Redox reactions and structure – properties relations in mixed alkali/alkaline earth silicate glasses
- The role of antimony oxides during the fining process
- A structural study of copper(I) and copper(II)
REDOX REACTIONS AND STRUCTURE – PROPERTIES RELATIONS IN MIXED ALKALI/ALKALINE EARTH SILICATE GLASSES

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LINA GRUND BÄCK

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It is important to optimize glass compositions for their specific purpose but also for the efficiency of the production process, the manufacturing of glass. This will be beneficial economically and environmentally. Today many processes and glass compositions are already optimized, but due to more strict legislation on toxic elements and substances there must be changes in many glass compositions. One of these elements is antimony; the oxide is used as fining agent to obtain a bubble free glass within a reasonable process time. One aim with this thesis is to obtain a deeper understanding of the fining mechanism in 20R2O-10MO-70SiO2 (R=Na and/or K, M = Ca and/or Ba, Mg, Sr) glasses in order to minimise the amount of Sb2O3. Another intention is to study the structure of 20R2O-10CaO-70SiO2 (R = Na, K) with Cu2+ as probe ion and thus get a deeper knowledge of the surrounding glass matrix. The optical basicity scale is used to determine the acid/base character of the different glass compositions.

Fining efficiency results showed a remarkable increase of the number of remaining bubbles when the glass contains either approximately equal amounts of Na and K or Ca and Ba, Mg or Sr. The much higher number of bubbles in the potassium containing glasses compared to the sodium containing is explained by the increase in viscosity, the increase in optical basicity and thus lower oxygen activity. The differences in the fining efficiency when altering alkaline earth ions cannot be explained by the optical basicity values, it seems to be a more complicated situation.

This thesis also reports maximum in Vickers hardness and packing density as well as minimum in glass transition temperature for the mixed alkali glasses. The mixed alkaline earth glasses do not exhibit any clear nonlinear behaviour. Raman spectroscopy measurements showed a variation in the network connectivity which has a clear relation to the optical basicity of the different glass compositions. The combination of UV-Vis-NIR and X-ray absorption spectroscopy measurements showed that the coordination sphere for Cu(II) is a tetragonal distorted octahedron with two elongated Cu-O bonds along the z axis. There were no trends in the degree of tetragonal distortion, thus it was about the same for all the investigated glass compositions. Cu(I) is found to be coordinated by two oxygen ligands in mainly linear coordination sphere, evidenced from X-ray absorption spectroscopy.

Keywords: Fining, oxygen activity, redox reactions, mixed alkali effect, mixed alkali silicate glasses, copper, antimony
Abstract


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I. Compositional effect on fining and oxygen activity in mixed alkali silicate glass
   Lina Grund and Bo Jonson

II. The influence of basicity on oxygen activity and antimony oxide fining efficiency in alkali alkaline earth aluminosilicate glasses
   Lina Grund, Bo Jonson and Karin Lundstedt

III. Electronic spectra and molar extinction coefficient of Cu²⁺ in alkali-alkaline earth-silica glasses
    Lina Grund Bäck

IV. Physical properties and Raman Spectroscopy of mixed alkali/alkaline earth silicate glasses
    Lina Grund Bäck, Sharafat Ali, Stefan Karlsson, Bo Jonson
    Submitted to Journal of Non-Crystalline Solids

V. X-ray and UV-Vis-NIR absorption spectroscopy studies of the Cu(I) and Cu(II) coordination sphere in (mixed) alkali -lime-silicate glasses
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Results related to this thesis have also been presented at scientific conferences:

**Compositional effect on fining and oxygen activity in mixed alkali silicate glass**
Lina Grund and Bo Jonson,  
*Poster session at the XXI International Congress on Glass, Strasbourg, France, 1-6th July 2007*

**Fining efficiency and oxygen activity in soda-alkaline earth-silica glasses**
Lina Grund, Bo Jonson, Karin Lundstedt, Christina Stålhandske,  
*Poster session at the 9th European Society of Glass Conference, Trencin, Slovakia, 22-26th June 2008*

**Application of perceptual representation of colour in glass – a tool for designers and glass industry - Part 2 Compositional effect on glass colour**
Lina Grund  
*60th Annual Meeting of Society of Glass Technology, Kosta, Sweden, 26-28th September 2010*

**Optical and physical properties of CuO-doped mixed alkali-alkaline earth silicate glasses**
Lina Grund Bäck, Sharafat Ali, Bo Jonson  
*Poster session at the 12th European Society of Glass Conference, Parma, Italy, 21-24th September 2014*
AUTHOR’S CONTRIBUTION

The following is the author’s contribution to the papers on which this thesis is based:

I  Performed the final method development for the oxygen activity measurements, prepared samples for oxygen activity measurements and performed the measurements, wrote the first draft of the text.

II  Prepared samples for oxygen activity measurements and performed the measurements, planned some of the experimental work and wrote the first draft of the text.

III  Planned the experimental work, performed the measurements (without the complementary UV-Vis-NIR measurement) and wrote the paper.

IV  Prepared the samples, planned some of the experimental work, interpreted all data and wrote the first draft to the paper.

V  Planned the experimental work, performed and interpreted the EXAFS-analysis, written the first draft to the manuscript.
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1. INTRODUCTION

1.1 General introduction

Glass is an amazing material which can exhibit many extraordinary properties. The transparency which makes all these windows transmit visible light, but not the dangerous part of the UV-light, is maybe the most important one. There are these wonderful glass pieces with spectacular colours and shapes, containers, glass wool, lamp bulbs, display glass, glass for solar panels, optical glasses etc. In all these products, the glass compositions are quite different and are optimized for the specific purpose and manufacturing process.

From the beginning of glass making, about 3000 B.C. in Middle East [1], the process was more or less trial and error, but since about 200 years ago more systematic and scientifically studies has been made on different glass compositions and properties [2]. Many of those questions raised back then concerning compositions and properties have been answered today, but there are still unanswered questions regarding unexpected properties when the glass composition is changed. One example is the peculiar non additive behaviour when mixing two alkali oxides, such as potassium and sodium, in about the same amount. The properties of both the melt and the glasses are affected of this so called mixed alkali effect and more studies are needed to be able to solve this puzzling manner.

Many metals and metalloids can exist in more than one oxidation state. When these are added to the glass melt, they will interact and give rise to a redox equilibrium. These elements can be impurities in the raw materials, such as iron (Fe₂⁺, Fe³⁺), or deliberately added, for example antimony as fining agent where the equilibrium will be between the oxidation states Sb³⁺ and Sb⁵⁺.
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Many colouring elements existing in the glass melt in at least two oxidation states, e.g. copper occur as both the colourless Cu\(^+\) and the Cu\(^{2+}\) ion which gives rise to a beautiful turquoise blue colour in silicate glasses. In reduced conditions, metallic copper can also be present. These redox equilibria are very dependent on the glass composition. Especially Cu\(^{2+}\) is used as a, so called, probe ion and provides information on the local structure in different glass compositions. As Cu\(^{2+}\) is relatively easy to study with different spectroscopic methods, i.e. UV-Vis-NIR, Electron Paramagnetic Resonance and X-ray Absorption Spectroscopy, the analytical data can provide useful structural information.

One aim of this thesis is to get a better understanding of how changes in the glass composition, particular mixed modifier alteration, affect the fining efficiency of antimony trioxide and if the partial pressure of oxygen in the melt can explain the differences in the fining results. The intention is as well to study the incorporation of Cu(I) and Cu(II) in the glass structure, for different glass compositions. Furthermore, another aim is to investigate the alterations in physical and structural properties of the glasses, especially the differences when mixing alkali or alkaline earth oxides on these properties.
1.2 The structure of alkali/alkaline earth silicate glasses

In paper IV, a Raman spectroscopy study provides structural information of some of the studied glasses, and below, a brief summary of the fundamental glass structure theory.

Glass making components are often divided in three classes based on the function of the component in the glass structure: network formers, network modifiers and property modifiers. Adding a network modifier such as alkali or alkaline earth oxides to a melt of vitreous silica alters the main structure by the formation of non-bridging oxygens (NBO), which decrease the connectivity of the melt, Figure 1.1. The non-bridging oxygens must be associated with an alkali ion or alkaline earth ion to maintain local charge neutrality. If the alkali oxide content is increased, the number of non-bridging oxygens is also increased. The network can no longer be maintained if there is too high amount alkali added, depolymerizing the silica beyond the point of network formation.

![Figure 1.1. The schematic structure of silica glass (left) respective soda-lime-silica glass (right). (illustrations from [3]).](image)

A common way to describe the degree of polymerization is the average number of NBO/SiO₄-tetrahedron, NBO/T=4 for orthosilicates, NBO/T=2 for chain silicates [4]. The fraction of the non-bridging oxygens (xNBO, NBO/(NBO+BO)) can be used or of the “Qⁿ notation” which expresses the concentration of bridging oxygens (BO) per tetrahedron by the value of superscript n. A tetrahedron fully linked to the network via four BO is a Q⁴ unit and a tetrahedron with no BO is a Q⁰ unit [5]. One model to express the Qⁿ distribution is the binary model where only two different kinds of Qⁿ species can exist at the same time. Another model is the Random distribution...
model where 3-4 different $Q^n$ species can exist [6]. The distribution can also be expressed as the disproportionate reaction [1.1].

\begin{equation}
2Q^n \rightarrow Q^{n+1} + Q^{n+1} \quad (1 \leq n \leq 3)
\end{equation} [1.1]

Measurements by means with $^{29}$Si MAS NMR and Raman spectroscopy have actually showed that the $Q^3$ distribution is somewhere in between the two above mentioned model’s [6]. An interesting observation is that reaction [1.1] shifts to the right when cations with high field strength are present in the glass. Therefore, in potassium silicate glass there are more $Q^3$ species and fewer $Q^2$ and $Q^4$ species compared to sodium silicate glass. In fact, it has been shown that in soda-lime-silicate glass, Ca$^{2+}$ will form bonds with non-bridging oxygens in $Q^2$ species and Na$^+$, with smaller cation field strength, will form bonds with non-bonding oxygens in $Q^3$ species [7, 8]. It is shown that in mixed cation glasses, cations with higher field strength have more non-bridging oxygen ions in their coordination shells, consequently the cations with lower field strength are surrounded by more bridging oxygens [9]. This means that the bond distances are shorter and stronger between “high field strength cations” and non-bridging oxygens than for the “low field strength cations” and bridging oxygens.

### 1.3 The mixed alkali effect

If two types of alkali oxide are used in a glass, some properties will change and be different from the data derived from single alkali glasses. E.g., the viscosity will be lower if two or more alkali oxides are mixed than those of corresponding melts containing the same total molar concentration of a single alkali oxide in alkali-lime-silicates [5]. The behaviour is decreasing with increasing temperature of the melt, and adding alumina decreases the mixed alkali effect on both the viscosity and electrical resistivity according to Kim and Lee [10]. Baucke and Werner [11] reports that the conductivity of glass melts in mixed alkali-lime-silica glass system has a minimum and the effect decreases with increasing temperature.

Properties like density, refractive index and hardness also exhibit non additive behaviour but not to the same extent as the dynamic properties mentioned above, as will be shown in paper IV. The mixing of alkaline earth oxides as well means that some properties also exhibit this non-additive behaviour. This is referred to as the mixed alkaline earth effect or mixed modifier effect [12, 13]. There have been many attempts to explain this phenomenon [14-17]. As mentioned, there is a structural difference when there are two modifier cations with different field strength present in the glass. This will lead to different
sizes of sites in the glass structure and is one of the suggested explanation for the decreased ion migration rates in mixed alkali glasses [9].

There is as yet very little published about how the mixed alkali affects the fining of glass melts [18], but Grund and Jonson [19] (paper I) showed that mixing sodium and potassium in alkali-lime-silica glasses results in a huge effect on the fining efficiency.

1.4 The basicity of glass melts

In this thesis, the optical basicity is chosen to express the acid-base character of the different glass compositions. The theory will be explained in the next section, 1.4.1; first a short general description of glass basicity is given.

The activity of the $O^{2-}$ ion is a measure of the basicity in glass melts, in analogy to aqueous solutions where the concentration of $H_3O^+$ ions is a measure of acidity as described by Lux [20]. In Lux-Flood theory, an acid is defined as an $O^{2-}$ acceptor, and a base is an $O^{2-}$ donor [21]. From equation [1.2], the reduced state of an element is expected to increase with increasing basicity.

$$\text{Cu}^{2+} + O^{2-} \rightleftharpoons \text{Cu}^+ + \frac{1}{2} O_2 (g) \quad [1.2]$$

As shown by many authors the relation is the opposite in silicate melts [22-27]; the higher oxidation states will be favoured when the basicity of the melt is increased, one exception is the redox pair $\text{Cu}^+/\text{Cu}^{2+}$ [28]. To overcome this paradox, further equations is proposed by Holmquist [29] and then later by Karlsson and Hirashima [30, 31] with the formation of complexes connected to the higher valence state of the redox ion, a more general form will be [28, 32]:

$$(\text{MO}_y)^{(m+n-2y)^{\text{-}}_r} \rightleftharpoons (\text{MO}_x)^{(m-2x)^{\text{+}}_r} + (y-x-n/2) O^{2-} + n/4 O_2 \quad [1.3]$$

Where m$^+$ is the lower and (m+n)$^+$ is the higher valence state, y and x are the number of oxygen atoms directly associated with the oxidized and reduced form of the multivalent element. Krämer suggested the following equation for antimony [32]:

$$[\text{SbO}_4]^{3\text{-}} \rightleftharpoons \text{Sb}^{3\text{+}} + 3O^{2\text{-}} + \frac{1}{2} O_2 \quad [1.4]$$

Araujo treated the paradox in a different way; he showed that $a_{O_2}$ does not directly enter into the equilibrium constant and hence the redox equilibrium contradiction does not exist [33].
The glass will aid the homogenisation of the melt. However, if no fining agent is added to the batch, the bubble disappearance is due only to the physical rise of relatively bubbles to the glass surface, i.e. physical fining. The density of the bubble is significantly lower than the glass melt, so when a bubble is large enough it will rise to the surface by the buoyancy effect. The velocity of bubble rise, $v_s$, is given by Stokes’ law for a special case of a gas bubble in a viscous liquid \[ \eta \rho g \frac{2}{r^2} \Delta = \] \[ \text{[1.6]} \]

Where $g$ is the gravitational acceleration, $\Delta \rho$ is the difference in density between bubble and the viscous liquid, $r$ is the radius of the bubble and $\eta$ is the viscosity of the liquid. The equation clearly shows that the rising velocity is inversely proportional to the viscosity and direct proportional to the bubble radius and the density of the melt.

The pressure inside the bubble, $p_i$, is given by Young–Laplace law \[ \frac{p_i}{2 \gamma} = \frac{p}{r} + \rho g (H - z) \] \[ \text{[1.7]} \]

Where $\gamma$ is the surface tension of the glass, $r$ is the bubble radius, $p$ is atmospheric pressure, $\rho$ the density of the glass, $H$ the distance between the bottom and the top of the glass bath and $z$ is the distance between the bottom of the bath and the bubble and $g$ is the acceleration of gravity. The pressure inside the bubble is equal to all partial pressures from the different gases.

The diffusion of gases through the melt and into the bubbles are important for the fining process, the diffusion coefficient, $D$, is related to the temperature and activation energy by the Arrhenius relation:

\[ D = D_0 \exp \left( -\frac{E_a}{RT} \right) \] \[ \text{[1.8]} \]

To accelerate the physical bubble rise, a so called fining agent is added to the batch. The most important criterion for a fining agent to work properly is the liberation of gas at high temperature (1350-1600°C). This process is called primary fining and usually the gases released are O$_2$ or SO$_2$ depending on which fining agent is used. This released gas is diffusing into the existing small bubbles and make them grow, which will make them rise faster to the surface. In the second stage of chemical fining, or refining, the temperature is...

There have been suggestions on how to calculate the basicity from the glass composition. This classification often place the oxides in a series characterized by decreasing tendency toward glass formation, gradual change of bond type from covalent ionic to highly ionic type, change of bond type from acidic type oxides through amphoteric to basic type oxides and decreasing ionic radius.

### 1.4.1 Optical basicity

Increasing the basicity of a glass leads to a greater degree of negative charge on the constituent oxygen atoms and to a greater electron donor power. The average electron donating power of the oxygen atoms in glass can be expressed numerically by the optical basicity value, $\Lambda$ \[ \text{[34, 35]} \]. The charge on the oxygen ion will vary with the glass composition and this can be measured if introducing probe ions such as Ti$^+$ or Pb$^{2+}$ with d$^{10}s^2$ as valence shell orbitals. The change in negative charge on the oxygen ion will affect the frequency of their $^1S_0 \rightarrow ^3P_1$ ultraviolet absorption band. The values of $\Lambda$ have been derived experimentally from UV-vis spectroscopy in a study by Duffy and Ingram \[ \text{[36]} \]. These experiments gave the basicity moderating parameter, $\gamma_0$, for cations. The optical basicity, $\Lambda$, is simply $1/\gamma_0$ for a single oxide, for glasses with several constituents, the expression will be:

\[ \Lambda = \sum_{i=n}^i X_i \cdot \Lambda_i \] \[ \text{[1.5]} \]

$\Lambda_i$ is the optical basicity of the constituent oxide, and $X_i$ is the proportions of oxygen atoms or ions which the oxide i contribute i.e. the equivalent fraction. The $\Lambda$ used is taken from \[ \text{[34]} \]. E.g., for a glass of molar composition Na$_2$O (16%), CaO (12%), SiO$_2$ (72%), $\Lambda = (16 \times 1.15 + 12 \times 1.00 + 144 \times 0.48) / 172 = 0.58$.

### 1.5 The fining of glass melts

In paper I and II the compositional effect on fining efficiency with Sb$_2$O$_3$ will be discussed, in this section the process of fining is described.

#### 1.5.1 Physical and chemical fining

When glass is melted, some of the raw materials (e. g. Na$_2$CO$_3$, K$_2$CO$_3$, CaCO$_3$, NaNO$_3$) will release a relatively large volumes of gas during the chemical melting reactions. Parts of the gaseous compounds are trapped as inclusions referred to as bubbles, blisters or seeds in the glass melt. Gases from carbonates, nitrates and hydrates evolved during the melting process of...
the glass will aid the homogenisation of the melt. However, if no fining agent is added to the batch, the bubble disappearance is due only to the physical rise of relatively bubbles to the glass surface, i.e. physical fining. The density of the bubble is significantly lower than the glass melt, so when a bubble is large enough it will rise to the surface by the buoyancy effect. The velocity of bubble rise, $V_s$, is given by Stokes’ law for a special case of a gas bubble in a viscous liquid [5]:

$$V_s = \frac{g\Delta \rho r^2}{3\eta}$$  \[1.6\]

Where $g$ is the gravitational acceleration, $\Delta \rho$ is the difference in density between bubble and the viscous liquid, $r$ is the radius of the bubble and $\eta$ is the viscosity of the liquid. The equation clearly shows that the rising velocity is inversely proportional to the viscosity and direct proportional to the bubble radius and the density of the melt.

The pressure inside the bubble, $p_i$, is given by Young–Laplace law [34]:

$$p_i = \frac{2\gamma}{r} + p_A + \rho \cdot g (H - z)$$  \[1.7\]

Where $\gamma$ is the surface tension of the glass, $r$ is the bubble radius, $p_A$ the atmospheric pressure, $\rho$ the density of the glass, $H$ the distance between the bottom and the top of the glass bath and $z$ is the distance between the bottom of the bath and the bubble and $g$ is the acceleration of gravity. The pressure inside the bubble is equal to all partial pressures from the different gases.

The diffusion of gases through the melt and into the bubbles are important for the fining process, the diffusion coefficient, $D$, is related to the temperature and activation energy by the Arrhenius relation:

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To accelerate the physical bubble rise, a so called fining agent is added to the batch. The most important criterion for a fining agent to work properly is the liberation of gas at high temperature ($1350-1600^\circ$C). This process is called primary fining and usually the gases released are $O_2$ or $SO_2$ depending on which fining agent is used. This released gas is diffusing into the existing small bubbles and make them grow, which will make them rise faster to the surface. In the second stage of chemical fining, or refining, the temperature is
decreased and this will cause an increase in the chemical solubility for the fining gases dissolving these into the melt again. Thus, O₂ has an crucial role for the fining process and its activity has therefore been measured in this work. When using the term fining it usually means the whole process, both primary fining and refining.

### 1.5.2 Fining by use of Sb₂O₃

Glass melting in factories producing art glass and hand blown tableware glasses are made at furnace temperatures lower than in the furnaces melting container or float glass. Sulphate, used for finings of float and container glass, is not an active fining agent at those low temperatures below, e.g. 1450°C. Arsenic oxide has been used in glass melts in that type of furnaces since at least the 17th century. During the 1920’s the first data on the fining with arsenic oxide were published [37]. In the 1980’s arsenic oxide was commonly replaced by antimony oxide due to the toxicity of arsenic, but still arsenic oxide is used in some countries. Antimony oxide is today broadly used in the industry, but there have been discusions concerning a substitution because of the lower antimony emission limits to both water and air [38, 39]. A criterion for a metal oxide with two different oxidation states to be active as a fining agent is the ability to release oxygen at a temperature that is not too high and not too low. Arsenic and antimony oxides are the only today known oxides which fulfil this criterion without colouring the melt. During the melting of glass in small glassworks, in pot furnaces, the temperature reaches maximum 1420°C. In the smaller tank furnaces, the temperature may reach 1450°C.

The fining active redox reaction of antimony can be described by:

\[
\text{Sb}^{5+} + \text{O}^{2-} \rightleftharpoons \text{Sb}^{3+} + \frac{1}{2} \text{O}_2 (g)
\]  

[1.9]

Where \(\text{O}^{2-}\) is the oxygen ion activity, to be considered as the basicity of the melt, \(\text{O}_2\) is the physically dissolved oxygen in the holes of the network structure. The equilibrium will be shifted to the right at higher temperature and the released \(\text{O}_2\) will diffuse into the quite small bubbles, enlarging them for faster rise to the surface. Equation [1.9] will go to the left at lower temperatures and the oxygen will dissolve chemically in the melt. Normally, Sb₂O₃ is added to the batch and in order to make the fining agent active, nitrate (sodium or potassium) is added to promote the oxidation of Sb³⁺ to Sb⁵⁺. This occurs at about 700-800°C. The simplified reaction is [5]:

\[
4\text{NaNO}_3 + 2 \text{Sb}_2\text{O}_3 \rightarrow 2\text{Na}_2\text{O} + 2\text{Sb}_2\text{O}_5 + 4\text{NO(g)} + \text{O}_2 (g)
\]  

[1.10]

There are many parameters that influence the fining efficiency of antimony trioxide (and other fining agents too). The two major ones are the glass
composition and the process temperature when melting the glass. The time of melting is also a very important factor for the industrial process.

Besides for art glass and hand blown tableware glasses antimony is also used when making CRT, cathode ray tube, glass and optical glasses [40]. However, nowadays when the conversion to flat glass televisions is almost completed, the CRT glass have been replaced by LCD glass with a completely different glass composition and fining agents [41].

1.6 Copper ions in silicate glass

The melting of alkali-lime-silicate glasses in air, means oxidizing conditions. The addition of CuO to such a melt give rise to both Cu$^+$ and Cu$^{2+}$ ions, the redox reaction is according to equation [1.2]. If no other polyvalent* ion is present, the ratio of the copper oxidation numbers depend on the glass composition, temperature of melting and the partial pressure of oxygen in the melt. The colour of the glasses will be turquoise blue, since the Cu$^{2+}$ ion will absorb light of the approximate wavelength 800 nm. The Cu$^{2+}$ ion is most likely coordinated with six O$^{2-}$ in a tetragonally distorted octahedral. This assumption is based on UV-Vis-NIR and EPR (Electron Paramagnetic Resonance) studies. From UV-Vis-NIR data the structure is proposed to be in a distorted octahedral coordination sphere because of the existence of a broad asymmetric absorption band at about 12600 cm$^{-1}$ [42]. A tetrahedral arrangement will give a lower ligand field splitting value and a square planar will give a higher value [42-44]. All reported EPR data on Cu$^{2+}$ in glass concludes that the coordination sphere is an elongated octahedron [45-49]. However, the conclusions from UV-Vis-NIR studies and EPR studies are not in agreement whether the elongation is most pronounced in sodium containing glasses or potassium containing glasses. The coordination sphere of Cu$^{2+}$ is discussed in paper III and V. The results from UV-Vis-NIR spectroscopy and for the copper containing glasses rarely used X-ray absorption spectroscopy are evaluated using the crystal field theory and the ligand field theory to interpret the analytical data.

*) Glass scientists often use the expression polyvalent where it means the ability of an element to exist in at least two different oxidations states at the same time. In this thesis it is used in that way and also in some of the papers.
1.6.1 Bonding theories for coordination complexes

A complex ion can be regarded as isolated from the surrounding, and thus bonding theories in a coordinated complex ion are somewhat different than for a solid material. Two common theories consider the bonding in complex ions and they are very briefly explained below. It is only the case of Cu$^{2+}$ surrounded by 6 oxygen ligands that will be described, i.e. a Cu$^{2+}$ ion in octahedral coordination.

1.6.1.1 The Crystal Field Theory

The Crystal Field Theory (CFT) treats the metal as a positive point charge and the ligands as negative point charges, i.e. only ionic binding is taken into account [50]. The theory has been used to explain colours originating from d-d transitions and measured by means of optical spectroscopy [51]. In an octahedral complex the dx$^2$-y$^2$ and dz$^2$ orbitals will be pointing directly against the ligands and due to stability reasons be raised in energy, see Figure 1.2. The differences between the t$_{2g}$ (dxy, dxz, dyz) and e$_g$ (dx$^2$-dy$^2$, dz$^2$) sets of orbitals, $\Delta_O$, is called the crystal field splitting and can also be referred to as 10Dq [50]. The factors influencing $\Delta_O$ are the type of metal ion, type of ligand, interatomic distance, pressure and temperature. If we consider the same cation, same ligands, same pressure and temperature, the distance between the metal ion and ligands is the only parameter that can influence the crystal field splitting. The interatomic distance influences $\Delta_O$ with the inverse fifth power, thus having a huge impact on the crystal field splitting.

The electron transition between the orbitals, t$_{2g}$ and e$_g$, can be observed in the absorption spectra in the visible region. In the case of a Cu$^{2+}$-O octahedron, this structure most likely will undergo “Jahn-Teller distortion” meaning that the axial bond length will increase and the equatorial bond lengths will decrease [52]. This will cause a splitting of the energy levels of the e$_g$ orbitals and the t$_{2g}$ orbitals. The dz$^2$, dxz and the dyz orbitals will lower their energy levels and becoming more stable than the dx$^2$-y$^2$ and dxy orbitals, see Figure 1.2. In the case of an elongated tetragonal distorted octahedron there will be three different electron transitions (dxz, dxy → dx$^2$-y$^2$, dxy → dx$^2$-y$^2$, dz$^2$ → dx$^2$-y$^2$) giving rise to three absorption peaks in the optical absorption spectra.
1.6.1.2 The Ligand Field Theory

The Ligand Field Theory includes Molecular Orbital Theory for the application on complex ions. The covalent binding is also taken into account and thus making the model more sophisticated. However, the outcome from CFT and LFT is often almost the same [50]. In an octahedral complex, the metal will form sigma-bonds with six sigma-donor ligands which will fill with the metal ion’s empty 4s (a1g), 4px, py and pz (t1u), dz2 and dx2-y2 orbitals (eg). The metal orbitals will form six bonding (σ) and six antibonding (σ*) molecular orbitals with the ligands because the mentioned atomic orbitals are pointed directly against the ligands, i.e. the components of the wave functions are directed along the x-, y- and z- axes [50]. The dxy, dxz and dyz orbitals (t2g) are located between the axes and can therefore not form σ-bonds and can either remain as non-bonding orbitals or form π-bonding molecular orbitals with the ligands. The nature of the ligands will control whether there will be a large or small splitting (ΔO) between the energy levels of t2g and eg* orbitals. In oxide glasses, oxygen ions are the ligands. These ions will possess filled π-
orbitals with lower energy than the non-binding $t_{2g}$ orbitals from the metal (black in the figure). The new $t_{2g}$ will have a new energy level which is filled with the electrons from the ligands (Figure 1.3) and the antibonding $t_{2g}^*$ orbital will be filled with the d electrons from the metal ion. Thus, the $\Delta_O$ is decreased when $\pi$-bonding is formed when oxygen ions (and other $\pi$-donor ligands) are ligands.

Figure 1.3. Molecular orbital diagram from an octahedral complex with $\pi$-donor ligands [54].
2. EXPERIMENTAL

2.1 Preparation of samples

2.1.1 Samples for fining and oxygen activity measurements
If nothing else stated, the samples were melted in an electrically heated Super Kanthal furnace at 1420°C. The fining agent used was 0.2 mol% Sb₂O₃ with 5 g of NaNO₃ or KNO₃ as oxidising agent /100g SiO₂. All raw materials were of industrial grade. The sand contained <0.01% Fe₂O₃ by weight and the glass batches weight about 200 g.

The first sample series, use the base glass R₂O-CaO-SiO₂ (R = Na and/or K) with varying R-ratio. For the sample codes 1.1 to 1.12, see Appendix A the \([\text{Na}_2\text{O}] / (\text{[Na}_2\text{O]} + \text{[K}_2\text{O]})\) ratio was altered from 1 to 0. The base glass composition was fixed to 70SiO₂-10CaO-20R₂O. For codes 1.13-1.17, the \([\text{Na}_2\text{O}] / (\text{[Na}_2\text{O]} + \text{[K}_2\text{O]})\) ratio was altered but instead of melting glasses at the same temperature they were melted at the same nominal viscosity \(\log \eta = 2\) (from 1317°C to 1446°C). The silica (from 75 to 65 mol%) and lime (from 17-24 mol%) content were varied for samples 1.18-1.21. In samples 1.22 to 1.28 the base glass composition was 75SiO₂-5CaO-20R₂O and again the \([\text{Na}_2\text{O}] / (\text{[Na}_2\text{O} + \text{K}_2\text{O]})\) ratio was altered from 1 to 0.

In the second series the base glass composition was 70SiO₂-10BaO-20R₂O and again the \([\text{Na}_2\text{O}] / (\text{[Na}_2\text{O]} + \text{[K}_2\text{O]})\) ratio was altered.

In the third series CaO was completely or partially replaced by BaO, MgO, ZnO, SrO, B₂O₃, Al₂O₃ or TiO₂ giving the base glass composition was 70SiO₂-zCaO-(10-z)MₓO₃-20Na₂O.
In the fourth sample series from, 4.1a to 4.4c, alumina silicate glasses with four different compositions and different basicity but with the same calculated viscosity were melted. The base glass was R₂O-CaO-Al₂O₃-SiO₂ (R=Na, K) and all the constituents were varied to get glasses and melts with the wanted properties.

The glasses in series 4 were only melted for 40 minutes because at 55 minutes sample 4.1a already was bubble free. All glasses used in the bubble counting test were melted in a ceramic crucible with the major composition of SiO₂ and Al₂O₃ and then casted on a graphite plate. The samples were annealed before the analysis of the number of bubbles. The annealing curve is found in Appendix B.

All the glass compositions, melting conditions and results can be found in Appendix A.

2.1.2 Samples containing Cu(I)/Cu(II)

Samples were melted in an electrically heated Super Kanthal furnace at 1420 °C during 1 h and then transferred to another electrically heated furnace held at 1300 °C during 1 h while stirring to make the samples homogeneous. The temperature was increased to 1420 °C, followed by continuous stirring during further 2 h and finally 1 h without stirring to make bubbles disappear. The melt was cast on an iron mould and transferred to the annealing furnace (see Appendix B for annealing curve).

The studied batched glass compositions are listed in Appendix A Table A8 and A9), the raw materials were of industrial grade with Fe₂O₃ maximum 0.01 wt% in the sand. All samples were melted in a Pt/Rh-crucible and the batches corresponded to 150 g of glass. The amount of copper was 0.4 mol%, i.e. close to the concentrations in industrial glasses coloured with CuO.

Furthermore, two more glasses with the same base glass composition containing 0.2 mol% CuO was studied. In one of these, 0.3 mol% Sb₂O₅ was added in order to favour the reduction of Cu²⁺ ions to Cu⁺. In the other glass 0.6 mol% CeO₂ was added to favour the oxidation of Cu⁺ ions to Cu²⁺.

UV-Vis-NIR spectroscopy

Samples were prepared by grinding and polishing plane parallel samples with a thickness of 3-5 mm. All samples were made in doublets or triplets.
X-ray Absorption Spectroscopy

Glass samples for the measurements were prepared by crushing and sieving to a particle size below 45 µm, using a 325 mesh sieve. The reference samples of Cu₂O and CuO were treated with mortar and pester and then mixed thoroughly with boron nitride in order to get homogenous samples with the approximately same concentration as the glass samples. Pure Cu₂O and CuO for reference were also spread on tape.

2.2 Fining efficiency - Bubble count tests

For the sample series from 1 to 3 the melting time was determined to 55 minutes, giving a feasible amount of bubbles for evaluation by the image processing/bubble counting equipment (an Image Pro Software).

2.3 Oxygen activity measurement

The oxygen activity was measured in melts for some of the glass compositions, specified in Table A2, Table A5 and Table A7 in Appendix A. The non-nitrate samples are marked with a, b denotes nitrate containing samples. The glasses were melted in a Pt/Rh crucible during 30 min and then cast on a graphite plate. The melting time was chosen to 30 minutes because at that time all the raw materials were melted or dissolved but the fining process was not yet completed. The samples were crushed in order to improve homogeneity and about 130 g glass was remelted in the Pt/Rh crucible. An yttria stabilized zirconia electrode was used as reference electrode and a platinum electrode as measuring electrode when measuring the oxygen activity, see Figure 2.1.
The measuring electrode is made of platinum, a wire and at the bottom there is a plate with an area that is much larger than the wire at the surface to avoid measuring a “mixed potential”[34]. To further minimise this experimental error, the platinum wire was covered with an insulator[55], alumina in this case. Similar methods are described by others [55-59] and the theory can be regarded as well-known and accepted. The oxygen activity in the melt, $a_{O_2}$, was calculated from the Nernst equation:

$$\Delta E = \frac{RT}{4F} \ln \frac{a_{O_2} \text{(melt)}}{p_{O_2} \text{(ref)}}$$ \hspace{1cm} [2.1]$$

In which $\Delta E$ is the electromotive force (EMF), R is the gas constant, T the temperature, F the Faraday constant and $p_{O_2}$ is 0.21 (the partial pressure of oxygen in air). Appendix C describes how the electrochemical cell was prepared for the experiments. When measuring the oxygen activity of the samples, the furnace was heated up to about 1200 °C with a rate of 500 K/h, and then the electrodes were immersed into the glass melt, about 1 cm from the surface. The furnace was then heated to 1350 or 1400 °C with the same rate, see Figure 2.2. This temperature was maintained during 30 min and then back again to 1200°C. The $\Delta E$ was measured with a Keithley 2700 Multimeter/data acquisition system.
2.4 Analysis of \([\text{Sb}^{3+}] / [\text{Sb}^{5+}]\) and \([\text{Cu}^+] / [\text{Cu}^{2+}]\)

The ratio of \(\text{Sb}^{3+}\) and \(\text{Sb}^{5+}\) were analysed in glass samples 4.1b-4.4c. In Appendix A, the glass compositions are listed. The \(\text{Cu}^+/\text{Cu}^{2+}\) ratio was determined for samples 0K-20K and 5Ba-10Ba, see Appendix A. The amount of \(\text{Sb}^{3+}\) and the total amount of \(\text{Sb}\) was determined, thus the part of \(\text{Sb}^{5+}\) could be calculated. The glasses were melted in the same way as described in section 2.1.2. The samples were crushed and further divided to very fine particles. The total amount of \(\text{Sb}\) was determined using a Perkin-Elmer AAnalyst 400 Atomic Absorption Spectrometer. The method for \(\text{Cu}^+\) and \(\text{Sb}^{3+}\) determination was first described by Zaman and Paul 1969 [60]. In this study it was modified and the procedure was according to following description: An appropriate amount of ground sample, depending on how much polyvalent ion the glass sample contains, are mixed with 20 ml \(\text{HCl}\) (1+1), 1 ml 0,75\% \(\text{ICl}\) 5 ml 40\% \(\text{HF}\). The samples have to be cooled during the 30 minutes before the titration of the amount of \(\text{I}_2\) with \(\text{KIO}_3\). The following reactions occur in aqueous solution:

**Oxidation of \(\text{Sb}^{3+}\) with \(\text{ICl}\):**

\[
2 \text{ICl} + \text{Sb}^{3+} \leftrightarrow \text{I}_2 + 2 \text{Cl}^- + \text{Sb}^{5+} \tag{2.2}
\]

**Determination of \(\text{I}_2\) in strong acid solution with \(\text{KIO}_3\):**

\[
2 \text{I}_2 + \text{IO}_3^- + 6 \text{H}^+ + 5 \text{Cl}^- \leftrightarrow 5 \text{ICl} + 3 \text{H}_2\text{O} \tag{2.3}
\]
2.5 Measurements/calculations of viscosity

2.5.1 Viscosity measurements

The viscosity was measured for some samples, see Appendix A, Table A1 and A7. A rotation viscometer was used. The viscometer consists of a small cylinder, or spindle, which is rotated inside a large cylindrical crucible containing the melt. The viscosity is determined from measurements of the torque on the spindle and use of equation [2.4], which relates the viscosity, \( \eta \), to the torque, \( T \), and the dimensions of the spindle and the cylinder [5]:

\[
\eta = \frac{1}{4\pi L} \left( \frac{1}{r^2} - \frac{1}{R^2} \right) \left( \frac{T}{\omega} \right) \tag{[2.4]}\]

Where \( L \) and \( r \) are the length and radius of the spindle, \( R \) is the inner radius of the cylinder holding the melt, and \( \omega \) is the angular velocity of the spindle rotation. The viscometer was calibrated with a standard container glass with known viscosity to give the necessary ratio between speed, torque and dimensions. The samples were measured stepwise between about 1450°C and 950°C and from these measurements the constants \( A \), \( B \) and \( T_0 \) was calculated from equation [2.5] (known as the Vogel-Fulcher-Tamman (VFT) equation [5]):

\[
T = \frac{B}{\log \eta + A} + T_0 \tag{[2.5]}\]

2.5.2 Viscosity calculations

For most glass compositions in this study, the temperature at a viscosity \( \log \eta = 2 \) was calculated, see Appendix A, Table A1-A7. The viscosity calculation program is based on equation [2.5] and the measured viscosity of numerous glasses in order to give reliable values for the constants \( A \), \( B \) and \( T_0 \) for certain compositions intervals in this program. If the composition of a certain glass lies within these intervals, the calculated value is very accurate. For the compositions outside these intervals, the calculated value is extrapolated and thus less accurate.
2.6 Determination of the molar extinction coefficient of Cu$^{2+}$

The extinction coefficient was calculated using the Lambert-Beer equation:

$$
\varepsilon_{\text{Cu}^{2+}} = \frac{A - A_0}{d \cdot C_{\text{Cu}^{2+}}} \quad [2.6]
$$

where $A$ is the absorbance at the peak wavelength, $A_0$ is the absorbance of a sample with no CuO for correction of reflection losses and internal absorption, $d$ is the thickness of sample in cm, $C_{\text{Cu}^{2+}}$ is the concentration of Cu$^{2+}$ in mol/dm$^3$. The densities were determined in order to calculate concentration of Cu$^{2+}$ needed to determine the extinction coefficient.

2.7 UV-Vis-NIR measurements

For the determination of the molar extinction coefficients, a Perkin Elmer Lambda 35, double beam UV-Vis-NIR spectrophotometer with tungsten as light source was used, with slit 4 nm and scan rate 480 nm/min. The slit was chosen because of the very broad absorption peak of Cu$^{2+}$, the (spectral bandwidth)/(natural bandwidth) is very small even with 4 nm slit. So, to get the largest possible $I_0$ (intensity of incident light), a slit of 4 nm was chosen. All samples were measured between 380 and 1100 nm with 2 nm steps. The CIE L*a*b* colour coordinate calculations were done with software from Perkin Elmer using wavelengths between 380 and 780 nm. Spectra in all figures are normalized to 1 mm thickness and for colour coordinate calculations a thickness of 2 mm was used.

When deconvoluting and the determining the integrated area of the absorption peaks, a wavelength up to 3300 nm was needed, an Agilent Technologies Cary 5000 was used for these measurements. The scan rate was 600 nm/min and the spectral bandwidth 2 nm. The samples were masked with a circular aperture with the diameter of 5 mm and were measured from 3300 nm to 200 nm with 1 nm steps. The lamp source changeover was at 350 nm and the detector as well as grating changeover at 700 nm. The broad absorption band was deconvoluted by using the software Peak Fit® [61].
2.8 Raman Spectroscopy

Raman spectra were recorded in the 100–3200 cm$^{-1}$ range on a micro-Raman spectrometer inVia Renishaw using the 488 nm line with Ar ion-laser as light source. The Raman spectra were baseline corrected and normalized to the intensity of the most intensive band, positioned around 1150 cm$^{-1}$, using the WiRE 4.0 software from Renishaw.

Deconvolution of the peaks in the region 800 to 1200 cm$^{-1}$ was done with the software PeakFit® [61]. The curve-fitting was done according to the procedure proposed by Mysen et al. [62] using four or five Gaussians to quantify the $Q^0$-species with the starting values at 870, 950, 1050, 1100 and 1150 cm$^{-1}$. Frequency, half-width and intensity were independent and unconstrained variables. The theory assuming that the peak areas are proportional to the concentration of the respective $Q^0$ specie is based on the hypothesis that the Raman scattering cross section is the same for all glass compositions [63]. In order to evaluate the network polymerization the area of the $Q^2$ peak is divided with the area of the $Q^2$ species (AQ$^2$/AQ$^2$) [64].

2.9 Differential thermal analysis

Glass transition temperatures (Tg) and crystallization temperatures (Tc) were measured by use of crushed pieces of glass, using a SETARAM Labsys Netzsch STA 409 PC/PG instrument. Samples were heated up to 1350 °C in flowing nitrogen in Alumina cups, using a heating rate of 15 °C/min. The onset point of the endothermic drift on the DTA curve was taken as representing Tg, and the onset of the exothermic peak as corresponding to Tc. The precision of the Tg and Tc measurement was estimated to be ±5 °C.

2.10 Measurements of Vickers hardness

The measurements were carried out on polished samples using two different indenters with two different loads during 10 seconds. For the 0.49 N load a FV-700 Futur Tech instrument fitted with a diamond pyramidal indenter and attached to an incident light microscope was used. A Zwick Roell Indentec equipped with a pyramidal diamond indenter was used for the applied load of 0.98 N. The indentation dimension for each sample was measured with a light microscope (Olympus PMG3, Japan) under a magnification of 200. Vickers hardness values were calculated in GPa, using the expression Hv = (18.42
P)/d2, where P [N] is the load applied on the indenter and d [µm] is the average indentation diagonal length. Ten indents per specimen were recorded and their mean value and standard deviation were calculated.

### 2.11 Density measurements

The densities were measured according to the Archimedes principle, weighing the samples in distilled water at 22 ± 1°C, assuming a density of 0.998 g/cm³ for water. Density values were calculated using the expression \( \rho = (m_d/m_w - m_w) \times \rho_{\text{water}} \), where \( m_d \) is the weight of the dry sample and \( m_w \) the weight of the immersed sample. Sample weights were between 2 and 4 g, and measured glass densities were reproducible to ±0.005 g/cm³.

### 2.12 Calculation of molar volume and compactness

The molar volume (MV) of a glass is equal to the volume of one mole of the glass and was derived by dividing the molecular weight of the glass by its density. The MV was calculated using the expression:

\[
MV = \frac{\sum x_i M_i}{\rho} \quad [2.7]
\]

with \( x_i \) and \( M_i \) being the mole fraction and molar mass of element \( i \) respectively, and \( \rho \) the density of the glass. The compactness of the glasses is expressed as the packing density (\( C_g \))[65]:

\[
C_g = \frac{\sum x_i V_i N}{MV} \quad [2.8]
\]

where \( V_i = 4/3\pi N(x r_A^3 + y r_B^3) \) is the molar volume of an oxide \( A_x B_y \), and the Avogadro’s constant \( N \). The ionic radii \( r_A \) and \( r_B \) of the respective anions and cations were taken from Shannon [66].
2.13 X-ray Absorption Spectroscopy

2.13.1 Data collection
Copper K-edge X-ray absorption measurements were made at the wiggler beamline I811 at the Max–II ring, Max-lab, Lund, Sweden, at two occasions. Max-II ring offered electron beam energies of 1.5GeV, maximum current of 200 mA and X-rays in the energy range 2.4-20 keV. The beamline was equipped with a Si [111] double crystal monochromator. In order to remove higher harmonics, 30% detuning was used. The sample spectra were collected in fluorescence mode by a solid state PIPS detector and a Cu-metal reference foil for energy calibration was simultaneously measured in transmission mode. The measurements were performed at ambient room temperature and the energy scale of the x-ray absorption spectra were calibrated by assigning the first inflection points of the K edges of foils of copper at 8980.3 eV. The ion chambers I0, I1 and I2 were filled with 1.1 bar N₂, 0.1 bar Ar and 2 bar Ar respectively. Every sample was scanned at least 5 times in continuous scanning mode.

2.13.2 Data analysis
The data analysis was carried out with the program package EXAFSPAK [67] and the pre-edge subtraction and spline removal was done in a standard procedure. The software FEFF7 [68] was used for the modelling in EXAFS region. The XANES region was only analysed qualitatively.
3. RESULTS AND DISCUSSION

3.1 Sb$_2$O$_3$ containing glasses and melts

This section contains an overview and summary of the most important results from the fining efficiency studies. For more detailed information about the results, see papers I-II and Appendix A for all glass compositions.

3.1.1 Fining efficiency

The number of bubbles was measured in order to evaluate the fining efficiency for mixed alkali glasses with the base composition 20R$_2$O-10CaO-70SiO$_2$, 20R$_2$O-5CaO-75SiO$_2$ and 20R$_2$O-10BaO-70SiO$_2$ (R = Na and/or K) respectively. In Figure 3.1, it can be seen that the number of bubbles increases with increasing K$_2$O content, i.e. decreasing [Na$_2$O]/([Na$_2$O] + [K$_2$O]) ratio. The glasses with higher silica content have fewer bubbles than the ones with lower silica content. The sudden decrease in the number of bubbles at a [Na$_2$O]/([Na$_2$O] + [K$_2$O]) ratio of about 0.5 is not so distinct for the 20R$_2$O-5CaO-75SiO$_2$ glass as for the 20R$_2$O-10CaO-70SiO$_2$ glass. When replacing potassium with sodium the viscosity of the glass melt will decrease with a negative deviation from linearity, see Figure 3.11b. Thus, the abrupt change in the number of bubbles is likely not only due to the decrease of the viscosity.

Another interesting detail of the fining behaviour is that the high silica glasses of higher viscosity show fewer bubbles than the glasses with lower silica content. This phenomenon has been noticed by others [69, 70]. The reason is probably that the oxygen release in the glass melt occurs at lower temperature since the high silica glass is more acidic [71]. This might also be one reason why the number of bubbles becomes higher when potassium content in the glass increases; these potassium enriched glasses will become more basic.
reasonable that Tonset is higher than the two lower temperatures, 1349°C and 1335°C. Another reason is that all processes go slower at a lower temperature, for example the diffusion of gases into the bubbles.

Figure 3.2. Number of bubbles/100g vs \([\text{Na}_2\text{O}]/([\text{Na}_2\text{O}]+[\text{K}_2\text{O}])\) ratio in 20R2O-10CaO-70SiO2, 20R2O-5CaO-75SiO2 and 20R2O-10BaO-70SiO2 glasses, 0.2% Sb2O3 and KNO3 or NaNO3 were used as fining agents.

The results for the glasses of the base composition 20R2O-10BaO-70SiO2 showed the same phenomenon as the glasses containing CaO, i.e. at a \([\text{Na}_2\text{O}]/([\text{Na}_2\text{O}]+[\text{K}_2\text{O}])\) ratio of about 0.5 there is a distinct increase in the number of bubbles, see Figure 3.1. This shows that not only calcium oxide containing glasses gives rise to this behaviour in mixed alkali glasses. The diffusion coefficient for sodium will decrease when the potassium content is increased and vice versa for potassium [5]. How the diffusion of oxygen will be affected when the Na/K ratio is altered is not known. Due to difficulties to determine \(D_{O2}\) there is a limited amount of data. However, most likely the diffusion of \(O_2\) is lower than alkali ions [72, 73].

Glasses of the base composition 20R2O-10CaO-70SiO2 (R= Na, K) were melted and investigated at different temperatures (1335°C - 1431°C) in order to keep the viscosity constant at 100 dPas. These samples had a large difference in the number of bubbles, see Figure 3.2. It is obvious that the temperature is too low for the glasses melted at temperatures of 1349°C and 1335°C. The fining is not working properly, there are much more bubbles when compared to Figure 3.1 for the same compositions. The reason might be that there is a certain temperature when there is a rapid increase in the oxygen release when fining with Sb2O3. This temperature is by Yamamoto et al [57] called \(T_{\text{onset}}\) and was found to be 1360°C for a 20Na2O-10CaO-70SiO2 glass with 0.2% Sb2O3 and no nitrate addition [paper I]. According to Yamamoto \(T_{\text{onset}}\) will be somewhat lower when adding nitrate to the batch. However, it is
reasonable that $T_{\text{onset}}$ is higher than the two lower temperatures, 1349°C and 1335°C. Another reason is that all processes go slower at a lower temperature, for example the diffusion of gases into the bubbles.

To overcome the experimental issue of glass melts having the same viscosity but at different temperatures, four samples having the same viscosity at the same temperature but different basicities were prepared. The batch compositions originates from the investigation of Hupa and Karlsson [74, 75] the 20R$_2$O-CaO-SiO$_2$-Al$_2$O$_3$ (R=Na and/or K) glass system, Appendix A, Table A6. The optical basicity concept was used for basicity calculations, see section 1.4.1. It is remarkable how the number of bubbles increase linearly with the calculated optical basicity of the melt, see Figure 3.3.

Figure 3.2. Number of bubbles/100g vs $[\text{Na}_2\text{O}]/([\text{Na}_2\text{O}]+[\text{K}_2\text{O}])$ ratio in 20R$_2$O-10CaO-70SiO$_2$ (R= Na, K) glasses, 0.2% Sb$_2$O$_3$ and same viscosity ($\log \eta = 2$).

Figure 3.3. Number of bubbles/100g glass versus optical basicity in 20R$_2$O—CaO-SiO$_2$-Al$_2$O$_3$ (R=Na and/or K) glasses with 0.2% Sb$_2$O$_3$ and NaNO$_3$ as fining agent.
The number of bubbles can have a positive effect on transport properties [78, 79]. When adding SrO at the cost of CaO, the number of bubbles is increased as expected, because of higher optical basicity and a slightly higher viscosity [80]. The effect of substituting BaO for CaO is not the expected from the basicity and the melt viscosity, the number of bubbles should be higher than the observed value. Yoshida et al estimated the [Sb\textsuperscript{3+}]/[Sb\textsuperscript{5+}] redox ratio in 10Na\textsubscript{2}O-10RO-74SiO\textsubscript{2} (mol%, R=Mg, Ca, Sr, Ba) glass melt using differential pulse voltammetry [81]. They showed that the ratio decreases with increasing size of alkaline earth ion, but there was a minimum in the SrO containing glasses. The [Sb\textsuperscript{3+}]/[Sb\textsuperscript{5+}] redox ratio for the glasses containing BaO was about the same as for the CaO containing glasses. As the [Sb\textsuperscript{3+}]/[Sb\textsuperscript{5+}] redox reaction is crucial for the fining process this can be the answer to the relatively small amounts of bubbles in the glasses containing BaO.

If 1 or 4 mol% of CaO was replaced by the three and four valent B\textsubscript{2}O\textsubscript{3}, Al\textsubscript{2}O\textsubscript{3} or Ti\textsubscript{2}O\textsubscript{3}, the base composition was 20Na\textsubscript{2}O-zCaO-(10-z)MxOy-70SiO\textsubscript{2}. The resulting pattern was quite different as when CaO was replaced with a divalent modifier ion just discussed, see Figure 3.5. The common denominator for these three oxides is that they act as network formers, even if Al\textsubscript{2}O\textsubscript{3} and Ti\textsubscript{2}O\textsubscript{3} cannot act as one by themselves.

The number of bubbles decreased to 0 for the 4 mol% B\textsubscript{2}O\textsubscript{3} containing glasses. This is quite logical since B\textsubscript{2}O\textsubscript{3} will decrease the viscosity and make the glass melt more acidic compared to CaO.

Ti\textsuperscript{4+} can both act as a network modifier and network former and the outcome are quite uncertain when adding TiO\textsubscript{2} to the melt [1]. Our results show an increase of the number of bubbles when 1 mol% TiO\textsubscript{2} is added. However, but when 4 mol% TiO\textsubscript{2} is added at the cost of CaO, the number of bubbles is decreased to an amount less than single CaO glass. The viscosity will increase somewhat with TiO\textsubscript{2}, but will contribute to a more acidic glass melt compare to CaO [82, 83].

When replacing CaO by Al\textsubscript{2}O\textsubscript{3}, the number of bubbles is increased, likely due to the increase of the viscosity. It is known that when Al\textsuperscript{3+} substitutes Si\textsuperscript{4+} in the tetrahedron of oxygen, modifiers need to charge compensate close to the Al\textsuperscript{3+} ion, however without forming any non-bridging oxygens. Thus, when 4 mol% Al\textsubscript{2}O\textsubscript{3} substitutes CaO, the network connectivity is increased and this leads to an increase of the viscosity.

If CaO is replaced completely or partially by BaO, MgO, ZnO or SrO in a 20Na\textsubscript{2}O-10MO-70SiO\textsubscript{2} glass composition, the number of bubbles increases for all the investigated compositions, see Figure 3.4. It is remarkable that the mixing of CaO with one of the other divalent metal oxides always results in more bubbles compared to the results for one single metal oxide in the glass. These results indicate that the mechanism of fining somehow is related to the transport of alkali and alkaline earth ions which is known to have a minimum in the diffusivity when there is about equal amount of two modifier ions with the same charge [76]. This pattern can be compared to the one shown in Figure 3.1, where the increase in the number of bubbles occurs at about equal mol% of Na\textsubscript{2}O and K\textsubscript{2}O. The basicity of the alkaline earth oxides increase with the size, i.e. MgO<CaO<SrO< BaO and in the previous section it was showed that in alkali-lime-silicate-alumina glasses an increase in basicity led to more bubbles. The fining efficiency of sodium-alkaline earth-silicate seems not to follow this basicity relationship.

MgO, which has lower optical basicity than CaO should have the lowest number of bubbles, but instead twice as many. When MgO is substituted for CaO, a higher viscosity was observed at 1400 °C [77] which will influence the bubble rise process, see section 1.5.1. Mg\textsuperscript{2+} is smaller than Na\textsuperscript{+}, the other

![Figure 3.4. Number of bubbles/100g glass vs MO in 20Na\textsubscript{2}O-10MO-70SiO\textsubscript{2} glass.](image-url)
modifier cation in the glass, while Ca$^{2+}$ has about the same size as Na$^+$. The same size on the cations can have a positive effect on transport properties [78, 79]. When adding SrO at the cost of CaO, the number of bubbles is increased as expected, because of higher optical basicity and a slightly higher viscosity of the melt [80]. The effect of substituting BaO for CaO is not the expected from the basicity and the melt viscosity, the number of bubbles should be higher than the observed value. Yoshida et al estimated the [Sb$^{3+}$/Sb$^{5+}$] redox ratio in 10Na$_2$O-10RO-74SiO$_2$ (mol%, R=Mg, Ca, Sr, Ba) glass melt using differential pulse voltammetry [81]. They showed that the ratio decreases with increasing size of alkaline earth ion, but there was a minimum in the SrO containing glasses. The [Sb$^{3+}$/Sb$^{5+}$] redox ratio for the glasses containing BaO was about the same as for the CaO containing glasses. As the [Sb$^{3+}$/Sb$^{5+}$] redox reaction is crucial for the fining process this can be the answer to the relatively small amounts of bubbles in the glasses containing BaO.

1 or 4 mol% of CaO was replaced by the three and four valent B$_2$O$_3$, Al$_2$O$_3$ or TiO$_2$, the base composition was 20Na$_2$O-zCaO-(10-z)M$_x$O$_y$-70SiO$_2$. The resulting pattern was quite different as when CaO was replaced with a divalent modifier ion just discussed, see Figure 3.5. The common denominator for these three oxides is that they act as network formers, even if Al$_2$O$_3$ and TiO$_2$ cannot act as one by themselves.

The number of bubbles decreased to 0 for the 4 mol% B$_2$O$_3$ containing glasses. This is quite logical since B$_2$O$_3$ will decrease the viscosity and make the glass melt more acidic compared to CaO.

Ti$^{4+}$ can both act as a network modifier and network former and the outcome are quite uncertain when adding TiO$_2$ to the melt [1]. Our results show an increase of the number of bubbles when 1 mol% TiO$_2$ is added. However, but when 4 mol% TiO$_2$ is added at the cost of CaO, the number of bubbles is decreased to an amount less than single CaO glass. The viscosity will increase somewhat with TiO$_2$, but will contribute to a more acidic glass melt compare to CaO [82, 83].

When replacing CaO by Al$_2$O$_3$, the number of bubbles is increased, likely due to the increase of the viscosity. It is known that when Al$^{3+}$ substitutes Si$^{4+}$ in the tetrahedron of oxygen, modifiers need to charge compensate close to the Al$^{3+}$ ion, however without forming any non-bridging oxygens. Thus, when 4 mol% Al$_2$O$_3$ substitutes CaO, the network connectivity is increased and this leads to an increase of the viscosity.
3.1.2 Oxygen activity and the [Sb$^{3+}$]/[Sb$_{\text{tot}}$] ratio

The results of the oxygen activity measurements in 20R$_2$O-10CaO-70SiO$_2$ glass melts containing 0.2 mol% Sb$_2$O$_3$, with or without nitrate, can be seen in Figure 3.6. There are two things that are quite apparent; firstly, the oxygen activity increases with an increase of the [Na$_2$O]/([Na$_2$O]+[K$_2$O]) ratio. Secondly, the oxygen activity is much higher in the nitrate containing batches. The fact that the oxygen activity is higher in the glass melts with a higher [Na$_2$O]/([Na$_2$O]+[K$_2$O]) ratio is one of the reasons why there are much fewer bubbles in these glasses than the ones with a lower Na$_2$O content (Figure 3.1). When the oxygen activity is higher, the amount of oxygen released to aid the fining of the melt is higher.

A third interesting observation is made for the most basic, potassium rich, glass melts. In these, the oxygen activity does not seem to be so much higher when nitrate was added to the batch. An oxygen activity that reach a pressure of 1 bar (lg a$_{O_2}$ = 0) is needed before the fining process starts. The measurement of the two glass melts with the lowest [Na$_2$O]/([Na$_2$O]+[K$_2$O]) ratio show that the a$_{O_2}$ is below this pressure. Most likely, this explains why there are so many bubbles remaining in these glasses, Figure 3.1.
A clear trend is observed, when the basicity is decreased, the oxygen activity is increased. At 1400 °C basic melts is expected to be capable of dissolving more O$_2$ than more acidic melts. As discussed, the T$_{onset}$ for the glass with a [Na$_2$O]/([Na$_2$O]+[K$_2$O]) ratio of 1 is determined to 1360 °C [paper I]. At this temperature, there is a rapid increase of the oxygen activity. Below this temperature, for a certain glass composition and fining agent, the glass melts cannot be fined. Therefore, the T$_{onset}$ probably is higher for a more basic glass composition [71].

There is another way of comparing the degree of O$_2$ saturation within the different melts. Rüssel et al let soda-lime-silica-glass be exposed for gas atmospheres with different oxygen partial pressure during some hours and then measured the oxygen activity in the melts at 1250°C and at 1400 °C [59]. The glass melt exposed for the highest oxygen partial pressure had a lower value of the difference between the two temperatures, lg a$_{O_2}$ at 1400°C and lg a$_{O_2}$ 1200 °C, i.e. Δlg a$_{O_2}$ was lower for the glass exposed for the highest P$_{O_2}$ and highest for the melts exposed for the lowest P$_{O_2}$.

In this study, the Δlg a$_{O_2}$ values were taken from 1350 °C and 1200 °C, but without changing the atmosphere. As the glass compositions were different and they were exposed for the same oxygen partial pressure, the Δlg a$_{O_2}$ value will be a way to express the degree of O$_2$ saturation in different melts. The Δlg a$_{O_2}$ increases from value of 0.65 for the most acidic glass melt,
The \([\text{Na}_2\text{O}] / ([\text{Na}_2\text{O}] + [\text{K}_2\text{O}])\) ratio was determined in the 20R-2O-CaO-SiO_2-Al_2O_3 (R=Na and/or K) glasses, both with nitrate and without nitrate added to the batch, Figure 3.9. When no nitrate was added the results are like the argumentation in section 1.4, the higher oxidation state will be favoured when the basicity of the melt is increased and when nitrate is added the results are the opposite. The behaviour is explained by the very high oxygen activity (see Figure 3.6) in the nitrate containing acidic glass melts which will shift the equilibrium towards more Sb_5^+, equation [1.8].

The data from the oxygen activity measurements were compared with the calculated optical basicity. The oxygen activity decrease when the optical basicity increases, Figure 3.8. This is in accordance with the expected trend from the other investigations.
The $\text{[Sb}^{3+}/\text{[Sb}_{\text{tot}}]$ ratio was determined in the $20\text{R}_2\text{O-CaO-SiO}_2-\text{Al}_2\text{O}_3$ ($R=\text{Na and/or K}$) glasses, both with nitrate and without nitrate added to the batch, Figure 3.9. When no nitrate was added the results are like the argumentation in section 1.4, the higher oxidation state will be favoured when the basicity of the melt is increased and when nitrate is added the results are the opposite. The behaviour is explained by the very high oxygen activity (see Figure 3.6) in the nitrate containing acidic glass melts which will shift the equilibrium towards more Sb$^{5+}$, equation [1.8].

![Graph showing the $\text{[Sb}^{3+}/\text{[Sb}_{\text{tot}}]$ ratio vs calculated optical basicity.](image)

Figure 3.9 $\text{[Sb}^{3+}/\text{[Sb}_{\text{tot}}]$ ratio vs calculated optical basicity.
3.2 Physical properties of alkali/alkaline earth silicate glasses

The results from the mixed alkali glasses in paper IV are compiled in this section. Density, molar volume, compactness, glass transition temperature, crystallisation temperature and Vickers hardness have been measured for five glasses in the (20-x)Na₂O-xK₂O-10CaO-70SiO₂ (x=0, 5, 10, 15, 20) and three glasses Na₂O-(10-x)CaO-xBaO-70SiO₂ (x=0, 5, 10) glass system. A structural characterization by means of Raman spectroscopy was performed.

3.2.1 Na₂O-K₂O-CaO-SiO₂ glasses

Density, molar volume and compactness
The density is increased and the molar volume is decreased when an increasing amount of sodium is contained in the glass, Figure 3.10a. However, there is a plateau in the density when there is a mix of sodium and potassium in the glasses. The increase in density when Na₂O substitutes potassium is a known phenomenon [2, 84]. Both the plateau and the increase in density with increasing [Na₂O]/([Na₂O]+[K₂O]) ratio is explained in terms of packing density of atoms, showed in Figure 3.10b. There is a more effective packing of atoms when there is a mix in the size of atoms [85]. Of course, this reasoning with compactness and density is only valid when the ion densities are similar as in this case with sodium and potassium.

![Figure 3.10a Density and molar volume vs [Na₂O]/([Na₂O]+[K₂O]) ratio)](image)
2.49 2.495 2.5 2.505 2.51 2.515 2.52 2.525 2.53 2.535
0.551 0.552 0.553 0.554 0.555 0.556 0.557
0 0.2 0.4 0.6 0.8 1
Density (g/cm^3)
Packing density

[Ta_2O]/([Ta_2O]+[K_2O]) (mol/mol)

3.2 Physical properties of alkali/alkaline earth silicate glasses
The results from the mixed alkali glasses in paper IV are compiled in this section. Density, molar volume, compactness, glass transition temperature, crystallization temperature and Vickers hardness have been measured for five glasses in the (20-x)Na_2O-xK_2O-10CaO-70SiO_2 (x=0, 5, 10, 15, 20) and three glasses Na_2O-(10-x)CaO-xBaO-70SiO_2 (x=0, 5, 10) glass system. A structural characterization by means of Raman spectroscopy was performed.

3.2.1 Na_2O-K_2O-CaO-SiO_2 glasses
Density, molar volume and compactness
The density is increased and the molar volume is decreased when an increasing amount of sodium is contained in the glass, Figure 3.10a. However, there is a plateau in the density when there is a mix of sodium and potassium in the glasses. The increase in density when Na_2O substitutes potassium is a known phenomenon [2, 84]. Both the plateau and the increase in density with increasing [Na_2O]/([Na_2O]+[K_2O]) ratio is explained in terms of packing density of atoms, showed in Figure 3.10b. There is a more effective packing of atoms when there is a mix in the size of atoms [85]. Of course, this reasoning with compactness and density is only valid when the ion densities are similar as in this case with sodium and potassium.

Tg and Tc
There is a minimum found when the [Na_2O]/([Na_2O]+[K_2O]) ratio is 0.5 for the glass transition temperature and crystallization temperatures (Figure 3.11a), as previously observed for mixed alkali glasses with at least 10 mol% alkali oxide [86]. These results can be compared to the minimum found when plotting measured temperatures at log η = 2 versus the [Na_2O]/([Na_2O]+[K_2O]) ratio, Figure 3.11b, however not so distinct as the minima for Tg and Tc.
The mechanism of permanent deformation of glass consists mainly of two processes, plastic flow (shear flow) and densification. Both these deformation processes are inelastic, densification with volume change and plastic flow without volume change but instead the matter is relocated to the surrounding area of the indentation. The resistance to these processes will be decisive for the penetration depth and the hardness value. The nature of the glass composition will control whether the resistance to densification or plastic flow will be most dominant. If the packing degree of atoms is high, then the resistance to densification most likely will be higher than a glass with lower packing density [91].

Yoshida et al developed a method for determining the volumes of densification respective total deformation volume of the indented glasses [92]. The volume change was estimated before and after annealing at a temperature of 0.9 x Tg (K). The densification part of the indentation corresponds to the volume of recovery, VR, i.e. when the glasses were annealed, the volume decrease caused by the densification process, was eliminated and the original volume was returned. Furthermore, Yoshida et al studied two sample series with three samples in each, 75SiO2–(10–x)MgO–xCaO–15Na2O and 65SiO2–(20–x)MgO–xCaO–15Na2O. The two sample series showed a maximum in hardness and minimum in Tg. The packing density, or compactness, of ions calculated using atomic radii is a very rough estimation of the real packing of ions, but it can be a useful measure when comparing the amount of free volume of different glass compositions. Therefore, the atomic packing density was calculated for the glass compositions taken from the paper of Yoshida et al. The compositions, packing densities, hardness values, and the recovery ratio, VR, are listed in Table D.1, Appendix D. The outcome from these calculations is plotted in Figure 3.13. There is a clear trend that the hardness increases as the packing density increases. The recovery ratio, VR, on the other hand decreases with increasing packing density. As seen, it is small changes in the packing density but both hardness and especially VR, the contribution to the hardness from densification, are affected quite much.

This is one demonstration that very small changes in the packing density can affect the hardness value and especially the densification part of the penetration volume. Therefore it is possible that the small changes in the packing density for the mixed alkali glasses in this investigation may affect the hardness value.

\[ \text{Figure 3.11b Temperature at a viscosity of } \log \eta = 2 (\text{Pa*s}) \text{ vs } [\text{Na}_2\text{O}]/([\text{Na}_2\text{O}]+[\text{K}_2\text{O}]) \text{ ratio for the } \text{Sb}_2\text{O}_3 \text{ containing glasses.} \]

\[ \text{Figure 3.12. Vickers hardness vs } [\text{Na}_2\text{O}]/([\text{Na}_2\text{O}]+[\text{K}_2\text{O}]) \text{ ratio).} \]

Vickers hardness
The trends observed for Vickers hardness are in accordance with previous investigations [84, 87-89]. There is a maximum when the molar ratio is about 0.5 for both the 0.49N indentation load and for the 0.98N indentation load, Figure 3.12. The hardness values are lower for the higher load and the maximum is not at all so pronounced as for the lower load. This is in line with the indentation size effect, which is manifested as an increase in hardness with decreasing depth of penetration when sharp indenters like pyramids are used [90].
The mechanism of permanent deformation of glass consists mainly of two processes, plastic flow (shear flow) and densification. Both these deformation processes are inelastic, densification with volume change and plastic flow without volume change but instead the matter is relocated to the surrounding area of the indentation. The resistance to these processes will be decisive for the penetration depth and the hardness value. The nature of the glass composition will control whether the resistance to densification or plastic flow will be most dominant. If the packing degree of atoms is high, then the resistance to densification most likely will be higher than a glass with lower packing density [91].

Yoshida et al developed a method for determining the volumes of densification respective total deformation volume of the indented glasses [92]. The volume change was estimated before and after annealing at a temperature of 0.9 x Tg (K). The densification part of the indentation corresponds to the volume of recovery, \( V_R \), i.e. when the glasses were annealed, the volume decrease caused by the densification process, was eliminated and the original volume was returned. Furthermore, Yoshida et al studied two sample series with three samples in each, 75SiO\(_2\)-(10-x)MgO-xCaO-15Na\(_2\)O and 65SiO\(_2\)-(20-x)MgO-xCaO-15Na\(_2\)O. The two sample series showed a maximum in hardness and minimum in Tg. The packing density, or compactness, of ions calculated using atomic radii is a very rough estimation of the real packing of ions, but it can be a useful measure when comparing the amount of free volume of different glass compositions. Therefore, the atomic packing density was calculated for the glass compositions taken from the paper of Yoshida et al. The compositions, packing densities, hardness values, and the recovery ratio, \( V_R \), are listed in Table D.1, Appendix D. The outcome from these calculations is plotted in Figure 3.13. There is a clear trend that the hardness increases as the packing density increases. The recovery ratio, \( V_R \), on the other hand decreases with increasing packing density. As seen, it is small changes in the packing density but both hardness and especially \( V_R \), the contribution to the hardness from densification, are affected quite much.

This is one demonstration that very small changes in the packing density can affect the hardness value and especially the densification part of the penetration volume. Therefore it is possible that the small changes in the packing density for the mixed alkali glasses in this investigation may affect the hardness value.
However, the differences of the Qn distribution for different glass compositions can explain the trends observed for the hardness values. As explained in section 1.2, Na\(^+\) ions are more inclined to form bonds with Q2 species than K\(^+\) ions which will form bonds to Q3 species. The mean Na\(^+\)-O bond length will be shorter and consequently the bond strength will be greater than in correspondingly K\(^+\)-O bond. In single alkali glasses, this can be a reason for the higher hardness value for 20Na\(_2\)O-10CaO-70SiO\(_2\) glass when compared to the analogous potassium glass. When sodium is replaced with potassium, there will be a more uneven distribution of the bond lengths and strengths if one assumes that sodium will bond to even more Q2 units than in the single alkali case and will be surrounded by more non-bridging oxygens than potassium ions. This small increase in the Na\(^+\)-O bond strength may cause the increase in hardness value until the \([Na_2O]/([Na_2O]+[K_2O])\) ratio is 0.5. For lower ratios, the higher bond strength of Na\(^+\)-O cannot compensate for the presence of more and weaker K\(^+\)-O and the decrease in hardness is very distinct, Figure 3.12.

3.2.2 Na\(_2\)O-CaO-BaO-SiO\(_2\) glasses

Both the density and the molar volume decrease almost linearly with substitution of CaO for BaO, see Figure 3.15a. These results are not surprising, since Ba\(^2+\) is larger than Ca\(^2+\) and the atomic weight is higher than the one for Ca\(^2+\).

In mixed alkali (Na-K) aluminosilicate glass the relation between densification and plastic deformation changed when the Na/K ratio was altered [84]. When the \([Na_2O]/([Na_2O]+[K_2O])\) ratio increased, the impression volume origin from densification part was increased and volume origin from plastic deformation was decreased. There was a minimum found for both the processes when the \([Na_2O]/([Na_2O]+[K_2O])\) ratio was of about 0.5, where the hardness value was highest.

However, in this study, the volume of recovery was not measured and thus the influence on the respective indentation processes, densification or plastic flow cannot be determined. Nevertheless, the small increase in packing density for the glasses containing both sodium and potassium (samples 10K and 15K) indicates that the increase in Vickers hardness origin from an increase resistance for densification.

Raman spectroscopy

The results of the Raman spectroscopy measurement show that the relative proportions of the Q\(^n\) units are different and depend on the modifier cations present in the melt. Figure 3.14 shows the area for the Q3 unit divided with area for the Q2 unit (AQ3/AQ2), which increases with increasing optical basicity. This is in good agreement with previous investigations [7, 8]. Even if there is an indication of an outlying value for the sample with a \([Na_2O]/([Na_2O]+[K_2O])\) ratio of 0.5, the experimental accuracy is not good enough to fully conclude this deviation from linearity.
However, the differences of the $Q^n$ distribution for different glass compositions can explain the trends observed for the hardness values. As explained in section 1.2, Na$^+$ ions are more inclined to form bonds with $Q^2$ species than K$^+$ ions which will form bonds to $Q^3$ species. The mean Na$^+$-O bond length will be shorter and consequently the bond strength will be greater than in correspondingly K$^+$-O bond. In single alkali glasses, this can be a reason for the higher hardness value for 20Na$_2$O-10CaO-70SiO$_2$ glass when compared to the analogous potassium glass. When sodium is replaced with potassium, there will be a more uneven distribution of the bond lengths and strengths if one assumes that sodium will bond to even more $Q^2$ units than in the single alkali case and will be surrounded by more non-bridging oxygens than potassium ions. This small increase in the Na$^+$-O bond strength may cause the increase in hardness value until the $[Na_2O]/([Na_2O]+[K_2O])$ ratio is 0.5. For lower ratios, the higher bond strength of Na$^+$-O cannot compensate for the presence of more and weaker K$^+$-O and the decrease in hardness is very distinct, Figure 3.12.

### 3.2.2 Na$_2$O-CaO-BaO-SiO$_2$ glasses

Both the density and the molar volume decrease almost linearly with substitution of CaO for BaO, see Figure 3.15a. These results are not surprising, since Ba$^{2+}$ is larger than Ca$^{2+}$ and the atomic weight is higher than the one for Ca$^{2+}$.
Both Tg and Tc exhibit a linear increase when plotted versus [CaO]/([CaO]+[BaO]) ratio, Figure 3.15b. Other studies of silicate glasses have found a minimum in Tg when two different alkaline earth ions with almost the same mole concentration [12, 93]. However, for bioactive phosphate glasses, an alteration of Tg was shown when SrO is substituted for CaO [94]. However, with only three samples in this study, it is not clear to identify a small minimum or maximum.

There is a linear relationship between Vickers hardness and the [CaO]/([CaO]+[BaO]) ratio for the 0.98N load, but for the 0.49N load there is a minimum when the [CaO]/([CaO]+[BaO]) ratio is 0.5, see Figure 3.15c. Other studies have found a maximum in hardness in mixed alkaline earth glasses [12, 13, 95], but there are studies reporting a linear relationship [95].

Data from Raman Spectroscopy showed that when BaO is substituted for CaO the AQ\textsuperscript{3}/AQ\textsuperscript{2} ratio increase with the barium content, Figure 3.14. Actually, there is a maximum observed when the [CaO]/([CaO]+[BaO]) ratio is 0.5. This ought to be further studied to confirm this indication of a non-additive behaviour of the Q\textsuperscript{n} distribution.

![Figure 3.15 a). Density and molar volume, b) Tg and Tc, c) Vickers hardness vs [CaO]/([CaO]+[BaO]) ratio.](image-url)
3.3 Cu(I) and Cu(II) in mixed alkali/mixed alkaline earth silicate glasses

In this section, the $[\text{Cu}^{2+}]/[\text{Cu}_{\text{tot}}]$ ratio and the molar extinction coefficients of $\text{Cu}^{2+}$, $\varepsilon_{\text{Cu}^{2+}}$, are reported and discussed. Furthermore has the Cu(I) and Cu(II) coordination spheres been determined in mixed alkaline glasses by means of X-ray absorption spectroscopy and Cu(II) was further characterised by UV-Vis-NIR spectroscopy.

3.3.1 $[\text{Cu}^{2+}]/[\text{Cu}_{\text{tot}}]$ and molar extinction coefficient of $\text{Cu}^{2+}$

The $[\text{Cu}^{2+}]/[\text{Cu}_{\text{tot}}]$ ratio increases with increasing sodium content, i.e. with decreasing basicity of the glass, Figure 3.16. Increasing basicity of the glass is expected to favour $\text{Cu}^{+}$, as mentioned in section 1.4. Even when taking the experimental error into account, one can identify this clear trend. As mentioned in the introduction, the $[\text{Cu}^{2+}]/[\text{Cu}_{\text{tot}}]$ ratio depend on the glass composition, the temperature and time of melting the glass. This makes it difficult to compare various values reported in other studies and to my data. The results from this investigation is, however, close to the results reported in another study using the same glass composition, almost the same temperature of melting and the same method used to determine the $[\text{Cu}^{+}]$ concentration [96].

![Figure 3.16](image-url)
The variation of the results reported in other studies of the ratio between \([Cu^+]\) and \([Cu^{2+}]\) concentration is large when using different methods or theoretical calculations. In paper III there is a more detailed discussion on this issue.

The molar extinction coefficient of \(Cu^{2+}\ (\varepsilon_{Cu^{2+}})\) is dependent on the concentration of copper \([Cu^{2+}]\). When the \([Cu^+]/[Cu_{tot}]\) ratio increases, the \(\varepsilon_{Cu^{2+}}\) decreases, and vice versa, Figure 3.16. The experimental uncertainty makes the results more difficult to interpret. Two studies found that the \(\varepsilon_{Cu^{2+}}\) in alkali-lime-silica glasses increase with decreasing size of alkali [97, 98], one show the opposite [96]. The extinction coefficient is principally a measure of the ease of electron transfers between the different energy levels involved, and thus it is dependent on the surrounding environment. From the EXAFS studies, paper V, it is shown that the size and distortion of the \(Cu^{2+}-O\) octahedron is about the same for all glass compositions in the study. However, even if the \(\varepsilon_{Cu^{2+}}\) vary to some degree in \((20-x)Na_2O-xK_2O-10CaO-70SiO_2\) glasses it is to a small extent.

In Figure 3.17, the \([Cu^{2+}]/[Cu_{tot}]\) ratio and extinction coefficient of \(Cu^{2+}\) is plotted for the \(20Na_2O-(10-x)CaO-xBaO-70SiO_2\) glasses. Even if the experimental error makes it difficult to draw conclusions from the data, it seems like the extinction coefficient is higher for the barium containing glasses than for the glass containing only calcium.

![Fig. 3.17. \([Cu^{2+}]/[Cu_{tot}]\) ratio and \(\varepsilon_{Cu^{2+}}\) vs \([CaO]/([CaO]+[BaO])\) ratio for \(20Na_2O-(10-x)CaO-xBaO-70SiO_2\) glasses.](image-url)
3.3.2 Coordination sphere of Cu(I) and Cu(II)

XANES
The XANES spectra for the samples 20KSB, 0KSB, 20K and 0KCe can be seen in Figure 3.18. The ratio $[\text{Cu}^+]/[\text{Cutot}]$ is most likely decreasing in the order $20\text{KSB}>0\text{KSB}>20\text{K}>0\text{KCe}$ due to basicity and oxidizing capacity. The compositions are listed in Table 1 paper V. Antimony was added to one sample containing potassium and to one sample containing sodium in order to reduce more Cu$^{2+}$ to Cu$^{+}$ (20KSB resp. 0KSB). Cerium was added to one sample in order to oxidize more Cu$^{+}$ to Cu$^{2+}$ (0KCe). The pre edge peak, at around 8985 eV, origin from the 1s-4p$_{x,y}$ transition in a linear coordination sphere of Cu$^{+}$ compounds [99] as observed in the spectra of Cu$_2$O. This peak is present in especially the spectra of the samples containing Sb, i.e. 20KSB and 0KSB. In the glass samples the peak is not as distinct as in the Cu$_2$O reference sample. The reason can be that the samples not only contain Cu$^{+}$, the sample 0KCe contains about 50% Cu$^{+}$ and the peak is much smaller than for the samples 0KSB and 20KSB where the $[\text{Cu}^+]/[\text{Cu}^{2+}]$ ratio is about 0.90. Another reason for the decreased peak intensity might be that not all Cu$^{+}$ is coordinated in a perfect linear coordination sphere and thus the peak becomes weaker. If the Cu$^{2+}$-site has no center of symmetry there will be a 1s-3d transition at about 8979 eV [44]. There is no such peak in none of the studied glass samples, thus the Cu$^{2+}$ coordination sphere ought to be centrosymmetric.
**EXAFS**

In paper V it is concluded that Cu$^+$ is coordinated with two oxygen ions mainly in linear coordination sphere. The final model concerning Cu$^{2+}$ was an elongated tetragonal distorted octahedron. The results showed no trends concerning the degree of tetragonal distortion for the five different glass compositions. The glass compositions and results are listed in Table 1 and 2 in paper V.

In EXAFS, there is a limitation in resolution between two shells of backscatters with similar atomic number and similar distances from the absorber (Cu$^+$ or Cu$^{2+}$) according to the equation [3.1] [100].

$$\Delta R = \pi/(2\Delta k)$$  \[3.1\]

$\Delta R$ is the distance between Cu and O and $k$ is the photoelectron wave vector. The $k$ range in this study is 3-12 Å$^{-1}$ which gives a $\Delta R$ of 0.17Å. The model used in paper V distinguishes between Cu$^+$-O and Cu$^{2+}$-O$_{eq}$ bond lengths and in this case there will be a $\Delta R$ of only about 0.10 Å, thus the model needs to be validated. In Table 3.1 the coordination number, CN, and Cu-O bond length, R are listed as the mean value for the Cu$^+$-O and Cu$^{2+}$-O$_{eq}$ bond length and coordination number. The CN for Cu$^+$ is expected to be two and the number of ligands in the equatorial plane for Cu$^{2+}$ is four, the [Cu$^{2+}$]/[Cu$_{tot}$] ratio can be calculated. This ratio has been compared with the [Cu$^{2+}$]/[Cu$_{tot}$] ratio determined with a wet chemical method (described in section 2.4) as well as with the model used when the Cu$^+$-O and Cu$^{2+}$-O bond lengths are separated, see Table 3.2.

### Table 3.1. The mean coordination number (CN), mean Cu-O distance (R) for Cu$^+$-O and Cu$^{2+}$-O$_{eq}$, EXAFS Debye-Waller factor $\sigma$, $k = 3$-12 Å$^{-1}$.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>CN</th>
<th>R (Å)</th>
<th>$\sigma^2$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0K</td>
<td>2.6 (±0.4)</td>
<td>1.86 (±0.02)</td>
<td>0.00562 (±0.001)</td>
</tr>
<tr>
<td>5K</td>
<td>2.6 (±0.4)</td>
<td>1.86 (±0.02)</td>
<td>0.00539 (±0.001)</td>
</tr>
<tr>
<td>10K</td>
<td>2.6 (±0.4)</td>
<td>1.86 (±0.02)</td>
<td>0.00589 (±0.001)</td>
</tr>
<tr>
<td>15K</td>
<td>2.6 (±0.4)</td>
<td>1.86 (±0.02)</td>
<td>0.00593 (±0.001)</td>
</tr>
<tr>
<td>20K</td>
<td>2.6 (±0.4)</td>
<td>1.86 (±0.02)</td>
<td>0.00578 (±0.001)</td>
</tr>
<tr>
<td>0KSb</td>
<td>2.3 (±0.3)</td>
<td>1.84 (±0.02)</td>
<td>0.00421 (±0.0008)</td>
</tr>
<tr>
<td>20KSb</td>
<td>2.2 (±0.3)</td>
<td>1.85 (±0.02)</td>
<td>0.00459 (±0.0008)</td>
</tr>
<tr>
<td>0KCe</td>
<td>2.7 (±0.4)</td>
<td>1.88 (±0.02)</td>
<td>0.00584 (±0.001)</td>
</tr>
</tbody>
</table>
The results in Table 3.2 show that the [Cu$^{2+}$/Cu$_{\text{tot}}$] ratios is comparable for all the used procedures, but there are three outliers which are highlighted in bold italic. The outliers for the samples 10K and 15K can be due to the issue of separation of the Cu$^{-}$-O and the Cu$^{2+}$-O distances. The odd value for the 0KCe sample is most probable due to the quite high uncertainty in the CN determination. However, the mean Cu-O bond length for 0KCe is 1.88 Å, in Table 3.1, and the mean bond length of Cu-O for a glass with no Sb$_2$O$_3$ added is 1.86 Å. This is indicates that the [Cu$^{2+}$/Cu$_{\text{tot}}$] ratio for the 0KCe sample should be higher than 0.35. The value from the model for the separated bond lengths is 0.49 and as the value from the wet chemical analysis is 0.50, the value of 0.35 is most likely not correct. The conclusion is that the model used in EXAFS calculations is reliable, but some refinements would be needed for the samples 10K and 15K.

Table 3.2. Comparison between [Cu$^{2+}$/Cu$_{\text{tot}}$] ratio determined using a wet chemical method, EXAFS results when Cu$^{-}$-O and Cu$^{2+}$-O$_{eq}$ distances are merged or separated.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>from paper III wet chemical analysis</th>
<th>merged Table 3.1</th>
<th>separated from paper V Table 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0K</td>
<td>0.34</td>
<td>0.30</td>
<td>0.33</td>
</tr>
<tr>
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<td>0.32</td>
<td>0.30</td>
<td>0.30</td>
</tr>
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<td>10K</td>
<td>0.31</td>
<td>0.30</td>
<td><strong>0.40</strong></td>
</tr>
<tr>
<td>15K</td>
<td>0.30</td>
<td>0.30</td>
<td><strong>0.38</strong></td>
</tr>
<tr>
<td>20K</td>
<td>0.30</td>
<td>0.30</td>
<td>0.33</td>
</tr>
<tr>
<td>20KSb</td>
<td>0.09*</td>
<td>0.10</td>
<td>-</td>
</tr>
<tr>
<td>0KCe</td>
<td>0.50*</td>
<td><strong>0.35</strong></td>
<td>0.49</td>
</tr>
</tbody>
</table>

*) Calculated from peak absorbance and $\varepsilon_{\text{Cu}^{2+}}$ from paper III.
If covalent bonding is taken into account, the ligand field theory, see section 1.6.1.2, can be the complement to CFT to explain the results. Results from EPR-studies, have shown that the degree of covalent character in the in-plane π-bonding will increase with increasing potassium content in Na₂O-K₂O-Al₂O₃-SiO₂ [46] and Na₂O-K₂O-SiO₂ glass [47]. According to ligand field theory the $\Delta_O$ will decrease with π-bonding when π-donor ligands such as O²⁻ are surrounding the Cu²⁺ ion. Increasing covalent character in π-bonds might explain the decrease in peak absorbance wavenumber for the samples in this study.

As the Cu(II) coordination sphere was interpreted as an elongated distorted octahedron, i.e. Jahn-Teller distorted. The expected electron transitions are $dxz, dyz \rightarrow dx^2-y^2$, $dxy \rightarrow dx^2-y^2$ and $dz^2 \rightarrow dx^2-y^2$ (Figure 1.2). Thus, three bands were used when the broad absorption band was deconvoluted. In paper V, the deconvoluted spectra and frequencies from the three bands are shown. The tetragonal distortion can be determined by comparing the energy needed for the $dz^2 \rightarrow dx^2-y^2$ and $dxy \rightarrow dx^2-y^2$ electronic transitions in the distorted octahedral [104]. The results from the comparison of the energies showed no difference in the degree of tetragonal distortion, except for the 20K glass which exhibited a somewhat lower degree of distortion than the rest of the glass compositions.

As expected from the high extinction coefficient of Cu²⁺ for the barium containing glasses, the intensity of their absorption bands are higher than the calcium containing glass 0K, see Figure 3.20. The peak positions are found at a somewhat lower wavenumber for the barium containing glasses than for the glass containing only calcium.

UV-Vis-NIR spectroscopy
When Na₂O is substituted for K₂O, the absorbance peak is shifted towards higher wavenumbers, as displayed in Figure 3.19. If considering an elongated distorted octahedron and the shift to higher wavenumber is interpreted by the crystal field theory, see section 1.6.1.1, the conclusion is that the most distorted octahedron will have the highest energy gap between the $dxz, dyz$ and $dx^2-dy^2$ energy levels. In this way to interpret the data, the crystal field splitting, $\Delta_O$, will remain the same for all studied samples. In this case, the glass containing most sodium will have the most distorted octahedron, i.e. the elongation in z – direction is greatest. Several authors came to this conclusion based on UV-Vis-NIR spectroscopy investigations [98, 101-103].

However, from the EXAFS measurements, it was concluded that there was no trend in the degree of tetragonal distortion for the studied samples, i.e. the distortion was about the same for all studied samples. With these results in mind, there must be another explanation, than only the CFT, to the change in the position of the absorbance peak.

![Figure 3.19. UV-Vis-NIR spectra of (20-x)Na₂O-xK₂O-10CaO-70SiO₂ glasses.](image)
If covalent bonding is taken into account, the ligand field theory, see section 1.6.1.2, can be the complement to CFT to explain the results. Results from EPR-studies, have shown that the degree of covalent character in the in-plane π-bonding will increase with increasing potassium content in Na₂O-K₂O-Al₂O₃-SiO₂ [46] and Na₂O-K₂O-SiO₂ glass [47]. According to ligand field theory the Δₒ will decrease with π-bonding when π-donor ligands such as O²⁻ are surrounding the Cu²⁺ ion. Increasing covalent character in π-bonds might explain the decrease in peak absorbance wavenumber for the samples in this study.

As the Cu(II) coordination sphere was interpreted as an elongated distorted octahedron, i.e. Jahn-Teller distorted. The expected electron transitions are dxz, dyz → dx²-y², dxy → dx²-y² and dz² → dx²-y² (Figure 1.2). Thus, three bands were used when the broad absorption band was deconvoluted. In paper V, the deconvoluted spectra and frequencies from the three bands are shown. The tetragonal distortion can be determined by comparing the energy needed for the dz² → dx²-y² and dxy → dx²-y² electronic transitions in the distorted octahedral [104]. The results from the comparison of the energies showed no difference in the degree of tetragonal distortion, except for the 20K glass which exhibited a somewhat lower degree of distortion than the rest of the glass compositions.

As expected from the high extinction coefficient of Cu²⁺ for the barium containing glasses, the intensity of their absorption bands are higher than the calcium containing glass 0K, see Figure 3.20. The peak positions are found at a somewhat lower wavenumber for the barium containing glasses than for the glass containing only calcium.

![Figure 3.20. UV-Vis-NIR spectra of 20Na₂O-(10-x)CaO-xBaO-70SiO₂ glasses.](image-url)
4 CONCLUDING REMARKS

The compositional effect on many properties, for both glasses and melts, are sometimes huge. It is important to know more about the relations of the properties to optimize the glass composition for certain purposes. In this section the most important conclusions from this thesis are compiled.

When sodium was substituted for potassium in (20-x)Na₂O-xK₂O-10CaO-70SiO₂ glass melts, the fining efficiency increased remarkably when the [Na₂O]/([Na₂O]+[K₂O]) ratio was about 0.5 or higher. The lower fining efficiency is explained by a much lower oxygen activity when the [Na₂O]/([Na₂O]+[K₂O]) ratio was lower than 0.5. The low oxygen activity in the potassium containing glasses is explained by the more basic character of the melt. In more basic glass melts, the temperature needs to be higher for the fining to start, i.e. for the oxygen activity to reach 1 bar. In this glass system the basicity of the melt was more important than the viscosity to receive a bubble free glass.

In 20Na₂O-(10-x)CaO-xMO-70SiO₂ (M = Mg, Sr, Ba) glasses the fining results could not be directly related to the basicity of the melts or the oxygen activity measurements. The barium containing glasses was easier fined than the Mg or Sr containing glasses. A mix of two different alkaline earth oxides resulted in a higher amount of remaining bubbles than was found for a single alkaline earth oxide.

The results from Raman spectroscopy showed an increase of the AQ⁵/AQ² ratio when the optical basicity was increased. This observation can also be explained by the cation field strength of the modifier ion, the AQ⁵/AQ² ratio decrease with increasing cation field strength.
The glasses in the (20-x)Na$_2$O-xK$_2$O-10CaO-70SiO$_2$ glass system exhibit an increase with a plateau in density and linear decrease in molar volume when increasing sodium content. There is a minimum in glass transition temperature and a maximum in Vickers hardness at a [Na$_2$O]/([Na$_2$O]+[K$_2$O]) ratio of 0.5. The maximum in hardness is explained by a maximum in packing density and an uneven distribution in Na$^+$-O and K$^+$-O bond strength in mixed alkali glasses.

In the 20Na$_2$O-(10-x)CaO-xBaO-70SiO$_2$ glass system, the density and molar volume decrease with calcium content. There is an increase in both glass transition temperature and Vickers hardness with increasing [CaO]/([CaO]+[BaO]) ratio.

XANES studies showed that Cu(I) is incorporated in the glass structure by two O$^{2-}$ mainly in linear coordination sphere. From EXAFS, the Cu(I)-O bond lengths were found to be 1.79-1.83 $\pm$ 0.02 Å for the different glass compositions.

Furthermore, EXAFS results showed that Cu(II) was present in a tetragonally distorted environment, an octahedron with four shorter Cu(II)-O bonds and two longer in axial position. The equatorial bond lengths were found to be 1.89-1.91 $\pm$ 0.02 Å and the axial 2.20-2.24 $\pm$ 0.02 Å. EXAFS and UV-Vis-NIR results showed no effects on the tetragonal distortion of the octahedron when the glass composition was altered.

In the (20-x)Na$_2$O-xK$_2$O-10CaO-70SiO$_2$ glass system, the variation of the Cu$^{2+}$ molar extinction coefficient is small. This is explained by the similar environment due to the same degree of tetragonal distortion of the octahedron.

The Cu$^{2+}$ molar extinction coefficient is higher for the barium containing glasses than for the glasses containing calcium, sodium and/or potassium.
ACKNOWLEDGEMENTS

Financial support from Sparbanksstiftelsen Kronan and KK-foundation is gratefully acknowledged.

My supervisor Prof. Bo Jonson, thank you for giving me this opportunity and for letting me go my own way, becoming an independent researcher. My co-supervisors Dr. Christina Stålhandske and Dr. Sharafat Ali, you are acknowledged for guiding me when I was totally lost and for all support you gave me during these years!

Thank you Dr. Stefan Karlsson, both as friend and scientist; among other things you did revise the entire thesis!

Prof. Ingmar Persson, thank you for help and support with EXAFS-analysis!

I would like to thank all colleagues in the Bioenergy group for all support and friendliness; it has been a pleasure knowing you all. Mario, Narges, Graciely, Anette and Farshid, I really liked having you PhD students around me to share anxiety and frustration with.

All personnel at Glafo; you are acknowledged for your practical help, kindness and support during these many years, soon I will finally be your colleague!

I would also like to thank:
Marianne G., for never stopped believing in me!
Ann-Charlotte L., for your pep-talks and good advices!
Ghazale N. for supporting the whole family!
Anna G., all those lunches really helped me to survive!
Stefan J. and Micael C for provide me with all computers that I needed, it made my life much easier!
Leo, I have felt your support on distance!

Daniel, Anna and Maria, I am happy to have you as my brother and sisters!
Mom and Dad, you have always done everything for me, thank you!

Vega and Olof, I am so grateful that I have you; from now on I will be home on weekends and evenings again! And finally, Andreas, thank you for always being there and listen to me, you really understood what I was talking about. Even this final chaotic period you still cared for me, I couldn’t have done this without you!
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### APPENDIX A - Glass compositions and results

#### Table A1. $R_2O$-CaO-SiO$_2$ glasses (R = Na, K) for bubble counting characterisation

Compositions in mol% and calculated optical basicity, $\Lambda_{\text{cal}}$, calculated viscosity, measured viscosity, number of bubbles.

Melting time is 55 minutes at either 1420°C or measured viscosity.

<table>
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<th>Sample code</th>
<th>$\text{SiO}_2$</th>
<th>$\text{Na}_2\text{O}$</th>
<th>$\text{K}_2\text{O}$</th>
<th>CaO</th>
<th>$\text{Sb}_2\text{O}_3$</th>
<th>$\Lambda_{\text{cal}}$</th>
<th>Calc. at viscosity log $\eta=2$ (°C)</th>
<th>Meas. at viscosity log $\eta=2$ (°C)</th>
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<td>1-1</td>
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<td>-</td>
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<td>10</td>
<td>10</td>
<td>0.2</td>
<td>0.604</td>
<td>-</td>
<td>1371</td>
<td>1894</td>
</tr>
<tr>
<td>1-16</td>
<td>69.8</td>
<td>5</td>
<td>15</td>
<td>10</td>
<td>0.2</td>
<td>0.612</td>
<td>-</td>
<td>1394</td>
<td>1458</td>
</tr>
<tr>
<td>1-17</td>
<td>69.9</td>
<td>0</td>
<td>19.9</td>
<td>10</td>
<td>0.2</td>
<td>0.619</td>
<td>-</td>
<td>1431</td>
<td>1113</td>
</tr>
<tr>
<td>1-18</td>
<td>74.8</td>
<td>16.6</td>
<td>0</td>
<td>8.3</td>
<td>0.2</td>
<td>0.568</td>
<td>1434</td>
<td>-</td>
<td>184</td>
</tr>
<tr>
<td>1-19</td>
<td>74.8</td>
<td>21.4</td>
<td>0</td>
<td>3.6</td>
<td>0.2</td>
<td>0.573</td>
<td>1408</td>
<td>-</td>
<td>257</td>
</tr>
<tr>
<td>1-20</td>
<td>74.8</td>
<td>20</td>
<td>0</td>
<td>5</td>
<td>0.2</td>
<td>0.571</td>
<td>1416</td>
<td>-</td>
<td>184</td>
</tr>
<tr>
<td>1-21</td>
<td>74.8</td>
<td>15</td>
<td>5</td>
<td>5</td>
<td>0.2</td>
<td>0.578</td>
<td>1446</td>
<td>-</td>
<td>209</td>
</tr>
<tr>
<td>1-22</td>
<td>74.8</td>
<td>12.5</td>
<td>7.5</td>
<td>5</td>
<td>0.2</td>
<td>0.582</td>
<td>-</td>
<td>203</td>
<td></td>
</tr>
<tr>
<td>1-23</td>
<td>74.8</td>
<td>10</td>
<td>10</td>
<td>5</td>
<td>0.2</td>
<td>0.586</td>
<td>1476</td>
<td>-</td>
<td>329</td>
</tr>
<tr>
<td>1-24</td>
<td>74.8</td>
<td>7.5</td>
<td>12.5</td>
<td>5</td>
<td>0.2</td>
<td>0.589</td>
<td>-</td>
<td>628</td>
<td></td>
</tr>
<tr>
<td>1-25</td>
<td>74.8</td>
<td>5</td>
<td>15</td>
<td>5</td>
<td>0.2</td>
<td>0.593</td>
<td>1506</td>
<td>-</td>
<td>569</td>
</tr>
<tr>
<td>1-26</td>
<td>74.8</td>
<td>0</td>
<td>20</td>
<td>5</td>
<td>0.2</td>
<td>0.600</td>
<td>1536</td>
<td>-</td>
<td>885</td>
</tr>
</tbody>
</table>
Table A2. $R_2O$-CaO-SiO$_2$ glasses ($R = \text{Na, K}$) for oxygen activity measurements

Compositions in mol% and calculated optical basicity, $\Lambda_{\text{cal}}$, EMF-data and $a_{O_2}$. The temperature of melting the glasses is 1420°C and melting time is 30 minutes for all samples in this table. In batches labelled with an a there are no NaNO$_3$ in the batch, in batches labelled with a b there are NaNO$_3$ added to the batch. There is 0.2 mol% Sb$_2$O$_3$ in all batches.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>SiO$_2$</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>CaO</th>
<th>$\Lambda_{\text{cal}}$</th>
<th>EMF (V)</th>
<th>$a_{O_2}$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2a</td>
<td>69.8</td>
<td>20</td>
<td>0</td>
<td>10</td>
<td>0.590</td>
<td>0.0694</td>
<td>1.436</td>
</tr>
<tr>
<td>1-4a</td>
<td>69.8</td>
<td>15</td>
<td>5</td>
<td>10</td>
<td>0.597</td>
<td>0.0601</td>
<td>1.107</td>
</tr>
<tr>
<td>1-8a</td>
<td>69.8</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>0.604</td>
<td>0.0383</td>
<td>0.605</td>
</tr>
<tr>
<td>1-10a</td>
<td>69.8</td>
<td>5</td>
<td>15</td>
<td>10</td>
<td>0.612</td>
<td>0.0367</td>
<td>0.578</td>
</tr>
<tr>
<td>1-12a</td>
<td>69.9</td>
<td>0</td>
<td>19.9</td>
<td>10</td>
<td>0.619</td>
<td>0.0133</td>
<td>0.302</td>
</tr>
<tr>
<td>1-18a</td>
<td>74.8</td>
<td>16.6</td>
<td>0</td>
<td>8.3</td>
<td>0.568</td>
<td>0.0836</td>
<td>2.126</td>
</tr>
</tbody>
</table>

Table A3. $R_2O$-BaO-SiO$_2$ glasses ($R = \text{Na, K}$) for bubble characterisation

Compositions in mol%, calculated optical basicity, $\Lambda_{\text{cal}}$, calculated temperature at log $\eta = 2$ and counted number of bubbles.

The temperature of melting the glasses is 1420°C and melting time is 55 minutes for all samples in this table.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>SiO$_2$</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>BaO</th>
<th>Sb$_2$O$_3$</th>
<th>$\Lambda_{\text{cal}}$</th>
<th>Calc. at viscosity log $\eta=2$ (°C)</th>
<th>Bubbles /100g glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>69.8</td>
<td>20</td>
<td>0</td>
<td>10</td>
<td>0.2</td>
<td>0.598</td>
<td>1454</td>
<td>1385</td>
</tr>
<tr>
<td>2-2</td>
<td>69.8</td>
<td>14</td>
<td>6</td>
<td>10</td>
<td>0.2</td>
<td>0.607</td>
<td>1493</td>
<td>1458</td>
</tr>
<tr>
<td>2-3</td>
<td>69.8</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>0.2</td>
<td>0.613</td>
<td>1519</td>
<td>1408</td>
</tr>
<tr>
<td>2-4</td>
<td>69.8</td>
<td>6</td>
<td>14</td>
<td>10</td>
<td>0.2</td>
<td>0.619</td>
<td>1544</td>
<td>1263</td>
</tr>
</tbody>
</table>

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Table A4. Na<sub>2</sub>O-M<sub>x</sub>O<sub>y</sub>-CaO-SiO<sub>2</sub> glasses (R = Na, K) for bubble counting characterisation
Compositions in mol%, calculated optical basicity, $\Lambda_{cal}$, calculated temperature at $\log \eta = 2$ and counted number of bubbles.
The temperature of melting the glasses is 1420°C and melting time is 30 minutes for all samples in this table. Nitrate and 0.2 mol% Sb<sub>2</sub>O<sub>3</sub> added.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>SiO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Na&lt;sub&gt;2&lt;/sub&gt;O</th>
<th>CaO</th>
<th>RO or R&lt;sub&gt;x&lt;/sub&gt;O&lt;sub&gt;y&lt;/sub&gt;</th>
<th>$\Lambda_{cal}$</th>
<th>Calc. at viscosity log $\eta = 2$ (°C)</th>
<th>Bubbles/100g glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-1</td>
<td>69.8</td>
<td>20</td>
<td>5</td>
<td>5 BaO</td>
<td>0.594</td>
<td>1385</td>
<td>461</td>
</tr>
<tr>
<td>3-2</td>
<td>69.8</td>
<td>20</td>
<td>5</td>
<td>10 BaO</td>
<td>0.599</td>
<td>1448</td>
<td>340</td>
</tr>
<tr>
<td>3-3</td>
<td>69.8</td>
<td>20</td>
<td>5</td>
<td>5 MgO</td>
<td>0.583</td>
<td>1362</td>
<td>465</td>
</tr>
<tr>
<td>3-4</td>
<td>69.8</td>
<td>20</td>
<td>5</td>
<td>10 MgO</td>
<td>0.577</td>
<td>1408</td>
<td>434</td>
</tr>
<tr>
<td>3-5</td>
<td>69.8</td>
<td>20</td>
<td>5</td>
<td>5 ZnO</td>
<td>-</td>
<td>1385</td>
<td>693</td>
</tr>
<tr>
<td>3-6</td>
<td>69.8</td>
<td>20</td>
<td>5</td>
<td>10 ZnO</td>
<td>-</td>
<td>1454</td>
<td>593</td>
</tr>
<tr>
<td>3-7</td>
<td>69.8</td>
<td>20</td>
<td>5</td>
<td>5 SrO</td>
<td>0.593</td>
<td>1386</td>
<td>1263</td>
</tr>
<tr>
<td>3-8</td>
<td>69.8</td>
<td>20</td>
<td>5</td>
<td>10 SrO</td>
<td>0.596</td>
<td>1458</td>
<td>959</td>
</tr>
<tr>
<td>3-9</td>
<td>69.8</td>
<td>20</td>
<td>9</td>
<td>1 B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.584</td>
<td>1313</td>
<td>172</td>
</tr>
<tr>
<td>3-10</td>
<td>69.8</td>
<td>20</td>
<td>6</td>
<td>4 B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.580</td>
<td>1283</td>
<td>0</td>
</tr>
<tr>
<td>3-11</td>
<td>69.8</td>
<td>20</td>
<td>9</td>
<td>1 Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.587</td>
<td>1349</td>
<td>341</td>
</tr>
<tr>
<td>3-12</td>
<td>69.8</td>
<td>20</td>
<td>6</td>
<td>4 Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.569</td>
<td>1446</td>
<td>910</td>
</tr>
<tr>
<td>3-13</td>
<td>69.8</td>
<td>20</td>
<td>9</td>
<td>1 TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-</td>
<td>1330</td>
<td>676</td>
</tr>
<tr>
<td>3-14</td>
<td>69.8</td>
<td>20</td>
<td>6</td>
<td>4 TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-</td>
<td>1372</td>
<td>183</td>
</tr>
</tbody>
</table>

Table A5. Na<sub>2</sub>O-M<sub>x</sub>O<sub>y</sub>-CaO-SiO<sub>2</sub> glasses (R = Na, K) for oxygen activity measurements
Compositions in mol%, calculated optical basicity, $\Lambda_{cal}$, EMF-data and $a_{O2}$.
The temperature of melting the glasses is 1420°C and melting time is 30 minutes for all samples in this table. There are no NaNO<sub>3</sub> added to these batch, therefore marked with a $a_{O2}$

<table>
<thead>
<tr>
<th>Sample code</th>
<th>SiO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Na&lt;sub&gt;2&lt;/sub&gt;O</th>
<th>CaO</th>
<th>BaO</th>
<th>SrO</th>
<th>B&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Sb&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</th>
<th>$\Lambda_{cal}$</th>
<th>EMF (V)</th>
<th>$a_{O2}$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-2a</td>
<td>69.8</td>
<td>20</td>
<td>10</td>
<td>0.2</td>
<td>0.598</td>
<td>0.0646</td>
<td>0.952</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-7a</td>
<td>69.8</td>
<td>20</td>
<td>5</td>
<td>0.2</td>
<td>0.593</td>
<td>0.0658</td>
<td>1.263</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-8a</td>
<td>69.8</td>
<td>20</td>
<td>10</td>
<td>0.2</td>
<td>0.596</td>
<td>0.0696</td>
<td>1.443</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-9a</td>
<td>69.8</td>
<td>20</td>
<td>9</td>
<td>0.2</td>
<td>0.584</td>
<td>0.0709</td>
<td>1.497</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table A6. R₂O-CaO-Al₂O₃-SiO₂ glasses (R = Na, K) for bubble counting characterisation
Compositions in mol%, calculated optical basicity, \( \Lambda_{cal} \), calculated temperature at \( \log \eta = 2 \) and counted number of bubbles. The temperature of melting the glasses is 1420°C and melting time is 40 minutes for all samples in this table. Nitrate and 0.2 mol% Sb₂O₃ added.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>SiO₂</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>Sb₂O₃</th>
<th>( \Lambda_{cal} )</th>
<th>Calc. Temp. in °C at viscosity ( \log \eta = 2 )</th>
<th>Meas. Temp. at viscosity ( \log \eta = 2 )</th>
<th>Bubbles /100g glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-1</td>
<td>75.51</td>
<td>16.92</td>
<td>0</td>
<td>7.22</td>
<td>0.14</td>
<td>0.2</td>
<td>0.566</td>
<td>1448</td>
<td>1423</td>
<td>395</td>
</tr>
<tr>
<td>4-2</td>
<td>73.31</td>
<td>16.08</td>
<td>2.09</td>
<td>7.24</td>
<td>1.06</td>
<td>0.2</td>
<td>0.576</td>
<td>1442</td>
<td>-</td>
<td>869</td>
</tr>
<tr>
<td>4-3</td>
<td>71.11</td>
<td>13.91</td>
<td>5.12</td>
<td>7.50</td>
<td>2.12</td>
<td>0.2</td>
<td>0.586</td>
<td>1448</td>
<td>-</td>
<td>1495</td>
</tr>
<tr>
<td>4-4</td>
<td>68.55</td>
<td>11.98</td>
<td>7.93</td>
<td>8.08</td>
<td>3.22</td>
<td>0.2</td>
<td>0.598</td>
<td>1447</td>
<td>1415</td>
<td>2068</td>
</tr>
</tbody>
</table>

Table A7. R₂O-CaO-Al₂O₃-SiO₂ glasses (R = Na, K) for \( a_{O₂} \) and Sb\(^{3+}/\)Sb\(^{5+}\) measurements
Compositions in mol% and calculated optical basicity, \( \Lambda_{cal} \), EMF-data, \( a_{O₂} \) and \([\text{Sb}^{3+}]/[\text{Sb}_{tot}]\). The temperature of melting the glasses is 1420°C and melting time is 35 minutes for all samples in this table. 0.2 mol% Sb₂O₃ is added and in batches marked with a there are no NaNO₃ in the batch, in batches marked with b there are NaNO₃ added to the batch.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>SiO₂</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>( \Lambda_{cal} )</th>
<th>EMF (V)</th>
<th>( a_{O₂} ) (bar)</th>
<th>([\text{Sb}^{3+}]/[\text{Sb}_{tot}]) (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-1a</td>
<td>75.51</td>
<td>16.92</td>
<td>0</td>
<td>7.22</td>
<td>0.14</td>
<td>0.566</td>
<td>-</td>
<td>-</td>
<td>0.92</td>
</tr>
<tr>
<td>4-2a</td>
<td>73.31</td>
<td>16.08</td>
<td>2.09</td>
<td>7.24</td>
<td>1.06</td>
<td>0.576</td>
<td>-</td>
<td>-</td>
<td>0.88</td>
</tr>
<tr>
<td>4-3a</td>
<td>71.11</td>
<td>13.91</td>
<td>5.12</td>
<td>7.50</td>
<td>2.12</td>
<td>0.587</td>
<td>-</td>
<td>-</td>
<td>0.85</td>
</tr>
<tr>
<td>4-4a</td>
<td>68.55</td>
<td>11.98</td>
<td>7.93</td>
<td>8.08</td>
<td>3.22</td>
<td>0.598</td>
<td>-</td>
<td>-</td>
<td>0.84</td>
</tr>
<tr>
<td>4-1b</td>
<td>75.51</td>
<td>16.92</td>
<td>0</td>
<td>7.22</td>
<td>0.14</td>
<td>0.566</td>
<td>0.111</td>
<td>4.596</td>
<td>0.74</td>
</tr>
<tr>
<td>4-2b</td>
<td>73.31</td>
<td>16.08</td>
<td>2.09</td>
<td>7.24</td>
<td>1.06</td>
<td>0.576</td>
<td>0.106</td>
<td>3.909</td>
<td>0.78</td>
</tr>
<tr>
<td>4-3b</td>
<td>71.11</td>
<td>13.91</td>
<td>5.12</td>
<td>7.50</td>
<td>2.12</td>
<td>0.587</td>
<td>0.085</td>
<td>2.188</td>
<td>0.87</td>
</tr>
<tr>
<td>4-4b</td>
<td>68.55</td>
<td>11.98</td>
<td>7.93</td>
<td>8.08</td>
<td>3.22</td>
<td>0.598</td>
<td>0.079</td>
<td>1.849</td>
<td>0.88</td>
</tr>
</tbody>
</table>
Table A8. Batched glass compositions in mol% for XAS measurements, determination of $\varepsilon_{\text{Cu}^{2+}}$, physical properties and Raman Spectroscopy measurements.

<table>
<thead>
<tr>
<th>Glass system</th>
<th>Sample code</th>
<th>SiO$_2$</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>CaO</th>
<th>CuO</th>
<th>Sb$_2$O$_3$</th>
<th>CeO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20R$_2$O-10CaO-70SiO$_2$</td>
<td>0K*</td>
<td>69.94</td>
<td>19.66</td>
<td>-</td>
<td>9.98</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(R= Na, K)</td>
<td>5K*</td>
<td>69.74</td>
<td>14.90</td>
<td>4.99</td>
<td>9.95</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>10K*</td>
<td>69.72</td>
<td>9.95</td>
<td>9.95</td>
<td>9.95</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>15K*</td>
<td>69.71</td>
<td>4.98</td>
<td>14.93</td>
<td>9.95</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>20K*</td>
<td>69.71</td>
<td>-</td>
<td>19.91</td>
<td>9.98</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Only for XAS

<table>
<thead>
<tr>
<th>Sample code</th>
<th>SiO$_2$</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>CaO</th>
<th>CuO</th>
<th>Sb$_2$O$_3$</th>
<th>CeO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0K</td>
<td>69.93</td>
<td>19.90</td>
<td>-</td>
<td>9.95</td>
<td>0.2</td>
<td>0.30</td>
<td>-</td>
</tr>
<tr>
<td>20K</td>
<td>69.92</td>
<td>-</td>
<td>19.91</td>
<td>9.95</td>
<td>0.2</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>0K</td>
<td>69.42</td>
<td>19.84</td>
<td>-</td>
<td>9.92</td>
<td>0.2</td>
<td>-</td>
<td>0.60</td>
</tr>
</tbody>
</table>

*) Contains maximum 0.02 mol% Al$_2$O$_3$ and <0.01 mol% Fe$_2$O$_3$.

Table A9. Batched glass composition in mol% for determination of $\varepsilon_{\text{Cu}^{2+}}$, physical properties and Raman Spectroscopy measurements.

<table>
<thead>
<tr>
<th>Glass system</th>
<th>Sample code</th>
<th>SiO$_2$</th>
<th>Na$_2$O</th>
<th>CaO</th>
<th>BaO</th>
<th>CuO</th>
<th>Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20Na$_2$O-10MO-70SiO$_2$</td>
<td>0K*</td>
<td>69.94</td>
<td>19.66</td>
<td>9.98</td>
<td>-</td>
<td>0.4</td>
<td>0.02</td>
</tr>
<tr>
<td>(M = Ca, Ba)</td>
<td>5Ba*</td>
<td>69.99</td>
<td>19.67</td>
<td>4.99</td>
<td>4.92</td>
<td>0.4</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>10Ba*</td>
<td>70.04</td>
<td>19.68</td>
<td>-</td>
<td>9.86</td>
<td>0.4</td>
<td>0.02</td>
</tr>
</tbody>
</table>

*) Contains maximum 0.02% mol% Al$_2$O$_3$ and <0.01 mol% Fe$_2$O$_3$. 
Table A10. Results physical properties

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Calc. optical basicity</th>
<th>ρ [kg/m³]</th>
<th>MV [cm³/mol]</th>
<th>C_g</th>
<th>T_g [°C]</th>
<th>T_c [°C]</th>
<th>H_v, 0.49N [GPa]</th>
<th>H_v, 0.98N [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0K</td>
<td>0.586</td>
<td>2.529</td>
<td>23.78</td>
<td>0.555</td>
<td>568</td>
<td>690</td>
<td>7.0(2)</td>
<td>5.5(2)</td>
</tr>
<tr>
<td>5K</td>
<td>0.593</td>
<td>2.518</td>
<td>24.53</td>
<td>0.554</td>
<td>555</td>
<td>695</td>
<td>7.1(3)</td>
<td>5.4(1)</td>
</tr>
<tr>
<td>10K</td>
<td>0.599</td>
<td>2.517</td>
<td>25.17</td>
<td>0.555</td>
<td>476</td>
<td>657</td>
<td>7.3(5)</td>
<td>5.5(4)</td>
</tr>
<tr>
<td>15K</td>
<td>0.605</td>
<td>2.515</td>
<td>25.82</td>
<td>0.556</td>
<td>565</td>
<td>715</td>
<td>6.7(3)</td>
<td>5.3(2)</td>
</tr>
<tr>
<td>20K</td>
<td>0.612</td>
<td>2.497</td>
<td>26.76</td>
<td>0.551</td>
<td>650</td>
<td>806</td>
<td>5.5(2)</td>
<td>4.8(1)</td>
</tr>
<tr>
<td>0K</td>
<td>0.586</td>
<td>2.529</td>
<td>23.77</td>
<td>0.555</td>
<td>568</td>
<td>690</td>
<td>7.0(2)</td>
<td>5.5(3)</td>
</tr>
<tr>
<td>5Ba</td>
<td>0.595</td>
<td>2.696</td>
<td>24.08</td>
<td>0.555</td>
<td>533</td>
<td>670</td>
<td>6.2(1)</td>
<td>5.2(3)</td>
</tr>
<tr>
<td>10Ba</td>
<td>0.605</td>
<td>2.847</td>
<td>24.51</td>
<td>0.553</td>
<td>494</td>
<td>625</td>
<td>6.2(3)</td>
<td>4.8(2)</td>
</tr>
<tr>
<td>Experimental uncertainties</td>
<td>-</td>
<td>±0.005</td>
<td>±0.05</td>
<td>±0.001</td>
<td>±5</td>
<td>±5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table A11. Calculated optical basicity, measured density, ε_{Cu^{2+}} is calculated according to equation [2.3] for glasses melted at 1420°C

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Calc. optical basicity</th>
<th>Density [kg/m³]</th>
<th>[Cu_2-]/[Cu_{tot}]</th>
<th>Log ([Cu^2+]/[Cu_{2-}])</th>
<th>Peak wavelength [nm]</th>
<th>A/mm (corrected value)</th>
<th>ε_{Cu^{2+}} [dm³ mol⁻¹ cm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0K</td>
<td>0.586</td>
<td>2.52945</td>
<td>0.336</td>
<td>0.30</td>
<td>787</td>
<td>0.2386</td>
<td>43 ± 6</td>
</tr>
<tr>
<td>5K</td>
<td>0.593</td>
<td>2.51823</td>
<td>0.320</td>
<td>0.33</td>
<td>796</td>
<td>0.2223</td>
<td>46 ± 6</td>
</tr>
<tr>
<td>10K</td>
<td>0.599</td>
<td>2.51665</td>
<td>0.308</td>
<td>0.35</td>
<td>806</td>
<td>0.2126</td>
<td>46 ± 6</td>
</tr>
<tr>
<td>15K</td>
<td>0.605</td>
<td>2.51475</td>
<td>0.305</td>
<td>0.36</td>
<td>825</td>
<td>0.1978</td>
<td>42 ± 6</td>
</tr>
<tr>
<td>20K</td>
<td>0.612</td>
<td>2.49740</td>
<td>0.301</td>
<td>0.37</td>
<td>853</td>
<td>0.1873</td>
<td>41 ± 6</td>
</tr>
<tr>
<td>5Ba</td>
<td>0.595</td>
<td>2.69576</td>
<td>0.309</td>
<td>0.38</td>
<td>794</td>
<td>0.2609</td>
<td>52 ± 6</td>
</tr>
<tr>
<td>10Ba</td>
<td>0.605</td>
<td>2.84661</td>
<td>0.314</td>
<td>0.34</td>
<td>796</td>
<td>0.2561</td>
<td>54 ± 6</td>
</tr>
</tbody>
</table>
APPENDIX B — Annealing curve

Annealing curve for glasses melted for bubble counting tests and the copper containing glass samples.

The annealing temperature is 500°C for most of the glasses. For glasses with calculated higher glass transition temperature, the annealing temperature is higher.
APPENDIX C — Electrochemical method

Verification of the thermodynamically correct response of oxygen sensors. According to method described in [34]. Since there are no standard melts with a defined oxygen pressure, the reversibility of the cell was verified thermodynamically.

The cell scheme for the isothermal measuring cell containing the melt with the ions \( \text{Sb}^{3+} \) and \( \text{Sb}^{5+} \) is

\[
\text{Pt, } \text{O}_2(r) | \text{melt, } \text{Sb}_2\text{O}_3(m), \text{Sb}_2\text{O}_5(m) | \text{Pt}
\]  

[C1]

The corresponding redox reaction between the polyvalent ions in the melt and the oxygen in the reference gas is

\[
\text{Sb}_2\text{O}_5(m) \rightleftharpoons \text{Sb}_2\text{O}_3(m) + \text{O}_2(r).
\]  

[C2]

The entropy change of the cell reaction is given by

\[
\Delta S_{\text{cell}} = S_{\text{Sb}_2\text{O}_5,m}^0 - S_{\text{Sb}_2\text{O}_3,m}^0 + S_{\text{O}_2,r}^0 - R \ln p_{\text{O}_2,r}
\]  

[C3]

The \( S^0 \) is standard entropies of the respectively compound. The entropy difference of the dissolved oxides is negligible compared to the entropy of oxygen gas, eq. C3 can be reduced to

\[
\Delta S_{\text{cell}} \approx \Delta S_{\text{O}_2,r} = S_{\text{O}_2,r}^0 - R \ln p_{\text{O}_2,r}
\]  

[C4]

This yields the temperature dependence of the EMF of the cell to

\[
\frac{dE_{\text{cell}}}{dT} = \frac{\Delta S_{\text{cell}}}{4F} \approx \frac{1}{4F} \left( S_{\text{O}_2,r}^0 - R \ln p_{\text{O}_2,r} \right)
\]  

[C5]

Calculated values of \( \frac{dE_{\text{cell}}}{dT} \) according to C5 are between 0.59 mV/K (1000°C) and 0.61 mV/K (1500°C) when pure \( \text{O}_2 \) was used as reference gas.

When measuring \( \frac{dE_{\text{cell}}}{dT} \) there need to be sufficient amount of \( \text{Sb}^{3+} \) and \( \text{Sb}^{5+} \) in the glass [63], so in our case 0.8 mol% \( \text{Sb}_2\text{O}_3 \) as 2 parts \( \text{Sb}_2\text{O}_3 \) and one part
NaSbO₃ (by weight) was added to the batch. The approximate base glass composition was 71SiO₂-19Na₂O-10CaO. The heating and cooling rate was 500 K/h, high enough to consider a “quasi-closed system” because the oxygen exchange with the environment is quite slow. See Figure C1.

The measured values for the cell varied from 0.59 mV/K at 1250°C to 0.44 mV/K at 1400°C and at higher temperature it was even lower, indicating that the cell cannot be used above 1400°C. It should be noticed that it was a 30 s delay from the measured voltage and the temperature, but anyhow the values should be slightly higher.

![Figure C1. Measurement of dE/dT for the cell with dT/dt = 500 K/h](image)

**Change of reference gas**

When changing the reference gas from air to pure oxygen, the emf between the reference electrode and the measuring electrode should be lower. This was studied, and the resulting diagram can be seen in figure C2. When switching from O₂ to air at 1200°C the theoretical E value for air should be -60.7 mV and the measured value is -61.3 mV. Those values are in very good agreement and this shows that the transport of air to the reference electrode works fine.

**Choice of raw materials**

Sand used in the industry contains impurities and especially Fe²⁺/³⁺ can interfere when studying a polyvalent element like Sb. Therefore results from oxygen activity measurements in glass melt made by industrial grade sand was compared to glass melts made by pure silica. There wasn’t any measureable difference between these two different silica materials and therefore the industrial grade was used in the sample melts.
**Inaccuracy of the method**

There are no commercially available standard samples with a fixed and specified O₂ activity/pressure. Results have been compared with other authors’ reported oxygen activities. But, if the amount of glass melted and melting time is not specified, the comparisons are less conclusive. During the initial melting the batch, the oxygen activity will increase to a certain level [55] (above 1 bar when fining) The oxygen activity will later decrease again, because the oxygen will diffuse into the air until the oxygen activity is similar to the oxygen partial pressure of the atmosphere. Nevertheless, it can be noted that our values are similar to those reported by others [40, 55, 56]. It should also be noted that the inaccuracy of the method cannot be neglected. If melting the glass samples in the same manner, crush them into similar size, heat the samples up with the same rate and measure the oxygen activity with electrodes that are fresh; there will still be differences in the values. These differences can be due to slight fluctuations in temperature, the heterogeneity of the melt because of high viscosity, corrosion of the reference electrode or the alumina covering of the measuring electrode or the fact that it can be glass left on the electrodes from previous measurements with different glass compositions. This means that there must be a sufficient number of samples for every glass composition to get representative values.
APPENDIX D — Packing densities

Table D.1. Glass compositions, Vickers hardness and Recovery Ratio taken from [92] and packing densities calculated using equation [2.5].

<table>
<thead>
<tr>
<th>Composition</th>
<th>Packing density, Cg = ρ(ΣfiVi/(ΣfiMi))</th>
<th>Vickers hardness, Hv GPa</th>
<th>Recovery Ratio, Vr</th>
</tr>
</thead>
<tbody>
<tr>
<td>75SiO₂-10CaO-15Na₂O</td>
<td>0.550</td>
<td>5.33</td>
<td>0.65</td>
</tr>
<tr>
<td>75SiO₂-5MgO-5CaO-15Na₂O</td>
<td>0.547</td>
<td>5.29</td>
<td>0.71</td>
</tr>
<tr>
<td>75SiO₂-10MgO-15Na₂O</td>
<td>0.539</td>
<td>5.02</td>
<td>0.79</td>
</tr>
<tr>
<td>65SiO₂-20CaO-15Na₂O</td>
<td>0.549</td>
<td>5.8</td>
<td>0.41</td>
</tr>
<tr>
<td>65SiO₂-10MgO-10CaO-15Na₂O</td>
<td>0.559</td>
<td>5.78</td>
<td>0.48</td>
</tr>
<tr>
<td>65SiO₂-20MgO-15Na₂O</td>
<td>0.551</td>
<td>5.46</td>
<td>0.71</td>
</tr>
</tbody>
</table>
Introduction

Antimony oxide has been used as fining agent for quite some time in "low temperature glass furnaces", in this context meaning industrial glass melting furnaces not capable of reaching temperatures high enough to activate decomposition of sulphate compounds that would contribute to the fining process. Many smaller sized glassworks still operate furnaces which have these process temperature limitations and are thus still dependant on the use arsenic or antimony oxide as the chemical fining agent. Substitution of arsenic oxide by antimony oxide has been demonstrated as a feasible route to reduce the industrial use of an environmentally hazardous element. However, antimony oxide will most likely not be a long term solution for chemically aided fining either, since questions are being raised about the environmental impact of antimony as well.

Thus finding an answer to the question of substitution of antimony oxide by a less toxic and non-colouring fining agent becomes more and more urgent. However, since all the details of the in situ conditions of fining/refining with antimony oxide are not fully known, it is necessary to study further the current fining process in order to evaluate possibilities for substitution. The redox active fining reaction of antimony can be described by

\[ \text{Sb}^{5+} + \text{O}_2^{-} \rightarrow \text{Sb}^{3+} + \frac{1}{2}\text{O}_2 \] (1)

The released oxygen will diffuse into the existing bubbles, increase the gas partial pressure and this will aid the physical removal of bubbles from the melt. Therefore, measurements of the melt oxygen activity \( a_{\text{O}_2} \) is a way to monitor in situ fining characteristics and conditions. Several investigations have been made that demonstrate that \( a_{\text{O}_2} \) increases with increasing temperature when the glass melt contains a polyvalent element like Sb.

However, very few studies have been published on how the glass composition is related to the fining efficiency and the \( a_{\text{O}_2} \) in the melt. The aim of this study is to observe how changes in the ratio \( \text{Na}_2\text{O}/\Sigma(\text{Na}_2\text{O}+\text{K}_2\text{O}) \) of a simple \( \text{R}_2\text{O}–\text{CaO}–\text{SiO}_2 \) glass affect the fining outcomes and the \( a_{\text{O}_2} \) of the melt.

Experimental

The approximate base glass composition studied was (in mol%) 20\( \text{R}_2\text{O}–\text{CaO}–70\text{SiO}_2 \) (\( \text{R}=\text{Na} \) and/or \( \text{K} \)). 0·2 mol% \( \text{Sb}_2\text{O}_3 \) was used as refining agent. In the majority of the glass batches, \( \text{NaNO}_3 \) or \( \text{KNO}_3 \) was added as oxidising agent (5·95 g \( \text{KNO}_3 \) or 5·00 g \( \text{NaNO}_3 \)/100 g \( \text{SiO}_2 \), corresponding to about 2·4 mol% nitrate). Most of the batches were melted at 1420°C. Some of the batches were melted keeping the melting viscosity at 100 dPa s, corresponding to temperatures between 1335–1431°C, depending on the glass composition. All raw materials were of industrial grade and the glass batch weight was about 200 g. The glasses used

Compositional effect on fining and oxygen activity in mixed alkali silicate glass

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Manuscript received 12 May 2008
Revised version received 15 August 2008
Accepted 18 August 2008

This study monitors, in situ, how alterations of the glass composition affect the results of fining and the oxygen activity \( a_{\text{O}_2} \) of the melt. The number of bubbles in annealed glass samples was determined in order to evaluate the fining efficiency. Electrochemical measurement of \( a_{\text{O}_2} \) was used to monitor in situ the fining characteristics and conditions of \( \text{Na}_2\text{O}–\text{K}_2\text{O}–\text{CaO}–\text{SiO}_2 \) glasses. The glasses investigated had a constant alkali oxide content, but a varying ratio \( \text{Na}_2\text{O}/\Sigma(\text{Na}_2\text{O}+\text{K}_2\text{O}) \). The \( \text{Sb}_2\text{O}_3 \) content was 0·2 mol% and \( \text{NaNO}_3 \) or \( \text{KNO}_3 \) was added as oxidising agent in most of the glasses. The results show that the number of bubbles decreases from approximately 1100 to around 200 bubbles/100 g glass and that \( a_{\text{O}_2} \) at 1400°C increases from 0·2 to 1·2 bar in the glass melt when increasing the \( \text{Na}_2\text{O}/\Sigma(\text{Na}_2\text{O}+\text{K}_2\text{O}) \) ratio from 0 to 1.

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Introduction

Antimony oxide has been used as fining agent for quite some time in “low temperature glass furnaces”, in this context meaning industrial glass melting furnaces not capable of reaching temperatures high enough to activate decomposition of sulphate compounds that would contribute to the fining process. Many smaller sized glassworks still operate furnaces which have these process temperature limitations and are thus still dependant on the use arsenic or antimony oxide as the chemical fining agent. Substitution of arsenic oxide by antimony oxide has been demonstrated as a feasible route to reduce the industrial use of an environmentally hazardous element. However, antimony oxide will most likely not be a long term solution for chemically aided fining either, since questions are being raised about the environmental impact of antimony as well.\textsuperscript{(1, 2)} Thus finding an answer to the question of substitution of antimony oxide by a less toxic and non-colouring fining agent becomes more and more urgent. However, since all the details of the \textit{in situ} conditions of fining/refining with antimony oxide are not fully known, it is necessary to study further the current fining process in order to evaluate possibilities for substitution. The redox active fining reaction of antimony can be described by

\begin{equation} \text{Sb}^{5+} + \text{O}^{2-} \leftrightarrow \text{Sb}^{3+} + 1/2\text{O}_{2} \end{equation}  

The released oxygen will diffuse into the existing bubbles, increase the gas partial pressure and this will aid the physical removal of bubbles from the melt. Therefore, measurements of the melt oxygen activity (a\textsubscript{O\textsubscript{2}}) is a way to monitor \textit{in situ} fining characteristics and conditions. Several investigations have been made that demonstrate that a\textsubscript{O\textsubscript{2}} increases with increasing temperature when the glass melt contains a polyvalent element like Sb.\textsuperscript{(3–7)} However, very few studies have been published on how the glass composition is related to the fining efficiency and the a\textsubscript{O\textsubscript{2}} in the melt. The aim of this study is to observe how changes in the ratio Na\textsubscript{2}O/(Na\textsubscript{2}O+K\textsubscript{2}O) of a simple R\textsubscript{2}O–CaO–SiO\textsubscript{2} glass affect the fining outcomes and the a\textsubscript{O\textsubscript{2}} of the melt.

Experimental

The approximate base glass composition studied was (in mol%) 20R\textsubscript{2}O–10CaO–70SiO\textsubscript{2} (R=Na and/or K). 0·2 mol% Sb\textsubscript{2}O\textsubscript{3} was used as refining agent. In the majority of the glass batches, NaNO\textsubscript{3} or KNO\textsubscript{3} was added as oxidising agent (5·95 g KNO\textsubscript{3} or 5·00 g NaNO\textsubscript{3}/100 g SiO\textsubscript{2}, corresponding to about 2·4 mol% nitrate). Most of the batches were melted at 1420°C. Some of the batches were melted keeping the melting viscosity at 100 dPa s, corresponding to temperatures between 1335–1431°C, depending on the glass composition. All raw materials were of industrial grade and the glass batch weight was about 200 g. The glasses used...
in the bubble counting test were melted in a ceramic crucible for 55 min in an electrically heated Super Kanthal furnace and the glasses for the oxygen activity measurement were melted in a Pt/Rh crucible for 30 min using the same furnace. All the samples were cast on a graphite plate. The samples used for determination of the number of bubbles were annealed before the analysis and the number of bubbles/100 g glass was calculated using Image Pro software. The samples used for electrochemical oxygen activity measurement were crushed in order to improve homogeneity and remelted in the Pt/Rh crucible. An yttria stabilised zirconia electrode was used as the reference electrode and platinum electrode as the measuring electrode. Similar methods have been described by others. \(^{(3-9)}\) The oxygen activity in the melt, \(a_{O2}\), was calculated from the Nernst equation

\[
\Delta E = \frac{RT}{4F} \ln \frac{a_{O2}(\text{melt})}{p_{O2}(\text{ref})}
\]

in which \(\Delta E\) is the electromotive force, \(R\) is the gas constant, \(T\) the temperature, \(F\) the Faraday constant and \(p_{O2}\) is 0·21 (the partial pressure of oxygen in air). The glasses were heated up to about 1100°C with a rate of 500 K/h, and then the electrodes were immersed while continuing heating to 1400°C. This temperature was maintained for 30 min. The \(\Delta E\) value was measured with a Keithley 2700 Multimeter/data acquisition system.

**Results and discussion**

Figure 1 shows the number of bubbles/100 g glass when changing the \(Na_2O/\Sigma(Na_2O+K_2O)\) ratio in the glass. The figure shows results for samples melted at the same temperature (1420°C) and for samples melted at the same calculated viscosity point (100 dPa, corresponding to 1335–1431°C). The samples prepared at 1420°C show a remarkable increase in the number of bubbles when changing the composition towards more \(K_2O\) in the glass. Around a \(Na_2O/\Sigma(Na_2O+K_2O)\) ratio of 0.5 there is a significant change in the curve with a maximum in the number of bubbles at a ratio of 0.4, then the number of bubbles decreases again. When adding more \(K_2O\) to the melt, the viscosity will increase and the change in bubble count will most likely depend on the impact of viscosity on the bubble rise velocity (according to Stokes’ law\(^{(19)}\)). The results when the effect of the viscosity on the bubble count was eliminated are, as mentioned earlier, shown in Figure 1. There are more bubbles in the glasses with higher \(Na_2O\) content. This is probably due to the oxygen activity in the melt, which is expected to decrease with decreasing temperature when polyvalent ions such as \(Sb^{+5}\) are present in the melt\(^{(2-7)}\).

According to Yamamoto et al.\(^{(4)}\) there is a certain temperature \(T_{\text{onset}}\), when fining with \(Sb_2O_3\) and \(NaNO_3\) where there is a rapid increase in \(a_{O2}\). This

**Figure 1. Bubbles/100 g glass versus the \(Na_2O/\Sigma(Na_2O+K_2O)\) ratio in 70SiO₂–10CaO–20R₂O glasses with 0·2% \(Sb_2O_3\) and \(KNO_3\) or \(NaNO_3\)**

**Figure 2. \(T_{\text{onset}}\) for 70SiO₂–10CaO–20Na₂O glass, with 0·2% \(Sb_2O_3\) and no nitrate, heating rate is 0·5 K/min**
temperature was about 1375°C for the TV-panel glass studied by Yamamoto. In this study there was such a $T_{onset}$ for the glass with the ratio Na$_2$O/$\Sigma$(Na$_2$O+K$_2$O)=1 and with 0·2% Sb$_2$O$_3$ and no nitrate at about 1360°C when heating the glass melt from 1300°C to 1420°C at a rate of 0·5 K/min, Figure 2. The fact that the temperature when melting glasses with higher Na$_2$O/$\Sigma$(Na$_2$O+K$_2$O) ratios is below $T_{onset}$ can explain the increase in the bubble count for these glasses. Figure 3 shows how the oxygen activity changes with the ratio Na$_2$O/$\Sigma$(Na$_2$O+K$_2$O) for glass melts with and without nitrate. It is obvious that the oxygen activity at 1400°C increases with increasing Na$_2$O content. As found by Yamamoto, this study also shows that the oxygen activity is higher when the batch contains nitrate and Sb$_2$O$_3$ compared to those only containing Sb$_2$O$_3$. The difference in oxygen activity is remarkable when nitrate is added to the batch and the difference is increased with increasing Na$_2$O/$\Sigma$(Na$_2$O+K$_2$O) ratio. The curves described in Figure 3 are inversely related to the curve in Figure 1 describing the bubble count monitored at constant melting temperature, 1420°C. There is a large change in the curve characteristic for $a_{O2}$ at a Na$_2$O/$\Sigma$(Na$_2$O+K$_2$O) ratio around 0·5 and this is at about the same composition when the number of bubbles is increased significantly, see Figure 1. The fining time in these tests was set to 55 min because this time resulted in a suitable number of bubbles for evaluation by the bubble counting equipment. From Figure 1 it is clear that 300 bubbles/100 g glass corresponds to a Na$_2$O/$\Sigma$(Na$_2$O+K$_2$O) ratio of about 0·68. In Figure 3, a glass composition with a Na$_2$O/$\Sigma$(Na$_2$O+K$_2$O) ratio of 0·68 will probably have an oxygen activity of about 3 bar at 1400°C in a melt with nitrate as oxidising agent. Melts of this composition and alkali ratio are typically used for industrial applications and give fully acceptable fining results.

**Conclusions**

This study shows that the number of bubbles decreases and that the $a_{O2}$ at 1400°C increases when the Na$_2$O/$\Sigma$(Na$_2$O+K$_2$O) ratio in the antimony fined alkali silicate glasses is increased. It also confirms the observations of other authors indicating that the $a_{O2}$ is higher for nitrate containing batches in which Sb$_2$O$_3$ has been added as the refining agent.

**Acknowledgement**

The authors are grateful to Karin Lundstedt at Glafo (the Glass Research Institute) who performed numerous experiments. The investigation was conducted with the financial support of Sparbanksstiften Kronan.

**References**

The influence of basicity on oxygen activity and antimony oxide fining efficiency in alkali alkaline earth aluminosilicate glasses

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Manuscript received 30 January 2009
Revision received 21 May 2009
Manuscript accepted 26 May 2009

The number of bubbles was monitored in antimony oxide fined \( R_2O - MxO_y - SiO_2 \) and \( R_2O - CaO - Al_2O_3 - SiO_2 \) glasses \((R=Na, K; M=Ca, Mg, Ba, Sr, Zn, B, Al, Ti, x=1 \text{ or } 2, y=1, 2 \text{ or } 3)\) in order to evaluate the fining efficiency. Electrochemical measurements of oxygen activity were used to, in situ, monitor the fining characteristics and conditions in some of the investigated glass melts. The results showed that an increase of the calculated optical basicity was related to an increased number of bubbles in the glass samples. The oxygen activity in the melt during fining decreased with increased optical basicity.

1. Introduction
Bubbles are generated in the glass melt when raw materials such as carbonates and nitrates are melted and/or when the atmospheric gases are trapped during the initial phase of batch melting. These bubbles will eventually rise to the surface by buoyancy, but this will take a long time if no mechanism speeds up the fining process. To aid the removal of bubbles, addition of a fining agent is necessary. In low temperature furnaces \((<1450^\circ\text{C})\) and the manufacturing of CRT glasses antimony oxide is used.(1,2) The fining active redox reaction of antimony can be described by

\[
Sb^{5+} + O_2^- \rightarrow Sb^{3+} + \frac{1}{2}O_2
\]

where \( O_2^- \) is the oxygen ion activity of the melt and \( O_2 \) is the physically dissolved oxygen within the holes of the network structure.

The released oxygen will diffuse into the existing bubbles, increase the gas partial pressure and this will aid the physical removal of bubbles from the melt – primary fining. In the second stage, or refining, the temperature is decreased and this will cause an increase in chemical solubility for the fining gases which will be dissolved into the melt again.

Antimony oxide is normally added as the compound of \( Sb_2O_3 \) and to make the fining agent active, sodium or potassium nitrate is added to oxidise \( Sb^{3+} \) to \( Sb^{5+} \). The simplified reaction is

\[
4NaNO_3 + 2Sb_2O_3 \rightarrow 2Na_2O + 2Sb_2O_5 + 4NO(g) + O_2(g)
\]

However, the use of antimony is questioned due to environmental issues and a reduction in the amount of \( Sb_2O_3 \) used or even a substitution is likely to be necessary in the near future. Even though antimony oxide has been used as fining agent for many years and investigations about the refining mechanism have been done,(4–8) the full mechanism of fining with antimony oxide and nitrate is still not understood. To be able to reduce the amount of \( Sb_2O_3 \) used or to find a substitute it is important to increase our knowledge of the fining mechanism with antimony.

Most previous investigations have been undertaken with the same glass composition and varying amounts of antimony oxide,(4,7,9,10) the fining time or temperature. (4,6,11,12) There are still some questions unanswered on how the fining reacts with modifications of the glass composition. Some investigations show that acidic melts, in general, are easier to fine than basic ones,(5,13) but there are no explanations as to why or, in some cases, not even a description of what glass compositions have been used. It is also reported that the oxygen release starts at a lower temperature in a more acidic glass melt than a basic melt(14) and in a previous study it has been shown that potassia–lime–silica glass melts are more difficult to get bubble free than equivalent (on a molar basis) soda–lime–silica melts and that the oxygen activities were higher in the melts containing soda than potassia.(15) \( K_2O \) is more basic than \( Na_2O \).(16)
The influence of basicity on oxygen activity and antimony oxide fining efficiency in alkali alkaline earth aluminosilicate glasses

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The number of bubbles was monitored in antimony oxide fined R₂O–MₓOᵧ–SiO₂ and R₂O–CaO–Al₂O₃–SiO₂ glasses (R=Na, K; M=Ca, Mg, Ba, Sr, Zn, B, Al, Ti, x=1 or 2, y=1, 2 or 3) in order to evaluate the fining efficiency. Electrochemical measurements of oxygen activity were used to, in situ, monitor the fining characteristics and conditions in some of the investigated glass melts. The results showed that an increase of the calculated optical basicity was related to an increased number of bubbles in the glass samples. The oxygen activity in the melt during fining decreased with increased optical basicity.

1. Introduction

Bubbles are generated in the glass melt when raw materials such as carbonates and nitrates are melted and/or when the atmospheric gases are trapped during the initial phase of batch melting. These bubbles will eventually rise to the surface by buoyancy, but this will take a long time if no mechanism speeds up the fining process. To aid the removal of bubbles, addition of a fining agent is necessary. In low temperature furnaces (<1450°C) and the manufacturing of CRT glasses antimony oxide is used. (1,2) The fining active redox reaction of antimony can be described by

\[ \text{Sb}^{5+} + \text{O}^{2-} \leftrightarrow \text{Sb}^{3+} + \frac{1}{2}\text{O}_2 \]  

where \( \text{O}^{2-} \) is the oxygen ion activity of the melt and \( \text{O}_2 \) is the physically dissolved oxygen within the holes of the network structure.

The released oxygen will diffuse into the existing bubbles, increase the gas partial pressure and this will aid the physical removal of bubbles from the melt – primary fining. In the second stage, or refining, the temperature is decreased and this will cause an increase in chemical solubility for the fining gases which will be dissolved into the melt again.

Antimony oxide is normally added as the compound of Sb₂O₃ and to make the fining agent active, sodium or potassium nitrate is added to oxidise Sb³⁺ to Sb⁵⁺. The simplified reaction is (3)

\[ 4\text{NaNO}_3 + 2\text{Sb}_2\text{O}_3 \rightarrow 2\text{Na}_2\text{O} + 2\text{Sb}_2\text{O}_5 + 4\text{NO}(g) + \frac{1}{2}\text{O}_2(g) \]  

However, the use of antimony is questioned due to environmental issues and a reduction in the amount of Sb₂O₃ used or even a substitution is likely to be necessary in the near future. Even though antimony oxide has been used as fining agent for many years and investigations about the refining mechanism have been done, (4–12) the full mechanism of fining with antimony oxide and nitrate is still not understood. To be able to reduce the amount of Sb₂O₃ used or to find a substitute it is important to increase our knowledge of the fining mechanism with antimony.

Most previous investigations have been undertaken with the same glass composition and varying amounts of antimony oxide, (4,7,10) the fining time or temperature. (4,6,11,12) There are still some questions unanswered on how the fining reacts with modifications of the glass composition. Some investigations show that acidic melts, in general, are easier to fine than basic ones, (5,13) but there are no explanations as to why or, in some cases, not even a description of what glass compositions have been used. It is also reported that the oxygen release starts at a lower temperature in a more acidic glass melt than a basic melt (14) and in a previous study it has been shown that potassium–lime–silica glass melts are more difficult to get bubble free than equivalent (on a molar basis) soda–lime–silica melts and that the oxygen activities were higher in the melts containing soda than potassium. (15) K₂O is more basic than Na₂O. (16)

The current study has been undertaken to investigate whether it is a general rule that the oxygen activity during fining is higher in more acidic melts.
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than in basic ones and whether the fining efficiency is related to the basicity of the glass. The possible correlation between basicity and fining results is discussed in terms of calculated optical basicity and the number of bubbles remaining in the glass.

2. Experimental

All samples were melted in an electrically heated Super Kanthal furnace at 1420°C and the fining agent used was 0.2 mol% Sb2O3 in most melts NaNO3 or KNO3 was added as oxidising agent (5 g KNO3; respective NaNO3/100 g SiO2).

The compositions for the investigated alkali calcium silicate, alkali alkaline earth silicate and alkali calcium aluminosilicate glasses and their respective calculated optical basicities can be found in Table 1. All raw materials were of industrial grade and glass batches weighed 200 g.

2.1. Fining tests – bubble counting

The fining was evaluated by determining the amount of bubbles remaining. Almost all samples used in the bubble counting test were melted in a ceramic crucible for 35 min and cast onto a graphite plate. Fining of sample 43 was completed after 55 min so the time was shortened to 40 min to be able to judge the fining for glasses 43–46. The glasses were annealed at 500°C for 1 h, and then the temperature was decreased by 0.5 °C/min to 400°C and thereafter down to room temperature.

Figure 1 with the number of bubbles in glasses in the left hand column are for non-nitrate melts and the right hand column for melts with nitrate. All samples contained 0.2 mol% Sb2O3. Temperatures in °C. Viscosity was calculated according to Lakatos correlation between basicity and fining results is related to the basicity of the glass. The possible correlation between basicity and fining results is discussed in terms of calculated optical basicity and the number of bubbles remaining in the glass.
0.5 °C/min to 350°C and thereafter down to room temperature by 5°C/min. After annealing the number of bubbles was analysed using Image Pro Software.

2.2. Oxygen activity measurement

Oxygen activity of the melts was measured for some of the glass compositions; in Table 1 these glasses are marked with an ‘a’. For these compositions the measurements were done both in melts with and without nitrate added to the batch. The samples were melted in a Pt/Rh crucible for 30 min (except for 43–46 which needed 35 min for complete dissolution) and then cast onto a graphite plate. The samples were crushed in order to improve homogeneity and remelted in the Pt/Rh crucible. An yttria stabilised zirconia electrode was used as reference electrode and a platinum electrode as measuring electrode. The methodology has been described by others. The oxygen activity in the melt, \( \alpha_{O_2} \), was calculated from the Nernst equation

\[
\Delta E = \frac{RT}{4F} \ln \frac{\alpha_{O_2} \text{(melt)}}{\alpha_{O_2} \text{(ref)}}
\]

where \( \Delta E \) is the electromotive force, \( R \) is the gas constant, \( T \) is temperature, \( F \) the Faraday constant and \( \alpha_{O_2} \) is 0.21 (the partial pressure of oxygen in air). The glasses were heated up to about 1100 °C at a rate of 500 K/h, and then the electrodes were immersed while continuing heating to 1400 °C. This temperature was maintained for 30 min. \( \Delta E \) was measured with a Keithley 2700 Multimeter/data acquisition system.

3. Results and discussion

3.1. Fining tests – bubble monitoring

In a previous study, the fining efficiency dependence of the Na/K ratio was studied in a 70SiO2–10CaO–20R2O glass. These results are compared in Figure 1 with the number of bubbles in glasses in the more acidic composition 75SiO2–5CaO–20R2O (R=Na and/or K).

It is clear that there are fewer bubbles in the glasses with higher silica contents and that in the higher silica glasses the potassia content can be higher before the increase in the number of bubbles. At a Na2O/(Na2O+K2O) ratio of about 0.65 the glass with 70 mol% silica has about the same number of bubbles as the glass with 75 mol% silica has at a Na2O/(Na2O+K2O) ratio of 0.5. There is a very large change in the number of bubbles when the Na2O/(Na2O+K2O) ratio is decreased from 0.65 to 0.5 for the glasses with 70 mol% silica and after that the number of bubbles is stabilised but decreases when the glass contains only K2O. This remarkable increase in the number of bubbles is not nearly so distinct in the glass with 75 mol% silica, but there is a slight increase in the number of bubbles at a somewhat lower Na2O/(Na2O+K2O) ratio. The decrease in number of bubbles for the K2O–CaO–SiO2 glass cannot be seen in the glass with 75 mol% silica and this may be due to the quite high viscosity arising from the K2O and SiO2 contents.

Interestingly, Orhon et al. reported a minimum in refining time when melting a mixed alkali glass. Their composition was 73SiO2–9CaO–18R2O (R=Na, K, wt%) and the minimum of refining time was obtained when the glass melt contained 9% K2O and 11% Na2O and not when the glass contained more Na2O. The refining behaviour can be explained by their use in wt% instead of mol%. When replacing Na2O for K2O and containing the same amount of wt% alkali in the glass, the molar amount of alkali will decrease when K2O is added instead of Na2O. This will probably make the glass less basic and easier to fine.

![Figure 1](image1.png)

**Figure 1. Bubbles/100 g glass versus Na2O/(Na2O+K2O) (in mol%) in alkali–lime–silica glasses – 0.2% Sb2O3 - nitrate**

![Figure 2](image2.png)

**Figure 2. Bubbles/100 g glass versus Na2O/(Na2O+K2O) in 70SiO2–10BaO–20R2O glasses – 0.2% Sb2O3 - nitrate**

![Figure 3](image3.png)

**Figure 3. Number of bubbles versus RO in Na2O–RO–SiO2 glasses with 0.2 mol% Sb2O3**

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The results for glasses with the base composition 70SiO\textsubscript{2}–10BaO–20RO showed the same phenomenon as the glasses with CaO, i.e. at a Na\textsubscript{2}O/(Na\textsubscript{2}O+K\textsubscript{2}O) ratio of about 0·5–0·6 there is a distinct increase in the number of bubbles, see Figure 2. This shows that not exclusively lime containing glasses give rise to this type of fining behaviour in mixed alkali glasses.

When substituting CaO completely or partially by BaO, MgO, ZnO or SrO in a 70SiO\textsubscript{2}–10CaO–20Na\textsubscript{2}O glass the number of bubbles increased in all of the investigated compositions as can be seen in Figure 3.

It is worth mentioning, that a mixture of CaO and another RO increases the amount of bubbles compared to when only one single metal oxide is present in the glass. The very high number of bubbles in the glasses containing SrO cannot be explained and therefore different ratios of SrO and CaO were melted and bubbles were counted. SrO was also combined with MgO and BaO and the resulting glasses were analysed. In Figure 4 it can be seen that all these samples contain quite high numbers of bubbles. This phenomenon cannot exclusively be explained by oxygen activity measurements or the fact that SrO has a particular high basicity, as other aspects such as material grain size, etc. must also be considered.

In Figure 5 the number of bubbles versus composition is shown when 1 or 4 mol\% of CaO is substituted by B\textsubscript{2}O\textsubscript{3}, Al\textsubscript{2}O\textsubscript{3} or TiO\textsubscript{2} so that the base composition was 70SiO\textsubscript{2}–2CaO–(10–\textit{z})RO–20Na\textsubscript{2}O. B\textsubscript{2}O\textsubscript{3} is known to be typically acidic in glasses and at the same time it will decrease the viscosity and surface tension. In this study it acted as an efficient fining aid. According to Sun,\textsuperscript{[8]} TiO\textsubscript{2} has a low basicity and therefore it was interesting to study the substitution of CaO by TiO\textsubscript{2}. When only 1 mol\% of CaO was substituted by TiO\textsubscript{2}, the amount of bubbles was increased, but a larger amount of TiO\textsubscript{2} improved the fining efficiency. Some raw materials, like feldspar, contain Al\textsubscript{2}O\textsubscript{3} and it is known as a property modifier in silicate glasses. It is quite acidic in glasses, but it also will increase the viscosity. When replacing CaO by Al\textsubscript{2}O\textsubscript{3} the number of bubbles increased.

In Figure 6, the number of bubbles is plotted against the calculated optical basicity for the investigated RO–R\textsubscript{2}O–SiO\textsubscript{2} glasses. It can be seen that the number of bubbles tends to increase with increasing optical basicity of the glasses. This behaviour can be explained from the oxygen activity measurements in the next section.

For the investigated samples in Figure 6, the viscosities also varied which makes it difficult to discuss whether the increase or decrease of bubbles is due to the viscosity or any other property such as the basicity. In Figure 7 the results are given for alkali calcium aluminosilicate glasses (sample codes 43–46).
with the same calculated viscosity and very different basicities. It is very clear that when the optical basicity is increased the number of bubbles is also increased.

The increase in the number of bubbles at about the same amount of K₂O as Na₂O presented in Figure 1 for the glasses with 70 mol% SiO₂ is not obviously explained from the relation between bubble count and optical basicity. The effect observed is suggested to be due to the so called mixed alkali effect. It is known that the diffusion coefficient for sodium will decrease when the potassium content is increased and vice versa in mixed alkali glasses. This relation between ionic diffusivity and glass composition gives rise to the mixed alkali effect in electric conductivity which passes through a deep minimum as the ratio of sodium to total alkali oxide varies from zero to one. It is possible that these properties affect the transport of oxygen to existing bubbles and make the number of bubbles vary so strongly. This is a suggestion and cannot be proven without further investigations. In addition it should be noted that there was no obvious mixed alkali effect in the glasses with 75 mol% SiO₂.

3.2. Oxygen activity measurements

The results from the oxygen activity measurements of the alkali-alkaline earth-silicate glass melts at 1400 °C are plotted against the calculated optical basicity in Figure 8 for non-nitrates glass melts and for the glass melts with nitrate in Figure 9. Some of the oxygen activity results were published in Grund & Jonson. It can be noted that oxygen gas evolution takes place if the oxygen activity of a melt exceeds the value attributed to an oxygen fugacity of 1 bar.

As was shown in Grund & Jonson there is a large difference in the oxygen activity when nitrate is present in the batches compared to those only having Sb₂O₃ as fining agent, especially for glass melts with low optical basicities. It is also obvious from Figures 8 and 9 that the oxygen activity is increased when the basicity is decreased, which is the opposite to the results of Thiemson et al. However, our samples were only melted for 30 min at 1420°C and then crushed and remelted to 1400°C and then oxygen activity was measured immediately, while Thiemson's samples were first melted during 4 h at 1450°C, then crushed and remelted for 5 h at the same temperature before starting measuring the oxygen activity in the melts. These differences in sample preparation procedures not only would explain the opposite results, but it is not clear if Thiemson's glass melts contained polyvalent ions or not. If the melts did not contain any polyvalent ions, it could explain why the oxygen partial pressure is higher in basic melts than in acidic ones, because there will be more O₂ in melts with higher basicity which are in equilibrium with free...
oxygen. El Harfouri & Hilger concluded that for glasses with higher alkali content (higher basicity), the maximum oxygen potential (i.e. during fining) tend to be lower than for more acidic melts, in accordance with the pattern shown in Figure 8.

The glasses with sample codes 1, 3 and 7 have the lowest amount of bubbles (Figure 1) and the highest oxygen activity (Figure 8). This is a likely reason why more acidic glass melts are more easily fined, i.e. the oxygen content (that can aid the fining) is higher in more acidic melts. The exceptions are the SrO containing glasses, which have a quite high oxygen activity but still have about 1000 bubbles/100 g glass and which is likely to be due to other, not investigated parameters.

The results from glass melts (numbers 43-46) with the same viscosity but very different basicities can be found in Figure 10, and there is a clear tendency that the more acidic melt the higher oxygen activity. The number of bubbles is lower in an acidic glass than in a more basic glass. In Figure 11 it can be seen that the oxygen activity is inversely proportional to the number of bubbles of these glass compositions.

4. Concluding remarks

It is easier to obtain bubble free glass melts with higher Na2O/(Na2O+K2O) ratios than with lower ratios in antimony oxide fined 20R2O–10CaO–70SiO2, 20R2O–5CaO–75SiO2 as well as 20R2O–10BaO–70SiO2 glasses. There is a sudden increase in the number of bubbles for these glasses containing roughly the same amount of sodium and potassium oxide. The clear trend observed is that more basic glass melts contain more bubbles than the acidic ones and this can be explained by the lower oxygen activity in these basic glass melts during the fining process. Measurements of antimony oxide fined Na2O–K2O–CaO–Al2O3–SiO2 glasses with the same viscosity and very different calculated optical basicities showed that the number of bubbles increased and the oxygen activity decreased with glass basicity. This indicates that the basicity of these melts strongly affects the fining efficiency.

Fining is a complex process. Additional parameters to the glass basicity, bubble monitoring or measured oxygen activity may be needed for a full picture. This is especially noticeable for the samples containing SrO and mixed alkaline earth oxides in sodium alkaline earth silicate glasses, where the basicity cannot explain why the number of bubbles is so high. Nevertheless, the study presented here makes it easier to predict how glass melts will behave when the chemical composition is modified.

Acknowledgements

The authors are grateful to the financial support of Sparbanksstiftelsen Kronan.

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Introduction

When adding CuO to a silicate glass melt without any reducing agents, copper will exist as two ions, Cu\(^+\) and Cu\(^{2+}\). The cuprous ion, Cu\(^+\), is colourless and absorbs light in the ultraviolet region. Cu\(^{2+}\) ions absorb light in the visible spectra with a broad peak at about 800 nm in soda–lime–silica glasses and thus give rise to a blue to turquoise-blue colour. This band is asymmetrical and this is caused by an elongated tetragonal distortion of the CuO\(_{6}\) octahedra which makes the complex consist of four short in-plane bond lengths and two longer axial bond lengths.\(^{(1–4)}\) This effect is known as Jahn–Teller distortion. The broad band most likely consists of two or three overlapping Gaussian curves, depending on the degree of tetragonal distortion.\(^{(2)}\)

As well as being a colorant Cu\(^{2+}\) is also a so called probe ion and can provide useful information of the local structure of the surrounding environment. This means that Cu\(^{2+}\) is a relatively easy ion to study and data from, for example, UV-vis-NIR spectroscopy will aid the investigation of the base glass structure. But, there are also difficulties in analysing the cupric ion, especially when it comes to determining the concentration of Cu\(^{2+}\) as well as Cu\(^+\) in glasses or glass melts. The equilibrium between the copper ions and oxygen is very dependent on the base glass composition and obviously also on the physically dissolved oxygen in the melt:

$$4\text{Cu}^{2+} + 2\text{O}^2^- \leftrightarrow 4\text{Cu}^+ + \text{O}_2$$ \(^{(1)}\)

The temperature during the melting procedure has also a big influence on the equilibrium; when temperature is increased, the cuprous concentration is increased. Due to the many factors that can affect the equilibrium, there have been several investigations in the past concerning the Cu\(^{2+}\) colouring of silicate glasses.\(^{(3–13)}\) In some of them the Cu-concentration is altered with a certain glass composition, \(^{(6,13)}\) but in most investigations the Cu-content is constant with varying glass composition.\(^{(3,4,7–12,14,15)}\) The compositional change is often in soda–lime–silica glasses by variation in the mutual proportion, \(^{(7,8,12,14)}\) by substituting one alkali by another, \(^{(3,8,9,15)}\) or by replacing lime by strontia or baria.\(^{(11)}\) Only a few investigations have been made with mixed alkali\(^{(15–17)}\) or mixed alkaline earth containing melts with more industrial-like compositions.\(^{(4,13)}\)

The previously reported results of the ratio of Cu\(^+\) and Cu\(^{2+}\) differ from each other and this is probably due to the difficulties analysing these different oxidation states and also a result of the many factors that influence the equilibria, as mention above. The extinction coefficient, \(\varepsilon\), is a measure of the absorbing strength of a colour centre and is very dependent of the concentration of the specific species. Consequently, when the concentrations of Cu\(^{2+}\) vary when different methods are used; \(\varepsilon_{\text{Cu}^{2+}}\) also vary.

In this paper, the varying results of the extinction coefficient and the \([\text{Cu}^+/\text{Cu}^{2+}]\) ratio in alkali–lime–silica glasses in previous investigations is discussed. The paper will also provide a new study of how \(\varepsilon_{\text{Cu}^{2+}}\) changes when replacing sodium by potassium gradually and also how \(\varepsilon_{\text{Cu}^{2+}}\) is affected when CaO is substituted by BaO in alkali–alkaline earth–silica glasses. Because, despite all investigations almost none have studied how mixed alkali or mixed alkaline earth affects the extinction coefficient of Cu\(^{2+}\).
Introduction

When adding CuO to a silicate glass melt without any reducing agents, copper will exist as two ions, Cu\(^{+}\) and Cu\(^{2+}\). The cuprous ion, Cu\(^{+}\), is colourless and absorbs light in the ultraviolet region. Cu\(^{2+}\) ions absorb light in the visible spectra with a broad peak at about 800 nm in soda–lime–silica glasses and thus give rise to a blue to turquoise-blue colour. This band is asymmetrical and this is caused by an elongated tetragonal distortion of the CuO\(_6\) octahedra which makes the complex consist of four short in-plane bond lengths and two longer axial bond lengths.\(^{(1–4)}\) This effect is known as Jahn–Teller distortion. The broad band most likely consists of two or three overlapping Gaussian curves, depending on the degree of tetragonal distortion.\(^{(2)}\)

As well as being a colorant Cu\(^{2+}\) is also a so called probe ion and can provide useful information of the local structure of the surrounding environment. This means that Cu\(^{2+}\) is a relatively easy ion to study and data from, for example, UV-vis-NIR spectroscopy will aid the investigation of the base glass structure. But, there are also difficulties in analysing the cupric ion, especially when it comes to determining the concentration of Cu\(^{2+}\) as well as Cu\(^{+}\) in glasses or glass melts. The equilibrium between the copper ions and oxygen is very dependent on the base glass composition and obviously also on the physically dissolved oxygen in the melt:

\[
4\text{Cu}^{2+} + 2\text{O}^{2−} \rightleftharpoons 4\text{Cu}^{+} + \text{O}_2
\] (1)

The temperature during the melting procedure has also a big influence on the equilibrium; when temperature is increased, the cuprous concentration is increased. Due to the many factors that can affect the equilibrium, there have been several investigations in the past concerning the Cu\(^{2+}\) colouring of silicate glasses.\(^{(3–13)}\) In some of them the Cu-concentration is altered with a certain glass composition,\(^{(6,13)}\) but in most investigations the Cu-content is constant with varying glass composition.\(^{(3,4,7–12,14,15)}\) The compositional change is often in soda–lime–silica glasses by variation in the mutual proportion,\(^{(7,8,12,14)}\) by substituting one alkali by another,\(^{(3,8,9,15)}\) or by replacing lime by strontia or baria.\(^{(11)}\) Only a few investigations have been made with mixed alkali\(^{(15–17)}\) or mixed alkaline earth containing melts with more industrial-like compositions.\(^{(4,13)}\)

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In this paper, the varying results of the extinction coefficient and the \([\text{Cu}^{+}] / [\text{Cu}^{2+}]\) ratio in alkali–alkaline earth–silica glasses in previous investigations is discussed. The paper will also provide a new study of how \(\varepsilon_{\text{Cu}^{2+}}\) changes when replacing sodium by potassium gradually and also how \(\varepsilon_{\text{Cu}^{2+}}\) is affected when CaO is substituted by BaO in alkali–alkaline earth–silica glasses. Because, despite all investigations almost none have studied how mixed alkali or mixed alkaline earth affects the extinction coefficient of Cu\(^{2+}\).
in mixed alkali–alkaline earth–silica glasses, even though many commercial coloured glasses contain a blend of these ions. The CIE L°a°b° colour system has been used to demonstrate the colour difference between 2 mm thick glass pieces. There will also be a short explanation concerning the shape and position of the cupric absorption band.

Experimental

Sample preparation

Samples were melted in an electrically heated Super Kanthal furnace at 1420°C for 1 h and then transferred to another electrically heated furnace held at 1300°C for 1 h while stirring to make the samples homogeneous. Then, the temperature was increased to 1420°C while continuously stirring for a further 2 h and finally held for 1 h without stirring to make all bubbles disappear. The melt was cast on an iron mould and transferred to an annealing furnace at 500°C. After 60 min the temperature was decreased at 0-5°C/min down to 350°C and thereafter at 5°C/min down to 50°C.

The studied batched glass compositions are listed in Table 1, the raw materials were of industrial grade.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>SiO₂</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>CaO</th>
<th>CuO</th>
<th>BaO</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>0K</td>
<td>69.94</td>
<td>19.66</td>
<td>9.88</td>
<td>-</td>
<td>0.4</td>
<td>0.02</td>
<td></td>
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<tr>
<td>5K</td>
<td>69.74</td>
<td>14.90</td>
<td>4.99</td>
<td>9.95</td>
<td>-</td>
<td>0.4</td>
<td>0.02</td>
</tr>
<tr>
<td>10K</td>
<td>69.72</td>
<td>9.95</td>
<td>9.95</td>
<td>-</td>
<td>-</td>
<td>0.4</td>
<td>0.02</td>
</tr>
<tr>
<td>15K</td>
<td>69.71</td>
<td>4.98</td>
<td>14.93</td>
<td>9.95</td>
<td>-</td>
<td>0.4</td>
<td>0.02</td>
</tr>
<tr>
<td>20K</td>
<td>69.71</td>
<td>-</td>
<td>19.91</td>
<td>9.98</td>
<td>-</td>
<td>0.4</td>
<td>0.02</td>
</tr>
<tr>
<td>20Na₂O–10MO–70SiO₂ (M=Ca, Ba)</td>
<td>69.99</td>
<td>19.67</td>
<td>-</td>
<td>4.99</td>
<td>4.92</td>
<td>0.4</td>
<td>0.02</td>
</tr>
<tr>
<td>5Ba</td>
<td>70.04</td>
<td>19.68</td>
<td>-</td>
<td>9.86</td>
<td>-</td>
<td>0.4</td>
<td>0.02</td>
</tr>
<tr>
<td>10Ba</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Batched glass compositions in mol%

and 780 nm. Spectra in all figures are normalized to 1 mm thickness and for colour coordinate calculations a thickness of 2 mm was used.

When deconvolution and the integrated area of the absorption peak was needed for a wavelength up to 3300 nm, an Agilent Technologies Cary 5000 was used. The scan rate was chosen to be 600 nm/min and slit size 2 nm. The samples were measured from 3300 nm to 200 nm with 1 nm steps.

Determination of the extinction coefficient of Cu²⁺

The amount of Cu⁺ and the total amount of Cu was determined, and then the amount of Cu²⁺ could be calculated as the difference between these two measurements. The glasses were melted in the same way as described above. The samples were crushed and then further divided to very fine particles. The total amount of Cu was determined using a Perkin-Elmer AAAnalyt 400 Atomic Absorption Spectrometer. The method for Cu⁺ determination was first described by Zaman & Paul. In this study the method was modified and the procedure followed was:

0-02–0.5 g sample as powder was blended with 1 ml 0.75% iodine monochloride, 20 ml HCl (1 part conc. HCl + 1 part H₂O) and with 5 ml 40% HF in a plastic container with lid. The sample containers were placed in an ice bath for 30 min and were shaken carefully some times. Then the liberated iodine was determined by titration with KI₃.

The extinction coefficient was calculated using the Lambert–Bouger–Beer equation:

\[
\epsilon_{Cu^{2+}} = A - A_0 \frac{A}{dC_{Cu^{2+}}}
\]

where \(A\) is the absorbance at peak wavelength, \(A_0\) is the absorbance of a sample with no CuO for correction of reflection losses and internal absorption, \(d\) is the thickness of sample in cm and \(C_{Cu^{2+}}\) is the concentration of Cu²⁺ in mol/dm³. Densities were determined in order to calculate concentration of Cu²⁺ needed to determine the extinction coefficient.

Results and discussion

Position of Cu²⁺ absorption band

As expected the absorption peak was shifted to a longer wavelength when the sodium was replaced by potassium. The 20Na₂O–10CaO–70SiO₂ glass peak was at 787 nm and the 20K₂O–10CaO–70SiO₂ glass peak at 852 nm. Other authors have seen the same trend, namely that the peak wavelength increases when sodium is replaced by potassium in alkali oxide–silica glasses or alkali oxide–lime–silica glasses. The peaks for the mixed alkali glasses were located in between these tertiary glasses, but not following the straight line (see Figure 1 and Table 2).

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**Table 1. Batched glass compositions in mol%**

**Sample code | SiO₂ | Na₂O | K₂O | CaO | CuO | BaO | Al₂O₃**
---|---|---|---|---|---|---|---|
0K | 69.94 | 19.66 | 9.88 | - | 0.4 | 0.02 | 
5K | 69.74 | 14.90 | 4.99 | 9.95 | - | 0.4 | 0.02 |
10K | 69.72 | 9.95 | 9.95 | - | - | 0.4 | 0.02 |
15K | 69.71 | 4.98 | 14.93 | 9.95 | - | 0.4 | 0.02 |
20K | 69.71 | - | 19.91 | 9.98 | - | 0.4 | 0.02 |
20Na₂O–10MO–70SiO₂ (M=Ca, Ba) | 69.99 | 19.67 | - | 4.99 | 4.92 | 0.4 | 0.02 |
5Ba | 70.04 | 19.68 | - | 9.86 | - | 0.4 | 0.02 |
10Ba | | | | | | |

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This nonlinearity of the ligand field strength is also shown in K2O–Na2O–Al2O3–SiO2 glasses,(26) in (30–x) Na2O–xK2O–70SiO2 glasses and in (30–x) Li2O–xCu2O–70SiO2 glasses.(11) Klonkowski suggested that the nonlinear variation in the bond character when mixing two alcalis is the reason for the deviation from linearity of the ligand field strength. It was mentioned in the introduction that Cu2+ is octahedrally coordinated with oxygen and that the octahedron is Jahn–Teller distorted. The degree of the distortion is unknown, but the centre of symmetry will be retained.(19) This Jahn–Teller elongation will split the eg and t2g energy levels,(20,21) see Figure 2, the limit is a square planar complex. When the distortion increases, the difference between the energy levels of dxy, dxz and dxyz orbitals is increased. The effect of the distorted CuO6 octahedron can be that the band position is shifted to a shorter wavelength and it can also intensify the absorption band when the distortion increases.(20) This is due to the fact that normally the d–d transitions in an octahedral complex is Laporte forbidden because octahedrals are centrosymmetric. The symmetry can be eliminated by asymmetrical vibrations and when the distortion increases these vibrations will also increase and this can increase the intensity of the absorption. This means that the 20Na2O–10CaO–70SiO2 glass should be the glass with the most distorted CuO6 octahedron and this is also what other authors have suggested,(18,22) There is a slight shift in the absorption band towards a longer wavelength when CaO is substituted by BaO (see Table 2).

**Absorption band shape**

All spectra are shown in Figure 3 and they are asymmetrical when absorption is plotted versus wavelength. It is obvious, without any measurement, that the absorption band generated from the most basic glass named 20K in Figure 3 (20K2O–10CaO–70SiO2) is the broadest. That basic glasses have broader bands than acidic ones (if the alkali ion is changing) was confirmed by Cable & Xiang in 22R–12CaO–66SiO2 glass(8) and also by Volotinen in R2O–MO–R“2O3–SiO2 (mol%, R=Li, Na, K and M=Mg, Ca, Ba, R“=B or Al) glasses.(4)

In order to deconvolve the broad peak, the samples were analysed with a different UV-vis-NIR instrument to cover the wavelengths needed for the whole 300-820 nm. The extinction coefficient was calculated using the absorption peak position as a function of [Na2O]/([Na2O]+[K2O]) in 20R2O–10MO–70SiO2 glass [Colour available online].

Figure 1. Absorption peak position as a function of [Na2O]/([Na2O]+[K2O]) in 20R2O–10MO–70SiO2 glass [Colour available online]

<table>
<thead>
<tr>
<th>Sample code</th>
<th>CaO</th>
<th>CuO</th>
<th>CuO'</th>
<th>CuO'2-</th>
<th>[CuO']2- / [CuO]</th>
<th>log([Cu'] / [CuO])</th>
<th>Peak wavelength</th>
<th>A/mm (corrected value)</th>
<th>εCu2+ [dm⁻¹ mol⁻¹ cm⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0K</td>
<td>0.596</td>
<td>2.52945</td>
<td>4.15</td>
<td>2.76</td>
<td>1.40</td>
<td>0.336</td>
<td>0.59</td>
<td>0.33</td>
<td>787</td>
</tr>
<tr>
<td>5K</td>
<td>0.593</td>
<td>2.51823</td>
<td>3.80</td>
<td>2.58</td>
<td>1.22</td>
<td>0.320</td>
<td>0.33</td>
<td>0.33</td>
<td>796</td>
</tr>
<tr>
<td>10K</td>
<td>0.599</td>
<td>2.51665</td>
<td>3.81</td>
<td>2.64</td>
<td>1.17</td>
<td>0.308</td>
<td>0.35</td>
<td>0.35</td>
<td>806</td>
</tr>
<tr>
<td>15K</td>
<td>0.605</td>
<td>2.51475</td>
<td>3.91</td>
<td>2.72</td>
<td>1.19</td>
<td>0.305</td>
<td>0.36</td>
<td>0.36</td>
<td>825</td>
</tr>
<tr>
<td>20K</td>
<td>0.612</td>
<td>2.49740</td>
<td>3.84</td>
<td>2.68</td>
<td>1.15</td>
<td>0.301</td>
<td>0.37</td>
<td>0.37</td>
<td>853</td>
</tr>
<tr>
<td>5Ba</td>
<td>0.595</td>
<td>2.69576</td>
<td>3.71</td>
<td>2.61</td>
<td>1.10</td>
<td>0.309</td>
<td>0.38</td>
<td>0.38</td>
<td>794</td>
</tr>
<tr>
<td>10Ba</td>
<td>0.605</td>
<td>2.84661</td>
<td>3.53</td>
<td>2.23</td>
<td>1.29</td>
<td>0.314</td>
<td>0.34</td>
<td>0.34</td>
<td>796</td>
</tr>
</tbody>
</table>

Figure 2. The splitting of the d-orbitals of Cu2+ as an octahedral becomes progressively distorted by the withdrawal of the two ligands lying on the z-axes(22) [Colour available online]
peak. In Figure 4 some of the samples are shown as absorption versus wavenumber. Deconvolution was done with the software PeakFit® and first, all spectra were fitted to one Gaussian peak with the intention of finding out the symmetry of the absorption bands. The results showed that the fit was best for the 20K glass and poorest for the 0K glass and the other mixed alkali glasses were in the following order from best fit to poorest fit 15K>10K>5K. This means that the distortion of the octahedron decreases with increasing K2O in the glass at the cost of Na2O. For the Ba-glasses, the distortion was between that of the 0K and 5K in the glass at the cost of Na2O. For the Ba-glasses, Cable & Xiang(6) measured the asymmetry of the cupric band in alkali–lime–silica glasses and came also to the conclusion that the distortion of the octahedron is decreased with increasing size of the alkali ion; i.e. the degree of asymmetry of the cupric band is smaller in the more basic glass.

As mentioned in the introduction the broad absorption band is most probably due to two or three overlapping absorption bands, depending on the degree of tetragonal distortion (see Figure 2). There have been earlier investigations about the number of peaks and the results are different depending on the type of glass. Durán & Fernández Navarro(5) concluded there is one strong band at wavenumber near 12500 cm⁻¹ and a weak one at 8500 cm⁻¹ in alkali–silica glasses. Volotinen recently suggested that these two Gaussian peaks are situated closer to each other in alkali–alkaline earth–silica glasses, only separated by 520–1250 cm⁻¹ which would be the energy difference between the d₋₋ and d₋₋ and d₋₋ levels.(16) In copper phosphate glasses Bae & Weinberg(2) concluded that there are three Gaussian peaks at about 8500, 12000 and 13250 cm⁻¹ assigned to the energy transitions between orbitals dₓz→dₓzₓₓ, dₓz→dₓzₓₓ and dₓz→dₓzₓₓ (see Figure 2).

Attempts were done to fit two or three Gaussian curves. The fit was best for three Gaussian curves, but the fit with two peaks was good enough to consider this option too. There should be three allowed transitions in a tetragonal distorted octahedral field dₓz→dₓzₓₓ, dₓz→dₓzₓₓ and dₓz→dₓzₓₓ (see Figure 2), and these correspond to three different overlapping absorption bands. But there is the possibility that there are two bands, depending on the degree of distortion. It is also thinkable that for some of the investigated glasses there are two bands and for some three bands. If the distortion of the octahedron is so extreme that it will be a square planar field it will probably seems like it is two peaks, but two of the peaks will be very close to each other (dₓz→dₓzₓₓ and dₓz→dₓzₓₓ transitions). All those scenarios can possibly be found when deconvolving the broad absorption peak of Cu²⁺. To end up with a meaningful conclusion about the degree of distortion and the different energy transitions there is a need for complementary analysis.

CIE L*a*b* colour space

The calculated L*a*b* coordinates can be seen in Figure 5. It is interesting to see that the samples almost follow a line when the colour getting more intense. In the investigated glasses no refining agent is added, which is unlike what happens in industrial batches. Common refining agents are antimony oxide and sulphate. They will both reduce Cu²⁺ to Cu⁺ and consequently the colour will be less intense(11,23) when one of these refining agents is added.

The [Cu²⁺]/[CuTot] ratio

The [Cu²⁺]/[CuTot] ratio is decreased with increasing potassium content (which means that the basicity is increased) in 20R₂O–10CaO–70SiO₂ glass, as is shown in Figure 6. Many other authors came to the same conclusion concerning basicity and [Cu²⁺]/[CuTot] ratio in soda– and soda–lime–silica glass(7,10,24–26) but the results of Thiemson et al showed the opposite trend.(14) There is a slight deviation from linearity in the [Cu²⁺]/[CuTot] ratio for the 20R₂O–10CaO–70SiO₂ where in the most basic glass the [Cu²⁺] value is the lowest. When CaO is substituted for BaO there is a minimum in the [Cu²⁺]/[CuTot] ratio when there is 5
mol% CaO and 5 mol% BaO in the glass. The existence of these deviations from linearity is rather uncertain and may due to the experimental error.

A problem with most wet chemical methods when the concentration of one oxidation state is to be determined is the relatively high uncertainty. It is often around 10%\(^{(27)}\) in the determination of [Cu\(^+\)] and then also a few percent when AAS is used to determine the total Cu content; finally the Cu\(^{2+}\) content is calculated as the difference between [Cu\(_{\text{tot}}\)] and [Cu\(^+\)]. The main difficulties when determining the Cu\(^{2+}\) concentration is to avoid anything happening with the equilibrium during cooling of the melt and during the solvation of the glass sample before the analysis of the Cu\(^{2+}\) content.\(^{(27)}\) When cooling the melt without having a second element with a variable valence the equilibrium is only dependent of the diffusion of oxygen in the melt, and if the concentration of copper in this case is 0-1 mol% than there should be no notable change in the equilibrium.\(^{(28)}\) The uncertainty in the method used to determine the [Cu\(^+\)] is 7% given from the standard deviation. The raw materials used are of industrial grade and there are iron impurities at a maximum 0-01 wt%. If the iron has reduced all Cu\(^{2+}\) to Cu\(^+\), equivalent to the Fe\(^{2+}\) content, the Cu\(^+\) concentration will be about 1-9% lower for all samples. When comparing with other methods (mentioned below) it seems like the values of [Cu\(^+\)] in present study are a few percent higher. Singh & Kumar used the same method as in this study and their value is almost identical for the same glass composition.\(^{(15)}\)

When not determining the concentration of the two different oxidation states of copper, it is convenient to use the [Cu\(^+\)]/[Cu\(^{2+}\)] ratio or log[Cu\(^+\)]/[Cu\(^{2+}\)] ratio as comparative data. The log[Cu\(^+\)]/[Cu\(^{2+}\)] value of this study is shown in Figure 7 and is compared with Bauke & Duffy’s calculated data from equilibrium constants and optical basicity values at 1400°C. As seen there is a huge difference between the results from this study and that of Bauke & Duffy. In the current study, the temperature is 1420°C, which means that the equilibrium shifts towards Cu\(^+\) compared to the lower temperature 1400°C but, of course, this is not the only explanation of the very different results. As mentioned in the introduction the results vary a lot from different authors and methods when it comes to the [Cu\(^+\)]/[Cu\(^{2+}\)] ratio. In some cases the differences in the values can depend on the fact that not every glass was melted long enough to reach equilibrium with the atmosphere. Because of the long time needed to reach this equilibrium, it is only done if it is of great interest. In this study the glasses were not melted for the time required to be in equilibrium with the atmosphere and the [Cu\(^+\)]/[Cu\(^{2+}\)] ratio is therefore higher than the equilibrium value should be. It was shown by Cable & Xiang\(^{(6)}\) that the concentration of Cu\(^{2+}\) increased, most probably due to oxygen diffusion, until it is in equilibrium with the atmosphere. But, the differences are often large and cannot be explained only by this.

Singh & Kumar’s\(^{(10)}\) value of 0-3 for log([Cu\(^+\)]/[Cu\(^{2+}\)]) in a 20Na\(_2\)O–10CaO–70SiO\(_2\) glass melted at 1400°C is almost identical with our value for the same composition that was melted at 1420°C. They also used the same wet chemical method to determined the cuprous ion concentration and their melt was not in equilibrium with the atmosphere. Duran & Valle also used an wet chemical method to determine the Cu\(^+\) content and electronic paramagnetic resonance spectroscopy was used to determine the percentage of Cu\(^{2+}\).\(^{(27)}\) They took all precautions to avoid reducing agents and oxygen during analysis of Cu\(^+\) content and for neutral melting conditions in 16Na\(_2\)O–10CaO–74SiO\(_2\), their log([Cu\(^+\)]/[Cu\(^{2+}\)]) value was 0-22. Duran & Valle also concluded that the redox equilibrium of cupric–cuprous is constant up to about 1-5 mol% CuO.

Cable & Xiang\(^{(6)}\) gave a log([Cu\(^+\)]/[Cu\(^{2+}\)]) value of ~0-4 at equilibrium with air at 1400°C in a 17-6Na\(_2\)O–12CaO–70-4SiO\(_2\) glass and as mentioned in the introduction they used a method where determining the chemical fraction of the oxide in either oxidation state was not needed when determining the log
(\([\text{Cu}^+]/[\text{Cu}^2+]\)) value. If Baucke & Duffy’s expression is used to calculate the equilibrium log\((\([\text{Cu}^+]/[\text{Cu}^2+]\))\) value of Cable & Xiang’s glass composition it gives –0.65. This is in the same region, but still is a relatively large difference.

In the paper of Kaufmann & Rüssel\(^{(29)}\) the equilibrium log\((\([\text{Cu}^+]/[\text{Cu}^2+]\))\) value of \(20\text{Na}_2\text{O}–10\text{CaO}−70\text{SiO}_2\) glass melt was 0.54, an extrapolated value at 1400°C determined by square wave voltammetry and this is really a huge difference from Cable & Xiang’s value, but it is in the same region that our value. So, when it comes to the differences in the log\((\([\text{Cu}^+]/[\text{Cu}^2+]\))\) values it seems to depend on the method used.

**Extinction coefficient of \(\text{Cu}^{2+}\)**

The results of the extinction coefficient of \(\text{Cu}^{2+}\) for the investigated glass compositions are shown in Figure 7, 8 and Table 2. The only glasses that distinguish themselves in the matter of extinction coefficient of \(\text{Cu}^{2+}\) are the barium containing glasses with 5 or 10 mol% \(\text{BaO}\), these results are 52 and 54 dm\(^3\)mol\(^{-1}\) cm\(^{-1}\), respectively. All other studied glasses have an extinction coefficient between 41 and 46. As mentioned before they used the same method and because of the great influence of \(\text{Cu}^{2+}\) on the extinction coefficient, the uncertainty for \(\varepsilon_{\text{Cu}^{2+}}\) is 14%.

In an earlier mentioned paper Singh & Kumar\(^{(10)}\) determined the \(\varepsilon_{\text{Cu}^{2+}}\) for \(20\text{Na}_2\text{O}–10\text{CaO}−70\text{SiO}_2\) and the result was 42.9 (as seen in Table 2, our value is 42.8). As mentioned before they used the same method to determine the amount of \(\text{Cu}^{2+}\).

Cable & Xiang\(^{(7)}\) investigated a number of soda–lime–silica glasses and came to the conclusion that the extinction coefficient varied from 20–26 dm\(^3\)mol\(^{-1}\) cm\(^{-1}\). They used a special method where determination of the chemical fraction of the oxide in either valence state was not needed. Instead they brought the melts to equilibrium at one temperature but two different oxygen partial pressures or made melts at one partial pressure but three different temperatures. Ståhlskärse compared Cable & Xiang’s method with the method used by Duran,\(^{(27)}\) and the results were 17 and 38 dm\(^3\)mol\(^{-1}\) cm\(^{-1}\), respectively.\(^{(13)}\)

The glass composition was \(72\cdot2\text{SiO}_2–10\cdot0\text{Na}_2\text{O}–5\cdot9\text{K}_2\text{O}–11\cdot0\text{CaO}–0\cdot9\text{BaO}_3\).

Duran,\(^{(3)}\) Cable\(^{(5)}\) and Singh\(^{(9)}\) investigated how the extinction coefficient of \(\text{Cu}^{2+}\) was affected if the sodium was replaced by lithium or potassium in binary and ternary silicate glass. Both Duran and Cable report that \(\varepsilon_{\text{Cu}^{2+}}\) decreases with increasing size of the alkali ion. Singh’s result, on the other hand, points out that \(\varepsilon_{\text{Cu}^{2+}}\) increases with increasing size of the alkali ion in alkali silicate glass. In present study the extinction coefficient is almost the same whether sodium or potassium is added to the batch, but there is a maximum for the 5K and 10K glasses and this may be due to mixed alkalis in these glasses. Klönkowski\(^{(16)}\) showed that it is a small positive deviation from linearity in electronic polarisability of \(\text{O}^{2−}\), \(\alpha_{\text{O}^{2−}}\), and in refractive index in mixed alkali glasses. This might be the reason for the higher extinction coefficients of the mixed alkali glasses.

The extinction coefficients in this paper and in the aforementioned ones above are determined using the peak absorption as the definition in Lambert–Bouger–Beer equation (Equation (2)). Considering the reasoning in the section about the band shape that the absorption band consists of two or three overlapping bands this might not be a correct value to use. Bae & Weinberg\(^{(26)}\) used the area of the integrated absorption band to determine the cupric extinction coefficient in copper phosphate glasses. If the peak height and area of the integrated absorption band has the same proportion to each other for all investigated glasses, then the peak heights can be used when the extinction coefficient is determined. The results were that all glasses, besides the 20K glass, have almost identical ratios between the peak height and the area. The peak height /area ratio for the 20K glass was about 10% lower than the other ratios. With these results in mind the decision was made to use the peak absorption. Therefore, the extinction coefficient most probably should be some units higher for the 20K glass.

The most remarkable about the results of extinction coefficient is that the values of the barium containing glasses are so high. Singh et al\(^{(11)}\) did measure the intensities of the \(\text{Cu}^{2+}\) absorption peak in \(20\text{Na}_2\text{O}–10\text{MO}–70\text{SiO}_2\) glasses (\(\text{M}=\text{Ca} \text{and/or} \text{K, M}=\text{Ca} \text{and/or} \text{Ba}\)) [Colour available online]

**Figure 8.** The extinction coefficient of \(\text{Cu}^{2+}\) (at peak position) in \(20\text{R}_2\text{O}–10\text{CaO}–70\text{SiO}_2\) glass (\(\text{R}=\text{Na} \text{and/or} \text{K} \text{and/or} \text{Ba}\)) together with \(0.40 \text{ mol% CuO}\) were studied.
the 5BaO glass and 10BaO glass. The molar extinction coefficient is thus higher for the 10BaO glass than for the 5BaO being 54 and 52 dm mol$^{-1}$ cm$^{-1}$, respectively. It is known that lead oxide glasses also give intense colours,\(^{[6,7]}\) and the reason that both barium and lead glasses provide high extinction coefficients might be the high refractive index and thus also high refractivity of these glasses.

**Summary**

Five glasses with a batched composition of 20R$_2$O–10CaO–70SiO$_2$ (mol%, R=Na, K) and three glasses with the composition 20Na$_2$O–10MO–70SiO$_2$ (mol%, M=Ca, Ba) together with 0-40 mol% CuO were studied.

The asymmetrical absorption band of Cu$^{2+}$ is dependent on the glass composition and the peak position is shifted to lower wavelengths if the tetragonal distortion of the CuO$_6$ octahedron is increased. The peak position of the 20Na$_2$O–10CaO–70SiO$_2$ glass is at the lowest wavelength of the investigated glasses and the shape of the absorption band is the most asymmetrical and consequently this glass has the most distorted CuO$_6$ octahedron. The peak position is about the same for the barium containing glasses as for the 20Na$_2$O–10CaO–70SiO$_2$ glass. The distortion will decrease when K$_2$O is substituted for Na$_2$O and will be lowest for the 20K$_2$O–10CaO–70SiO$_2$ glass. The exact degree of the distortion has not been determined and this will be further investigated with the aim of determining the different electron transitions.

The extinction coefficient was almost the same for sodium or potassium containing glasses and was higher for the mixed alkali glasses and this might be due to the positive deviation in electronic polarisability and refractive index in mixed alkali glasses. The highest extinction coefficient was in the barium containing glasses and this cannot be explained by the basicity values or the distortion of the CuO$_6$ octahedron, but the higher refractivity of barium containing glasses may be the reason.

The [Cu$^{2+}$/Cu$_{tot}$] ratio is decreased with increasing potassium content (which means that the basicity is increased) in 20R$_2$O–10CaO–70SiO$_2$ glass and there is a slight deviation from linearity when plotting this ratio against potassium content.

**Acknowledgements**

The author gratefully acknowledges the financial support by KK-stiftelsen, the Knowledge-foundation in Sweden.

**References**

Physical properties and Raman spectroscopy of mixed alkali/alkaline earth-silicate glasses

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Abstract

The mixed alkali - and mixed alkaline earth effect is still a common research area and the reason is that many properties are influenced by this phenomenon, as yet poorly understood. It is still not possible to predict several properties of mixed alkali glasses, without melting the glasses and actually do the necessary measurements. In this study five glasses in the mixed alkali system (20R 2O-10CaO-70SiO2 (R=Na and/or K)) and three glasses in mixed alkaline earth system (20Na 2O-10MO-70SiO2 (M=Ca and/or Ba)) were investigated. We observed maximum in micro hardness and packing density as well as minimum in glass transition temperatures for the mixed alkali glasses. The mixed alkaline earth glasses do not exhibit any clear nonlinear behavior, but the hardness and glass transition temperatures decreases while the density and molar volume increases with increasing BaO content. The different Qn species in the glasses were determined by Raman spectroscopy and the relative area originating from Q3 species was increased with calculated optical basicity. The maximum in hardness for the mixed alkali glasses is explained by the maximum in packing density and by the structural changes in the glasses.

Keywords: mixed modifier effect; silicate glass; glass transition temperature; hardness; Raman spectroscopy

Introduction

It was almost 100 years ago Peddle showed that the chemical durability in a soda-potash-lead-glass was highest when the K 2O:Na2O weight ratio was about 7:3 [1], and nearly a century before that, in 1837, Kavalier prepared a soda-potash glasses with outstanding resistance against water and acids [2]. The composition in Kavalier’s 1900 century glass was about 4Na2O-10K2O-10.5CaO-0.5Al2O3-75SiO2 weight %. Nowadays borosilicate glasses are commonly used to get a glass with low thermal expansion and resistance against chemical attack. However, the approach to use a combination of sodium and potassium oxides in a certain ratios to get a glass with desired properties has been known for a long time. A number of review articles have been written on the subject of mixed alkali effect in glass [3-6]. During the last years the research on mixed alkali and mixed alkaline earth effect become common because it is still an unsolved phenomenon [7-20].

The pronounced mixed alkali effect affecting the chemical durability is due to the decrease in the ion migration rates of Na + and K+ when mixing two alkalis. Dynamic properties such as viscosity and conductivity also show a significant mixed alkali effect while static properties like density, molar volume, refractive index and hardness do not exhibit a particular distinct
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The pronounced mixed alkali effect affecting the chemical durability is due to the decrease in the ion migration rates of Na⁺ and K⁺ when mixing two alcalis. Dynamic properties such as viscosity and conductivity also show a significant mixed alkali effect while static properties like density, molar volume, refractive index and hardness do not exhibit a particular distinct
deviation from linearity [3]. As the mixed alkali effect depend on the singly charged mobile species and therefore includes not only alkalis but e.g. silver as well, the effect is sometimes called the “mixed mobile ion effect” [21] and the “mixed modifier effect” is also a frequently used expression for including both alkali- and mixed alkaline earth oxides [10].

From a structural point of view, it has been proven both experimentally and by use of MD (molecular dynamics) simulations, that the alkalis and alkaline earths are mixed randomly in the silicate network [22]. The cations are predominantly bonded to non-bridging oxygens (NBO), but also to bridging oxygens as confirmed with MD modelling and EXAFS [23, 24]. The influence of the structure on the non additive properties concerning ion migration in mixed alkali- and mixed alkaline earth glasses has been investigated [22], while other properties has not been related to structural changes in the same amount.

The connectivity of the silicate network is commonly described in terms of Qn species. The silicate structural units are divided in Q0-Q4 species, where Q0 species have 4 NBO and Q4 have to other Si-O tetrahedra bridging oxygens only [25]. Studies of these structural units have been made by use of NMR [26], but they have also been investigated with Raman spectroscopy [27]. The higher frequency region in Raman spectra, 850 cm⁻¹ – 1300 cm⁻¹, is the most investigated region concerning silicate glasses. The bands found are attributed to Si-O asymmetric stretching vibrations of the different Qn species [25, 28-36]. The authors of previous papers are in agreement about the position of the specific Q1, Q2, Q3 and Q4 species, namely at about 870 cm⁻¹, 950 cm⁻¹, 1100 cm⁻¹ and 1150 cm⁻¹ respectively. During the deconvolution of the Raman spectra there is evidence for at least one more peak at about 1050 cm⁻¹ in alkali silicate glasses which has not yet been interpreted in previous studies [30, 32-34].

The Qn units distribution changes with the field strength of the cation e.g. the number of Q3 species increase with decreasing field strength of the cation [22, 34, 37, 38]. When mixing sodium and calcium in silicate glass results from Neuville [34] show the same trend while Karlsson et al [39] did not notice any change in the Qn distribution in mixed Na2O-CaO-SiO2 glass. Both these investigations were performed with glasses of about 60 mol% SiO2 and 40% Na2O and/or CaO. MD studies on ternary mixed alkali silicate glasses that have shown that there is a minimum in the disproportionation of Q3 species to Q2 and Q4 species when there is about the same proportions of Na2O and Rb2O [40]. Because of the contradictory results of these three studies, there is a need for more studies concerning the network connectivity in mixed modifier glasses. The intention of the present study is to investigate the Qn distribution in mixed alkali- and mixed alkaline earth silica glasses. Furthermore, these structural changes are related to physical properties that usually exhibit a mixed alkali or mixed alkaline earth effect.

In the present study, we have investigated five glasses in the system (20R2O-10CaO-70SiO2 (R=Na and/or K)) and three glasses in the system (20Na2O-10MO-70SiO2 (M=Ca and/or Ba)). The studied glasses also contain 0.4 mol% CuO which was introduced and the content of the rest of the components were proportionally reduced. The molar extinction coefficient of Cu²⁺, the [Cu²⁺]/[Cu⁺] ratio and the optical spectra have been reported in a previous paper [41]. In the present paper we report on the influence of the mixed Na2O/K2O and mixed CaO/BaO on hardness, density, molar volume, packing density, glass transition temperature (Tg) and crystallization temperature (Tc) in the silicate glass system. The structure of the glasses were investigated using Raman spectroscopy and the deconvolution of Raman peaks were performed in order to determine the Qn distribution. There is also a short review from
the most recent papers concerning microhardness in glasses containing mixed alkali- or mixed alkaline earth oxides. The relationship between the structure and physical properties are discussed.

Experimental procedures

Sample preparation

The approximate glass compositions studied are 20R2O-10CaO-70SiO2 (R=Na and/or K) or 20Na2O-10MO-70SiO2 (M=Ca and/or BaO) and 0.4 mol% of CuO was also added to the batch. The target glass compositions are listed in Table 1. The raw materials were of industrial grade with maximum degree of impurities 0.01 wt% Fe2O3 and 0.04 wt% Al2O3 contamination respectively. All samples were melted in a Pt-Rh crucible at 1420°C and the batch weight corresponds to 150 g of glass. Samples were melted in a standard procedure described elsewhere [41].

Density and calculation of molar volume and compactness

Densities were measured according to the Archimedes principle in distilled water at 22 ± 1°C, assuming a density of 0.998 g/cm3 for water. Density values were calculated using the expression ρ = (m_d/ m_d-m_w)×ρ_water, where m_d is the weight of the dry sample and m_w the weight of the immersed sample. Sample weights were between 2 and 4 g, and measured glass densities were reproducible to ±0.005 g/cm³.

The molar volume (MV) of a glass is equal to the volume of one mole of the glass and was obtained by dividing the molecular weight of the glass by its density. The MV was calculated using the expression

\[ MV = \frac{\sum x_i M_i}{\rho} \]  

(1)

with x_i and M_i being the mole fraction and molar mass of element i respectively, and ρ the density of the glass. The compactness of the glasses is expressed as the packing density (C_g)[42]:

\[ C_g = \frac{\sum x_i V_i N}{MV} \]  

(2)

where \( V_i = \frac{4}{3}\pi N(x r_A^3 + y r_B^3) \) is the molar volume of an oxide A\_x B\_y, and the Avogadro’s constant N. The ionic radii r_A and r_B of the respective anions and cations were taken from Shannon [43].
Calculation of optical basicity

Duffy and Ingram developed a method to measure the acid-base character of an oxidic material and thereafter also a way to calculate a theoretical value of the so called “optical basicity” for different compositions [44]. In this paper the values obtained from refractivity data was used [45]:

\[ \Lambda = \frac{XA(\text{oxide } A)}{yA} + \frac{XB(\text{oxide } B)}{yB} + \cdots \]  

(3)

where \( \Lambda \) is the optical basicity, \( X \) the mole fraction and \( \gamma \) the basicity moderating parameter.

Differential thermal analysis

Glass transition temperatures (T_g) and crystallization temperatures (T_c) were measured on crushed pieces of glass, using a SETARAM Labsys Netzsch STA 409 PC/PG instrument. Samples were heated up to 1350°C in flowing nitrogen in Alumina cups applying, a heating rate of 15°C/min. The onset point of the endothermic drift on the DTA curve was taken as representing T_g, and the onset of the exothermic peak as corresponding to T_c. The precision of the T_g and T_c measurement is estimated to be ±5°C.

Microhardness

The measurements were carried out on polished samples using two different indentors with two different loads during 10 seconds. For the 0.49 N load a FV-700 Futur Tech instrument fitted with a diamond pyramidal indenter and attached to an incident light microscope was used. A Zwick Roell Indentec equipped with a pyramidal diamond indenter was used for the applied load of 0.98 N. The indentation dimension for each sample was measured with a light microscope (Olympus PMG3, Japan) under a magnification of 200. Vickers hardness values, expressed in GPa, were calculated by the expression \( H_v = \frac{(18.42 \text{ P})}{d^2} \), where \( P \) [N] is the load applied on the indenter and \( d \) [µm] is the average indentation diagonal length. Ten indents per specimen were recorded and their mean value and standard deviation were calculated.

Raman spectroscopy

Raman spectra were recorded in the 100–3200 cm\(^{-1}\) range on a micro-Raman spectrometer (inVia Renishaw) using the 488 nm line of an Ar ion-laser. The Raman spectra were baseline corrected and normalized to the intensity of the most intensive band, positioned around 1150 cm\(^{-1}\), using the WiRE 4.0 software from Renishaw. Deconvolution of the peaks from 800 to 1200 cm\(^{-1}\) were done with the software PeakFit®. The curve-fitting was done according to Mysen et al. [46] using four or five Gaussians to quantify the Q\(^5\)-species with the starting values at 870, 950, 1050, 1100 and 1150 cm\(^{-1}\). Frequency, half-width and intensity were independent and unconstrained variables. An example of a peak-fitted spectra is shown in Figure 1. The theory that the peak areas are proportional to the concentration of the respective Q\(^5\) specie is based on the hypothesis that the Raman scattering cross section is the same for all glass compositions [39]. As indication of the degree the network depolymerization, the ratio of the areas of the Q\(^5\) peak and the Q\(^2\) peak (AQ\(^5\)/AQ\(^2\)) has been used [34].
Results

Density, molar volume and packing density

The measured densities and calculated molar volumes for the glasses are given in Table 2. The variation of the density and molar volume as function of the \([\text{Na}_2\text{O}]/(\text{Na}_2\text{O}+\text{K}_2\text{O})\) ratio for \(20\text{R}_2\text{O}-10\text{CaO}-70\text{SiO}_2\) (R= Na, K) glasses and the \([\text{CaO}]/(\text{CaO}+\text{BaO})\) ratio for \(20\text{Na}_2\text{O}-10\text{MO}-70\text{SiO}_2\) (M=Ca and/or BaO) is shown in Figure 2a and 2b respectively. When substituting \(\text{K}_2\text{O}\) by \(\text{Na}_2\text{O}\) the density decreases from 2.53 to 2.50, but remains constant around 2.52 in a plateau in the middle of the graph. The molar volume on the other hand decrease linearly with the substitution of \(\text{K}_2\text{O}\) by \(\text{Na}_2\text{O}\). In the case of mixed alkaline earth glasses, both density and molar volume decrease linearly when substituting BaO by CaO. The packing density of both systems, alkali and alkaline earth mixed glasses are not changing much (the change is in the 3rd decimal), see Table 2, but it is worth noting that there is a maximum of the packing density for both glass systems at about equal amount sodium and potassium respectively calcium and barium. The 5K glass have a lower value than the 0K glass and obviously does not behaves as the other glasses which contain both \(\text{Na}_2\text{O}\) and \(\text{K}_2\text{O}\).

Glass transition and the crystallization temperature

The glass transition temperature, \(T_g\), and the crystallization temperature, \(T_c\), in Figure 3a and 3b be seen as a function of the \([\text{Na}_2\text{O}]/(\text{Na}_2\text{O}+\text{K}_2\text{O})\) ratio and the \([\text{CaO}]/(\text{CaO}+\text{BaO})\) ratio respectively. The substitution of \(\text{K}_2\text{O}\) by \(\text{Na}_2\text{O}\) results in a decrease of both \(T_g\) and \(T_c\) with a pronounced minimum at the ratio of about 0.5. The \(20\text{Na}_2\text{O}-10\text{MO}-70\text{SiO}_2\) (M=Ca and/or BaO) glass system exhibit an almost linear increase in \(T_g\) and \(T_c\) when substituting BaO by CaO.

Microhardness

The glass series \(20\text{R}_2\text{O}-10\text{CaO}-70\text{SiO}_2\) (R= Na, K) exhibit a clear nonlinear variation in microhardness with a maximum value for the mixed alkali glass \(10\text{Na}_2\text{O}-10\text{K}_2\text{O}-10\text{CaO}-70\text{SiO}_2\), as can be seen in Figure 4a. Results from the two different loads and two different instruments show approximately the same trend. The hardness values for mixed alkaline earth glasses are almost additive and the glass sample having a composition of \(20\text{Na}_2\text{O}-10\text{BaO}-70\text{SiO}_2\) shows the lowest hardness. Though with 0.49 N load there is a visible maximum in hardness and with 0.98 N load there is a noticeable minimum. For both glass series the values are higher for the 0.49 N load than for the 0.98 N load which can be attributed to the indentation size effect.

Raman Spectroscopy

The Raman spectra are shown in Figure 5a and 5b, the positions of the Gaussian bands from the deconvolution fits of the species \(Q^4\), \(Q^3\) and \(Q^2\) are listed in Table 3 and the apparent maxima from the low and mid wavenumber region in Table 4. There is a noticeable shoulder at about 480 cm\(^{-1}\) in the spectra for all glass compositions, but it is most pronounced for the 20K, 5Ba and 10Ba glasses. At 520-710 cm\(^{-1}\) there is a strong asymmetric band observed in the spectra of the 10K, 15K and 20K glasses, there is evidence of two peaks, one at approximately 560 and one at about 600 cm\(^{-1}\). All glasses have a shoulder at about 780 cm\(^{-1}\), a
weak peak at 950 cm$^{-1}$ and a very strong band at about 1100 cm$^{-1}$. The results from the deconvolution shows that in every sample $Q^1$, $Q^3$ and $Q^2$ species are present. $Q^1$ species in very low concentrations appears to be present in the samples 5K, 15K, 20K and 10Ba, respectively. It is clear that this ratio increases with increasing potassium content respective barium content by the cost of sodium or calcium. When plotting the $AQ^1/AQ^2$ ratio against calculated optical basicity there is a strong relationship between the area ratios and increasing calculated optical basicity, see Figure 6.

Discussion

In the present work, CuO was introduced as probe ion with the concentration of 0.4 mol% in every glass sample. The role of CuO is expected to be as a modifier as proved by others [47-49], but as the amount is small in all glasses, it is assumed not to affect the trends of the studied physical properties nor the structural differences when the other components are altered.

Glass properties

The density of the mixed alkali glasses labelled 5K, 10K and 15K is quite similar to each other compared to the extremes 0K and 20K containing only one alkali oxide, figure 2a. The “plateau” in density when both sodium and potassium are present in the glass was also observed by Hand and Tadjiev in 20R$_2$O-10CaO-65SiO$_2$ glass (R=Na and/or K) [8]. The deviation from linearity concerning density has also been shown by others, though without the “plateau” [3, 6, 50]. It is obvious that the packing of the atoms is influenced when alkalis of two different sizes is mixed. This was suggested to be the major reason for the mixed alkali effect by Stevels back in 1951 [51]. There will be a much more effective packing of ions with different sizes. The packing density of ions calculated using atomic radii is a rough estimation of the real packing of ions, but it can be a useful measure when comparing the amount of free volume of the different glass compositions. The error in the measurement of the density is $\pm 0.005$ g/cm$^3$, which will lead to an error of only $\pm 0.001$ of the packing density. There is a small maximum in the packing density for both mixed alkali- and mixed alkaline earth series, and this is in accordance with previous studies of mixed alkaline earth glasses [52].

The negative deviation in $T_g$ and the positive deviation in microhardness are in good agreement with previous studies [3, 20, 50, 53]. The mechanism of permanent deformation of glass consists mainly of two processes, plastic flow (shear flow) and densification. Both these deformation processes are inelastic, densification with volume change and plastic flow without volume change but instead a relocation of the matter is to the surrounding area of the indentation. The activation energy associated with the densification is much smaller than the one for plastic flow [53, 54], that means that if the loading time (and/or load) is increased, the deformation origin from densification should decrease [55].

Yoshida et al developed a method for determining the volumes of densification respective total deformation volume of the indented glasses [52]. The volume change was estimated before and after annealing at a temperature of 0.9 x $T_g$ (K). The densification part of the indentation corresponds to the volume of recovery, $V_R$, i.e. when the glasses were annealed, the volume decrease caused by the densification process, was eliminated and the original volume was returned. Furthermore, Yoshida et al showed that density, compactness and hardness decrease when substituting MgO for CaO (from 0 to 20 mol%) in two different soda-
lime-silica glass series and that the densification part of the indentation increased. However, there was a maximum in compactness for the glasses containing both magnesium and calcium for both glass series. In these two glass series Vickers hardness changes from 5 to 5.8 (16%) and $V_R$ varies from 79% to 41% (38%) and thus densification is much more sensitive for compositional changes than hardness. The packing density for the two mentioned glasses is 0.539 respective 0.549, which means that the increase in packing density is only 0.010 when $V_R$ decrease with 38%. It was also shown by Rouxel et al [54] that densification dominates over plastic flow in glasses with relatively low packing density. For example, in silica glass the packing density is about 0.45 [56] and the ratio of densification to total indentation volume is 92%, while the corresponding figures for a float glass (71 mol% SiO$_2$, 13 mol% Na$_2$O, 10 mol% CaO, 6 mol% MgO) is 0.62 and 61% [52]. It is important to understand that even if the densification part of the indentation will be higher this will not necessarily mean that the glass will have a lower hardness value e.g. the mentioned silica glass has a higher hardness value than the float glass.

As mentioned above there is a slight trend that the hardness is increased with increasing packing density of the mixed alkali glasses. For the mixed alkaline earth glasses there is no such trend. However, the changes in packing density is, as mentioned, relatively small and if the degree of densification compared to plastic deformation only is dependent on the packing density this should not be the only explanation to the mixed alkali effect (or mixed alkaline earth effect) as pointed out by Mohajerani and Zwanziger [57]. This suggests that the resistance to plastic flow also influences the hardness values in mixed alkali glasses [10, 57, 58]. Faiivre et al explained it with that the lack of ion mobility prevented plastic deformation and was not due to viscous flow [58].

Kjeldsen et al [20] studied the microhardness of aluminosilicate glasses with mixing Na$_2$O and K$_2$O in varying proportions. They estimated the densification part of the microhardness value and the part from plastic flow and came to the conclusion that both the resistance for densification and plastic flow have a positive deviation from linearity. They also showed that the densification part was about four to five times larger than the part origined from plastic flow and that the percentage deviation from linearity for both mechanisms was about the same. This means that in mixed alkali aluminosilicate glasses the resistance for both densification and plastic deformation contribute to the hardness in about equal parts. In relation to the present study, the positive deviation for the microhardness values should be further studied specifically concerning the influence from the respective indentation processes, densification or plastic flow.

When mixing two alkaline earth oxides there is often a minimum in hardness or a linear relationship between hardness and composition [8, 9, 52]. Furthermore in mixed alkaline earth glasses, there is a minimum in ionic conductivity, but less pronounced than for mixed alkali glasses, and there should therefore be a small maximum in hardness if the lack of mobility of the ions prevented plastic flow, as previously proposed by Kjeldsen et al [9]. Kjeldsen also suggested that a minimum in hardness is reflected by a minimum of $T_g$ and $T_c$ etc. and that plastic deformation is due to viscous flow.

For the mixed alkaline earth glasses in this study density, molar volume, $T_g$, $T_c$, ligand field strength [41] and data from Raman spectroscopy data all exhibit a relatively linear dependency as expected from the composition. This means that there is a correlation between the glass transition temperatures and hardness in this study for the mixed alkaline earth glasses; when $T_g$ decrease also hardness decrease. Hardness is often related to the cation field strength (CFS) and effective cation field strength (ECFS) in case of mixed modifier
are shown in Table 3 and 4. The asymmetric frequency band at about 600 cm\(^{-1}\) is most likely and Q\(^2\) species in glasses with higher calculated optical basicity, see Figure 6. This is in agreement with earlier observations in single alkali or alkaline earth glasses, i.e. that the number of Q\(^3\) species will increase with decreasing cation field strength, as mentioned in the introduction [22, 34, 37, 38]. In this paper, with mixed alkali- and mixed alkaline earth oxides, the different glasses could not be correlated with the cation field strength, therefore the optical basicity concept was chosen to classify the different glass compositions. There is neither a maximum or minimum in the AQ\(^3\)/AQ\(^2\) ratio and this was in fact not what MD simulations showed for mixed alkali silicate glasses [40], these showed a minimum in Q\(^3\) species.

Further information from the Raman spectra is shown in Figure 5a-b and the peak frequencies are shown in Table 3 and 4. The asymmetric frequency band at about 600 cm\(^{-1}\) is most likely due to bending and rocking motions of the Si-O network and consists of at least two peaks [34]. The peak at about 570 cm\(^{-1}\) is assigned to rocking vibrations of the fully polymerized SiO\(_2\) i.e. Q\(^4\) units [35]. This peak will move towards lower frequency when the silica content is increased (polymerization of the network) [28, 33, 36], probably due to the change in the average Si-O-Si bond angle [25, 28]. The shoulder at 600 cm\(^{-1}\) is assigned to Si-O-Si bending motions in depolymerized structural units [28]. This shoulder is more pronounced in the spectra of glasses with more potassium and less sodium, i.e. 10K, 15K and 20K. The broad peak at about 780 cm\(^{-1}\) seems to evolve from pure silica and the motion of Si against its tetrahedral oxygen cage [25]. This peak will shift to a higher frequency when alkali or alkaline earth oxide is added [27]. This peak for the investigated glasses will shift to lower frequency with increasing potassium content with the cost of sodium. The peaks at 950 and 1100 cm\(^{-1}\) is shifted to lower frequency as glasses are more depolymerized, i.e. when more metal oxides are added [27, 32, 33, 36, 66]. When the K\(_2\)O content is increased in the mixed alkali glasses in this study, both these peaks shift to higher frequency while the peaks move to lower wavenumber when calcium is substituted by barium, this confirms the results by Neuville [27].

Raman Spectroscopy and other structural aspects

The polymerization degree of the silicate network evaluated by Raman spectroscopy show that the number of Q\(^3\) species will increase accompanied by the subsequent decrease of Q\(^4\) and Q\(^2\) species in glasses with higher calculated optical basicity, see Figure 6. This is in agreement with earlier observations in single alkali or alkaline earth glasses, i.e. that the number of Q\(^3\) species will increase with decreasing cation field strength, as mentioned in the introduction [22, 34, 37, 38]. In this paper, with mixed alkali- and mixed alkaline earth oxides, the different glasses could not be correlated with the cation field strength, therefore the optical basicity concept was chosen to classify the different glass compositions. There is neither a maximum or minimum in the AQ\(^3\)/AQ\(^2\) ratio and this was in fact not what MD simulations showed for mixed alkali silicate glasses [40], these showed a minimum in Q\(^3\) species.
It is clear from the Raman spectroscopy analysis that when sodium is replaced by potassium and calcium is replaced by barium the degree of polymerization is altered, this has also been shown for alkali silicate glass [27]. The AQ²/AQ³ ratio increase with optical basicity confirms that the interrelation of the structural units changes with glass composition. As the proportion of Q³ species increases relatively with the potassium and barium content, this means that the relatively number of Q² and Q⁴ species will decrease and thus the network connectivity is influenced. This change in Qⁿ distribution is probably due to the different cation field strength of K⁺ and Na⁺ respective Ca²⁺ and Ba²⁺. Stebbins have shown, with NMR data, that cations with higher field strength will have a relatively low coordination number and a higher fraction of NBO’s than cations with lower field strength, which will have a higher proportion of BO’s and consequently a longer mean bond length [67]. Furthermore, bonds between alkali cations and NBO’s are stronger and shorter than are bonds with BO’s. In mixed alkali glasses it has been shown both with NMR [68] and EXAFS [69] that the metal-oxygen bond length distribution is high. When it comes to the Si-O bond lengths these are longer for non bridging oxygens than for bridging oxygens and the difference increase with the modifier content [22]. On the other hand, there is a trend that the bridging oxygen angle decrease with increasing modifier content and makes the SiO₄ (Q⁴) species come closer together [70]. To sum up, when both sodium and potassium are present in the glass it means that the surrounding of sodium is different from the environment of potassium. Sodium ions will due to the higher field strength coordinate to fewer oxygens, but more NBO’s and have shorter bond lengths than potassium ions will have which are stuck with fewer NBO’s but more BO’s. This means that the sizes of the sites are different from each other and this is suggested to be the reason for the decreased ion migration rates in mixed alkali glasses, a certain cation have a decreased number of sites which they can “jump” to [67]. How this structural change will affect the properties in current study is not clear. The density is supposed to increase with modifier content in silicate glasses both, because of the smaller angle in the Si-O tetrahedral (as mentioned above) and also because of the introduction of heavier elements to fill the interstices. Considering glass transition temperature it is as all other viscosity related reference points affected by the network connectivity [71], but the present structural study cannot explain the minimum in T_g and T_c for the glasses with both sodium and potassium. It is proposed by Fluegel that mixed alkali effect in viscosity is caused by non-linear and independent alkali-silica interactions [72]. It is possible that the change in network connectivity can affect the part from shear flow on hardness value.

To summarise, all trends exhibit an almost linear dependency for every studied property for the glasses in the mixed alkaline earth system, and even if there is only three samples in the series it appears like there is no clear mixed alkaline earth effect for the studied glasses, similar trends were also observed for oxynitride glasses containing alkaline earth elements. It should be noted that other authors with mixed alkaline earth oxides in silica and aluminosilicate glasses have noted a distinct mixed alkaline earth effect [9, 52].

Concerning the mixed alkali glass series, the explanations of the trends are not that easily interpreted. In comparison between the 20K glass which contain no Na₂O and 0K glass which contain no K₂O, the 20 K glass has the lowest hardness, density and compactness and the highest glass transition temperature as well as the largest relative number of Q⁴ units. On the other hand the 0K glass by contrast has a relatively high hardness, highest density and compactness, lowest glass transition temperature and the lowest relative number of Q³ species. However, the mixed alkali glasses (5K, 10K, 15K) have the highest hardness values, quite high densities and compactness, lowest glass transition temperatures and a relatively
high AQ³/AQ² ratio. The reasons for the high hardness values for the mixed alkali glasses are suggested to be a combined resistance to densification and plastic flow. Even if there is a very small change in the compactness that probably will have an influence on the densification part on the hardness value and the changing in the network connectivity can alter the resistance to plastic flow.

Conclusions

In this study we have investigated mixed alkali glasses (20R₂O-10CaO-70SiO₂ (R=Na, K)) and mixed alkaline earth glasses (20Na₂O-10MO-70SiO₂ (M=Ca, Ba)). For the mixed alkali glasses, the substitution of Na₂O for K₂O increase density and decrease molar volume of the glasses. Furthermore the mixed alkali effect manifests itself as a minimum in Tg, maximum in hardness as well as increasing the atomic packing density when mixing alkalis in the glass. The mixed alkaline earth glasses exhibit an additive behavior in density, molar volume, glass transition and microhardness. The density and molar volume increase with increasing substitution of Ba for Ca, Tg and hardness decrease with increasing substitution of Ba for Ca. The structure evaluated from the Q⁰ distribution determined by curve fitting for high wavenumber region (830-1300 cm⁻¹) of the Raman spectra showed an increase in the AQ³/AQ² ratio when sodium and calcium was replaced by potassium and barium respectively. The positive deviation in packing density is suggested to contribute to the higher microhardness value (densification part will be less) when mixing sodium and potassium in the glass.

Acknowledgement

The authors gratefully thank the Laboratory of Glass Science at the Otto Schott Institute of Materials Science, Friedrich Schiller University of Jena for giving us the opportunity to measure Raman spectra of the investigated glasses. Furthermore, the Marie-Curie Fellowship granted to Dr. Stefan Karlsson via the VINNMER programme (Vinnova) co-funded by Marie Curie Actions FP7-PEOPLE-2011-COFUND (GROWTH 291795) is gratefully acknowledged.

References


[59] A. Sharafat, J. Grins, S. Esmaeilzadeh, Properties of high nitrogen content mixed alkali earth oxynitride glasses (AE(x)Ca(1-x))(1.2(1))SiO1.9(1)N0.86(6), AE = Mg, Sr, Ba, Journal of Non-Crystalline Solids, 355 (2009) 1259-1263.
Table 1. Batched glass compositions in mol%.

<table>
<thead>
<tr>
<th>Glass system</th>
<th>Sample code</th>
<th>SiO₂</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>CaO</th>
<th>BaO</th>
<th>CuO</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>20R₂O-10CaO-70SiO₂ (R= Na, K)</td>
<td>0K</td>
<td>69.94</td>
<td>19.66</td>
<td>-</td>
<td>9.98</td>
<td>-</td>
<td>0.4</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>5K</td>
<td>69.74</td>
<td>14.90</td>
<td>4.99</td>
<td>9.95</td>
<td>-</td>
<td>0.4</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>10K</td>
<td>69.72</td>
<td>9.95</td>
<td>9.95</td>
<td>9.95</td>
<td>-</td>
<td>0.4</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>15K</td>
<td>69.71</td>
<td>4.98</td>
<td>14.93</td>
<td>9.95</td>
<td>-</td>
<td>0.4</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>20K</td>
<td>69.71</td>
<td>-</td>
<td>19.91</td>
<td>9.98</td>
<td>-</td>
<td>0.4</td>
<td>0.02</td>
</tr>
<tr>
<td>20Na₂O-10MO-70SiO₂ (M = Ca, Ba)</td>
<td>0K</td>
<td>69.94</td>
<td>19.66</td>
<td>-</td>
<td>9.98</td>
<td>-</td>
<td>0.4</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>5Ba</td>
<td>69.99</td>
<td>19.67</td>
<td>-</td>
<td>4.99</td>
<td>4.92</td>
<td>0.4</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>10Ba</td>
<td>70.04</td>
<td>19.68</td>
<td>-</td>
<td>-</td>
<td>9.86</td>
<td>0.4</td>
<td>0.02</td>
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</tbody>
</table>

Table 2. Physical properties of mixed alkali and alkaline earth glasses: glass designation, calculated optical basicity, density (ρ), molar volume (MV), packing density (Cₙ), glass transition temperature (Tₛ), crystallization temperature (Tₓ), hardness (Hᵥ). Numbers in parenthesis are estimated standard deviations.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Calc. optical basicity</th>
<th>ρ [kg/m³]</th>
<th>MV [cm³/mol]</th>
<th>Cₙ</th>
<th>Tₛ [°C]</th>
<th>Tₓ [°C]</th>
<th>Hᵥ, 0.49 N [GPa]</th>
<th>Hᵥ, 0.98 N [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0K</td>
<td>0.586</td>
<td>2.529</td>
<td>23.78</td>
<td>0.555</td>
<td>568</td>
<td>690</td>
<td>7.0(2)</td>
<td>5.5(2)</td>
</tr>
<tr>
<td>5K</td>
<td>0.593</td>
<td>2.518</td>
<td>24.53</td>
<td>0.554</td>
<td>555</td>
<td>695</td>
<td>7.1(3)</td>
<td>5.4(1)</td>
</tr>
<tr>
<td>10K</td>
<td>0.599</td>
<td>2.517</td>
<td>25.17</td>
<td>0.555</td>
<td>476</td>
<td>657</td>
<td>7.3(5)</td>
<td>5.5(4)</td>
</tr>
<tr>
<td>15K</td>
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<td>2.515</td>
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<td>5.3(2)</td>
</tr>
<tr>
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<td>26.76</td>
<td>0.551</td>
<td>650</td>
<td>806</td>
<td>5.5(2)</td>
<td>4.8(1)</td>
</tr>
<tr>
<td>0K</td>
<td>0.586</td>
<td>2.529</td>
<td>23.77</td>
<td>0.555</td>
<td>568</td>
<td>690</td>
<td>7.0(2)</td>
<td>5.5(2)</td>
</tr>
<tr>
<td>5Ba</td>
<td>0.595</td>
<td>2.696</td>
<td>24.08</td>
<td>0.555</td>
<td>533</td>
<td>670</td>
<td>6.2(1)</td>
<td>5.2(3)</td>
</tr>
<tr>
<td>10Ba</td>
<td>0.605</td>
<td>2.847</td>
<td>24.51</td>
<td>0.553</td>
<td>494</td>
<td>625</td>
<td>6.2 (3)</td>
<td>4.8(2)</td>
</tr>
</tbody>
</table>

Experimental uncertainties - ±0.005 ±0.05 ±0.001 ±5 ±5 - -
Table 3. Positions (cm⁻¹) of fitted Gaussian peaks from the Raman Spectra (800-1300 cm⁻¹), normalized peak areas and AQ³/AQ² (dimensionless).

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Peak</th>
<th>Norm. area</th>
<th>Peak</th>
<th>Norm. area</th>
<th>Peak</th>
<th>Norm. area</th>
<th>Peak</th>
<th>Norm. area</th>
<th>AQ³/AQ²</th>
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<td>950</td>
<td>0.084</td>
<td>1056</td>
<td>0.329</td>
<td>1106</td>
<td>0.424</td>
<td>1151</td>
<td>0.163</td>
<td>5.05</td>
</tr>
<tr>
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<td>0.077</td>
<td>1050</td>
<td>0.227</td>
<td>1107</td>
<td>0.454</td>
<td>1154</td>
<td>0.135</td>
<td>5.88</td>
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<tr>
<td>10K</td>
<td>949</td>
<td>0.068</td>
<td>1053</td>
<td>0.240</td>
<td>1108</td>
<td>0.463</td>
<td>1155</td>
<td>0.144</td>
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<tr>
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<tr>
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<td>0.191</td>
<td>1109</td>
<td>0.531</td>
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<td>0.132</td>
<td>7.82</td>
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<table>
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<td>1106</td>
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<td>0.163</td>
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<tr>
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<td>6.59</td>
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<td>0.154</td>
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<tr>
<td>Exper. Uncert.</td>
<td>-</td>
<td>±7%</td>
<td>-</td>
<td>±7%</td>
<td>-</td>
<td>±7%</td>
<td>-</td>
<td>±7%</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4. Apparent peak maxima region 400-800 cm⁻¹ (data in cm⁻¹).

<table>
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<th>[Na₂O]/([Na₂O]+[K₂O])</th>
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<th>600</th>
<th>790</th>
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<tbody>
<tr>
<td>0K</td>
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<td>568</td>
<td>792</td>
<td></td>
</tr>
<tr>
<td>5K</td>
<td>0.75</td>
<td>571</td>
<td>789</td>
<td></td>
</tr>
<tr>
<td>10K</td>
<td>0.5</td>
<td>571</td>
<td>601</td>
<td>786</td>
</tr>
<tr>
<td>15K</td>
<td>0.25</td>
<td>571</td>
<td>607</td>
<td>787</td>
</tr>
<tr>
<td>20K</td>
<td>0</td>
<td>568</td>
<td>603</td>
<td>784</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample code</th>
<th>[CaO]/([CaO]+[BaO])</th>
<th>580</th>
<th>600</th>
<th>790</th>
</tr>
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<tbody>
<tr>
<td>0K</td>
<td>1</td>
<td>568</td>
<td>792</td>
<td></td>
</tr>
<tr>
<td>5Ba</td>
<td>0.5</td>
<td>565</td>
<td>789</td>
<td></td>
</tr>
<tr>
<td>10Ba</td>
<td>0</td>
<td>568</td>
<td>792</td>
<td></td>
</tr>
</tbody>
</table>
Figure 2a. The density and molar volume as a function of the molar ratio of \([\text{Na}_2\text{O}]/(\text{Na}_2\text{O}+\text{K}_2\text{O})\) for the 20R2O-10CaO-70SiO2 (R= Na, K) glasses.

Figure 2b. The density and molar volume as a function of the molar ratio of \([\text{CaO}]/(\text{CaO}+\text{BaO})\) for the 20Na2O-10MO-70SiO2 (M= Ca, Ba) glasses.

Figure 1: Example of curve-fitted spectra, sample 0K.
Figure 2a. The density and molar volume as a function of the molar ratio of $[\text{Na}_2\text{O}] / ([\text{Na}_2\text{O}+\text{K}_2\text{O}])$ for the 20R$_2$O-10CaO-70SiO$_2$ (R = Na, K) glasses.

Figure 2b. The density and molar volume as a function of the molar ratio of $[\text{CaO}] / ([\text{CaO}+\text{BaO}])$ for the 20Na$_2$O-10MO-70SiO$_2$ (M = Ca, Ba) glasses.
Figure 3a. The glass transition temperature and crystallization temperature as a function of the molar ratio of $[\text{Na}_2\text{O}] / ([\text{Na}_2\text{O}+\text{K}_2\text{O})$ for the 20Na$_2$O-10MO-70SiO$_2$ (M= Ca, Ba) glasses.

Figure 3b. The glass transition temperature and crystallization temperature as a function of the molar ratio of $[\text{CaO}] / ([\text{CaO}+\text{BaO})$ for the 20Na$_2$O-10MO-70SiO$_2$ (M= Ca, Ba) glasses.
Figure 4a. Vickers hardness as a function of molar ratio of alkali oxides.

Figure 4b. Vickers hardness as a function of molar ratio of alkaline earth oxides.
Figure 5a. Raman spectra for the mixed alkali glasses (Na/K).

Figure 5b. Raman spectroscopy for the mixed alkaline earth glasses (Ca/Ba).
Figure 6. $AQ^3/AQ^2$ as a function of calculated optical basicity.
X-ray and UV-Vis-NIR absorption spectroscopy studies of the Cu(I) and Cu(II) coordination sphere in (mixed) alkali-lime-silicate glasses

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c Otto Schott Institute of Materials Research, Friedrich Schiller University of Jena
Fraunhoferstraße 6, D-07743 Jena, Germany
d The Abbe Center of Photonics, Friedrich Schiller University of Jena, Max -Wien-Platz 1, D -07743 Jena, Germany

Abstract

The local structures of Cu+ and Cu2+ have been investigated by Cu K-edge extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) in (20-x)Na2O-xK2O-10CaO-70SiO2 glasses with a copper content of 0.4 mol%. Further data on the surrounding structure of the Cu2+ ion were derived using UV-Vis-NIR spectroscopy. The glasses were melted and quenched in a standard procedure. Evidence for mainly linear coordination of the Cu+ ion is given from both EXAFS and XANES. The Cu(I)-O bond lengths were found to be 1.79-1.83 ± 0.02 Å. EXAFS results showed that Cu(II) was present in a tetragonally distorted environment, an octahedron with four shorter Cu(II)-O bonds and two longer in axial position. The equatorial bond lengths were found to be 1.89-1.91 ± 0.02 Å and the axial 2.20-2.24 ± 0.02 Å. EXAFS and UV-Vis-NIR results showed no effects on the tetragonal distortion of the octahedron when the glass composition was altered.

Introduction

As CuO is added to the glass melt, the redox equilibria between the Cu+ and Cu2+ ions is dependent on the glass composition. It is known that the proportion of Cu+ will increase if the basicity of the silicate glass increases [1]. Cu2+ absorbs light of the higher wavelengths in the visible region which makes silicate glasses turquoise blue. Cu+ ions, on the other hand, have a d10 electron configuration and thus no empty d-orbitals and are therefore colorless.

Furthermore, the Cu2+ and Cu+ are incorporated in the glassy structure in different ways. In general, as the charge increases, the number of oxygen ligands increases. Due to the absorption of Cu2+ in the visible region and its paramagnetic behavior, it is an easier ion to analyze from a structural point of view than the colorless, diamagnetic Cu+ ion. Several papers on the structural features of Cu2+ in oxide glasses have been published and the data has mainly been derived from studies using UV-Vis-NIR spectroscopy and/or EPR (Electron Paramagnetic Resonance Spectroscopy) as major techniques [2-8].

The expected coordination sphere for Cu2+ from these studies is a tetragonally distorted octahedron with two elongated bonds along the z-axis. However, the degree of distortion and in which glass composition the distortion is most pronounced is still not clear, since the previous studies are somewhat contradictory.

EXAFS (Extended X-ray Absorption Fine Structure) studies of the coordination sphere of Cu+ and Cu2+ ions have to some extent been made for ion exchange d and ion-implanted glasses [9-14]. However, copper oxide was incorporated in the glass matrix during the melting process in aluminosilicate glasses with a CuO concentration of about 20 wt% [15]. The study concluded that the Cu+ ion was coordinated by two oxygen ions and the Cu2+ ion was coordinated by four oxygen ions in a square planar geometry. In another paper, EXAFS investigations concerning the Cu+ and Cu2+ in blue Paleo-Christian glass mosaic showed that Cu+ was incorporated with two oxygen ions and Cu2+ with four oxygen ions in square planar coordination sphere [16]. There are also examples on green copper glasses, where the Cu2+-O2- coordination geometry is square planar [17]. Thus, EPR and UV-Vis-NIR studies do not show the same result as the EXAFS studies do. Therefore, in order to fully...
X-ray and UV-Vis-NIR absorption spectroscopy studies of the Cu(I) and Cu(II) coordination sphere in (mixed) alkali-lime-silicate glasses

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Abstract

The local structures of Cu+ and Cu2+ have been investigated by Cu K-edge extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) in (20-x)Na2O-xK2O-10CaO-70SiO2 glasses with a copper content of 0.4 mol%. Further data on the surrounding structure of the Cu2+ ion were derived using UV-Vis-NIR spectroscopy. The glasses were melted and quenched in a standard procedure. Evidence for mainly linear coordination of the Cu+ ion is given from both EXAFS and XANES. The Cu(I)-O bond lengths were found to be 1.79-1.83 ± 0.02 Å. EXAFS results showed that Cu(II) was present in a tetragonally distorted environment, an octahedron with four shorter Cu(II)-O bonds and two longer in axial position. The equatorial bond lengths were found to be 1.89-1.91 ± 0.02 Å and the axial 2.20-2.24 ± 0.02 Å. EXAFS and UV-Vis-NIR results showed no effects on the tetragonal distortion of the octahedron when the glass composition was altered.

Introduction

As CuO is added to the glass melt, the redox equilibria between the Cu2+ and Cu3+ ions is dependent on the glass composition. It is known that the proportion of Cu+ will increase if the basicity of the silicate glass increases [1]. Cu2+ absorbs light of the higher wavelengths in the visible region which makes silicate glasses turquoise blue. Cu+ ions, on the other hand, have a d10 electron configuration and thus no empty d-orbitals and are therefore colorless.

Furthermore, the Cu2+ and Cu+ are incorporated in the glassy structure in different ways. In general, as the charge increases, the number of oxygen ligands increases. Due to the absorption of Cu2+ in the visible region and its paramagnetic behavior, it is an easier ion to analyze from a structural point of view than the colorless, diamagnetic Cu+ ion. Several papers on the structural features of Cu2+ in oxide glasses have been published and the data has mainly been derived from studies using UV-Vis-NIR spectroscopy and/or EPR (Electron Paramagnetic Resonance Spectroscopy) as major techniques [2-8]. The expected coordination sphere for Cu2+ from these studies is a tetrahedrally distorted octahedron with two elongated bonds along the z-axis. However, the degree of distortion and in which glass composition the distortion is most pronounced is still not clear, since the previous studies are somewhat contradictory.

EXAFS (Extended X-ray Absorption Fine Structure) studies of the coordination sphere of Cu+ and Cu2+ ions have to some extent been made for ion exchanged and ion-implanted glasses [9-14]. However, copper oxide was incorporated in the glass matrix during the melting process in aluminosilicate glasses with a CuO concentration of about 20 wt% [15]. The study concluded that the Cu+ ion was coordinated by two oxygen ions and the Cu2+ ion was coordinated by four oxygen ions in a square planar geometry. In another paper, EXAFS investigations concerning the Cu+ and Cu2+ in blue Paleochristian glass mosaic showed that Cu+ was incorporated with two oxygen ions and Cu2+ with four oxygen ions in square planar coordination sphere [16]. There are also examples on green copper glasses, where the Cu2+ -O2- coordination geometry is square planar [17]. Thus, EPR and UV-Vis-NIR studies do not show the same result as the EXAFS studies do. Therefore, in order to fully
clarify the coordination sphere of Cu$^{2+}$ and to sort out the previous contradictory results about the degree of distortion in different silicate glass compositions further studies are needed.

The present study investigates the coordination of Cu$^{2+}$ and Cu$^{+}$ as well as the degree of distortion of Cu$^{2+}$ in mixed alkali-lime silicate glasses. Five glasses with the base glass composition 70SiO$_2$-20R$_2$O-10CaO (R=Na, K) doped with 0.4 mol% CuO have been investigated by means of UV-Vis-NIR spectroscopy and X-ray Absorption Spectroscopy. Furthermore, another two glasses with the same base glass composition containing 0.2 mol% CuO were studied. In one glass 0.3 mol% Sb$_2$O$_5$ added in order to shift the equilibria and favor the reduction of Cu$^{2+}$ ions to Cu$^{+}$ and in the other glass 0.6 mol% CeO$_2$ was added to favor the oxidation of Cu$^{+}$ ions to Cu$^{2+}$.

**Experimental procedure**

**Sample preparation**

The glass compositions studied have the approximate molar composition 20R$_2$O-10CaO-70SiO$_2$ (R=Na and/or K). 0.4 mol% of CuO was also added to the batch. The glass compositions are listed in Table 1. The raw materials were of industrial grade with maximum 0.01 wt% Fe$_2$O$_3$ and 0.04 wt% Al$_2$O$_3$. All samples were melted in a Pt-Rh crucible at 1420°C and the batches weight corresponds to 150 g of glass. Samples were melted in a standard procedure described elsewhere [5].

**UV-Vis-NIR spectroscopy**

Samples were prepared by grinding and polishing plane parallel samples with a thickness of 3-5 mm. All samples were made in doubles or triplets.

An Agilent Technologies Cary 5000 was used for the measurements. The scan rate was 600 nm/min and the spectral bandwidth 2 nm. The samples were masked with a circular aperture with the diameter of 5 mm and were measured from 3300 nm to 200 nm with 1 nm steps. The lamp source changeover was at 350 nm and the detector as well as grating changeover at 700 nm. The broad absorption band was deconvoluted by using the software Peak Fit® [18].

**X-ray Absorption Spectroscopy – data collection**

Glass samples for the measurements were prepared by crushing and sieving to a particle size below 45 μm, using a 325 mesh sieve. The crystalline reference samples of Cu$_2$O and CuO were treated with mortar and pester and were mixed thoroughly with boron nitride in order achieve homogenous samples with the approximately the same concentration as the glassy samples. Pure crystalline Cu$_2$O and CuO for reference were also spread on tape.

Copper K-edge X-ray absorption measurements were performed at the wiggler beamline I811 at the Max–II ring, Max-lab, Lund, Sweden, at two occasions. The Max-II synchrotron ring offered electron beam energies of 1.5GeV, maximum current of 200 mA and X-rays in the energy range 2.4-20 keV. The beamline was equipped with a Si [111] double crystal monochromator. In order to remove higher harmonics, 30% detuning was used. The sample spectra were collected in fluorescence mode by a solid state PIPS detector and a metallic Cu reference foil for energy calibration was simultaneously measured in transmission mode. The measurements were performed at ambient room temperature and the energy scale of the x-ray absorption spectra were calibrated by assigning the first inflection points of the K edges of foils of copper at 8980.3 eV. The ion chambers I$_0$, I$_1$ and I$_2$ were filled with 1.1 bar N$_2$, 0.1 bar Ar and 2 bar Ar respectively. Every sample was scanned at least 5 times in continuous scanning mode.
X-ray Absorption Spectroscopy – data analysis

The data analysis was carried out with the program package EXAFSPAK [19] and the pre-edge subtraction and spline removal was performed in a standard procedure. The software FEFF7 [20] was used for modeling the EXAFS region. The XANES region was only analyzed qualitatively.

The structural modelling in FEFF7

Cu(I)

In previous investigations, when Cu⁺ was introduced in the glass by additive to the batch or by ion exchange, Cu⁻ has been suggested to be coordinated by two oxygen ions [9-13, 15]. In one of the previous studies there was evidence for a linear coordination sphere of Cu⁺ [13]. However, Kaufmann and Rüssel have proposed a coordination of six oxygen ions surrounding the Cu⁺ ion in a compressed octahedral site [21]. Both models were tried in the fitting process but the linear coordination sphere was chosen for the Cu⁺ ions and the surrounding oxygen ions. The Cu-O distance in crystalline Cu₂O has been determined by Troger et al to be 1.85 Å [22] and in the previous mentioned EXAFS studies of Cu₂O containing glasses the distance ranged from 1.83-1.85 Å [9-15, 17]. Thus 1.85 Å was chosen as the Cu(I)-O distance starting value.

Cu(II)

Former studies of the structural coordination of Cu²⁺ in different glass compositions by UV-Vis spectroscopy and EPR have proposed a structural coordination sphere consisting of an elongated octahedron [2-5, 23-28]. On the contrary, EXAFS analysis carried out on ordinary melt-quenched glass, ion-exchanged glass and also historic blue glasses have suggested a square planar coordination with four oxygen ions surrounding the Cu²⁺ ion [13, 15, 16]. However, EXAFS data from sol-gel derived silicate glasses [29] and in phosphate glasses [30] has given evidence for an elongated octahedron of Cu²⁺ coordinated to O²⁻. Therefore, the both structural models were built in FEFF7, the square planar and the elongated octahedron configurations. The starting value of the Cu(II)-O distance was 1.95 Å for the four equatorial bonds and 2.30 for the Cu(II)-O axial bond. These starting values was chosen because of the distances in crystalline CuO (1.95 Å) [22] and previous EXAFS results from Cu²⁺ in silica gel [31] and Cu²⁺ in water solution [32]. The sample containing CeO₂ was the first sample to be tested as this was the sample with supposedly the highest proportion of Cu²⁺ and therefor it was anticipated to be the easiest sample to try the Cu(II) coordination model on.

All previous suggestions of the structure of Cu⁺ and Cu²⁺ with surrounding O²⁻ in glass were considered during the fitting process for the primary coordination sphere. Silicon was chosen as backscatterer for the second coordination shell. No further shell was tried to be fitted. Multiple scattering paths were fitted, but the contribution to the fit was very small. Different redox ratios of Cu⁺ and Cu²⁺ were used during the fitting procedure with starting values taken from ref [5] where the samples were analyzed by means of a wet chemical method. The coordination number, CN was used to express the redox ratio parts of Cu⁺ respective Cu²⁺ in the glass samples. For example, if a coordination with two oxygen ions was expected for Cu⁺ and the CN is 1.3, it means that 1.3/2, i.e. 65%, of the total Cu content in the sample is Cu⁺ and the rest is Cu²⁺ (and the CN for Cu²⁺ is (1-0.65)x4 (for the equatorial bonds) and half that value for the axial Cu(II)-O bonds.
Results

Cu K-edge EXAFS

The model with Cu⁺ in linear coordination with oxygen and Cu²⁺ surrounded with six oxygen ions in an elongated octahedron was found to be the best model (lowest F-factor). The results from the fitted model can be seen in Table 2. The Fourier transforms of the k³ weighted EXAFS spectra and the corresponding fits are displayed in Figure 1.

The shortest Cu-O distance (1.81-1.83 Å) origins from the Cu(I)-O bond. The EXAFS Debye-Waller factor, σ², which is the variation in bond lengths, was found to be: 0.0017-0.0044 Å².

The Cu(II)-O bond distances are ranging from 1.89 Å to 1.91 Å for the equatorial (x-y) Cu(II) - O binding, the axial (z) Cu(II)-O bonds have distances ranging from 2.20 to 2.24 Å, see Figure 2. EXAFS Debye-Waller factor, σ², ranging from 0.0006 to 0.0048 Å² for the equatorial bond lengths, but for the axial Cu(II)-O distance it is higher (0.0098 - 0.0169 Å²). This means that the bond length distribution for this axial Cu(II) - O is higher than for the shorter bonds.

The distances from the Cu⁺ ion and Cu²⁺ ion to silicon was found to be 2.80-2.85 Å and 3.01-3.06 Å respectively for the different glass compositions.

Cu K-edge XANES

Spectra from the XANES region is shown in Figure 3. The very characteristic pre edge peak at about 8985 eV, which is seen in the crystalline Cu₂O sample is from the 1s-4px,y transition and is attributed to a linear coordination [33]. In the spectra of the glassy samples the same band is present too. The peak is more intense as the Cu⁺ concentration increase, the ([Cu⁺]/([Cu+tot]) ratio is about 85-90 % in the 0KSb and 20KSb sample and about 50% in the 0KCe sample. It confirms the EXAFS results suggesting a linearly coordination sphere of Cu⁺ and two O²⁻. There are no such obvious transitions in the XANES spectra known concerning Cu²⁺, hence you cannot conclude that there is Cu²⁺ other than the indication of less pronounced 1s-4px,y transition for Cu⁺. However, if the Cu-site has no center of symmetry there will be a 1s-3d³ transition at about 8979 eV [33]. There is no such peak in the studied glass samples, thus the Cu²⁺ coordination sphere is centrosymmetric.

UV-Vis-NIR Spectroscopy

The geometry of an elongated octahedron was expected to give rise to three absorption bands in the UV-Vis-NIR spectra originating from the electron transitions; dxz, dzy → dx²-y², dxy → dx²-y² and dz² → dx²-y². In all spectra three Gaussian curves were used to resolve the broad absorption band. Results from the deconvolution of the optical absorption spectra can be seen in Figure 4 and Table 3.

Tetragonal distortion of the octahedral complex

The degree of tetragonal distortion of the octahedral complex can be expressed as the ratio between the shorter equatorial bond length and the longer bond length of the complex, Cu-Oeq/Cu-Oax [34]. The EXAFS results gave us these bond lengths (Table 2). When the ratio is 1 there is no distortion at all [34]. The Cu-Oeq/Cu-Oax ratio was found to vary only to a small extent, between 0.84 and 0.86 and is obviously not changing much as the glass composition is altered.

Another way to determine the degree of the tetragonal distortion is to compare the energy needed for the dz² → dx²-y² and dxy → dx²-y² electronic transitions in the distorted octahedral [2]. If the distortion increases (when the axial bond lengths increase) the energy level of the dz² orbital will
Another way to determine the degree of the tetragonal distortion is to compare the energy needed for obviously not changing much as the glass composition is altered.

The shortest Cu-O distance (1.81-1.83 Å) origins from the Cu(I)-O bond. The EXAFS Debye-Waller factor, \(\sigma\), ranging from 0.0006 to 0.0048 Å\(^2\) for the equatorial bond lengths, but for the axial Cu(II)-O distance it is higher (0.0098 - 0.0169 Å\(^2\)). This means that the bond length distortion increases (when the axial bond lengths increase) the energy level of the \(dz^2\) orbital will decrease due to longer distance to the oxygen ligands. The energy levels of \(dx^2-y^2\) and \(dxy\) will both increase, but the difference between them will still be the same, i.e. the orbital energy increase is constant. The ratio between the transitions \(dz^2 \rightarrow dx^2-y^2\) and \(dxy \rightarrow dx^2-y^2\) is a measure of the degree of tetragonal distortion (T) and the values are found in the range 0.72 to 0.74 for all samples except for the 20K sample which have a value of 0.69. The results are summarized as the absorption wavenumbers from UV-Vis-NIR spectroscopy and are presented in Table 3. In this way to express the distortion, the ratio is 0 when there is a regular octahedral, i.e. no distortion at all. The reason why the deconvoluted absorption band for the 20K glass look so different from the other glass compositions and thus gives a lower value of the tetragonal distortion is not clear.

### Discussion

#### \(Cu(I)-O\) bond length

The Cu(I)-O distance found in this investigation is somewhat shorter than previous investigations of Cu in glass received [9-13, 15, 16]. Some of the previous studies chose the distance to be constrained to the same distance as crystalline CuO which has been evidenced to be 1.847 Å with X-ray diffraction [22]. On the other hand, when calculating the Cu-O bond length by adding the ionic radii (according to Shannon [35]) of Cu\(^+\) (0.46 Å) and O\(^2-\) (1.35 Å), the expected Cu-O bond length is 1.81 Å, which is almost identical to our result.

#### \(Cu(II)-O\) bond length

The Cu(II)-O distance found in the present study is shorter compared to most previous studies [13, 15, 16], but almost the same as found by D’Acapito et al [10]; a Cu(II)-O distance of 1.92 Å in soda-lime glass implanted with Cu ions.

In two crystalline silicates, \(MCuSi_4O_{10}\) (M = Ca and Ba), with Cu(II) coordinated to four oxygen ions in square planar arrangement, the Cu(II)-O distances can be 1.928 Å and 1.921 Å, respectively [36]. Thus, in silicates, Cu(II)-O distances are shorter than in, e.g. crystalline CuO (1.95 Å [22]). In water Cu\(^{2+}\) is surrounded by six or five ligands and the Cu-O\(_{eq}\) were measured to 1.96 and Cu-O\(_{ax}\) to 2.29 Å with EXAFS [32, 37]. However, in an aerogel silicate the Cu(II)-O\(_{eq}\) distance was found to be 1.96-2.00 Å and the Cu(II)-Oax 2.25-2.35 Å by Kristiansen et al [31]. The axial bond lengths found in present study are between 2.20 and 2.24 Å, which is somewhat shorter than the Cu(II) - O\(^{2-}\) distance in aerogel or the hexaqua Cu(II) complex. The Cu(II)-O bond length expected from Shannons ionic radii [35] of Cu\(^{2+}\) (0.73 Å) and O\(^2-\) (1.40 Å) is approximately 2.13 Å. However, this bond length would be found in a symmetrical octahedron only. When the coordination sphere is distorted towards an elongated octahedron, the axial bond lengths will be longer and the equatorial bond lengths shorter.

#### Distortion of the \([Cu^{2+} O^{2-}]^{10}\) octahedral coordination sphere

It has been proposed from UV-Vis-NIR and EPR studies that the degree of tetragonal distortion is altered when for example Na is replaced with K in the glass structure [3, 4]. When increasing the size of the alkali ion, the broad absorption band at about 800 nm in the UV-Vis-NIR spectra is shifted to lower energy (higher wavelengths) [3, 5, 38, 39]. This shift has also been attributed to the difference in the distortion of the octahedron, i.e. when the elongation is not that pronounced, the ligand field strength is decreased and the absorption band is shifted to a longer wavelength.

According to the crystal field theory (CFT), the difference between the lowest energy levels, the dxy and yz orbitals, and the highest energy level, the dx\(^2\)-y\(^2\)orbital, would be higher if the distortion is increased. It means that the difference between the distance of Cu-O\(_{eq}\) and Cu-O\(_{ax}\) will increase. The results from this investigation show that the distortion of the octahedral geometry is almost the same for all studied glass compositions as can be seen in Table 2 and Table 3. The exception for this is the sample named 20K where the deconvoluted UV-Vis-NIR spectrum looks somewhat different than the
others and the calculated distortion is somewhat lower than the others, see Table 3. However, this study also shows that the bond lengths are very similar for all compositions; at least there is no trend in the bond lengths that can explain the decrease in ligand field strength when Na is replaced with K. The term $\Delta_0$ is influenced by the type of ligand, the metal ion and the distance from the metal ion to the ligands with the inverse fifth power [40]. This means, if all Cu(II)-O bond lengths in the potassium containing glass would have been longer than the bonds in the glasses with more sodium, that could also (except for being less distorted) have explained the decrease of the ligand field strength as the radii of alkali ion is increased. However, according to the EXAFS measurements, there is no such difference of the Cu(I)-O bond lengths in the octahedral sphere when the glass composition is altered. Thus, there must be another explanation to the observed difference in $\Delta_0$ which cannot be described by CFT.

In the CFT only ionic bonds are considered. In the more realistic ligand field theory, based on Molecular Orbital theory, the covalent bonding is taken into account. The $dz^2$ and $dx^2-y^2$ orbitals of the Cu$^{2+}$ ion and the six $O^{2-}$ ligands form $\sigma$-bonds and $\pi$-bonds are formed from $dxy$, $dxz$ and $dyz$ orbitals. As the $O^{2-}$ ions are so called $\pi$-donating ligands they will already have a filled $t_{2g}$ orbital and thus force the metal ion’s electrons to the antibonding orbital ($t_{2g}*$) which has a higher energy, see Figure 5. This will lead to a decrease of $\Delta_0$ between the $t_{2g}$* and e* energy levels compare to when $\pi$ bonding is neglected. It means that an increase of the covalent character of the Cu(II)-O bond will actually decrease the ligand field strength, $\Delta_0$, compare to the case when the bond has more ionic character. It has been shown that in copper containing potassium aluminosilicate glasses the degree of covalent character (i.e. proportion of $\pi$-bonds) for the Cu(II)-O bond is higher than for the Cu(II)-O bond in sodium aluminosilicate glasses [6]. It is possible that the fraction of covalent bonds is higher in the potassium containing glasses in this study too, thus it would explain the decrease in $\Delta_0$. This explanation was suggested by Lee and Brückner [4] based on EPR and UV-Vis-NIR spectroscopy results from Cu containing alkali silicate glass. However, they concluded that the tetragonal distortion increased with the size of alkali ion.

Both the crystal field theory and the ligand filed theory assume the complex-ion to be isolated from the rest of the solvent or the glassy matrix and this is of course a huge simplification. It was recently suggested that the surrounding structure (secondary, third, fourth sphere… etc.) affects the $\Delta_0$ of the metal complex in tetragonal distorted Cu$^{2+}$ complex in crystalline samples such as $K_2CuF_4$ and $KCuF_3$ [41]. Based on ab initio calculations, it was stressed that the potential energy of the neighboring lattices will contribute to the difference in $\Delta_0$, and therefore cannot be explained by different tetragonal distortions of Cu$^{2+}$ coordination sphere. In the present study, the higher field strength of Na$^+$ compared to K$^+$ will result in a higher internal electric field (i.e. higher potential energy) which most likely will affect the Cu(II)-oxygen octahedron. This might also explain the differences in ligand field strength in the sodium containing glasses compare to the potassium containing glasses.

The above described picture of how Cu(I) and Cu(II) is structured in silicate glass is quite idealistic, it is more likely that copper is not that ordered and this is reflected by the quite large F-factor. However, the very significant 1s-4p transition which is only seen in linear coordinated Cu(I), is more clearly observed in the samples with higher [Cu(I)]/[Cu tot] ratio (i.e. the Sb containing glasses). Therefore, the conclusion is that Cu(I) is most linearly coordinated with two oxygen ions. Concerning the Cu(II) coordination it should though be noted that the results from an elongated five coordinated square pyramidal coordination sphere around Cu(II) look about the same as for the six coordinated elongated octahedron, in analogy with Cu$^{2+}$ in water [32, 37]. The transitions in UV-Vis-NIR would be at the same energies and as this hypothetical coordination was tried during the EXAFS analysis the fit was almost as good as for the tetragonal distorted elongated octahedron.
Summary and conclusions

The results from EXAFS and XANES study show that Cu(I) in the glass matrix (20-x)Na2O-xK2O-10CaO-70SiO2 is coordinated by two oxygen ions mainly in a linear structure. The Cu(I)-O bond lengths were found to be 1.79-1.83 Å (±0.02 Å). The EXAFS analysis showed that Cu(II) has a coordination sphere consisting of six oxygen ions in an elongated tetragonal distorted octahedral geometry. This structural configuration was confirmed by UV-Vis-NIR spectroscopy. The four equatorial Cu(II)-O bond lengths were found to be 1.89-1.91 Å (±0.02 Å) and the two axial Cu(II)-O bond lengths were found to be 2.20-2.24 Å (±0.02). The degree of tetragonal distortion of the Cu(II)-oxygen octahedron was found to be about the same for all investigated glass compositions.

Acknowledgements

Portions of this research were carried out at beamline I811, MAX-lab synchrotron radiation source, Lund University, Sweden. Funding for the beamline I811 project was kindly provided by The Swedish Research Council and The Knut och Alice Wallenbergs Stiftelse. The authors thank Dr. Stefan Carlsson at the beamline I811 for help during the measurements and Professor Ingmar Persson, Swedish Agricultural University, Uppsala, for helpful discussions during EXAFS data analysis.


Table 1. Batched glass compositions in mol%.

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*: Goodness of fit parameter; the sum of the squares of the differences between experimental and calculated values.

**Exp. uncertainty**: ±15% ±0.02 ±20% ±0.015

Table 2. Fitted EXAFS parameters; coordination number (CN), interatomic distance (R), EXAFS Debye-Waller factor (σ²), goodness of fit parameter (F-factor), degree of tetragonal distortion (Cu-Oeq/Cu-Oax), (Cu²+/Cutot)-ratio. The range of within the data has been fitted k=3-12Å⁻¹, except for 0K k= 3-11 Å⁻¹.
Table 2. Fitted EXAFS parameters: coordination number (CN), interatomic distance (R), EXAFS Debye-Waller factor ($\sigma^2$), goodness of fit parameter (F-factor), degree of tetragonal distortion ($Cu$-$O_{eq}$/Cu-$O_{ax}$), ($Cu^{2+}$/Cu$_{tot}$)-ratio. The range of within the data has been fitted $k=3$-$12\,\text{Å}^{-1}$, except for 0K $k=3$-$11\,\text{Å}^{-1}$)

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Exp. uncertainty: ±15% ±0.02 ±20% ±0.015

*) Goodness of fit parameter; the sum of the squares of the differences between experimental and calculated values.
Figure 1. Fourier transforms of k3-weighted EXAFS spectra (solid lines) and fits (dotted lines). Not corrected for phase shift. 20K = 70SiO2-10CaO-20K2O, 0K = 70SiO2-10CaO-20Na2O

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<th>dxy → dx^2-y^2 (cm(^{-1}))</th>
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</table>
Figure 1. Fourier transforms of k3-weighted EXAFS spectra (solid lines) and fits (dotted lines). Not corrected for phase shift. 20K = 70SiO2-10CaO-20K2O, 0K = 70SiO2-10CaO-20Na2O

Table 3. Deconvoluted absorption spectra and tetragonal distortion

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<tr>
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<th>dxy → dx²-y² (cm⁻¹)</th>
<th>dz² → dx²-y² (cm⁻¹)</th>
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<tr>
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<td>7030</td>
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</tbody>
</table>

Experimental uncertainty ±100 ±100 ±100 ±0.02
Figure 2. The elongated tetragonal distorted Cu$^{2+}$-O complex.

Figure 3. XANES spectra of selected samples. The dotted lines marks the pre edge peak for the transition 1s → 4px,y in Cu(I) complex with linear coordination.
Figure 3. XANES spectra of selected samples. The dotted lines marks the pre edge peak for the transition 1s - 4p_x,y in Cu(I) complex with linear coordination.
Figure 4. Deconvoluted UV-Vis-NIR spectra for the different glass compositions.
Figure 5. In case A, π-bonding is ignored and in situation B ligand π-orbitals are full and at lower energy than metal t_{2g} (π-donating ligands) and case C is for π-accepting ligand.
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