Redox behavior of glasses doped with copper and arsenic, antimony or tin.

Dissertation

Zur Erlangung des akademischen Grades doctor rerum naturalium

(Dr. rer. nat.)

vorgelegt dem Rat der Chemisch-Geowissenschaftlichen Fakultät

der Friedrich-Schiller-Universität Jena

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geboren am 21. Juli 1977 in Chiangmai, Thailand

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Tag der öffentlichen Verteidigung: 16 Juni 2010

Zusammenfassung.

In der vorgelegten Arbeit werden die Redoxreaktionen von Kupfer mit den Redoxpartnern As_2O_3, Sb_2O_3 und SnO in zwei Grundgläsern der Zusammensetzung i) $16Na_2O$-10CaO-$74SiO_2$ und ii) $25Na_2O$-$15B_2O_3$-$60SiO_2$ (Zusammensetzungen in Mol%) in einem Temperaturbereich zwischen 25 und 800 °C mittels Hochtemperatur-vis-NIR-Spektroskopie im Spektralbereich von 400 bis 1.100 nm (das entspricht einem Wellenzahlenbereich von 25.000 bis 9.000 cm^{-1}) untersucht.

Das so genannte Natron-Kalk-Silicatglas i) ist das am häufigsten genutzte Modellglas für viele industriell verwendete Gläser. Es erlaubt sowohl grundlegende Untersuchungen von Glaseigenschaften an einem einfach zusammengesetzten Grundglas und ermöglicht aber auch deren Umsetzung auf die komplizierter zusammengesetzten Glassysteme der industriellen Praxis. Das Natriumborosilicatglas ii) wurde als ein Grundglas mit hoher Aktivierungsenergie des viskosen Fließens im Temperaturbereich oberhalb der Transformationstemperatur ausgewählt. Es hat einen im Vergleich zu Grundglas i) steileren Verlauf der Viskositäts-Temperaturkurve (so genanntes ‚kurzes' Glas).

Die Glasgemenge wurden aus für die Herstellung optischer Gläser verwendeten Rohstoffen hergestellt: Na_2CO_3, $CaCO_3$, SiO_2, H_3BO_3 sowie CuO, As_2O_3, Sb_2O_3 und $Sn(COO)_2$. Die Glasschmelze erfolgte in Platintiegeln in einem induktiven Mittelfrequenzschmelzofen. Besonderer Wert wurde auf die Homogenität der Gläser gelegt (Blasenfreiheit, Vermeiden von Schlieren).

Für die Hochtemperatur-vis-NIR-Messungen kam ein modulares Spektrometer mit optischem Chopper und LockIn-Verstärker zu Einsatz, das mit einem Heiztisch für die Mikroskopie gekoppelt war. Als Strahlungsquelle diente eine Halogenlampe, die spektrale Zerlegung erfolgte in einem Gittermonochromator und die Intensität der Strahlung wurde mit einem Si-Detektor gemessen. Mit diesem Spektrometer kann der Spektralbereich zwischen 400 und 1100 nm

untersucht werden. Im Prinzip lässt sich mit dem Spektrometer bis 5000 nm messen, wenn in einem zweiten Schritt ein PbSe-Detektor (und ein geeignetes Gitter) verwendet wird. Allerdings verlängert sich dadurch die Messzeit deutlich, so dass die Zeitauflösung der Experimente schlechter wird und den (geringen) Informationsgewinn bezüglich der Cu^{2+}-Bande nicht rechtfertigt. Durch die besondere Anordnung der Module wird dafür Sorge getragen, dass die thermische Strahlung der Probe, des Heiztisches und anderer erhitzter Teile im Strahlengang die Absorptionsmessungen an der zu untersuchenden Probe nicht beeinflussen.

Die Konzentrationen der polyvalenten Elemente, die den entsprechenden Grundgläsern zugesetzt wurden, waren immer klein genug, um die optische Basizität der Grundgläser nicht zu beeinflussen. Daher blieben sowohl die Lage des Maximums der Cu^{2+}-Absorptionsbande als auch deren Halbwertsbreite für unterschiedliche dem Grundglas zugesetzte Mengen an CuO konstant. Die vis-NIR-Spektren der untersuchten Glasproben trat im oben angegebenen Spektralbereich nur eine Absorptionsbande auf, die bekannte Cu^{2+}-Bande an der Grenze zwischen sichtbarem und NIR-Bereich. Auf den ersten Blick handelt es sich dabei um eine einzige Bande mit GAUSS-Form, aber eine genauere Analyse offenbart, dass es sich um die Überlagerung von drei Einzelbanden handelt, die durch die Jahn-Teller-Aufspaltung entstehen. Dessen ungeachtet konnten die aufgenommenen Cu^{2+}-Absorptionsspektren durch eine einzige GAUSS-Bande gefittet werden, ohne dass nennenswerte Fehler auftraten. Die zugesetzten Redoxmittel Arsen, Antimon und Zinn haben im vis-NIR-Spektralbereich keine Absorptionsbanden. Die Banden für diese polyvalenten Elemente liegen im UV-Bereich und werden von der Absorptionskante des Grundglases überlagert. Mit steigender Temperatur wird diese Absorptionskante langwellig verschoben. Das ist ein lange bekanntes Verhalten.

Nur mit Kupfer dotierte Gläser

Die Spektren der nur mit CuO dotierten Grundgläser (Natron-Kalk-Silicat- und Natriumborosilicatglas) zeigen die Cu^{2+}-Absorptionsbande bei etwa 12.500 cm^{-1}, die vom $^2E \rightarrow {}^2T_2$-

Übergang stammt. Die Bande zeigt nahezu GAUSS-Form und stammt von sechsfach (oktaedrisch) koordinierten Cu^{2+}-Ionen. Während des Aufheizens verschiebt sich die Position des Bandenmaximums zu kleineren Wellenzahlen (von 12.650 cm^{-1} bei Raumtemperatur nach 11.500 cm^{-1} bei 800 °C). Gleichzeitig wird die Bande breiter (von 7.200 auf 7.600 cm^{-1}) und ihre Intensität sinkt etwas, allerdings nur um etwa 5%. Diese Veränderungen sind völlig reversibel, wenn die Proben wieder abgekühlt werden. Die Redoxreaktion entsprechend $Cu^{2+}+\frac{1}{2}O^{2-}\rightleftharpoons Cu^{+}+\frac{1}{4}O_2$ wird in diesen Gläsern beim Aufheizen und Abkühlen in dem beschriebenen Temperaturbereich bis 800 °C nicht verschoben, da die Diffusion von Sauerstoff (O_2) in die Schmelze auch bei höheren Temperaturen ein sehr langsamer Prozess ist.

Allerdings ist es möglich in den Glasproben unterschiedliche $[Cu^{2+}]/[Cu^{+}]$-Verhältnisse einzustellen, indem die entsprechenden Glasproben bei hohen Temperaturen (größer als 1250 °C) äquilibriert werden. Mit steigender Temperatur verschiebt sich dabei die Redoxreaktion $Cu^{2+}+\frac{1}{2}O^{2-}\rightleftharpoons Cu^{+}+\frac{1}{4}O_2$ nach rechts. Das kann genutzt werden, um den molaren Absorptionskoeffizienten für Cu^{2+} in dem Natron-Kalk-Silicatglas zu bestimmen, er beträgt 25 $Lmol^{-1}cm^{-1}$. Das Verhalten war bereits bei Natron-Kalk-Silicatgläsern beschrieben worden und konnte nun auch für Natriumborosilicatgläser bestätigt werden.

Mit Kupfer und Zinn dotierte Gläser

Im Prinzip zeigen Gläser, die mit Kupfer und Zinn dotiert wurden, das gleiche Verhalten beim Aufheizen und Abkühlen wie die nur mit Kupfer dotierten Gläser. Allerdings wird die Intensität der Cu^{2+}-Bande durch die Zugabe von Zinn in Form von Zinn(II)-oxalat gegenüber einer nur mit der gleichen Konzentration an Kupfer dotierten Probe um etwa 30% erniedrigt. Das ist aber wohl der Reduktionswirkung des Oxalates während des Einschmelzens der Rohstoffe zuzuschreiben. Im Gegensatz zur Wirkung, die As_2O_3- und Sb_2O_3-Zugaben zeigen, konnte kein Hinweis auf eine temperaturabhängige Redoxreaktion $2Cu^{2+}+Sn^{2+}\rightleftharpoons 2Cu^{+}+Sn^{4+}$ gefunden werden. Die Intensität der Cu^{2+}- Bande nimmt mit steigender Temperatur leicht ab. Die Position des Bandenmaximums verschiebt sich zu kleineren Wellenzahlen und die Bande wird breiter. Diese Änderungen sind vollständig reversibel während des Abkühlens auf Raumtemperatur. Ein solches Verhalten ist verständlich, wenn man die kleine Standardreaktionsenthalpie $\Delta H^0_{Cu/Sn} = 6\ kJmol^{-1}$ für die oben angegebene Reaktion betrachtet.

Mit Kupfer und Arsen oder Antimon dotierte Gläser

Die Zugabe von Arsen oder Antimon zu mit Kupfer dotierten Natron-Kalk-Silicat- oder Natriumborosilicatgläsern hat einen viel stärkeren Einfluss auf die Cu^{2+}-Konzentration und damit auf die Intensität der Cu^{2+}-Absorptionsbande als die Zugabe von Zinn. Während des Aufheizens der entsprechenden Proben nimmt die Intensität der Cu^{2+}-Bande bei Temperaturen unter 400 °C leicht ab, die Proben verhalten sich wie Proben, die nur mit Kupfer oder mit Kupfer und Zinn dotiert wurden. Oberhalb 400 °C nimmt die Intensität der Cu^{2+}-Bande (und damit also auch die Cu^{2+}-Konzentration) mit steigender Temperatur deutlich stärker ab und geht durch ein Minimum. Je kleiner die Aufheizgeschwindigkeit, desto ausgeprägter erscheint das Minimum und desto kleiner ist die Temperatur, bei der es erreicht wird. Nachdem das Minimum in der Intensität der Cu^{2+}-Bande durchschritten ist, steigt deren Intensität beim weiteren Erhitzen sehr deutlich an. Die Kurven für unterschiedliche Aufheizgeschwindigkeiten liegen übereinander, die Intensität der Cu^{2+}-Bande ist nicht mehr von der Aufheizgeschwindigkeit abhängig sondern nur noch von der Temperatur.

Dieses Verhalten kann durch von der Temperatur abhängige Redoxreaktionen der Art $2Cu^{2+} + As^{3+} \rightleftharpoons 2Cu^{+} + As^{5+}$ bzw. $2Cu^{2+} + Sb^{3+} \rightleftharpoons 2Cu^{+} + Sb^{5+}$ erklärt werden. Mit steigender Temperatur werden diese Redoxreaktionen auf die linke Seite verschoben und dabei die Cu^{2+}-Konzentration erhöht. Die Werte für die Standardreaktionsenthalpie betragen $\Delta H^0_{Cu/As} = 46$

kJmol^{-1} bzw. $\Delta H^0_{Cu/Sb}$ = 102 kJmol^{-1} und sind damit deutlich größer als für die Reaktion zwischen Kupfer und Zinn.

Bei Temperaturen, die höher sind als die Temperatur, bei der das Minimum in der Cu^{2+}-Intensitätskurve auftritt, sind die oben angeführten Redoxreaktionen im Gleichgewicht. Bei Temperaturen unterhalb 400 °C sind diese Redoxreaktionen eingefroren. In dem Temperaturbereich dazwischen spielt die Kinetik eine wichtige Rolle und deshalb wird der Einfluss der Aufheizgeschwindigkeit offensichtlich.

Die entsprechenden Intensitätskurven, die während der Abkühlung von Temperaturen im Gebiet, wo die Redoxreaktionen im Gleichgewicht sind (also von 750 °C für Natron-Kalk-Silcatgläser und von 650 °C für Natriumborosilicatgläser), aufgenommen wurden, zeigen einen anderen Verlauf. Zuerst nimmt die Intensität der Cu^{2+}-Bande deutlich und linear mit sinkender Temperatur ab und zeigt das umgekehrte Verhalten wie während des Aufheizens in diesem Temperaturbereich. Ab einer bestimmten Temperatur wird diese Abnahme aber deutlich geringer und geht dann schließlich in einen leichten und im Prinzip linearen Anstieg mit sinkender Temperatur über. Das passiert dann, wenn die Redoxreaktion und damit die entsprechende Cu^{2+}-Konzentration eingefroren wird, folglich bleibt diese auch während des weiteren Abkühlens unverändert. Auch beim Abkühlen macht sich die Geschwindigkeit der Temperaturänderung bemerkbar: je geringer die Abkühlgeschwindigkeit ist, desto kleiner wird die Intensität der Cu^{2+}-Bande und folglich auch die Cu^{2+}-Konzentration.

Aus diesen Abkühlexperimenten lassen sich fiktive Einfriertemperaturen ermitteln. Die fiktive Einfriertemperatur T_f ist die Temperatur, unterhalb derer sich das Redoxverhältnis – im hier untersuchten Fall also das $[Cu^{2+}]/[Cu^{+}]$-Verhältnis – wegen der kinetischen Behinderung der Redoxreaktion nicht mehr verändert. Die fiktive Einfriertemperatur hängt von der Abkühlgeschwindigkeit ab: je größer die Abkühlgeschwindigkeit, desto höher ist die fiktive Einfriertemperatur. Für Abkühlgeschwindigkeiten von 10 bis 0,5 Kmin^{-1} ändert sich die fiktive Einfriertemperatur von 554 auf 536 °C für Natriumborosilicatgläser, die mit Kupfer und Arsen dotiert waren, und von 560 auf 539 °C für die mit Kupfer und Antimon dotierten Gläser. Sie sind um 20 bis 50 K niedriger als die für entsprechende Natron-Kalk-Silicatgläser bestimmten fiktiven Einfriertemperaturen.

Im mittleren Temperaturbereich lässt sich die Relaxation der Redoxreaktionen verfolgen. Dazu wurden entsprechende Glasproben auf (drei) bestimmte Temperaturen in diesem Bereich aufgeheizt und dann die Abnahme der Intensität der Cu^{2+}-Bande (und somit der Cu^{2+}-Konzentration) als Funktion der Zeit bei konstanter Temperatur gemessen. Aus den exponentiellen Abklingkurven kann die (temperaturabhängige) Relaxationszeit bestimmt werden, mit deren Hilfe sich über die Geschwindigkeitskonstanten für die entsprechende Redoxreaktion deren Aktivierungsenergie bestimmen lässt.

Bei Untersuchungen an Natron-Kalk-Silicatgläsern, die mit dem Redoxsystem $Cr^{3+}/Cr^{6+}//Mn^{2+}/Mn^{3+}$ dotiert waren, konnte die Relaxation einer Redoxreaktion in Gläsern erstmalig nachgewiesen werden. Die Aktivierungsenergie für die Redoxreaktion $3Mn^{3+}+Cr^{3+} \rightleftharpoons 3Mn^{2+}+Cr^{6+}$ wurde zu 535 $kJmol^{-1}$ bestimmt und liegt damit in einer zur Aktivierungsenergie des viskosen Fließens (560 $kJmol^{-1}$) vergleichbaren Größenordnung. Für die hier untersuchten Redoxreaktionen ergaben sich deutlich geringere Aktivierungsenergien: 210 $kJmol^{-1}$ für die Reaktion $2Cu^{2+}+As^{3+} \rightleftharpoons 2Cu^{+}+As^{5+}$ im Natron-Kalk-Silicatgrundglas (gemessene Aktivierungsenergie des viskosen Fließens: 560 $kJmol^{-1}$), 270 $kJmol^{-1}$ für die Reaktion $2Cu^{2+}+As^{3+} \rightleftharpoons 2Cu^{+}+As^{5+}$ sowie 265 $kJmol^{-1}$ für die Reaktion $2Cu^{2+}+Sb^{3+} \rightleftharpoons 2Cu^{+}+Sb^{5+}$ im Natriumborosilicatgrundglas (berechnete Aktivierungsenergie des viskosen Fließens: 850 $kJmol^{-1}$). Damit kann angenommen werden, dass in den hier untersuchten Redoxpaaren andere Mechanismen die Reaktionsgeschwindigkeit bestimmen als in dem oben genannten Redoxsystem $Cr^{3+}/Cr^{6+}//Mn^{2+}/Mn^{3+}$, für das strukturelle Umordnungen während der Redoxreaktion als geschwindigkeitsbestimmender Schritt beschrieben wurden: Cr^{3+} ist sechsfach koordiniert, während Cr^{6+} vierfach koordiniert ist (für Mn^{3+} und Mn^{2+} könnte sich die Koordinationszahl auch von 6 auf 4 ändern oder bei 6 bleiben).

Eine solche strukturelle Umordnung ist bei den hier untersuchten Gläsern weder für Cu^{2+} und Cu^{+} (beide verzerrt oktaedrisch, wenn auch gestreckt bzw. gestaucht koordiniert) noch für $As^{3+/5+}$ oder $Sb^{3+/5+}$ (beide jeweils tetraedrisch koordiniert) notwendig. Der geschwindigkeitsbestimmende Schritt sollte also die Diffusion der Cu^{2+}-Ionen sein, denn die Aktivierungsenergie für die Diffusion anderer zweiwertiger Ionen (z.B. Ca^{2+}, da entsprechende Daten für die Diffusion von Cu^{2+} in diesem Temperaturbereich nicht zur Verfügung stehen) in einem Natron-Kalk-Silicatglas liegt in der gleichen Größenordnung wie die oben aufgeführte Aktivierungsenergie für die Redoxreaktionen zwischen Kupfer und Arsen bzw. Antimon.

Contents.

1. **Introduction and aim of the project**.

Glass is a material that is fascinating people already since a long time. Obviously, it is the unique combination of properties, such as light transparency, the possibility to colourize glasses in rather simple and many different ways together with the easy malleability at high temperatures which made glass an interesting material over the centuries. Nevertheless, glass making often seemed to be mystique and, despite increasing scientific results, alchemistic, a combination of materials science and art.

The transmission of light is probably the most known property of glasses, and coloured glasses are one of the most important glassy materials. They are used in many applications such as optical materials, container glass, sensors etc. Often, glasses are coloured by doping with transition-metal ions (d- or f-ions). Transition metals are often polyvalent and can occur in more than one oxidation state. Different oxidation states absorb the light in different ways, thus, the colour of the respective glass samples depends not only on the concentration but also on the ratio between the ions in different oxidation states. The ratio is influenced by the base glass composition, by the atmosphere during melting and by redox agents added to the batch. Thus, the colour of a glass depends on many factors. A certain colour of a glass sample can be the desired result of glass makers' work, but it also can be undesired. Therefore, the control of glass colours demands the understanding of the influencing factors. Although many of the factors with effects on the colour of the glasses are already known, some questions and unsolved problems are still remaining. The aim of this work is to deepen the understanding of and to explain the mutual interaction between pairs of polyvalent elements in a glass melt especially in the temperature range around the glass transition temperature.

The colour of a glass is also of technological importance especially during the glass melting process. The degree of absorption of the thermal radiation by the glass melt depends for example on the concentration of ions which are absorbing in the near Infrared (NIR) region, such as Fe^{2+} and Cu^{2+}. Thus, the transport of heat (thermal radiation) into and within the glass melt is strongly affected by these polyvalent elements and the respective concentrations of the NIR absorbing ions. It is thus obvious that this depends on the redox ratio of the polyvalent element.

It is very common to investigate (coloured) glasses by different physical methods at room temperature, more especially by UV-vis-NIR optical spectroscopy. This way, information results on the kind of the colouring species and on their concentrations using the well known Lambert-Beer's law. Though, investigations using UV-vis-NIR spectroscopy at room temperature provide only limited information on the conditions at higher temperatures. It is hardly possible to freeze in the high temperature conditions by rapid quenching of a glass melt and to investigate these samples at room temperature. In molten glasses, square-wave voltammetry has become an important method to investigate the redox behavior in glass melts. But for temperatures from room temperature to glass softening temperature is still a large gap remaining. (UV-)vis-NIR absorption spectroscopy using a modular spectrometer in combination with a microscope heating stage opens up possibilities to investigate the absorption behavior and the redox reactions of polyvalent elements in this temperature range. It is the most suited method to study the course, the mechanism and the dynamics of redox reactions of polyvalent elements in glass melts in the temperature range around the transition temperature.

The aim of this thesis is the better understanding of redox phenomena in soda-lime-silica ($16Na_2O$-$10CaO$-$74SiO_2$, in mol%) and sodium borosilicate ($25Na_2O$-$15B_2O_3$-$60SiO_2$, in mol%) glass systems doped either solely with copper or simultaneously with copper and tin, arsenic or antimony as redox agents at temperatures in the range from 25 up to 800 °C. The soda-lime-silica glass is a model glass for the most frequently used glass compositions in the glassmaking industry. The sodium borosilicate glass was chosen because of its different viscosity behavior (different activation energies of viscous flow in the interesting viscosity range) in comparison to the soda-lime-silica glass.

The course of the redox reactions is different in glasses solely doped with a polyvalent element and in glasses co-doped with a second polyvalent element due to the mutual interaction between the two polyvalent elements during heating and cooling. This behavior should be investigated *in situ* by high temperature optical absorption spectroscopy. The main topics of the work are the kinetics of the mutual redox interaction, its relaxation behavior, the connection between fictive redox freezing temperatures and glass viscosity, and an explanation of the possible mechanisms of the redox reactions.

2. State of the art.

Many properties of glasses doped with polyvalent elements are influence by the type and the concentration of the species which are formed by redox reactions either with the atmosphere (oxygen) or by mutual interaction with a second polyvalent element. The investigation of glasses, especially the coloured ones, by optical UV-vis-NIR spectroscopy is very common and widely used to characterize and study the glasses and their structure.

In principle, three different types of coloured glasses exist [1]:

i) glasses coloured by various colouring ions (transition metal ions) [2], [3],

ii) glasses coloured by noble metal colloids [4], [5] and

iii) glasses coloured by semiconductor nanocrystals [6], [7].

The glasses under investigation belong to type i), to the most common coloured glasses. Since at least one of the different oxidation levels of the polyvalent elements included in the redox reaction absorbs in the visible range, UV-vis-NIR absorption spectroscopy is well suited to investigate these glasses. Measurements at room temperature result in information on the type of absorbing species, their coordination number and concentration provided that the molar absorptivity of the respective species is known. It is also possible to draw conclusions about the acid-basic properties of the base glass using the colouring ions as probe ions [8]. Nevertheless, spectroscopic investigations at room temperature provide only limited information on the relationships at higher temperatures, i.e. in the glass melt.

Redox reactions in glass melts are best studied by electrochemical methods [9]. This way, the standard potential of a redox pair can directly be measured. If the measurements are done at different temperature, then thermodynamic parameters, such as standard enthalpy, ΔH^0, and standard entropy, ΔS^0, can be calculated. Soda-lime-silica glass melts containing different polyvalent elements including copper, antimony, arsenic and tin, were investigated using square-wave voltammetry [10]. Their normal potentials are described as a function of temperature. From this dependence, the values of AH° and AS° for redox reactions

$$A^{(n-z)+} + \frac{z}{4} O_2 \rightleftharpoons A^{n+} + \frac{z}{2} O^{2-} \tag{1}$$

have been calculated as well as the redox ratio $[A^{n+}]/[A^{(n-z)+}]$ for the different multivalent ions. The effect of basic glass composition on polyvalent ions was studied by square wave voltammetry on soda-lime-silica glass melts doped with 0,2 mol% Fe_2O_3 [11]: decreasing Na_2O content and increasing CaO content lead to an increase in the standard potentials of Fe^{3+}/Fe^{2+} redox pair although the decrease in melt basicity is not large.

Diffusion coefficients of various polyvalent ions (Sn^{2+}, As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, V^{4+}, V^{5+}, Cr^{3+}, Cr^{6+}, Fe^{3+}, Cu^{+}) were measured in a Na_2O-$2SiO_2$ glass melt with the aid of square-wave voltammetry [12]. Within the temperature range from 850°C to 1550°C, a linear correlation between log D and 1/T was observed. At the same temperature, diffusion coefficients varied by up to the factor of 2800. Polyvalent elements showing two redox steps (As, V, Cr) always possess higher diffusion coefficients in the lower valence state. The diffusion coefficients measured correlate with those reported for a soda-lime-silicate melt.

Self diffusion coefficients of various polyvalent elements were measured with the aid of square-wave voltammetry [13]. For all elements, a linear correlation between log(D) and 1/T was observed. Difference is large in the soda-lime-silica glasses. Self diffusion coefficients of polyvalent ions differ by two orders of magnitude at 1300°C, and at 800°C by more than six orders of magnitude. Usually diffusion coefficients of ions with lower charge are higher than those of polyvalent ions with higher charge. Extrapolation of voltammetrically determined diffusion coefficients towards lower temperatures leads to a good agreement with data obtained from tracer experiments [14]. By comparison to diffusion coefficients measured in soda-lime-silica glasses, those in the borosilicate glass are notably higher at the same temperature. This is an effect of the lower viscosities of the borosilicate melt investigated.

A recent square-wave voltammetric study on thermodynamics of the Cu^+/Cu^{2+}-redox equilibrium in soda-lime-silica glass (xNa_2O-$10CaO$-$(90-x)SiO_2$ with x = 10, 16, 20 and 26) melts is given in [15]. The voltammograms exhibit two peaks. That at less negative or (depending on temperature and glass composition) even positive potential is attributed to the reduction of Cu^{2+} to Cu^+, while that observed at more negative potential is caused by the reduction of Cu^+ to metallic copper. For both redox steps, the peak potentials decrease linearly with temperature. Those of the composition with 10 mol% Na_2O show the most negative values. The diffusion coefficients can be fitted to Arrhenius equation. If referenced to the same viscosity, the diffusion coefficients decrease with increasing Na_2O-concentration. The effect of composition on the thermodynamics as well as on diffusivities is explained by the incorporation of the copper ions into the melt structure. Unfortunately, voltammetric methods will not work at temperatures below the softening point when a glass-forming melt is cooled down.

In a glass melt that contains only one polyvalent element, the redox ratio will not change during cooling if its concentration in the reduced form is large compared with the real amount of physically dissolved oxygen (O_2), because the diffusion of oxygen into the melt is too slow. If the glass melt contains at least two polyvalent elements, a redox reaction between the polyvalent elements is expected. At sufficiently high temperatures, the redox reaction is in equilibrium. Though, during cooling of the glass melt it could be possible that the reaction is no longer in the thermodynamic equilibrium. Then, kinetic effects play an important part. Rüssel calculated that the redox reaction will be frozen in at temperatures near to the transformation temperature of the respective glass [16] and that the freezing temperature depends on cooling rate. These calculations were confirmed by ESR experiments of glasses doped with Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+} in the temperature range from room temperature to 680 °C [17]. Glasses containing only one polyvalent element revealed the predicted behavior: during cooling, the

$[Fe^{2+}]$ and $[Fe^{3+}]$ (alternatively, the $[Mn^{2+}]$ and the $[Mn^{3+}]$) are not changed. Glasses containing both Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+} revealed the mutual interaction according to

$$Mn^{3+} + Fe^{2+} \underset{T\uparrow}{\overset{T\downarrow}{\rightleftharpoons}} Mn^{2+} + Fe^{3+} \qquad (2)$$

The signal intensity of the Fe^{3+} peaks is increased compared to a glass containing only iron. The redox reaction was found to be completely frozen-in at 400 °C.

NIR optical absorption spectroscopic investigations on glass melts using a reflection method were first reported by Genzel and Neuroth [18], [19], 60 years ago. Coenen [20] used the transmission method to measure absorption behavior of glasses doped with iron, chromium, cobalt, manganese or nickel at temperatures up to 1400 °C and discovered that absorption bands of the coloring ions normally become weaker and broader with increasing temperature. These results were confirmed by Tiquin et al. [21], [22]: the d-d absorption bands of Cr^{3+} in a sodium silicate glass are shifted towards longer wavelengths and become broader at 1000 °C. Additionally, it was found that with increasing oxygen partial pressure the concentration of the $[CrO_4]^{2-}$ charge transfer band was increased in the glass melts.

Endrys [23] proved that the change of the absorption coefficient (molar absorptivity) with temperature of the Fe^{2+} and of the OH^- absorption bands is reversible. Thus, it was concluded that the molar absorptivity depends on temperature.

If the glasses contain more than one coloring polyvalent element, then a band separation is required for the recorded spectra to specify the influence of temperature on intensity, position and width of the individual absorption bands. For example, Cr^{3+} has four d-d absorption bands in the visible region and Fe^{2+} has two d-d absorption bands in the NIR region. But there is only a limited number of works that performed a band separation for the high temperature spectra of glasses, e.g. [24], [25].

Gödeke investigated the behavior of soda-lime-silica glasses doped with iron or chromium by high-temperature absorption spectroscopy in the UV-vis-NIR range between room temperature and 1400 °C [26]. With increasing temperature, the (charge-transfer and d-d) absorption bands become weaker and broader and were shifted to larger wavelengths with the exception of the Cr^{3+} absorption band at 450 nm ($^4A_2 \rightarrow ^4T_1(F)$). The intensity of this band is increased with increasing temperature due to a weakening of the Laporte rule caused by increasing thermal vibrations of the octahedral coordination complex of the Cr^{3+} ions. The parameters of the chromium and iron absorption bands (position, intensity and width) were given as function of temperature so that absorption spectra could be modeled for any temperature up to 1400 °C. These data were used to describe the light emission properties of the respective glass melts.

The occurrence of redox reactions between the polyvalent elements $Fe^{2+/3+}$ and $As^{3+/5+}$ during cooling of a melt was first time proved using high-temperature UV-VIS-NIR spectroscopy [27]. During cooling of a melt containing both iron and arsenic oxide, a redox reaction takes place and the equilibrium $2Fe^{3+} + As^{3+} \rightleftharpoons 2Fe^{2+} + As^{5+}$ is shifted to the right. At temperatures larger than 650°C, the redox reaction is in equilibrium and gets frozen-in at lower temperatures. The larger the iron and arsenic concentrations, the lower are the freezing-in temperature. The thermodynamic behavior can qualitatively be explained by calculating the concentration of the redox species from thermodynamic data ΔH^o and ΔS^o measured voltammetrically at high temperatures. The freezing-in of the redox reaction can be explained by numerical simulations of the respective differential equation assuming the redox reaction to be controlled by diffusion.

UV-vis-NIR spectra of soda-lime-silica glasses doped either solely with copper or with copper and antimony or tin as a function of temperature are discussed in [28]. Glasses doped solely with copper showed a slight and steady decrease of absorption in the range from room temperature up to 800°C. Glasses additionally doped with antimony showed smaller absorptions at room temperature. During heating, the absorption is decreased in the same manner as in the glass doped solely with copper up to a temperature of around 600°C. On further heating, the absorption increases again. This was explained by the redox reaction $2Cu^{+} + Sb^{5+} \rightleftharpoons 2Cu^{2+} + Sb^{3+}$. Thermodynamic calculations based on ΔH^0 and ΔS^0 values determined by high temperature square-wave voltammetry quantitatively explain the shift in the redox ratios observed during heating (or cooling) in the temperature range 600 to 1600°C. Below 600°C, the redox reaction is frozen-in due to kinetic hindrance. In melts doped with copper and tin, the Cu^{2+} concentration is slightly smaller than in melts doped solely with copper. This can easily be explained by the small standard reaction enthalpy (6 kJmol^{-1}) of the reaction $2Cu^{+} + Sn^{4+} \rightleftharpoons 2Cu^{2+} + Sn^{2+}$.

First experimental evidence for redox relaxation in glasses was reported in [25-27]. A soda lime silica glass doped with manganese and chromium was studied by high-temperature UV-vis-NIR spectroscopy in the range from 25 to 800 °C. The spectra were deconvoluted especially with respect to the absorption peaks caused by Cr^{6+} and Mn^{3+}. Up to a temperature of around 520 °C, the absorptivities of peaks due to Cr^{6+} and Mn^{3+} decreased with temperature in the same way as in glasses doped with only one of these polyvalent elements. At higher temperature, the absorptivity of peaks caused by Cr^{6+} increases while those attributed to Mn^{3+} decreases. This is due to the redox reaction $Cr^{6+} + 3Mn^{2+} \rightleftharpoons Cr^{3+} + 2Mn^{3+}$, which is shifted to the left with increasing temperature. At temperatures below 520 °C, the redox reaction is frozen in. If the glass is heated more slowly, the intensity of the Cr^{6+} peaks decreases at temperatures larger than 520 °C and re-increases at temperatures larger than 600 °C. If a temperature in the range from 530 to 550 °C is kept, the intensity of the Cr^{6+} decreases steadily according to an exponential law. From this dependency, redox relaxation times were calculated. Thermodynamics and kinetics of the redox reaction are illustrated by numerical calculations.

The optical spectra of copper ions and the redox behavior of the Cu^+/Cu^{2+} in soda-lime-silica glasses and melts are reported in [29], [30]. A method to calculate the molar absorptivity of Cu^{2+} in soda-lime-silica glasses is proposed in [31]: three (at least) glass samples containing three different copper concentrations were equilibrated with air at three temperatures in the high temperature range. The recorded Cu^{2+} absorptivity and its dependence on nominal copper concentration and on equilibration temperature is used to estimate the molar absorptivity. The redox interaction of copper with cerium, tin, arsenic or antimony in these glasses is discussed in [32]. Cerium was found to be an oxidizing agent during cooling of melts, whereas antimony, arsenic and tin (Sb > As > Sn) are reducing agents with respect to copper.

It is complicated to study the time dependence of physical properties in the transformation range of glass due to the "memory effect" and the inherent nonlinearity which are characteristic of structural relaxation. A multi-parameter model of structural relaxation is presented in [33] that differs from earlier models that it takes into account both effects. This model fits available experimental data well; these data were predominantly obtained by observing the evolution of properties (such as density or refractive index) following a step change in temperature. The present model also permits prediction of the physical properties of glass subjected to arbitrary and more complex temperature-time histories. It should, therefore, also be useful in the rational design of heat-treating processes such as annealing.

A theory of relaxation (the time-dependent change of macroscopic properties) of glasses is presented in [34]. The fluid is described by a set of quasi-equilibrated structures, and a master equation gives the transitions among these structures. Any structural change is presumed to require a cooperative rearrangement involving many atoms, and this rearrangement entails a fluctuation to a high-energy transition state. The resulting kinetic equation describes very well the main features of observed relaxation, namely, the broad distribution of relaxation times and the nonlinearity (in ΔT) of relaxation following a temperature jump ΔT, where the apparent activation energy for relaxation depends on time.

The activation energy ΔH^* for structural relaxation in the glass transition region can be determined from the heating rate dependence of the glass transition temperature T_g or the cooling rate dependence of the limiting fictive temperature T'_f measured using DSC or DTA [35]. ΔH^* values determined this way are in good agreement with the shear viscosity activation energies ΔH_η^*. ΔH_η^* for inorganic glasses (i.e.: glasses with high T_g) can also be estimated from the width $\Delta(1/T_g)$ of the glass transition region measured by DSC or DTA using an empirical constant $C = (\Delta H_\eta^*/R)\Delta(1/T_g)$.

3. Theoretical Introduction.

3.1 Thermodynamics of redox reaction

At high temperatures, the polyvalent elements are in equilibrium with the physically dissolved oxygen in the glass melt [36], [37], [38], [39]:

$$A^{(n-z)+} + \frac{z}{4} O_2 \xrightleftharpoons{K'_A(T)} A^{n+} + \frac{z}{2} O^{2-} \tag{3}$$

The equilibrium constant $K'_A(T)$ in Eq. (3) is defined as

$$K'_A(T) = \frac{a_{A^{n+}} a_{O^{2-}}^{z/2}}{a_{A^{(n-z)+}} a_{O_2}^{z/4}} \tag{4}$$

with a_i as the activities of the respective species.

For small total concentrations of A (smaller than 1 mol%), the redox ratio $[A^{n+}]/[A^{(n-z)+}]$ does not change with the concentrations if the melt is equilibrated with a certain atmosphere and only one type of polyvalent ion is present [40]. Therefore, the activity coefficients can be considered to be unity (if referenced to infinitely diluted solutions), and the activities can be replaced by the respective concentrations.

$$K_A(T) = \frac{\left[A^{n+}\right]}{\left[A^{(n-z)+}\right]} \frac{1}{a_{O_2}^{z/4}} \tag{5}$$

Then, the equilibrium constant $K_A(T)$ depends on the glass composition. $K_A(T)$ increases with decreasing temperature for all polyvalent elements studied up to now in glass melts. Thus, if a melt is cooled down, the equilibrium is shifted towards the oxidized species [16], [17], [38], [39], [41]. However, the concentration of physically dissolved oxygen in the melt is very small, and hence, cooling the melt does not lead to a noticeable increase in the concentration of the oxidized species, if only one redox pair is present. In highly viscous silicate melts, oxygen diffusion is usually a very slow process and does only occur in a noticeable extend, if the cooling rates supplied are very small. It is justified to assume that in (boro-)silicate melts containing solely one polyvalent element in a concentration greater than 0.1 mol%, the redox ratio $[A^{n+}]/[A^{(n-z)+}]$ remains constant [17] during cooling.

In melts doped solely with copper, arsenic, antimony, and tin, respectively, the following redox equilibria are formed:

$$\mathrm{Cu^{+}} + \frac{1}{4}\mathrm{O_2} \rightleftharpoons \mathrm{Cu^{2+}} + \frac{1}{2}\mathrm{O^{2-}} \tag{6}$$

$$\mathrm{Sn^{2+}} + \frac{1}{2}\mathrm{O_2} \rightleftharpoons \mathrm{Sn^{4+}} + \mathrm{O^{2-}} \tag{7}$$

$$\mathrm{As^{3+}} + \frac{1}{2}\mathrm{O_2} \rightleftharpoons \mathrm{As^{5+}} + \mathrm{O^{2-}} \tag{8}$$

$$\mathrm{Sb^{3+}} + \frac{1}{2}\mathrm{O_2} \rightleftharpoons \mathrm{Sb^{5+}} + \mathrm{O^{2-}} \tag{9}$$

The attributed equilibrium constants $K_i(T)$ (see Eq. 5) of these reactions depend on temperature:

$$-RT \ln K_i = \Delta G_i^0 = \Delta H_i^0 - T\Delta S_i^0 \tag{10}$$

with ΔG^0 equal to standard free enthalpy, ΔH^0 equal to standard enthalpy and ΔS^0 equal to standard entropy of the assigned redox reactions in the given glass matrix in a state of infinite dilution.

If, however, another polyvalent ion is present in the melt, redox reactions during cooling (and heating) may play an important part [16], [17], [27], [28], [42], [43], [44]. At high temperature, a melt containing two polyvalent ions, A and B, equilibrated with an atmosphere of a certain oxygen fugacity will exhibit the same redox ratios $[A^{n+}]/[A^{(n-z)+}]$, $[B^{m+}]/[B^{(m-y)+}]$ as the melts solely containing the polyvalent ion A or B [16] and the following redox equilibria are formed:

$$A^{n+} + \frac{z}{4} O_2 \rightleftharpoons A^{(n+z)+} + \frac{z}{2} O^{2-} \tag{11}$$

$$B^{(m+y)+} + \frac{y}{4} O_2 \rightleftharpoons B^{m+} + \frac{y}{2} O^{2-} \tag{12}$$

The attributed equilibrium constants $K_A(T)$ and $K_B(T)$ depend on temperature.

$$-RT \ln K_A = \Delta G_A^0 = \Delta H_A^0 - T\Delta S_A^0 \tag{13}$$

$$-RT \ln K_B = \Delta G_B^0 = \Delta H_B^0 - T\Delta S_B^0 \tag{14}$$

If more than one polyvalent element is present in the glass melt, the redox ratios can not longer be considered as constant during cooling. The following redox reaction with the equilibrium constant $K_{Sb/Cu}(T)$ may take place if copper and antimony, as an example of the redox agents used in this work, are simultaneously present in the melt:

$$2Cu^{+} + Sb^{5+} \rightleftharpoons 2Cu^{2+} + Sb^{3+} \tag{15}$$

The equilibrium constant $K_{Sb/Cu}(T)$ and its temperature dependence can then be calculated from Eq. 10 inserting the values for copper and the respective redox agent (see [16], [28], [39]).

$$\begin{aligned} K_{Sb/Cu}(T) &= \frac{K_{Sb}(T)}{\left(K_{Cu}(T)\right)^2} = \exp\left(\frac{-\Delta G_{Sb}^0 + 2\Delta G_{Cu}^0}{RT}\right) \\ &= \exp\left(\frac{-\Delta H_{Sb}^0 + 2\Delta H_{Cu}^0}{RT}\right)\exp\left(\frac{\Delta S_{Sb}^0 - 2\Delta S_{Cu}^0}{R}\right) \end{aligned} \tag{16}$$

The equilibrium constant $K_{Sb/Cu}(T)$ depends on temperature, provided that $\Delta H_{Sb}^0 \neq 2\Delta H_{Cu}^0$ In that case, also the respective redox ratios $[Cu^{+}]/[Cu^{2+}]$ and $[Sb^{3+}]/[Sb^{5+}]$ depend on temperature and will be changed during cooling and heating. For this mutual interaction of two polyvalent elements, diffusion of oxygen into the melt is not necessary, but it may play an additional part at high temperatures and/or very small cooling rates.

3.2 Kinetics of the redox reaction

The kinetics of the redox reaction described in Eq. (15) is given by:

$$\frac{dx}{dt} = \left(\left[Cu^{2+}\right]_0 + x\right)^2 \left(\left[Sb^{5+}\right]_0 + x/2\right)k_+ - \left(\left[Cu^{+}\right]_0 - x\right)^2 \left(\left[Sb^{3+}\right]_0 - x/2\right)k_- \qquad (17)$$

with k_+ equal to the rate constant of the forward and k_- equal to that of the backward reaction, $[M^{x+}]_0$ equal to the initial concentration of the species M^{x+}, and x is the change in concentration of the respective species during the redox reaction.

The quotient of the rate constants k_+ and k_- is equal to the equilibrium constant $K_{Sb/Cu}(T)$

$$K_{Sb/Cu} = \frac{k_+}{k_-} \qquad (18)$$

The rate constants k_+ and k_- depend on temperature:

$$k_+ = C_1 \exp\left(\frac{E_a}{RT}\right) \qquad (19)$$

$$k_- = C_1 \exp\left(\frac{\Delta S^0_{Sb/Cu}}{R}\right) \exp\left(-\frac{E_a + \Delta H^0_{Sb/Cu}}{RT}\right) \qquad (20)$$

with E_a equal to activation energy.

The kinetics of this redox reaction during cooling (provided cooling rate q is constant) can be described by the following differential equation:

$$\frac{dx}{dT} = \frac{\left(\left[Cu^{+}\right]_0 + x\right)^2 \left(\left[Sb^{5+}\right]_0 - \frac{x}{2}\right)k_+ - \left(\left[Cu^{2+}\right]_0 - x\right)^2 \left(\left[Sb^{3+}\right]_0 - \frac{x}{2}\right)k_-}{K_{Sb/Cu}(T)} C_1 \frac{\exp\left(\frac{E_a}{RT}\right)}{q} \qquad (21)$$

Eq. 21 can be solved numerically.

When the redox reaction in a glass melt is in equilibrium at a certain temperature T and the temperature is changed, then the system will react according to Eq. (15) until a new equilibrium at the actual temperature is reached (after infinitely long times). The concentrations of the reactants and products are then changed by ΔC_0 with respect to the former equilibrium. At the time t, the change in concentrations is given by ΔC:

$$\Delta C = \Delta C_0 \exp\left(-\frac{t}{\tau}\right) \tag{22}$$

In Eq. (22), τ is the relaxation time. It depends on the respective rate constant and, for reaction orders >1, on the concentration of reacting species. For the reaction according to Eq. (15) τ can be expressed as follows [16]:

$$\tau = \left\{ k_+ \left(2\left[Sb^{3+}\right] + \frac{1}{2}\left[Cu^{2+}\right] \right)\left[Sb^{3+}\right]^2 + k_- \left(2\left[Sb^{5+}\right] + \frac{1}{2}\left[Cu^{+}\right] \right)\left[Sb^{5+}\right]^2 \right\}^{-1} \tag{23}$$

From the temperature dependence of the rate constants k, the activation energy E_a can be calculated using Arrhenius equation (see Eq. (19)).

3.3 Relaxation

It should be noted that the redox relaxation has already been described in glasses doped with manganese and chromium [42]. In general, the relaxation kinetics with respect to viscosity relaxation and electric relaxation was subject of numerous papers and theoretical considerations. According to Maxwell's kinetics of relaxation, Newtonian flow behavior is assumed. The attributed relaxation times τ are proportional to the viscosity [16]:

$$\tau = \frac{\eta}{q} \tag{24}$$

At glass transition temperature, viscosity η is set to 10^{13} dPas. Assuming a shear modulus $q = 2*10^{11}$ Pa, τ is approximately 50 s [45]. More complex concepts assume more than one [46] or even a distribution of relaxation times, include non-Newtonian flow [47]. The effect of the cooling rate q on the glass transition temperature T_g is described by the Bartenev equation [48]:

$$q = A\exp\left(\frac{E_q}{RT_g}\right) \tag{25}$$

A is a constant depending on the glass composition. E_q is the Bartenev energy which is approximately equal to the activation energy of the viscous flow.

3.4 Calculation of molar absorptivity of Cu^{2+}

The molar absorptivity of Cu^{2+} in the glasses can be estimated using some of the relations shown in 3.1.

Method proposed by Cable [31]:

For a given temperature, the absorptivity at maximum position of the Cu^{2+} band depends linearly on total copper concentration $[Cu] = [Cu^{2+}] + [Cu^{+}]$ and is

$$A = A_0 + b[Cu] \tag{26}$$

provided that the $[Cu^{2+}]/[Cu^{+}]$ ratio is constant and does not depend on total copper concentration (these pre-conditions are satisfied in the glasses under investigation according to 3.1). Appling Lambert-Beer’s law to Eq. 26, it results

$$A = A_0 + \varepsilon_{Cu^{2+}}\left[Cu^{2+}\right] \tag{27}$$

Unfortunately, only the total copper concentration [Cu] is known whereas $[Cu^{2+}]$ and the $[Cu^{2+}]/[Cu^{+}]$ ratio are unknown. Therefore, $[Cu^{2+}]$ has to be replaced by [Cu]:

$$A = A_0 + \varepsilon_{Cu^{2+}}\frac{[Cu]}{1+\frac{\left[Cu^{+}\right]}{\left[Cu^{2+}\right]}} \tag{28}$$

The slope b of the straight line from Eq. (1) is

$$b = \frac{\varepsilon_{Cu^{2+}}}{1+\frac{\left[Cu^{+}\right]}{\left[Cu^{2+}\right]}} \tag{29}$$

The redox reaction in the glass matrix is given in Eq. (6) and the respective equilibrium constant K′ can be written

$$K' = \frac{\left[Cu^{2+}\right]\left[O^{2-}\right]^{\frac{1}{2}}}{\left[Cu^{+}\right]p\left(O_2\right)^{\frac{1}{4}}} \tag{30}$$

For the [Cu^{+}]/Cu^{2+}] ratio results

$$-\log\frac{\left[Cu^{+}\right]}{\left[Cu^{2+}\right]} = \log K' + Z \tag{31}$$

Since redox reactions in glass melts behave regularly, K′ can be represented by

$$\log K' = \frac{-\Delta H}{2.303RT} + \text{const.} \tag{32}$$

and it results in:

$$\log\frac{\left[Cu^{+}\right]}{\left[Cu^{2+}\right]} = \frac{\Delta H}{2.303R}\frac{1}{T} - Z' \tag{33}$$

For a simplification of the mathematical treatment, the temperatures of the experiments should be chosen in a way that

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{1}{T_2} - \frac{1}{T_3} \tag{34}$$

Combining Eq. (33) and (34), it follows that

$$\left(\frac{\left[Cu^{I}\right]}{\left[Cu^{II}\right]}\right)_{T_2}^{2} = \left(\frac{\left[Cu^{I}\right]}{\left[Cu^{II}\right]}\right)_{T_1}\left(\frac{\left[Cu^{I}\right]}{\left[Cu^{II}\right]}\right)_{T_3} \tag{35}$$

and from Eq. (29) the [Cu^{I}]/[Cu^{II}] ratio results in

$$\frac{\left[Cu^{+}\right]}{\left[Cu^{2+}\right]} = \frac{\varepsilon_{Cu^{2+}}}{b} - 1 \tag{36}$$

Eq. (35) becomes

$$\left(\frac{\varepsilon_{\mathrm{Cu}^{2+}}}{b_{T_2}}-1\right)^2=\left(\frac{\varepsilon_{\mathrm{Cu}^{2+}}}{b_{T_1}}-1\right)\left(\frac{\varepsilon_{\mathrm{Cu}^{2+}}}{b_{T_3}}-1\right) \tag{37}$$

and the molar absorptivity is then

$$\varepsilon_{\mathrm{Cu}^{2+}}=\frac{b_{T_2}^2\left(b_{T_1}+b_{T_3}\right)-2b_{T_1}b_{T_2}b_{T_3}}{b_{T_2}^2-b_{T_1}b_{T_3}} \tag{38}$$

Alternative method:

It follows from thermodynamics used for the calculation of the redox reaction in glasses containing solely one polyvalent element that the equilibrium constant K depends on temperature [30], cf. Eq. (10). K is given by

$$\ln K=\frac{-\Delta H^0}{RT}+\frac{\Delta S^0}{R} \tag{39}$$

In case of glasses doped with copper, the equilibrium constant K is then

$$K=\frac{[\mathrm{Cu}^{2+}]}{[\mathrm{Cu}^{+}]p_{O_2}^{1/2}}=\frac{[\mathrm{Cu}^{2+}]}{\left([\mathrm{Cu}]-[\mathrm{Cu}^{2+}]\right)p_{O_2}^{1/2}}=\exp\left[\frac{-\Delta H^0+T\Delta S^0}{RT}\right] \tag{40}$$

and it results in:

$$\frac{[\mathrm{Cu}]}{[\mathrm{Cu}^{2+}]}=\exp\left[\frac{\Delta H^0}{RT}\right]\exp\left[\frac{\Delta S^0}{R}\right]-1 \tag{41}$$

According to Lambert-Beer's law (see 4.2.1), the spectroscopically measured absorptivity α is

$$\alpha=\varepsilon_{\mathrm{Cu}^{2+}}\left[\mathrm{Cu}^{2+}\right] \tag{42}$$

and it follows that $[\mathrm{Cu}^{2+}]=\alpha/\varepsilon$. This can be inserted in Eq. (41):

$$\frac{\varepsilon_{\mathrm{Cu}^{2+}}\left[\mathrm{Cu}\right]}{\alpha}=\exp\left(\frac{\Delta H^0}{RT}\right)\exp\left(\frac{\Delta S^0}{R}\right)-1 \tag{43}$$

If $\exp(\Delta S^0/R)$ is named constant B and $\Delta H^0/R$ is named constant C, it results in:

$$\frac{\left[\mathrm{Cu}\right]}{\alpha}=\frac{B}{\varepsilon}\exp\left(\frac{C}{T}\right)-\frac{1}{\varepsilon} \tag{44}$$

and finally

$$\ln\frac{[\mathrm{Cu}]}{\alpha}=\left(\frac{\Delta H^0/R}{T}\right)\ln\left(\frac{1}{\varepsilon}\exp\left(\frac{\Delta S^0}{R}\right)\right)-\ln\left(\frac{1}{\varepsilon}\right) \tag{45}$$

The expressions $\Delta H^0/R$, $\frac{1}{\varepsilon}\exp(\Delta S^o/R)$ and $1/\varepsilon$ are constants.

Applying Eq. (45), molar absorptivity ε can be estimated from the spectroscopically (at room temperature) measured absorptivities α_i of samples of a glass with the total copper concentration [Cu] which melts were equilibrated at (at least) three temperatures.

In principle, during cooling the redox equilibrium according to Eq. (6) is shifted to the oxidized species [41], [49]. Simultaneously, the viscosity of the melt is increased and the diffusion of oxygen into the melt is drastically decreased. Consequently, if the concentration of the polyvalent element is larger than 0.1 mol% then the redox ratio remains constant [16]. But in optical glasses the concentrations of polyvalent elements are very low, and the concentration of physically dissolved oxygen (O_2) in the glass melt is high enough so that the redox equilibrium can be shifted. At higher concentrations of polyvalent elements, the redox ratio remains constant during cooling [16], [17].

4. Experimental part.

4.1 Preparation and characterization of the samples

For the experiments, two base glass compositions were used. First glass was a soda-lime-silicate glass with the nominal composition $16Na_2O$-$10CaO$-$74SiO_2$ (mol %). This glass is known and widely used as a model glass for sheet and other industrial glasses in glass research. The second glass was a borosilicate glass with the nominal composition $25Na_2O$-$15B_2O_3$-$60SiO_2$ (mol %). The second glass is 'shorter' than the soda-lime-silica glass. This means that the viscosity of the glass is changed steeper with changing temperature. Furthermore, the activation energy of viscous flow is higher than that for the soda-lime silicate glass. The investigated redox reaction of polyvalent elements can be explained more clearly comparing their behaviour in the two different base glass compositions. Soda-lime silicate glasses were prepared for two experiments. First, glasses were doped with copper as the only polyvalent element to investigate the Cu^+/Cu^{2+} redox equilibrium at high temperature. Second, glasses were doped with copper and arsenic, antimony or tin to investigate the kinetics and mechanism of redox reactions during heating and cooling of the doped glasses between room temperature and 800 °C. The borosilicate glasses were doped with copper and arsenic, antimony or tin to investigate the kinetics and mechanism of redox reaction at temperatures up to 650 °C.

4.1.1 Glass preparation

(i) Soda-lime-silicate glasses for the estimation of Cu^{2+} molar absorptivity

Glass batches were mixed from reagent grade raw materials: SiO_2, Na_2CO_3, $CaCO_3$ and doped with copper oxide CuO. The CuO concentrations of the samples are given in Table 1. Batches were calculated for 300 g glass and melted in silica crucibles for 1 h at 1,500 °C in a Superkanthal furnace. The glasses were casted into a carbon mould (preheated to 550 °C), subsequently put into a cooling furnace and cooled to room temperature using a cooling rate of about 30 K/min. Pieces of the glasses were heat treated in 90Pt/10Au crucibles at 1500, 1425 and 1350 °C for 24 h and at 1225 °C for 36 h to equilibrate the Cu^+/Cu^{2+} ratio. After cooling to room temperature, samples were investigated using UV-vis-NIR spectroscopy to estimate the Cu^{2+} absorptivity.

Table 1: Total copper concentration in soda-lime-silica glasses (series (i))

Sample	[CuO] in mol %	[CuO] in $molL^{-1}$
A	0.079	0.025
B	0.238	0.074
C	0.486	0.148
D	0.794	0.250

(ii) Soda-lime-silicate glasses for redox reaction studies

Batches for the base glass were mixed from reagent grade raw materials: SiO_2, Na_2CO_3, and $CaCO_3$. Copper was added as CuO, arsenic as As_2O_3, antimony as Sb_2O_3 and tin as $Sn(COO)_2$, all of reagent grade. The concentrations of the polyvalent elements added to the glasses compositions are shown in Table 2. Again, batches were calculated for 300 g of glass. All these glasses were melted in a middle frequency induction furnace using a 250 ml platinum crucible. In order to produce comparable (with respect to their redox state) samples, a strict temperature-time schedule has to be kept for the melting process. The batches were put in portions into the pre-heated platinum crucible at 1300 °C. After that, the temperature was stepwise increased by 50 K until the melting temperature of 1500 °C was reached. For 2 h, glass melts were homogenised by stirring and simultaneously gas bubbles were removed. The glass melts were then casted into a carbon mould (preheated 15 minute at annealing temperature), put into a cooling furnace and cooled down to room temperature with a cooling rate of about 30 K/min.

(iii) Borosilicate glasses for redox reaction studies

These glasses were prepared mostly like the soda-lime-silica glasses mentioned above. Glass batches were mixed from reagent grade raw materials: SiO_2, Na_2CO_3 and H_2BO_3 and doped with reagent grade CuO and with or without the reducing agents As_2O_3, Sb_2O_3 or SnO, all of reagent grade. Concentrations of the polyvalent elements in the respective samples are given in Table 2. Batches for these glasses were calculated for 180 g of glass. All compositions were melted in a middle frequency induction furnace using a platinum crucible. The batches were put in portions into the pre-heated platinum crucible at 1050 °C. After that, the temperature was stepwise increased by 50 K until the melting temperature of 1160 °C was reached. For 2 h, glass melts were homogenised by stirring and simultaneously gas bubbles were removed. The glass melts were then casted into a carbon mould (preheat 15 minute at annealing temperature), put into a cooling furnace and cooled down to room temperature with a cooling rate of about 30 K/min.

In principle, it has to be marked that the concentrations of the redox dopants are notably higher than in most industrial glasses in order to improve the quality of the spectroscopic measurements. The molar absorptivity of Cu^{2+} is much smaller than the molar absorptivities of the most other polyvalent elements, especially of chromium, iron and manganese. Nevertheless, the concentration of copper was limited to $\leq$ 1mol%. For these concentrations, the redox ratio of the polyvalent elements will not depend on their total concentration [41] and the Lambert-Beer's law is still valid.

Table 2: Nominal concentration (in mol%) of the polyvalent elements added to the samples studied

(X and Y are soda-lime-silica glass, Z sodium borosilicate glass)

Sample	[CuO]	[As_2O_3]	[Sb_2O_3]	[SnO]
X	0.475	-	-	-
X1	0.475	0.294	-	-
X2	0.475	0.586	-	-
X3	0.475	1.165	-	-
Y	0.238	-	-	-
Y1	0.238	0.147	-	-
Y2	0.238	0.294	-	-
Y3	0.238	0.586	-	-
Z	1.2	-	-	-
Z1	1.2	1.2	-	-
Z2	1.2	-	1.2	-
Z3	1.2	-	-	1.2

4.1.2 General characterisation of the base glasses

The important characteristics of the two base glasses were measured and the results are summarized in Table 3. The glass transformation temperature, T_g, was estimated by differential thermal analysis, DTA, (Shimadzu DTA-50) and by thermal expansion measurements: the linear thermal expansion coefficient, α, was measured in the temperature range from 100 to 300 °C by dilatometry (Netzsch 402 ES). For high temperature spectroscopic investigations, the softening point of the glasses is important. The temperature at which the thermal expansion curve goes through its maximum was taken as the softening point temperature. The densities of the glasses were measured using a Helium pycnometer (Micrometrics AccuPyc 1330).

Table 3: Base glass characteristics

Properties	Soda-lime-silica glass	Sodium borosilicate glass
T_g (°C)	545±5	530±5
Softening point (°C)	605±5	580±5
α (10^{-7} K^{-1})	94±3	97±2
Density (gcm^{-3})	2.487	2.570

4.2 UV-vis-NIR spectroscopic studies

4.2.1 General introduction

In the glasses under investigation, Cu^{2+} is the only species out of the studied redox pairs which absorbs in the visible and NIR region. As^{3+}/As^{5+}, Sb^{3+}/Sb^{5+} and Sn^{2+}/Sn^{4+} absorption bands are situated in the UV region and covered by the base glass absorption edge. Thus, only the change in Cu^{2+} concentration can be used to describe the course of the respective redox reactions as a function of temperature and time.

In glasses doped with copper, three different oxidation states of copper are possible. The most common is the Cu^{2+} which is the origin of the (greenish-) blue colour of the respective glasses. Under normal ('oxidizing') conditions, Cu^{2+} is in equilibrium with Cu^{+}, which is colourless. Under reducing conditions, the formation of Cu^{0} is possible which can lead to a red colour of the glass samples by the formation of colloidal Cu^{0} particles in the glass matrix (so called ‘copper ruby glasses’). In the glasses investigated, only Cu^{2+} and Cu^{+} were observed due to the oxidizing conditions (melting in air).

The electronic configuration of Cu^{2+} is $3d^9$, whereas the electronic configuration of Cu^{+} is $3d^{10}$. In case of Cu^{2+}, electron transitions between the d-orbitals are possible provided that the d-orbitals are splitted by ligands. Cu^{2+} ions are sixfold (octahedrally) coordinated by ligands. Therefore, the d-orbitals are splitted into ^2E (d_{xy}, d_{xz}, d_{yz}) and $^2T_2$ $\left(d_{x^2-y^2}, d_{z^2}\right)$ and $^2E \rightarrow {}^2T_2$ transitions are possible. Due to the Laporte selection rule, transitions between d energy levels are forbidden and therefore only week absorption bands result unless there are no other effects that repeal at least partially the selection rules. Cu^{2+} absorption band in oxide glasses is found in the visible region at wavenumbers at around 12,500 cm^{-1}. Often, the band is asymmetric on account of Jahn-Teller distortion [50] which leads to three electron transitions instead of one. Therefore, the seemingly single Cu^{2+} absorption band can be decomposed into three absorption bands of Gaussian shape. For the investigations presented here, it was found that the recorded Cu^{2+} spectra could be fitted in a sufficient approximation by only one single band. The concentration of Cu^{2+}, $[Cu^{2+}]$, was correlated with the intensity of this single band.

Cu^{+} ($3d^{10}$) does not show d-d transitions but strong oxygen-to-metal charge transfer bands in the near UV region that are superimposed by the base glass absorption edge. Thus, it was not possible to evaluate these bands properly.

Lambert-Beer’s law describes the relation between the ratio of the incident intensity $\mathbf{I_0}$ and of the intensity passed through the sample **I** and the specific absorption properties of the absorbing species $\boldsymbol{\varepsilon}$, their concentration **c** and sample thickness **d**:

$$\ln\frac{I}{I_0} = A = -\varepsilon(\lambda, T)cd = -\alpha(\lambda, T)d \tag{46}$$

A is the absorbance, and spectra were recorded as absorbance A vs. wavenumbers ν (linear with energy) in this work. The molar absorptivity ε is a distinguishing feature of the respective species (in $Lmol^{-1}cm^{-1}$) and depends on wavelength λ and on temperature T, c is its concentration ($molL^{-1}$), and d is the sample thickness (cm).

In glasses doped with polyvalent elements, the concentration c of the respective absorbing ion, for example Cu^{2+}, is not equal to the nominal concentration of CuO which was added to the glass batch because of the redox interaction with the (physically and chemically) solved oxygen or with other polyvalent elements in the melt. Unfortunately, the molar absorptivity ε of the absorbing species is normally unknown, and it depends among other things on acid-base properties of the glass matrix. Thus, any change in base glass composition will change the respective molar absorptivity of the absorbing species. It is possible to estimate molar absorptivity ε for polyvalent elements in glasses by the method described in 3.4, but it is very time consuming and, therefore, restricted to a few special investigations.

Normally, absorptivity $\alpha = A/d = \varepsilon c$ is given to compare the results of samples with different base glass composition, with different concentrations of polyvalent elements and/or melted under different redox conditions.

At room temperature, absorption spectra (i.e. absorbance A vs. wavenumbers υ) were measured by double-beam UV-vis-NIR spectrophotometer UVPC 3101 (Shimadzu Corporation, Kyoto, Japan). The measuring range is between 3,100 and 52,500 cm^{-1}. The recorded absorbance A was divided by the sample thickness d and the obtained absorptivity α is given in the respective figures. At higher temperatures, spectra were recorded using a modular spectrometer in combination with a microscope heating stage (cf. 4.2.2).

The spectra (absorptivity α vs. wavenumbers υ) were decomposed into background, base glass absorption edge and a single Cu^{2+} absorption band. Peakfit 4.02 program (SYSTAT software Inc) was used for these purposes.

4.2.2 Absorption spectroscopic measurements at high temperatures

High temperature vis-NIR spectra were recorded in the temperature range from 25 to 800 °C in a specially constructed spectrometer (see Fig. 1). The sample was placed inside the heating chamber of a microscope heating stage (TS 1500, LINCAM, Waterfield, Great Britain). A halogen lamp was used as light source. The light was reflected by a planar mirror; it passed through a chopper (chopper frequency: 113 s^{-1}) and subsequently through the sample. The transmitted light was reflected by 90° using an off-axis parabolic mirror and focused to the entrance slit of a monochromator (TRIAX 320, Jobin-Yvon, Edison, N. Y., USA). The signals collected by an Si-detector were given to a lock-in amplifier (SR830, Stanford Research Systems, Stanford, CA, USA) adjusted to the chopper frequency. The spectrometer is described in details in [27], [28]. At constant temperature, the temperature error is ±5 K; while it increases with increasing heating rates up to ±20 K at a heating rate of 5 $K{\cdot}min^{-1}$. The samples had a diameter of 6 mm and thicknesses between 0.2 and 2 mm. The surfaces were ground and polished to optical quality.

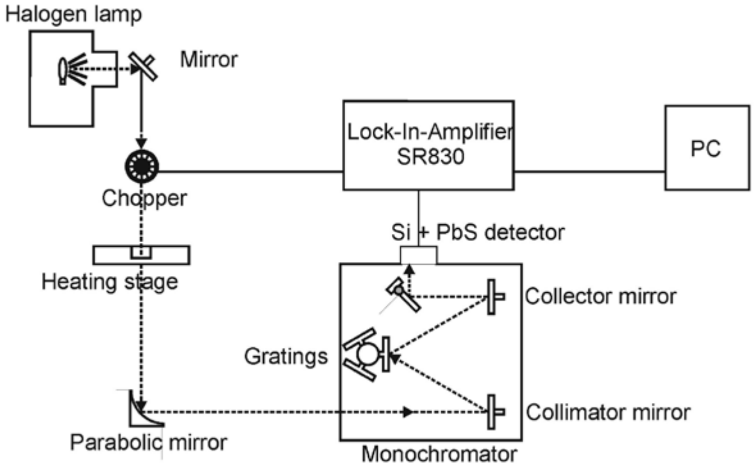


Figure 1: Schematic drawing of the high temperature spectrometer

This spectrometer is especially useful for samples containing ions with absorption bands in the boundary region between visible and NIR region like Cu^{2+}. It is necessary to exclude the thermal radiation of the heating stage and of the sample. According to Kirchhof's radiation law [50], the sample emits radiation in the spectral range where light is absorbed, i.e. where the Cu^{2+} absorption band occurs. With respect to the emitted radiation, the furnace (heating stage) behaves as a gray emitter. With increasing temperature the thermal radiation emitted by the furnace and the sample is increased. With the spectrometer described above only the chopped light beam of the lamp is measured by the lock-in amplifier and, therefore, we obtain only the absorption of the sample.

Though, this advantage is connected with the disadvantage of increased measuring times (in comparison with the diode array spectrometer used for high temperature spectroscopic investigations of chromium and manganese containing glasses [52]). For a given wavenumber region between 10,000 and 25,000 cm^{-1}, measuring time depends on the number of steps. The more steps, i.e. the smaller the wavenumber distance between the measured υ-A data points, the better is the resolution of the recorded spectra, but the longer is the measuring time, and vice versa. Usually, measuring time (at constant temperature) was between 1 and 3 minutes. Therefore, time resolution of kinetic experiments is within this order of magnitude.

In principle, it is possible to measure up to a wavenumber of 4,000 cm^{-1} with the modular spectrophotometer. In this case, the silicon detector has to be changed by a PbSe detector. The measuring time is increased, but the gain in information on the Cu^{2+} absorption band is comparatively low. It should be mentioned, that in case of glasses doped with iron the measurements were carried out down to 4,000 cm^{-1} [26], [27].

4.3 Measuring procedure

Soda-lime silica glasses and sodium borosilicate glasses both doped with copper or with copper and additionally with arsenic, antimony or tin are spectroscopically measured using different temperature-time schedules.

First step: Spectra were recorded at different temperatures between 25 and 800 °C during heating. All investigated samples were heated up from room temperature to 300 °C with a rate of 5 K/min. Above 300 °C, different heating rates of 10, 5, 2, 1 and 0.5 K/min were used. These measurements were carried out to characterize the absorption behaviour of the samples and its temperature dependence in general.

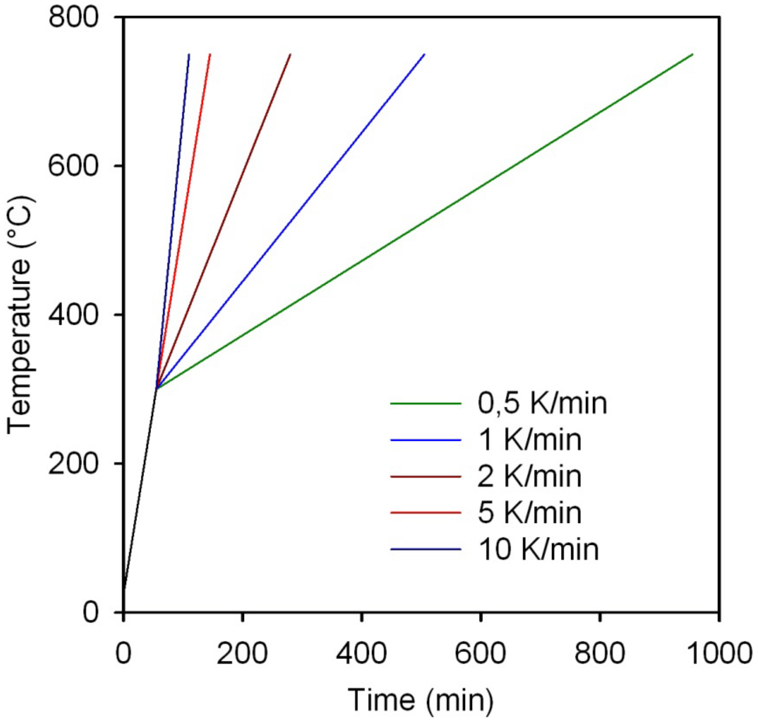


Figure 2: Temperature-time schedule of heating experiments with different heating rates

Second step: The samples were heated up to 300 °C with a heating rate of 5 K/min, followed by further heating with a heating rate of 2 K/min to one of three temperatures slightly above T_g, where the samples were hold at constant temperature and the spectra were recorded after different times. These experiments were carried out to investigate the relaxation of the redox reaction.

Third step: The samples were heated up to 650 °C with a heating rate of 5 K/min, held at this temperature for 30 min and subsequently cooled down with different cooling rates of 10, 5, 1 and 0.5 K/min to 300 °C to study the kinetics of the redox reaction during cooling.

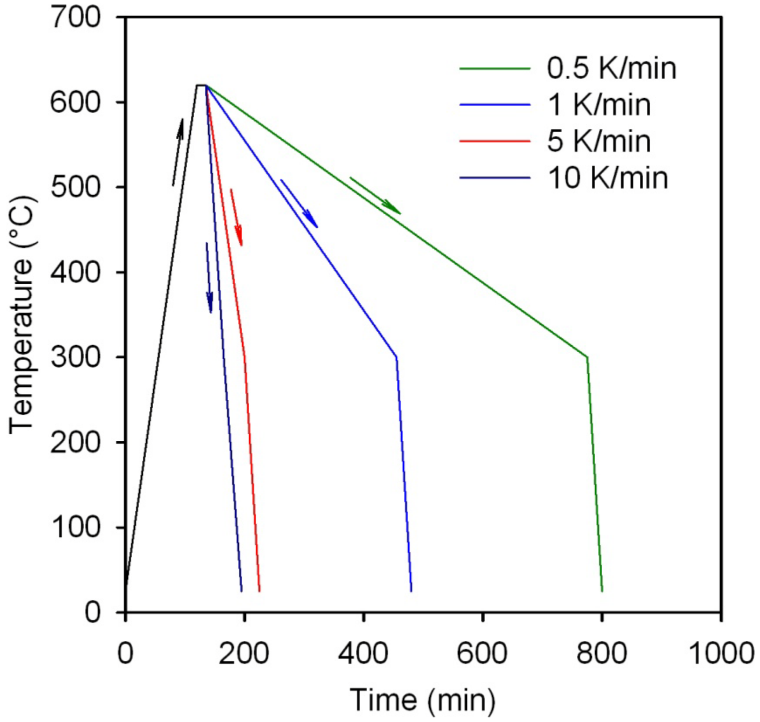


Figure 3: Temperature-time schedule of cooling experiments with different cooling rates

4.4 Analysis of the absorption spectra

After measuring the samples either with the UV-vis-NIR spectrophotometer Shimadzu UVPC 3101 or normally with the modular high temperature spectrophotometer, the software Peakfit 4.02 (SYSTAT Software Inc) was used to fit the part of the absorption spectra showing the Cu^{2+} absorption band (cf. Fig. 4) by one Gaussian shaped band and to estimate the band parameters height = intensity of the band, maximum position and full width at half maximum

(FWHM). The intensity of the Cu^{2+} absorption band was used to describe the concentration of Cu^{2+} as a function of the nominal concentration of CuO and redox agents, of temperature, of time and of heating or cooling rates to analyze the thermodynamics and the kinetics of the redox reaction.

Figure 4 presents the absorption spectra measured with the UVPC3101 (curve A) and with the modular spectrophotometer (curve B). Curve C is the calculated Cu^{2+} absorption band to fit the recorded spectra. The fit is not perfect but fairly good. The differences between the calculated band (curve C) and the measured band (curve A) (additional bands caused by Jahn-Teller splitting) are visible at wavenumbers larger than 10,000 cm^{-1}.

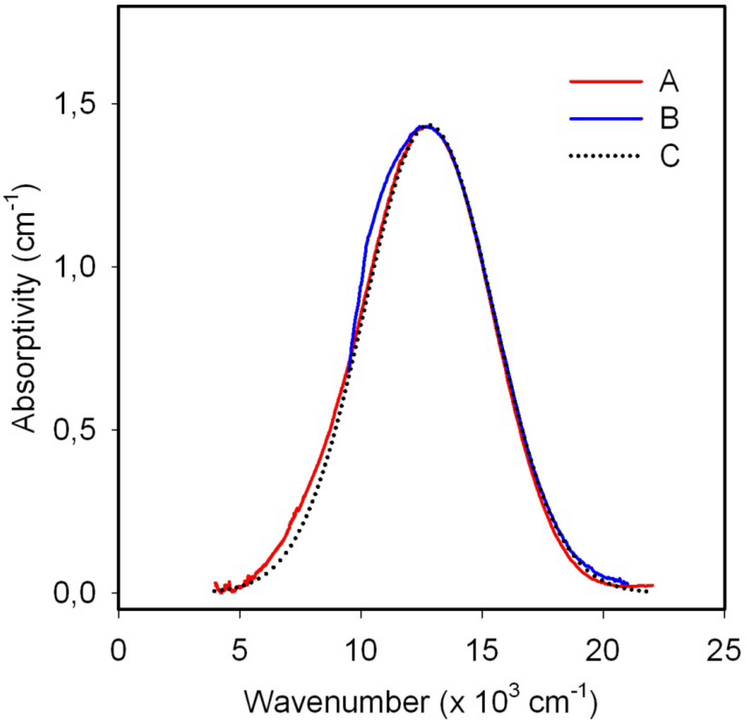


Figure 4: Absorption spectra of the soda-lime-silica glass doped with 0.475 mol% CuO and with 0.294 mol% As_2O_3
A: recorded with UV3100PC
B: recorded with modular high temperature spectrometer
C: simulated Cu^{2+} absorption band

In the same way, absorption spectra of the sodium borosilicate glass samples were interpreted. The absorption spectra for soda-lime-silica and for sodium borosilicate glasses closely resemble each other. The maximum position of the Cu^{2+} absorption band is shifted to lower wavenumbers in the latter glasses. Figure 5 presents the absorption spectra measured by UVPC3101 and by the modular spectrophotometer together with the calculated Cu^{2+} band to fit the recorded spectra.

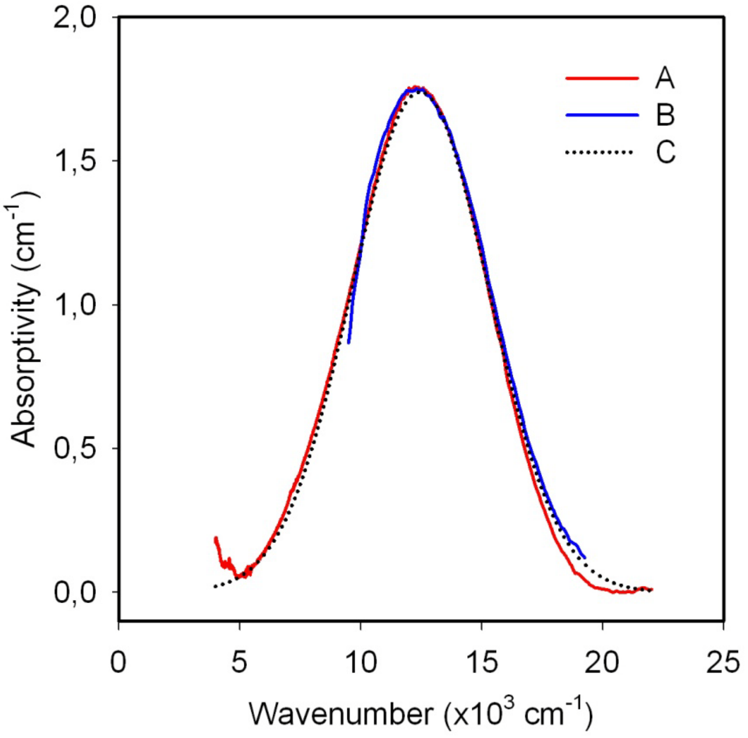


Figure 5: Absorption spectra of a sodium borosilicate glass sample doped with 1.2 mol% CuO and 1.2 mol% As_2O_3
A: recorded with UV3100PC
B: recorded with modular high temperature spectrometer
C: simulated Cu^{2+} absorption band

In case of the sodium borosilicate glasses, the appearance of the additional Cu^{2+} bands is less pronounced compared to the soda-lime-silica glasses.

4.5 Calculation of kinetic parameters

The results of the heating and cooling experiments were summarized by presentations of absorptivity of the Cu^{2+} band vs. temperature or vs. time.

For the calculation of **relaxation times** $\boldsymbol{\tau}$, the measured absorptivity values as a function of time at constant temperatures were fitted by an exponential decay function representing Eq. 22, $\Delta C = \Delta C_0 \exp(-t/\tau)$:

$$y = y_0 + a * \exp(-bx)$$

In this function, y is equal to the absorptivity at maximum position of the Cu^{2+} band (i.e. proportional to the $[Cu^{2+}]$), x equal to the time and b equal to $1/\tau$. The fits resulted in regression coefficients values R^2 larger than 0.99.

For a redox reaction $yA^{n+} + zB^{(m-y)+} \rightleftharpoons yA^{(n-z)+} + zB^{m+}$, the equilibrium constant K_{AB} is

$$K_{AB}(T) = \frac{(K_A(T))^y}{(K_B(T))^z} = \frac{\left[A^{n+}\right]^y \left[B^{(m-y)+}\right]^z}{\left[A^{(n-z)+}\right]^y \left[B^{m+}\right]^z}$$

The equilibrium constants $K_{AB}(T)$ can also be expressed by thermodynamic values ΔH_i^0 and ΔS_i^0 as is given for the redox reaction $2Cu^{2+} + Sb^{3+} \rightleftharpoons 2Cu^{+} + Sb^{5+}$ in Eq. 16:

$$\begin{aligned} K_{Sb/Cu}(T) &= \frac{K_{Sb}(T)}{(K_{Cu}(T))^2} = \exp\left(\frac{-\Delta G_{Sb}^0 + 2\Delta G_{Cu}^0}{RT}\right) \\ &= \exp\left(\frac{-\Delta H_{Sb}^0 + 2\Delta H_{Cu}^0}{RT}\right) \exp\left(\frac{\Delta S_{Sb}^0 - 2\Delta S_{Cu}^0}{R}\right) \end{aligned} \qquad (16)$$

Using the respective values for Cu and Sb or As, the $K_{Sb/Cu}(T)$ and $K_{As/Cu}(T)$ can be calculated. With the help of the $K_{AB}(T)$, it is possible to calculate the concentrations of the respective species $[Cu^{2+}]$, $[Cu^{+}]$ and $[Sb^{5+}]$, $[Sb^{3+}]$ or $[As^{5+}]$, $[As^{3+}]$ at a certain temperature in equilibrium. Inserting the respective relaxation time τ and the calculated concentrations into Eq.

23, and replacing k_- by $k_+/K_{Sb/Cu}$ (or $K_{As/Cu}$), the **rate constant**s, $\mathbf{k_+}$, could be calculated for the (three) temperatures at which the relaxation times were estimated.

An Arrhenius plot of the rate constants k_+ ($\ln k_+$ vs. $1/T$) was used to calculate the attributed **activation energy E_A** of the redox reaction which corresponds to the slope (multiplied by the gas constant R).

5. **Result and Discussion.**

5.1 Determination of molar absorptivity of Cu^{2+} in the soda-lime-silica base glass

Glass samples containing at least three different total concentrations of copper (about 50g for each sample) were heat treated at 1275 °C for 36 h and at 1350, 1425 and 1500 °C for 24 h, respectively, in order to equlibrate the Cu^{2+}/Cu^{+} ratio. The spectra of the samples recorded at room temperature using the Shimadzu UVPC3101 spectrophotometer are given in Figures 6 to 9.

The results of these investigations are summarized in Table 4 and Figure 10. The maximum of the Cu^{2+} absorption band was found at wavenumbers between 12,600 and 12,700 cm^{-1}. It is shifted to larger wavenumbers with increasing total copper concentration and with increasing equilibration temperature. With decreasing equilibration temperature, the maximum absorptivity of the respective samples is increased. That is: the concentration of Cu^{2+}, $[Cu^{2+}]$, is increased with decreasing temperature whereas the $[Cu^{+}]$ is decreased.

Applying the method proposed in [31], the molar absorptivity $\varepsilon(Cu^{2+})$ was calculated to be 24.3 $L mol^{-1} cm^{-1}$.

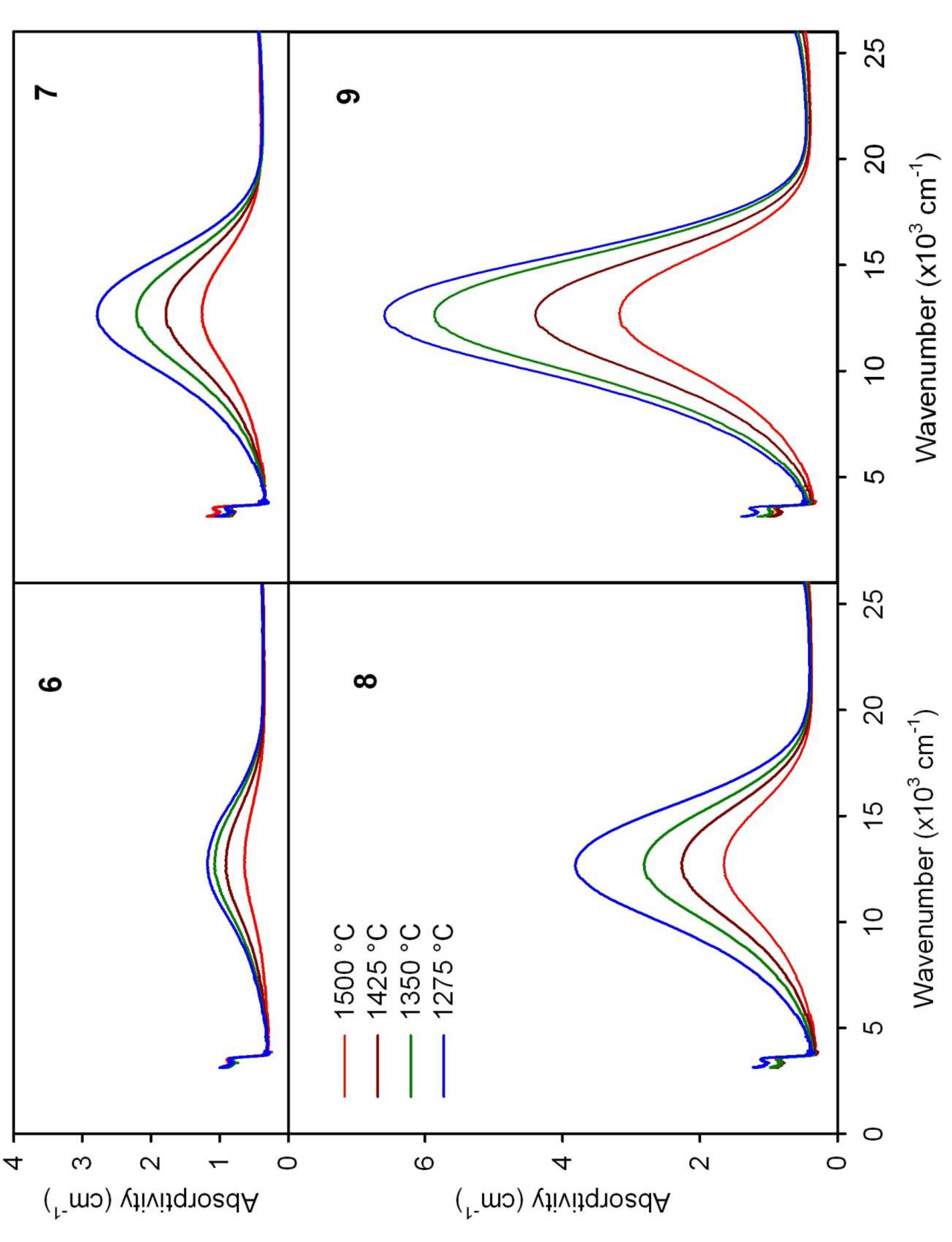


Figure 6 to 9: Absorption spectra (measured at room temperature) of samples doped with different amounts of copper after equilibration at the given temperatures
6: 0.079 mol% CuO
7: 0.238 mol% CuO
8: 0.486 mol% CuO
9: 0.794 mol% CuO

Table 4: Absorptivity (cm^{-1}) of soda-lime-silica glass samples containing different copper concentration after equilibrating at different temperatures

	Glass A (0.079 Cu^{2+})	Glass B (0.238 Cu^{2+})	Glass C (0.486 Cu^{2+})	Glass D (0.794 Cu^{2+})
1275 °C	0.448	1.595	3.081	5.213
1350 °C	0.428	1.357	2.729	4.605
1425 °C	0.388	1.118	2.013	3.682
1500 °C	0.285	0.712	1.484	2.489

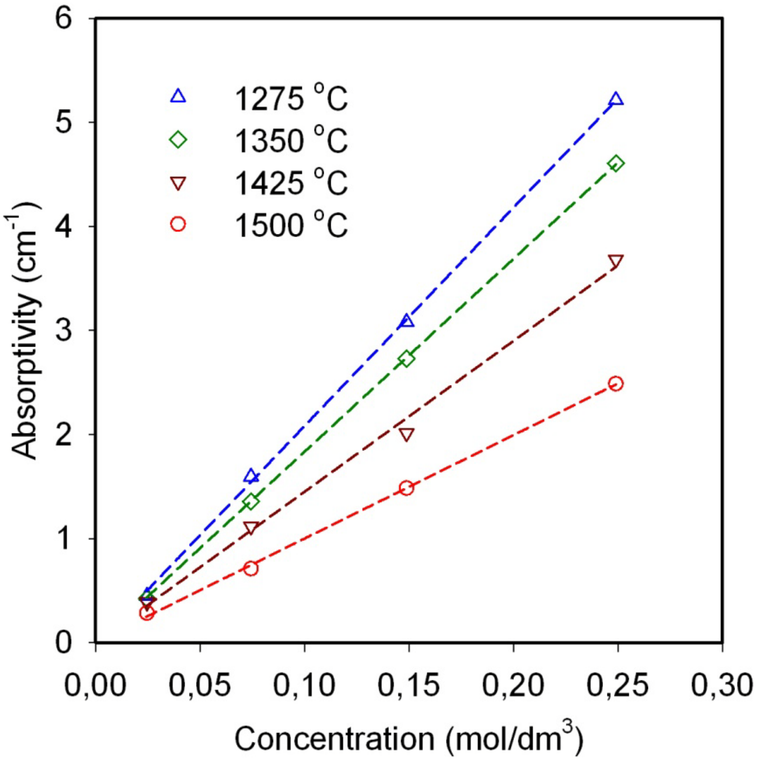


Figure 10: Absorptivity (cm^{-1}) of soda-lime-silica glass samples containing different copper amounts after equilibrating at different temperatures
The intersections with the y-axis are at -0.0186, -0.0191, -0.0012 and 0.0065.

In Figure 11, the relation of $\ln \frac{[Cu_{total}]}{\alpha}$ as a function of $1/T$ is given according to Eq. 45. For the calculation of $\varepsilon(Cu^{2+})$, the data for temperatures of 1350, 1425 and 1500 °C were used. The molar absorptivity ε was calculated for four different total copper concentrations. The linear plots of the samples with higher total copper concentrations are quite similar to each other, but in case of lowest copper concentration (0.079 mol%), the slope is quite different. Therefore, data obtained for 1275 °C were not used for the calculation of the molar absorptivity. Molar absorptivity values were given from the intersection with the y axis.

For total copper concentrations [Cu] of 0.238, 0.486 and 0.794 mol %, Cu^{2+} molar absorptivities $\varepsilon(Cu^{2+})$ were calculated to be 31.2, 24.8 and 23.2 $L*mol^{-1}*cm^{-1}$, using only the results for 1500, 1425 and 1350 °C. A mean value of $\varepsilon(Cu^{2+})$ = 25 $L*mol^{-1}*cm^{-1}$ was assumed for the thermodynamic and kinetic calculations. This is the same value which was already obtained by the first method. The advantage of the second method is that molar absorptivity of the respective species can be calculated using data obtained for (at least three) different temperatures of glass samples with only one concentration of copper provided that the total copper concentration is high enough but does not exceed 1 mol% [40].

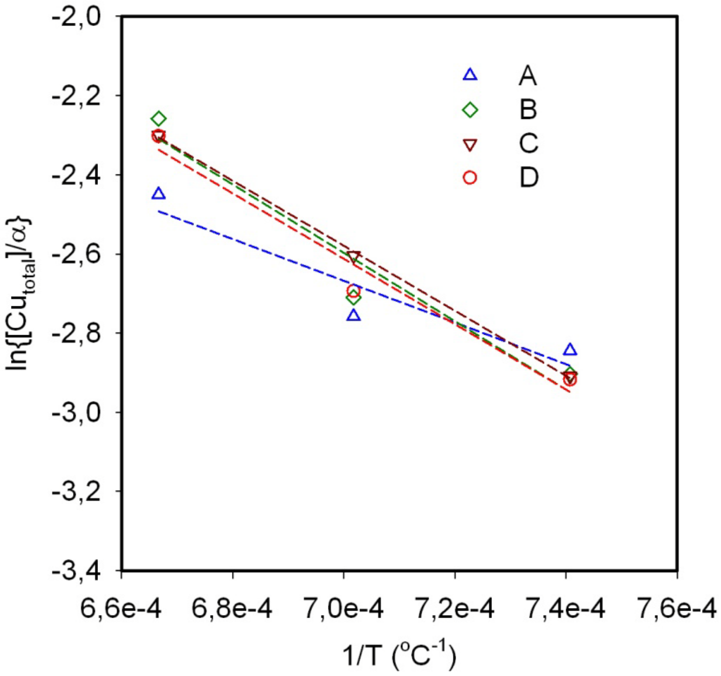


Figure 11: Relation between $\ln\frac{[Cu_{total}]}{\alpha}$ and $1/T$

Table 5: Molar absorptivity $\varepsilon(Cu^{2+})$ calculated using Eq. 45

[CuO] in mol%	$\ln\frac{1}{\varepsilon}$ (according to Eq. 45)	molar absorptivity in $L*mol^{-1}*cm^{-1}$
0.079	1.02	2.77
0.238	3.44	31.2
0.486	3.17	23.8
0.794	3.17	23.8

5.2 Temperature dependence of Cu^{2+} absorption in both base glasses doped solely with copper

In glasses doped solely with copper, the redox ratio $[Cu^{2+}]/[Cu^{+}]$ remains constant during cooling from glass melting temperature (1500 °C for soda-lime-silica glass, 1160 °C for sodium borosilicate glass) to room temperature [10] due to the fact that the diffusion of O_2 into the melt normally is too slow and the equilibrium $Cu^{2+}+\frac{1}{2}O^{2-} \rightleftharpoons Cu^{+}+\frac{1}{4}O_2$ cannot be changed due to the lack of a reaction partner and provided that the total copper concentration is high enough. For the soda-lime-silica glass doped solely with copper, it was already shown by Kido [28]: i) Only a slight decrease in the absorptivity during heating from room temperature to 800 °C is observed. This decrease is completely reversible during subsequent cooling. ii) The position of the maximum of the Cu^{2+} absorption band is shifted from 12,650 cm^{-1} (25 °C) to 11,500 cm^{-1} (800 °C), and iii) the absorption band becomes broader (FWHM from 7,250 cm^{-1} to 7,550 cm^{-1}).

Sodium borosilicate glass samples doped solely with copper show the corresponding behaviour. It should be mentioned, that soda-lime-silica glasses doped with the same amount of CuO show a much lower absorptivity of the Cu^{2+} absorption band compared to the sodium borosilicate glasses. The higher melting temperatures of the latter glasses shift the redox equilibrium to reduced species (right side of the redox equation above).

Figure 12 shows a set of vis-NIR spectra of a sodium borosilicate glass sample with 1.2 mol% CuO recorded at temperatures in the range from 25 to 650 °C. All spectra have very similar shape and possess only one maximum attributed to the absorption of Cu^{2+}. With increasing temperature, the position of the maximum of the Cu^{2+} absorption band is shifted from 12,700 cm^{-1} (at 25 °C) to smaller wavenumbers until at 650 °C a value of 11,800 cm^{-1} is reached. The absorptivity at room temperature is 8.8 cm^{-1} and then decreases slightly (~5%) in the temperature range studied.

In Figure 13, the absorptivity measured at the maximum position of the Cu^{2+} absorption band is given as a function of temperature during heating from room temperature to 650 °C and subsequent cooling. For any given temperature in this range, the estimated absorptivity remains (within the experimental error limits) the same during heating and cooling (see also Fig. 18).

In order to calculate the Cu^{2+}-concentration from Lambert-Beer's law, the molar absorptivity must be known. Unfortunately, the molar absorptivity has not yet been determined for the sodium borosilicate glass composition, but according to the literature does not depend much on the base glass composition. Assuming the molar absorptivity of 25 $L*mol^{-1}*cm^{-1}$ experimentally estimated for soda-lime-silica glass samples, the Cu^{2+} concentration is 0.95 mol%. This means 80% of the total copper occurs as Cu^{2+} in the sample containing solely copper. This value is much larger than those found for the respective soda-lime-silica glass samples. It should be noted, however, that the borosilicate glass studied was melted at 1160 °C while the silicate glasses usually were prepared using maximum temperatures in the range from 1450 to 1550 °C. The higher the temperature, the more pronounced is the shift in the equilibrium between Cu^{+} and Cu^{2+} towards the reduced state Cu^{+} (see Eq. (4)).

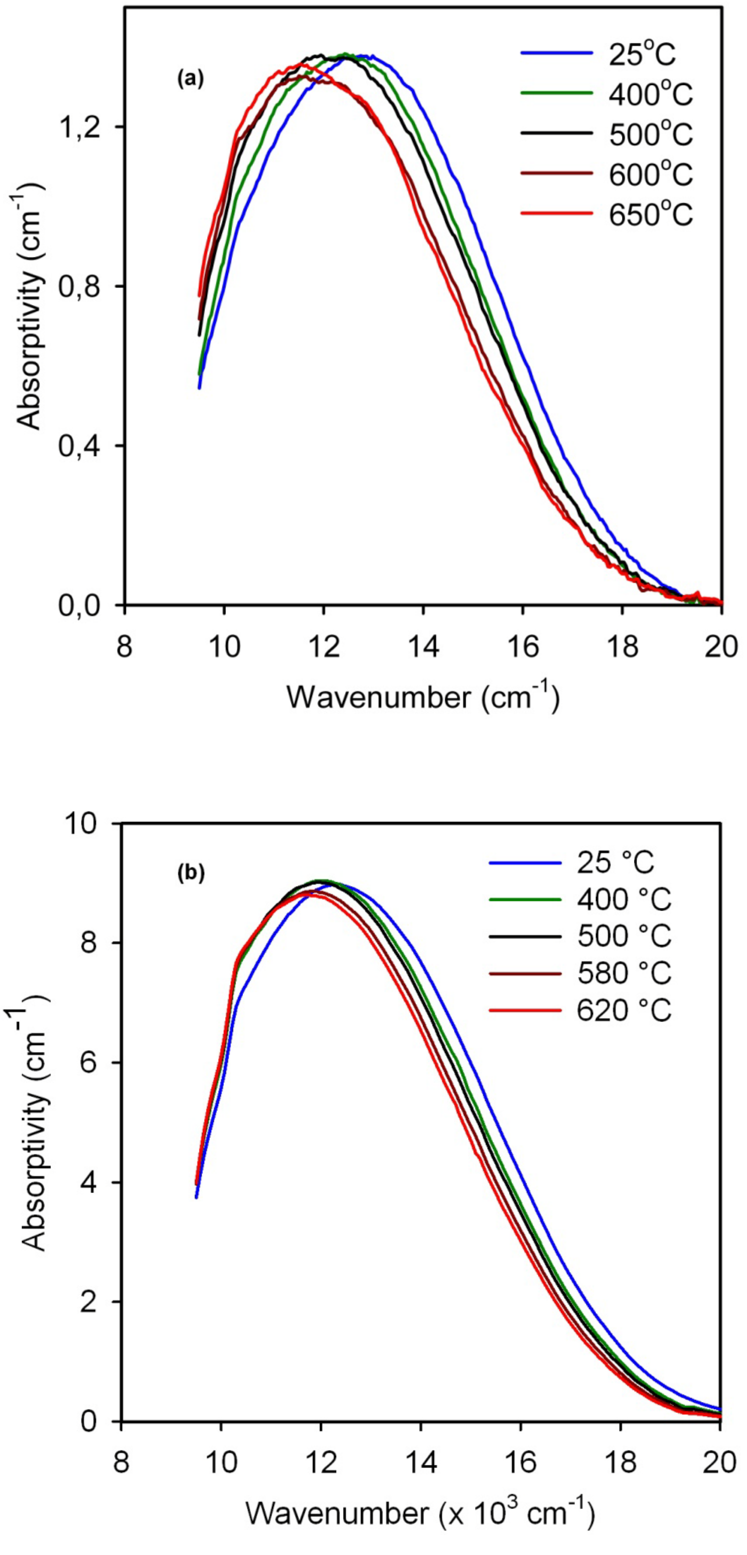


Figure 12: Absorption spectra of the soda-lime-silica glass doped with 0.475 CuO (a) and of the sodium borosilicate glass doped with 1.2 mol% CuO (b) at different temperatures.

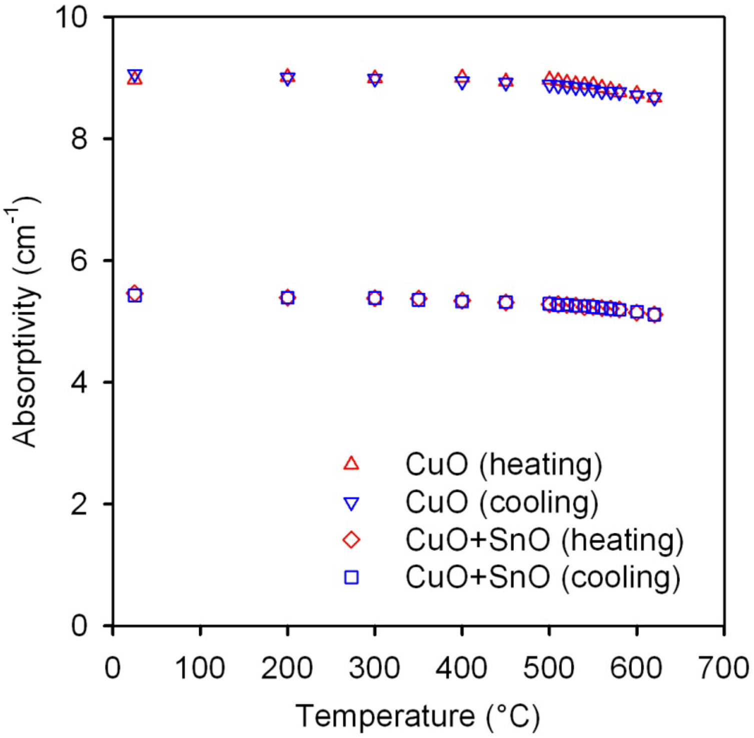


Figure 13: Absorptivity at maximum position of the Cu^{2+} absorption band in the sodium borosilicate glass as a function of temperature during heating and subsequent cooling for the sample doped with 1.2 mol% CuO and for the sample doped with 1.2 mol% CuO and 1.2 mol% SnO

5.3 Temperature dependence of the Cu^{2+} absorption in both base glasses doped with copper and tin

The absorptivities at maximum position of the Cu^{2+} absorption band measured at different temperatures during heating and subsequent cooling for a sodium borosilicate glass sample doped with CuO and SnO are also shown in Figure 13. In analogy to the soda-lime-silica glass for this sample, the absorptivities at any temperature during heating and cooling are the same within the accuracy of measurement. But glass samples additionally doped with tin show the same behaviour at a lower Cu^{2+} concentration level as the glasses solely doped with copper. It is already known that tin is not such a strongly reducing agent in soda-lime-silica glasses in comparison to arsenic and antimony [53]. By contrast, the results presented here demonstrate that a redox reaction, according to $2Cu^{+}+Sn^{4+} \rightleftharpoons 2Cu^{2+}+Sn^{2+}$ will not occur in a noticeable extend in these samples during heating and cooling. The reaction enthalpy for this reaction in a soda-lime-silica glass was calculated to be only 6 $kJmol^{-1}$ [28]. It is reasonable to assume that the reaction enthalpy in this sodium borosilicate glass is in the same order of magnitude. Therefore, no evidence of a redox reaction in the studied temperature range was found for this glass. This is in contrast to [54], where Sn^{2+} is described as an effective reducing agent towards Cu^{+}. The decreased Cu^{2+} concentration in the sample investigated here is the result of the reducing ability of the (tin) oxalate during its thermal decomposition when the glass batch is heated up.

5.4 Temperature dependence of redox reactions in glasses doped with copper and arsenic or antimony during heating

5.4.1 Experimental results

The Cu^{2+} concentration in the investigated glass samples is strongly influenced by the redox agents added. Obviously, SnO has the smallest effect: the Cu^{2+} concentration is decreased by 33% with respect to the sample without any added redox agent, whereas additional doping with Sb_2O_3 and As_2O_3 decreased the Cu^{2+} concentration by 80% or even more. At room temperature, the shape of the spectrum and the position of the maximum is the same for all four samples, (see Fig. 14).

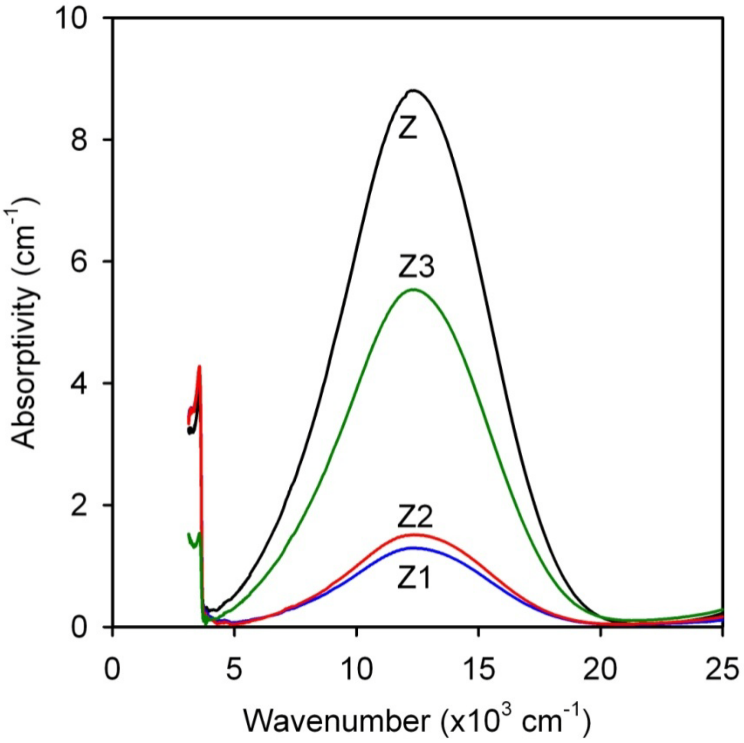


Figure 14: Absorption spectra (recorded with SHIMADZU UV3100PC) at room temperature of glasses doped with 1.2 mol% CuO (curve Z), with 1.2 mol% CuO with 1.2 mol% As_2O_3 (curve Z1), with 1.2 mol% CuO and 1.2 mol% Sb_2O_3 (curve Z2), and with 1.2 mol% CuO and 1.2 mol% SnO (curve Z3)

Absorption spectra of sodium borosilicate base glass doped with different concentrations of copper (a: 0.475 mol% and b: 0.238 mol% CuO) and arsenic (see Table 2) are shown in Figure 15. As expected, the intensity of the Cu^{2+} absorption band is decreased with decreasing copper concentration and with increasing arsenic concentrations. The redox reaction $2Cu^{2+}+As^{3+} \rightleftharpoons 2Cu^{+}+As^{5+}$ is shifted to the right side. This can also be seen by the increase of the absorptivity at 25,000 cm^{-1}. The increase is probably caused by increasing [Cu^{+}] and is more obvious with smaller total copper concentration.

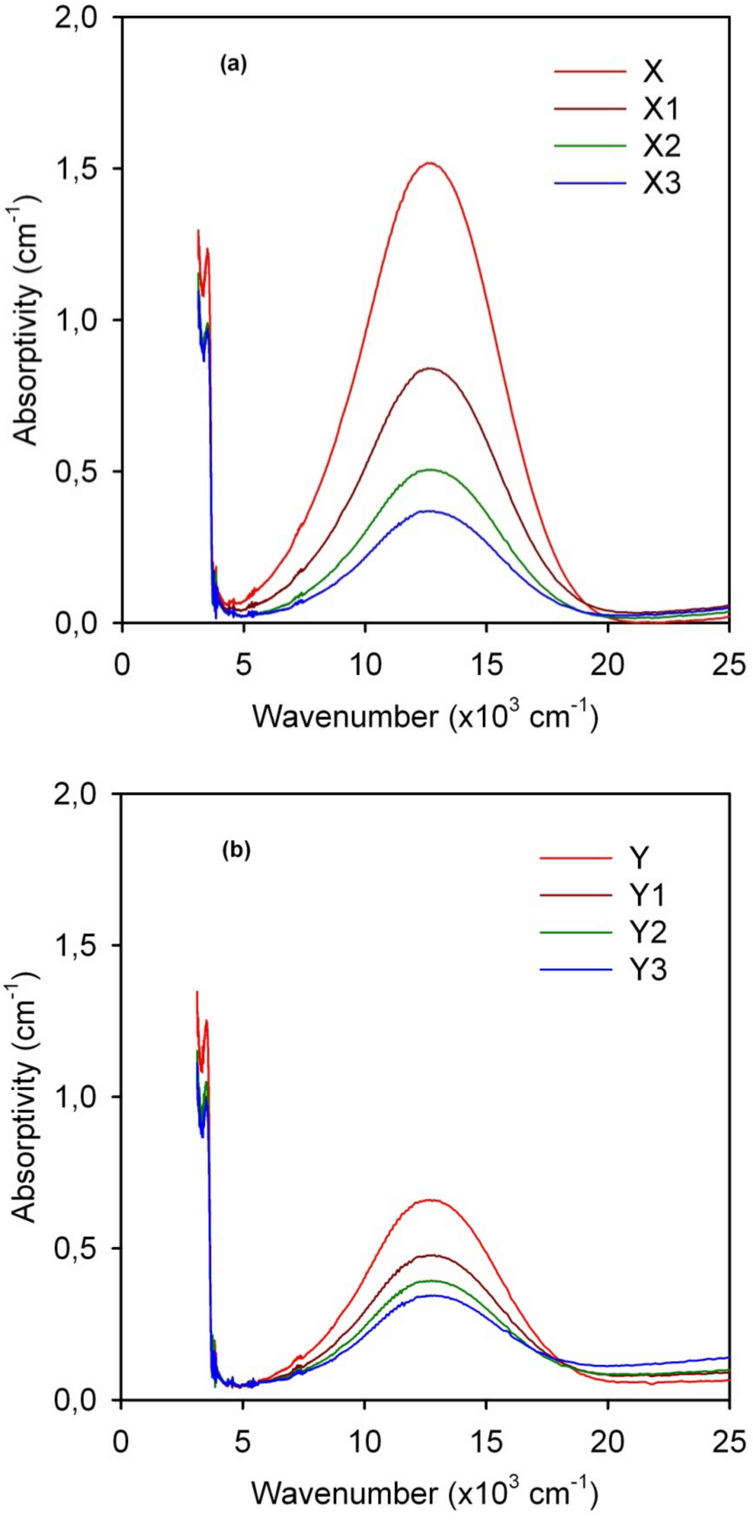


Figure 15: Absorption spectra at room temperature of glasses doped with 0.475 mol% CuO (a) (curve X), 0.475 mol% CuO with 0.294 mol% As_2O_3 (curve X1), 0.475 mol% CuO with 0.586 mol% As_2O_3 (curve X2), 0.475 mol% CuO with 1.165 mol% As_2O_3 (curve X3), 0.238 mol% CuO (b) (curveY), 0.238 mol% CuO with 0.147 mol% As_2O_3 (curve Y1), 0.238 mol% CuO with 0.294 mol% As_2O_3 (curve Y2), 0.238 mol% CuO with 0.586 mol% As_2O_3 (curve Y3)

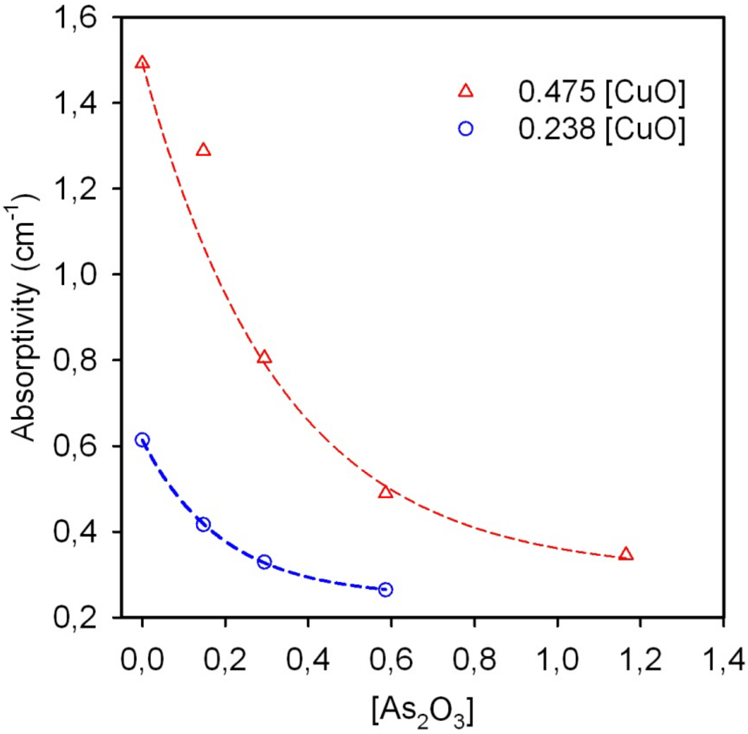


Figure 16: Absorptivity at the maximum of the Cu^{2+} absorption band at room temperature of glassed doped with CuO as a function of the As_2O_3 concentration.

Figure 16 shows that the reducing effect of arsenic is fairly similar for both total copper concentrations. With increasing arsenic concentration, the [Cu^{2+}] approaches seemingly saturation.

Absorption spectra of a soda-lime-silica base glass doped with 0.475 mol% CuO and 0.294 mol% As_2O_3 recorded at different temperatures in the range from 25 to 750 °C are shown in Figure 17.

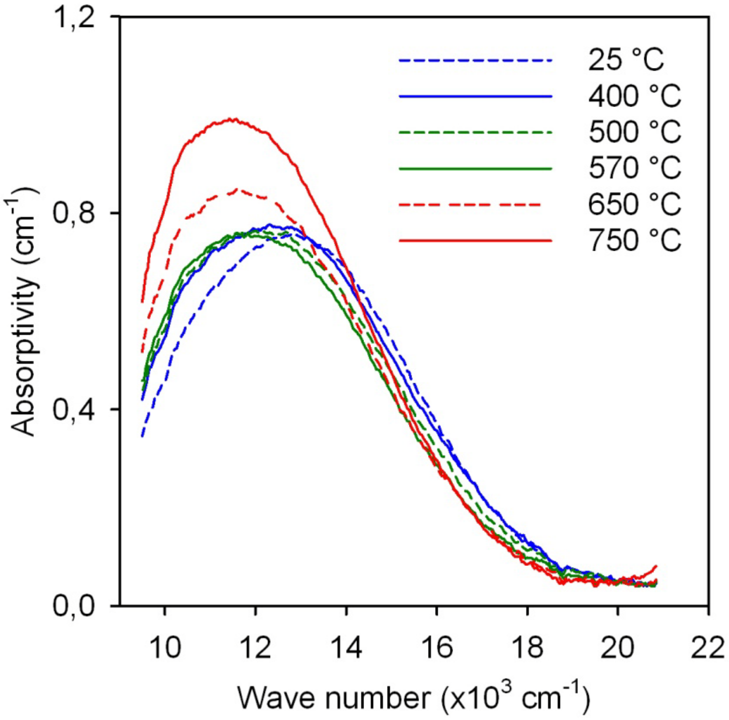


Figure 17: Absorption spectra of the soda-lime-silica base glass doped with 0.475 mol% CuO and 0.294 mol% As_2O_3 as a function of temperature (heating rate 10 Kmin^{-1})

With increasing temperature, the position of the maximum of the Cu^{2+} absorption band is shifted from 12,700 cm^{-1} (at 25 °C) to smaller wavenumbers until at 750 °C a value of 11,700 cm^{-1} is reached. At temperatures below T_g, (T_g = 545 °C) the intensity of the absorption band decreases with increasing temperature. At temperatures above T_g, a re-increase of the intensity is observed.

The temperature dependence of the absorbance at the maximum position of the Cu^{2+} absorption band is shown in Figure 18 for glasses doped with 0.475 CuO and various As_2O_3 concentrations.

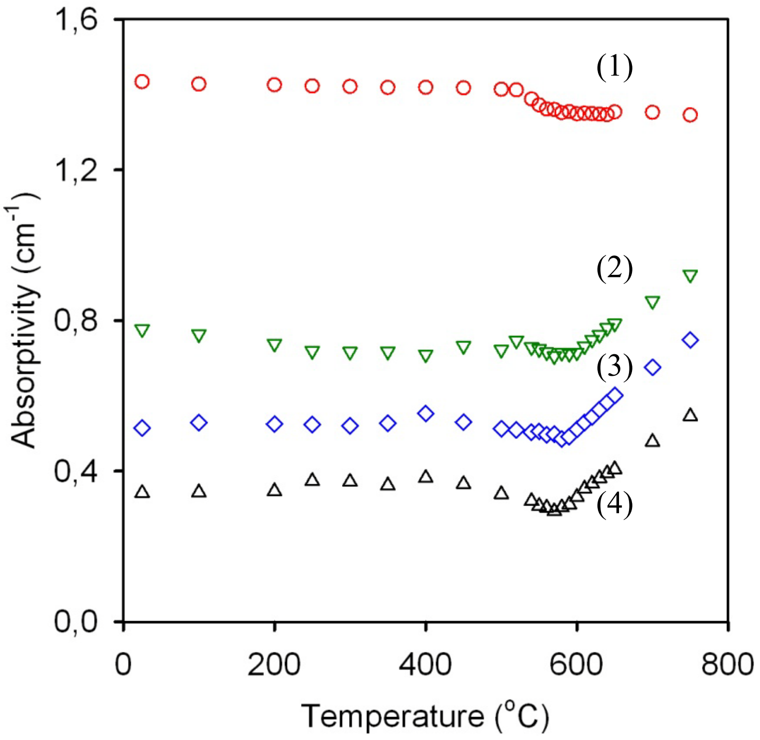


Figure 18: Intensity of the Cu^{2+}-absorption band of samples doped with 0.475 mol % CuO and 0.0 (1), 0.294 (2), 0.586 (3) and 1.163 (4) mol % As_2O_3 as a function of temperature

The spectra were recorded during heating of quenched samples (casted melt cooled to room temperature) using a heating rate of 10 Kmin^{-1}. In the sample solely doped with CuO, only a slight temperature dependency was observed. The absorptivities decreased from 1.434 cm^{-1} at 25 °C to 1.413 cm^{-1} at 550 °C. Approximately the same behavior was observed in glasses doped with both CuO and As_2O_3 at temperatures below T_g. At temperatures above T_g, the absorbance increases. The latter effect depends strongly upon the As_2O_3-concentration.

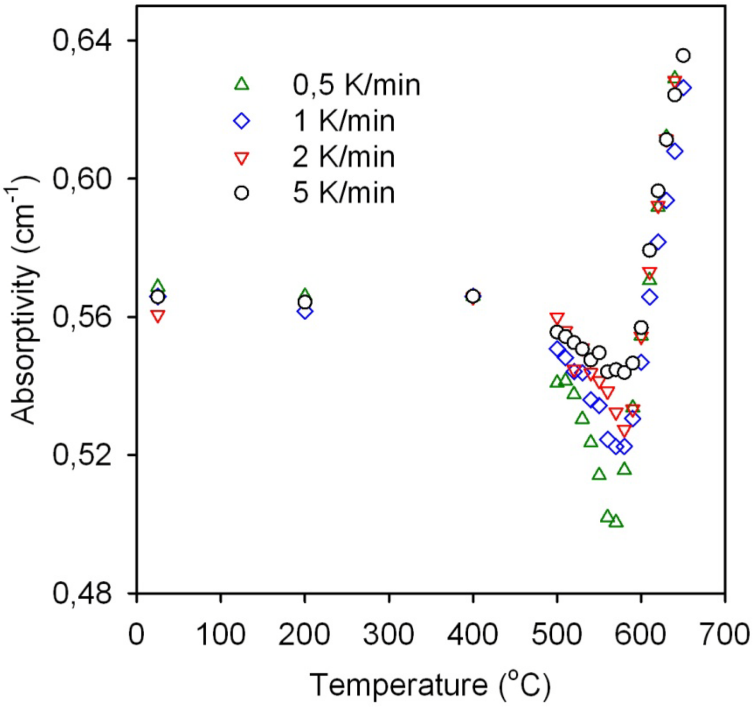


Figure 19: Absorptivity at maximum position of the Cu^{2+}-absorption band of a glass doped with 0.475 mol% CuO and 0.586 mol% As_2O_3 as a function of temperature for different heating rates.

In Figure 19, the absorptivities at the maximum position of the Cu^{2+} absorption band of a soda-lime-silica glass doped with 0.475 mol% CuO and 0.586 mol% As_2O_3 are shown as a function of temperature for different heating rates (from 0.5 to 5 Kmin^{-1}). Up to 500 °C, the effect of the temperature on the absorptivity is small and does not depend on heating rate. At temperatures above 500 °C, the curves exhibit a minimum at temperatures in the range from 580 to 600 °C and increases strongly for larger temperatures. The heating rate strongly affects the absorptivity especially the minimum: The smaller the heating rates, the smaller are the absorptivities at the minimum (i. e. the more pronounced is it). Furthermore, this minimum is shifted to lower temperatures at smaller heating rates. At temperatures more than 30 K larger than that attributed to the minimum, the absorptivities of all samples are approximately equal again, and hence do not depend on the heating rate. The difference of the absorptivity in the respective minima between heating rates of 5 and 0.5 K/min was 0.043 cm^{-1}. This is an evidence of the effect of the heating rate on the redox reaction (time dependence of redox reactions) according to theory of structural relaxation [33], [55].

The room temperature vis-NIR spectra of sodium borosilicate glass samples doped both with copper and additionally with arsenic, antimony or tin are already discussed in chapter 5.2 and 5.3: the Cu^{2+} concentration in the samples is influenced by the redox agents added. Sodium borosilicat glasses doped solely with copper or doped with copper and with tin behave like the respective soda-lime-silica glasses and do not show evidence of redox reaction during heating and cooling.

All spectra recorded exhibit a well pronounced absorption peak of Cu^{2+} which according to the literature, e.g. [3], is attributed to the $^2E \rightarrow {}^2T_2$ transition. The dependency of absorption upon wavenumbers can fully be described by a fit to a curve of Gaussian shape. The wavenumbers attributed to the peak maximum are slightly shifted to smaller values with increasing temperature as already reported in references [28], [43]. In principle, the dependencies of the absorptivity on temperature are similar for all glasses studied both during heating and cooling for temperatures larger than 450 °C. Since in the glass solely doped with copper the Cu^{2+}-concentration can be considered as constant, the slight decrease in absorptivity is due to the temperature dependence of the molar absorptivity. A similar behaviour has already been reported for the Cu^{2+} molar absorptivity in soda-lime-silicate glasses [42], [43].

In the glasses studied, the absorptivities of the glass solely doped with copper are approximately 50% larger than those in the glass doped with both copper and tin and more than five times larger than those in the glasses doped with both copper and arsenic or antimony. In order to calculate the Cu^{2+}-concentration from Lambert-Beer's law, the molar absorptivity must be known. Unfortunately, the molar absorptivity has not yet been determined for the studied glass composition, but according to the literature does not depend much on the base glass composition [31]. Assuming a molar absorptivity of 25 $Lmol^{-1}cm^{-1}$ [31], the Cu^{2+} concentration is 0.95 mol%. This means 80% of the total copper occurs as Cu^{2+} in the sample containing solely copper. This value is much larger than those given in the literature for example for soda-lime-silica glasses. It should be noted, however, that the borosilicate glass studied was melted at 1160 °C while the silicate glasses usually were prepared using maximum temperatures in the range from 1450 to 1550 °C. The higher the temperature, the more the equilibrium between Cu^+ and Cu^{2+} is shifted towards the reduced state Cu^+ (see Eq. 6).

The sodium borosilicate glass additionally doped with tin shows the same behaviour at a lower Cu^{2+} concentration level. It is already known that tin is not such a strongly reducing agent in soda-lime-silica glasses in comparison to arsenic and antimony [32]. On the contrary, the results presented here demonstrate that a redox reaction $2Cu^{+}+Sn^{4+} \rightleftharpoons 2Cu^{2+}+Sn^{2+}$ will not occur in a noticeable extend in this sample during heating and cooling. The reaction enthalpy for this reaction was calculated to be only 6 $kJmol^{-1}$ in a soda-lime-silica glass [28].

In Figures 20 and 21, the absorption spectra at different temperatures of two glasses doped with 1.2 mol% CuO and 1.2 mol% Sb_2O_3 (Fig. 20) and 1.2 mol% CuO and 1.2 mol% As_2O_3 (Fig. 21) are shown for two heating rates: 10 $Kmin^{-1}$ (upper case) and 0.5 $Kmin^{-1}$ (lower case), and in Figure 22, the absorptivity at maximum position of the Cu^{2+} band as a function of temperature is shown for different heating rates for the two samples. During heating from room temperature up to about 420 °C, all samples (containing solely CuO or containing CuO and an additional redox agent) exhibit a similar behavior; although the Cu^{2+} concentrations are different (cf. Figs. 13 and 18). At temperatures above 420 °C, the curves for the samples doped with CuO and As_2O_3 or Sb_2O_3 exhibit a minimum in the range from 540 to 570 °C and increases drastically at larger temperatures. The heating rate strongly affects the absorptivity, especially the development of the minimum. The smaller the heating rates, the smaller is the absorptivity at the minimum, i.e. the more pronounced is the minimum. Furthermore, this minimum is shifted to lower temperatures at smaller heating rates. At temperatures more that 30 K larger than that attributed to the minimum, the absorptivity of all samples is approximately equal again, and hence does not depend on the heating rate. The differences of the absorptivities in the respective minima between heating rates of 10 and 0.5 Kmin^{-1} were approximately 0.1 cm^{-1}.

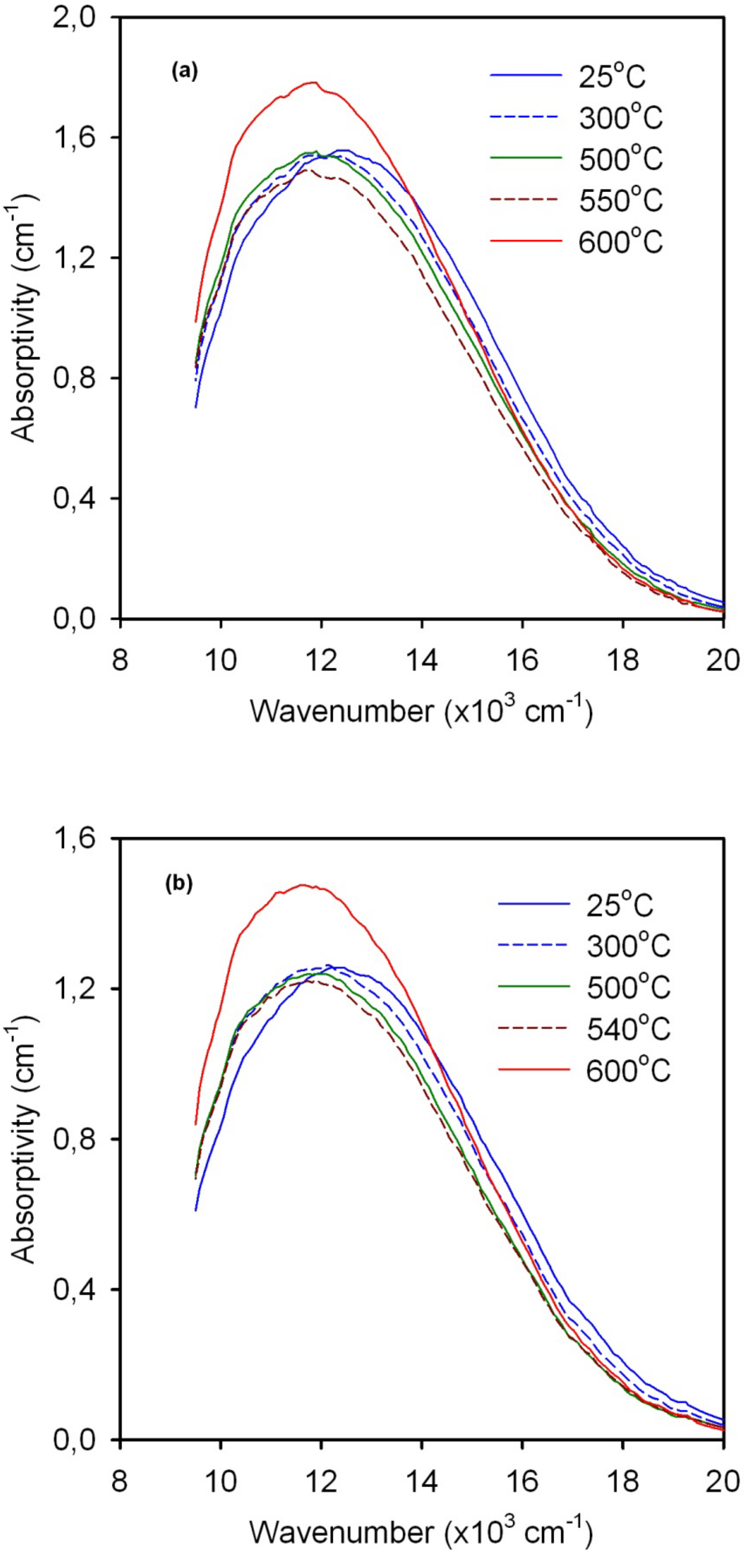
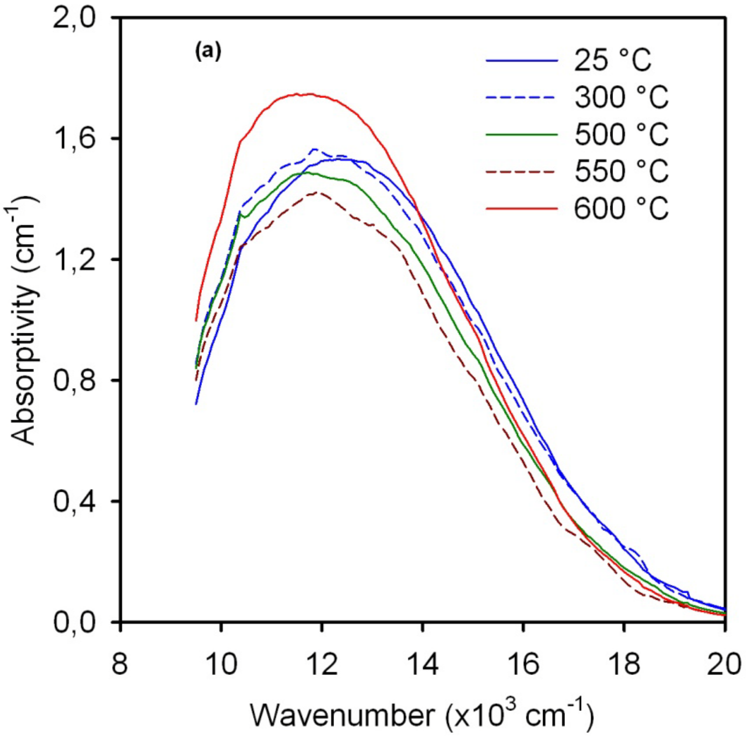


Figure 20: Absorption spectra of a sodium borosilicate glass doped with 1.2 mol% CuO and 1.2 mol% Sb$_2$O$_3$ (a) and 1.2 mol% CuO and 1.2 mol% As$_2$O$_3$ (b) at temperatures of 25, 300, 500, 540, 550 and 600 °C during heating using a rate of 10 K·min^{-1}



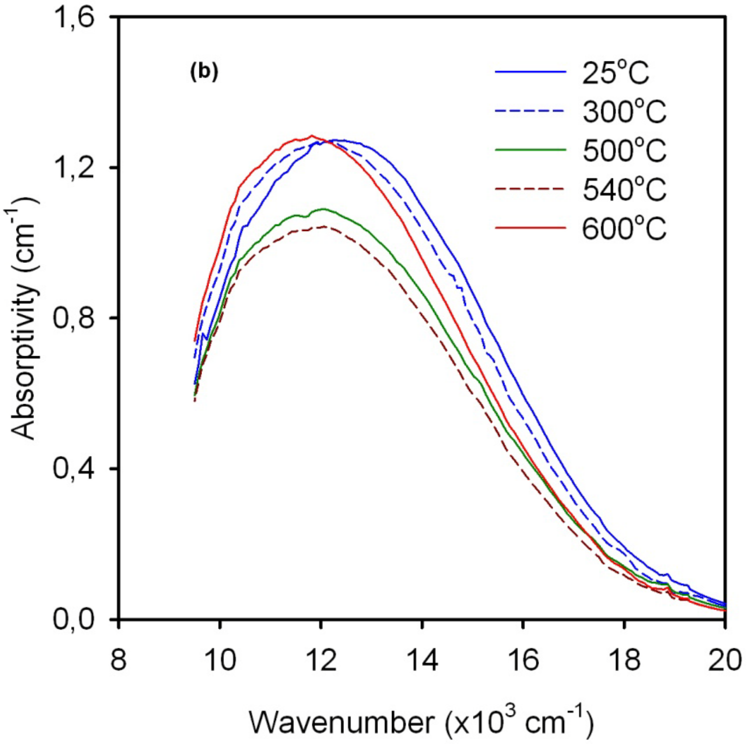
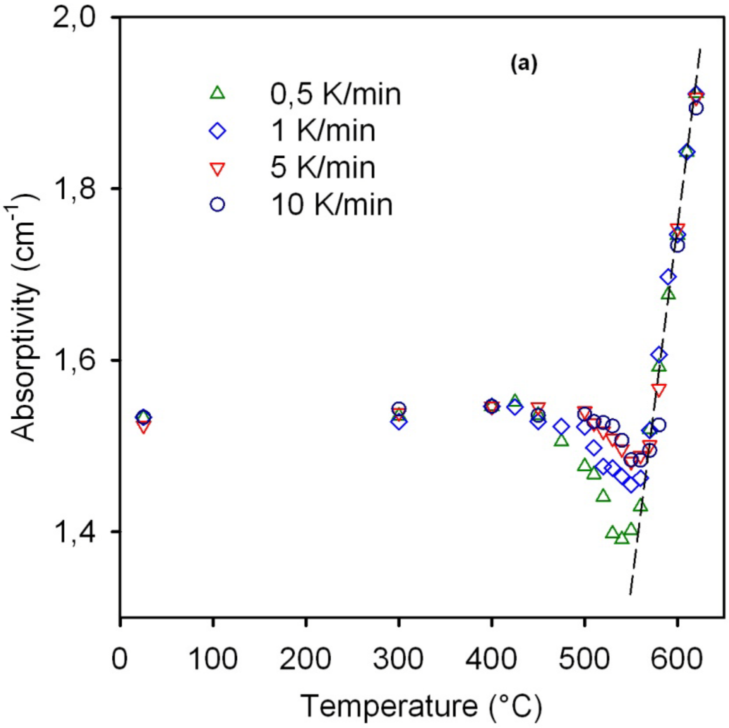


Figure 21: Absorption spectra of a sodium borosilicate glass doped with 1.2 mol% CuO and 1.2 mol% Sb_2O_3 (a) and 1.2 mol% CuO and 1.2 mol% As_2O_3 (b) at temperatures of 25, 300, 500, 540, 550 and 600 ^{o}C during heating using a rate of 0.5 K·min^{-1}.



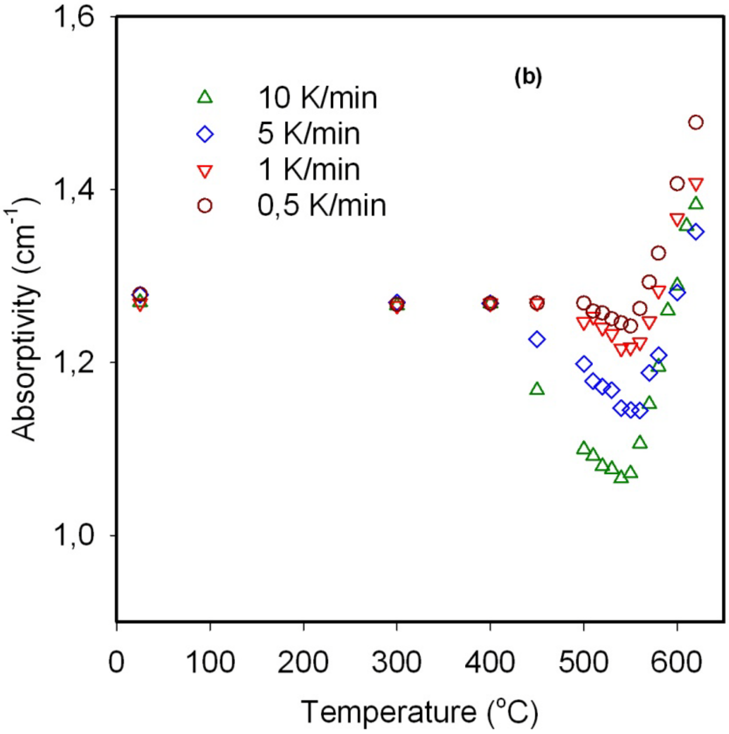


Figure 22: Absorptivity at maximum position of the Cu^{2+} band of a sodium borosilicate glass doped with 1.2 mol% CuO and 1.2 mol% Sb_2O_3 (on top) and 1.2 mol% CuO and 1.2 mol% As_2O_3 (beneath) as a function of temperature using different heating rates.

5.4.2 Thermodynamics of the redox reaction

Quenched glasses solely doped with copper show absorptivities which increase as a function of the copper concentration according to Lambert-Beer's law. Samples doped with both copper and arsenic, show decreasing Cu^{2+} absorptivities with increasing arsenic concentrations. Since the glasses were prepared from oxidized components (CuO), the redox ratio Cu^{2+}/Cu^{+} at maximum melting temperature (1500 °C) should be approximately the same. That means, the redox ratio Cu^{2+}/Cu^{+} is changing during cooling. This can be illustrated with the aid of high temperature spectroscopic measurements. In the glasses solely doped with copper, the absorptivity slightly decreases with temperature. Due to the lack of a reaction partner, this decrease cannot be caused by a redox reaction and hence, is attributed to the temperature dependence of the molar absorptivity ε of Cu^{2+} (which is a function of wavelength and temperature).

In glasses doped with both copper and arsenic, the same behavior is observed up to a temperature of around 470 °C. During further heating, first a minimum and then a steady increase in absorbance occur. The latter effect proves that a redox reaction according to Eq. 15 took place:

$$2Cu^{2+} + As^{3+} \rightleftharpoons 2Cu^{+} + As^{5+} \tag{47}$$

According to Eq. 16,

$$\begin{aligned} K_{As/Cu}(T) &= \frac{K_{As}(T)}{\left(K_{Cu}(T)\right)^2} = \exp\left(\frac{-\Delta G^0_{As} + 2\Delta G^0_{Cu}}{RT}\right) \\ &= \exp\left(\frac{-\Delta H^0_{As} + 2\Delta H^0_{Cu}}{RT}\right)\exp\left(\frac{\Delta S^0_{As} - 2\Delta S^0_{Cu}}{R}\right) \end{aligned} \tag{16}$$

the redox equilibrium is shifted if $2\Delta H^0_{Cu} \neq \Delta H^0_{As}$.

It follows from Figures 18 and 19 that the redox reaction is in equilibrium at temperatures larger than 600 °C. The molar absorptivity of cupric (Cu^{2+}) ions at the maximum of absorption at room temperature is 25 $Lmol^{-1}cm^{-1}$. For sample 1 in Figure 18, the Cu^{2+}-concentration is then 0.1296 mol%. That means: 28% of the copper occurs as Cu^{2+} in that soda-lime-silica glass sample. In order to prepare the glasses, oxidized raw materials were used and hence excess oxygen is evaporated from the melt (in glass technology denoted as “fining”) and the polyvalent compounds are transferred to the respective reduced species. In the following it was assumed that the oxygen activity of the melt is attributed to an equilibrium with oxygen (1 bar). Thermodynamic values of the Cu^+/Cu^{2+}-equilibrium in glass melts, obtained by electrochemistry are given in Ref. [15]. Unfortunately, the thermodynamics were studied at temperatures (900 – 1100 °C) much lower than the melting temperature in the present study. Nevertheless, the value of ΔS^0_{Cu} = 42 $JK^{-1}mol^{-1}$ was taken from the electrochemical studies while the value for ΔH° (60 $kJmol^{-1}$) was fitted to the Cu^{2+}-concentration of the glass solely doped with copper, assuming an oxygen activity of 1 bar.

Data for the As^{3+}/As^{5+}-equilibrium are scarcely available in literature. For a soda-lime-silica melt, a ΔS^0_{As} value of 138 $JK^{-1}\cdot mol^{-1}$ is given for temperatures in the range from 900 to 1300 °C [56]. The reaction enthalpy was now fitted to the absorbance of Cu^{2+} at room temperature in glasses doped with both copper and arsenic (see Fig. 18) assuming a freezing temperature of 550 °C. This resulted in optimum agreement with the experimental values if ΔH° was assumed to be 172.5 $kJmol^{-1}$.

In Figure 23, the Cu^{2+}-concentrations obtained from this calculation are shown as a function of temperature. It is seen that the redox reaction is continuously shifted towards Cu^+ and As^{5+} with decreasing temperatures. Since, as shown in Figure 19, the reaction is frozen in below around 550 °C, the experimental Cu^{2+} absorptivities are plotted against the calculated Cu^{2+}-concentrations attributed to an equilibrium at 550 °C (see Fig. 24), a linear correlation is observed.

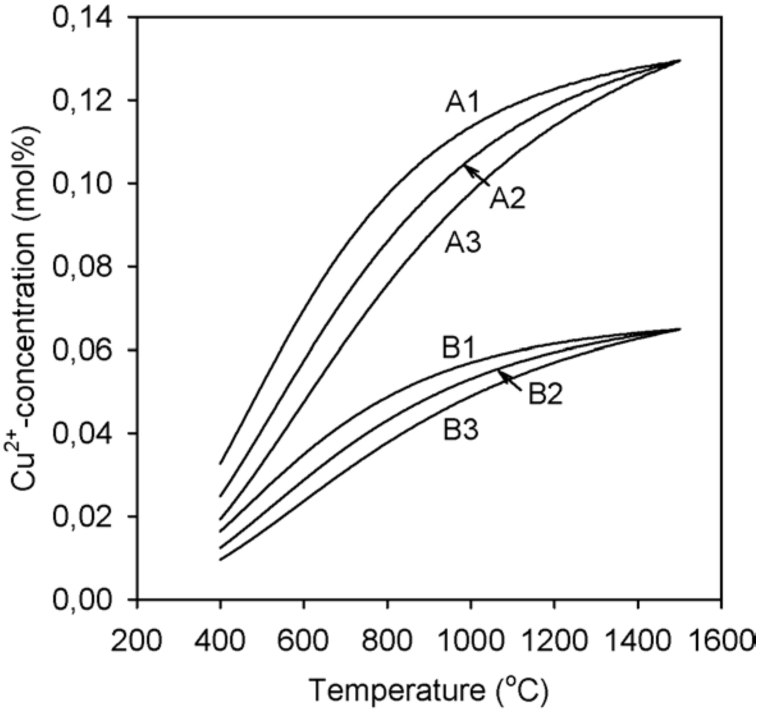


Figure 23: Calculated Cu^{2+} equilibrium concentrations as a function of the temperature.

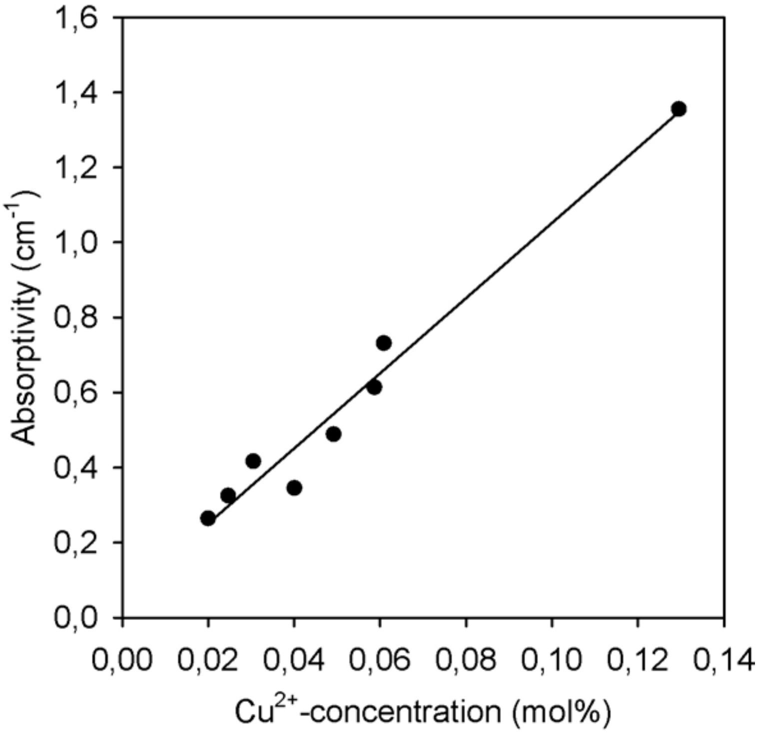


Figure 24: Absorptivity at maximum position of the Cu^{2+}-absorption band at room temperatures versus the calculated Cu^{2+}-concentrations for an equilibrium at 550 °C.

5.5 Time dependence of redox reactions in glasses doped with copper and arsenic or antimony during holding at certain temperatures

5.5.1 Experimental results

During the next series of experiments, samples of the glass doped with 0.475 mol% CuO and 0.586 mol% As_2O_3 were heated to 550, 560 and 570 °C, and held at these temperatures. Then the change in the absorbance was measured as a function of time. As shown in Figure 25, the absorbance at maximum position of the Cu^{2+} absorption band decreases as a function of time. From the decay, the relaxation times can be calculated assuming an exponential law according to Eq. 22: $\Delta C = \Delta C_0 \exp\left(-\frac{t}{\tau}\right)$

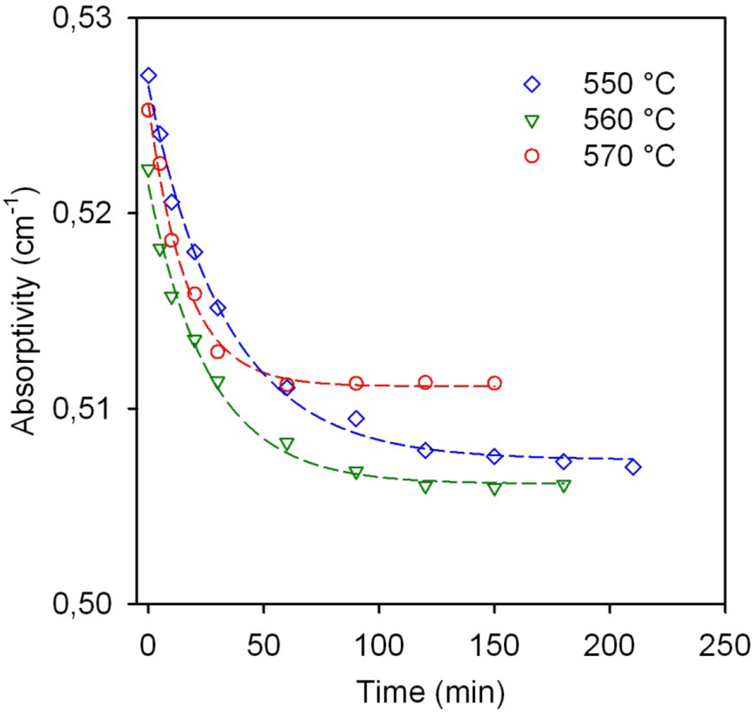


Figure 25: Absorptivity at maximum position of the Cu^{2+}-absorption band of samples doped with 0.475 mol% CuO and 0.586 mol% As_2O_3 as a function of time. The samples were held at 550, 560, and 570 °C.

The time dependences of the Cu^{2+} concentrations at three temperatures in the range between the frozen-in (< 420 °C) and the equilibrium state (>550 °C) of the redox reactions are given in Figure 26 for a glass doped with both 1.2 mol% CuO and 1.2 mol% As_2O_3 and for the glass doped both with 1.2 mol% CuO and 1.2 mol% Sb_2O_3. Eq. 22 was used to calculate the respective relaxation times: 3261 s (510 °C), 2158 s (520 °C) and 1156 s (530 °C) for the glass with arsenic and 7059 s (520 °C), 5128 s (530 °C) and 2620 s (540 °C) for the glass with antimony.

Using Eq. 23, rate constants k_+ were calculated from these relaxation times: $1.02 \cdot 10^{-3}$, $1.54 \cdot 10^{-3}$ and $2.87 \cdot 10^{-3}$ $s^{-1}mol\%^{-3}$ for the glass with arsenic, and $1.36 \cdot 10^{-3}$, $1.87 \cdot 10^{-3}$ and $3.36 \cdot 10^{-3}$ $s^{-1}mol\%^{-3}$ respectively, for the glass with antimony. An Arrhenius plot of the rate constants k_+ is shown in Figure 27. The attributed activation energies are very similar to each other: 270 $kJmol^{-1}$ (Cu/As) and 265 $kJmol^{-1}$ (Cu/Sb). These activation energies are slightly larger (20%) than that determined for the soda-lime-silica glass but drastically smaller than the activation energy for viscous flow in this sodium borosilicate glass which was calculated to be about 850 $kJmol^{-1}$. Thus, it is concluded that the diffusion of Cu^{2+} is the rate determining step for the redox reactions between copper and arsenic or antimony also in this sodium borosilicate glass.

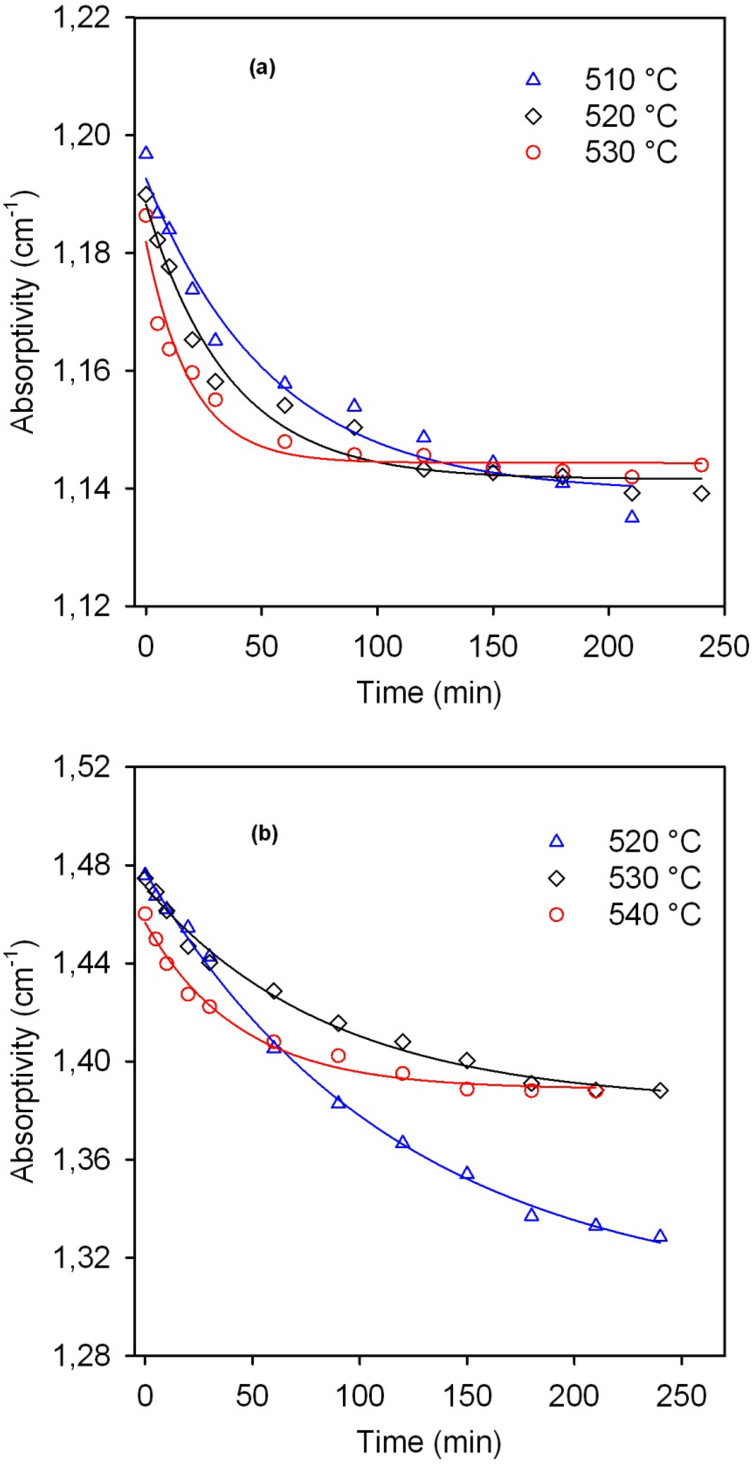


Figure 26: Absorptivity at maximum position of the Cu^{2+}-absorption band of a glass doped with 1.2 mol% CuO and 1.2 mol% As_2O_3 (a) 1.2 mol% CuO and 1.2 mol% Sb_2O_3 (b) as a function of time. The samples were held at the given temperatures.

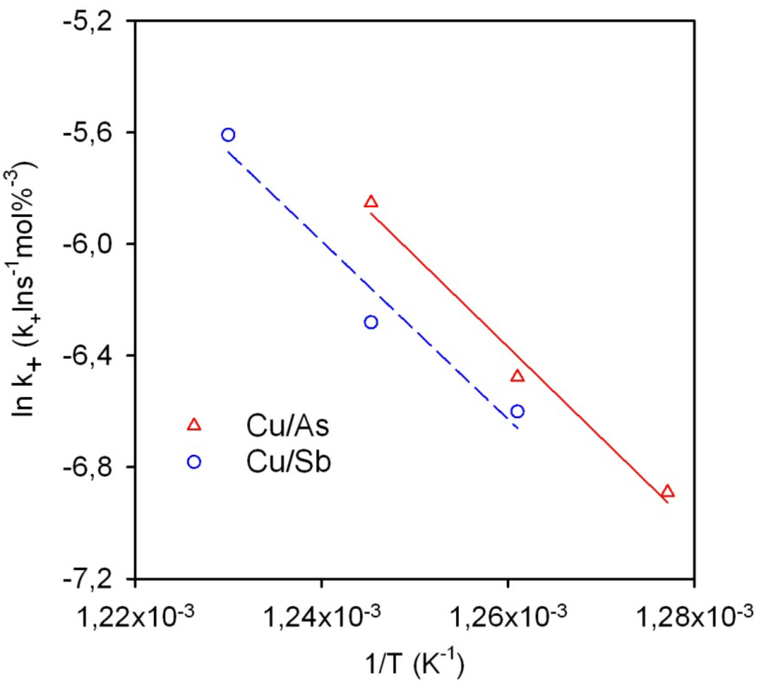


Figure 27: Arrhenius plot of the rate constants k_+ for the samples doped with 1.2 mol% CuO and 1.2 mol% As_2O_3 or Sb_2O_3 for the borosilicate glass

As expected, the results obtained for the sodium borosilicate glass correspond to the results obtained during the investigations of the soda-lime-silica glasses and the already discussed conclusions were confirmed.

5.5.2 The kinetics of the redox reaction

The redox reaction according to Eq. 47 is hence in equilibrium (within the time scale of the performed experiments) at temperatures above 600 °C. At temperatures below 470 °C, the absorptivities have the same temperature dependency as the glasses solely doped with CuO and hence the equilibrium is frozen in. At temperatures in the range from 470 to 600 °C, the absorptivities depend on cooling rate or time. In this range, the kinetics of the redox reaction play an important part. From the time dependence shown in Figure 25, the relaxation times according to Eq. 22 can be calculated.

For the temperatures of 550, 560 and 570 °C, the relaxation times are 2034, 1587 and 985 s, respectively. The rate constants, k_+, calculated here of using Eq. 23 are $1.68{\cdot}10^{-3}$, $2.16{\cdot}10^{-3}$ and $3.48\cdot10^{-3}$ $s^{-1}mol\%^{-3}$.

Figure 28 presents an Arrhenius plot of the rate constant k_+. The attributed activation energy is 210 $kJmol^{-1}$ and the pre-exponential factor $3.33{\cdot}10^{10}$ $s^{-1}mol\,\%^{-3}$.

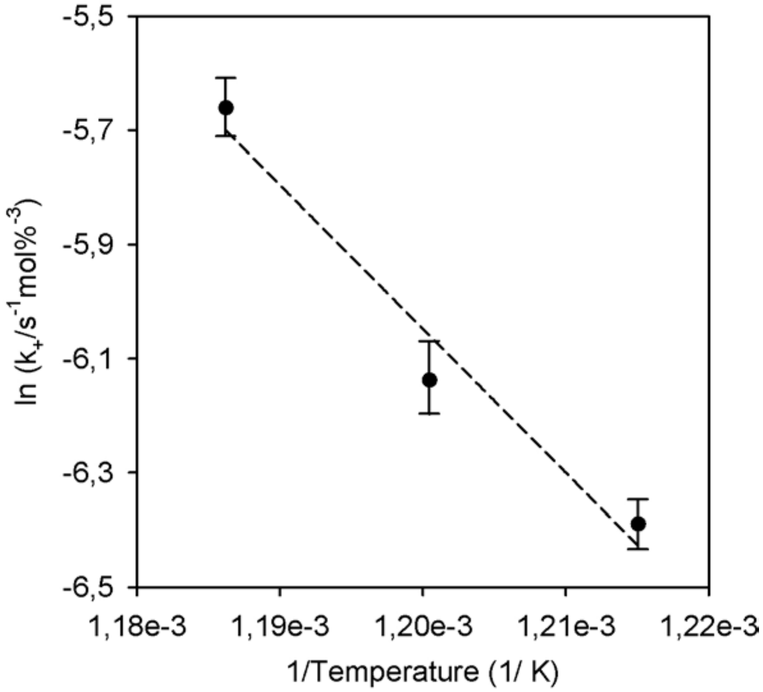


Figure 28: Arrhenius plot of the rate constants k_+ for the soda-lime-silica glass

The activation energy, the pre-exponential factor and the ΔS° values as well as the fitted ΔH° values were inserted into Eq. 48:

$$\frac{dx}{dt}=\left([As^{5+}]_0+\frac{x}{2}\right)\left([Cu^{+}]_0+x\right)^2k_+-\left([As^{3+}]_0-\frac{x}{2}\right)\left([Cu^{2+}]_0-x\right)^2k_- \qquad (48)$$

Figure 29 presents numerical solutions of the differential equations for the compositions A1, A2 and A3 for cooling the respective melts with a rate of 10 $Kmin^{-1}$. The full lines are attributed to the thermodynamics as described above while the kinetics are shown by the short dashed lines. It is shown that above 650 °C, the redox reaction is still in equilibrium, however, the values deviate from equilibrium at smaller temperatures. For T smaller than 470 °C, the Cu^{2+}-concentrations do no longer change with temperature and hence are frozen in.

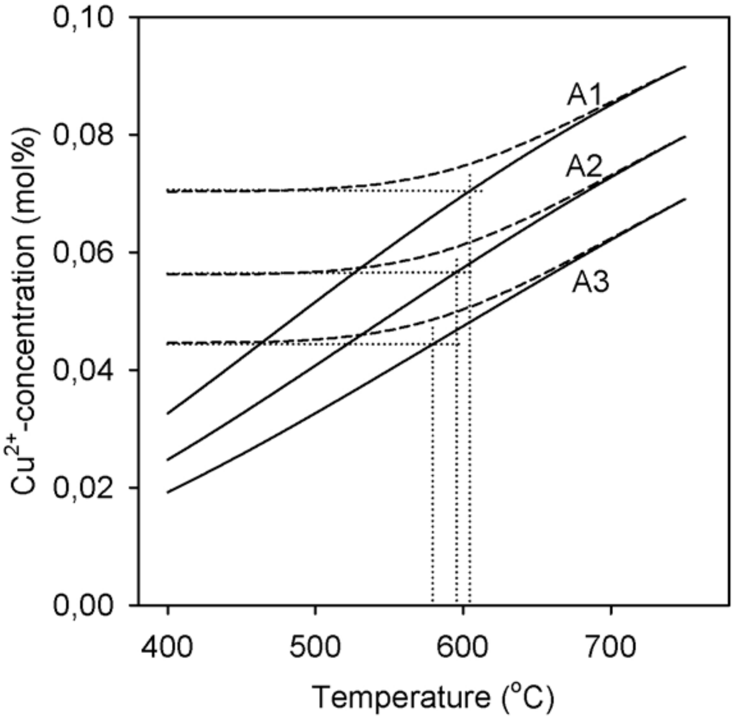


Figure 29: Calculated Cu^{2+}-concentrations as a function of temperature for samples A1, A2 and A3 during cooling the sample using a rate of 10 $Kmin^{-1}$.
Full lines: equilibrium values, dashed lines: kinetic values. The dotted lines are shown to illustrate the determination of the fictive redox freezing temperatures.

The fictive redox freezing temperatures (defined as those temperatures, the equilibrium values are equal to the Cu^{2+}-concentration obtained at room temperature) depend on the composition. For the samples A1, A2 and A3, they are 604, 592 and 581, respectively. The larger the As_2O_3 concentrations, the lower is the fictive redox freezing temperatures.

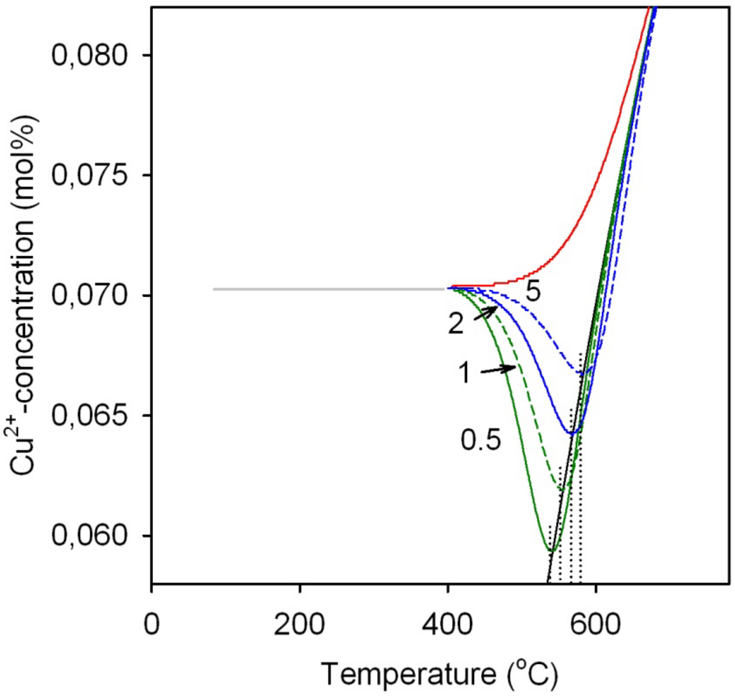


Figure 30: Calculated Cu^{2+}-concentrations as a function of temperature for sample A 1 during heating the sample with rates of 0.5, 1, 2 and 5 K/min which was previously cooled with 10 K/min. Full red line: equilibrium values, dashed lines: kinetic values. The dotted lines are attributed to the minimum of the dashed curves.

In Figure 30, numerical solutions are shown for reheating sample A1 with different rates (after cooling with 10 K/min). It is seen that the curves show a constant [Cu^{2+}] value up to 400 °C and then exhibit a minimum. Using smaller heating rates results in more pronounced minima shifted to lower temperatures. The temperatures attributed to the minima are 582, 567, 555 and 541 °C for the heating rates of 5, 2, 1 and 0.5 Kmin^{-1}.

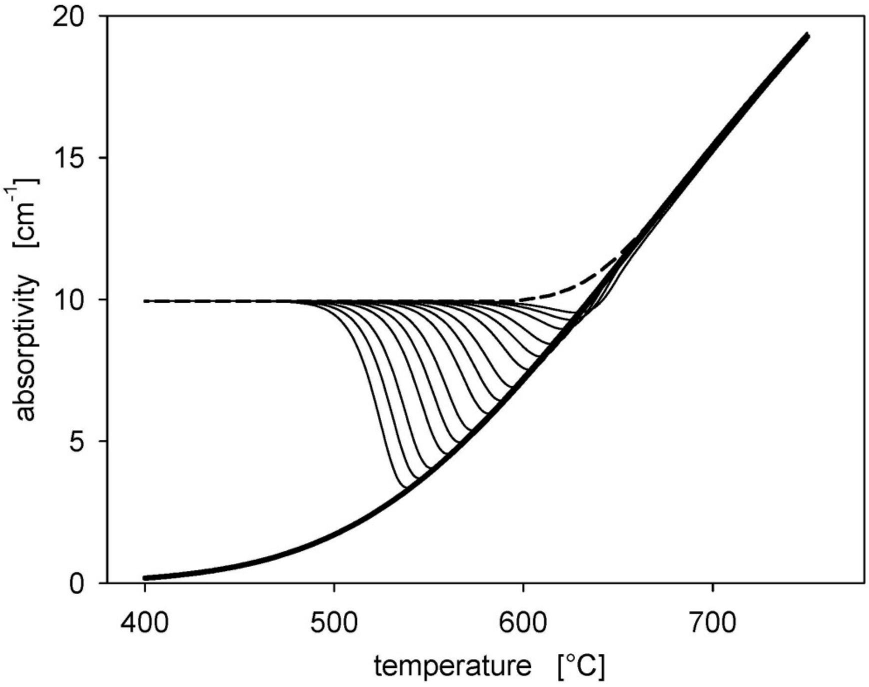


Figure 31: Theoretically calculated Cr^{6+} absorptivities (normalized to room temperature for different heating rates)
full lines: 2000, 1000, 500, 200, 100, 50, 20, 10, 5, 2, 1, 0.5, 0.2, 0.1 and 0.05 $Kmin^{-1}$ (from the top)
dashed line: during cooling, thick line: equilibrium values.

A comparison with theoretically calculated Cr^{6+} absorptivities (see Fig. 31) [42] shows the same mechanism of the relaxation during heating. The difference is that evidently the $[Cr^{6+}]$ is more affected by heating rate than the $[Cu^{2+}]$ in the $2Cu^{2+} + As^{3+} \rightleftharpoons 2Cu^{+} + As^{5+}$ system.

Concerning the experimental values obtained during heating the sample (see Fig. 19), a very similar behaviour is observed. The minima are less pronounced using larger heating rates and the minima are shifted to higher temperatures. The temperatures attributed to the minima are 588, 576, 582 and 568 °C for heating rates of 5, 2, 1 and 0.5 $Kmin^{-1}$, respectively. Taking into account the larger error in temperature with increasing heating rates, the agreement of measured and simulated values is fairly good.

5.6 Temperature dependence of redox reactions in glasses doped with copper and arsenic or antimony during cooling

5.6.1 Experimental results

In Figure 32, vis-NIR absorption spectra of a sodium borosilicate glass sample with 1.2 mol% CuO and 1.2 mol% Sb_2O_3 are shown for different temperatures in the range from 25 to 620 °C. The spectra were recorded during cooling the samples from 620 °C using a rate of 0.5 $Kmin^{-1}$. As already mentioned, the absorptivity at 600 °C was much smaller than in the glass solely doped with CuO. Furthermore, a steep decrease in absorptivity was observed in the temperature range from 600 to 500 °C. During further cooling, a slight decrease in the absorptivity was observed. If larger cooling rates (10, 5 or 1 $Kmin^{-1}$) were supplied, the decrease in absorptivity in the temperature range from 600 to 500 °C was not as large, (see Fig. 33).

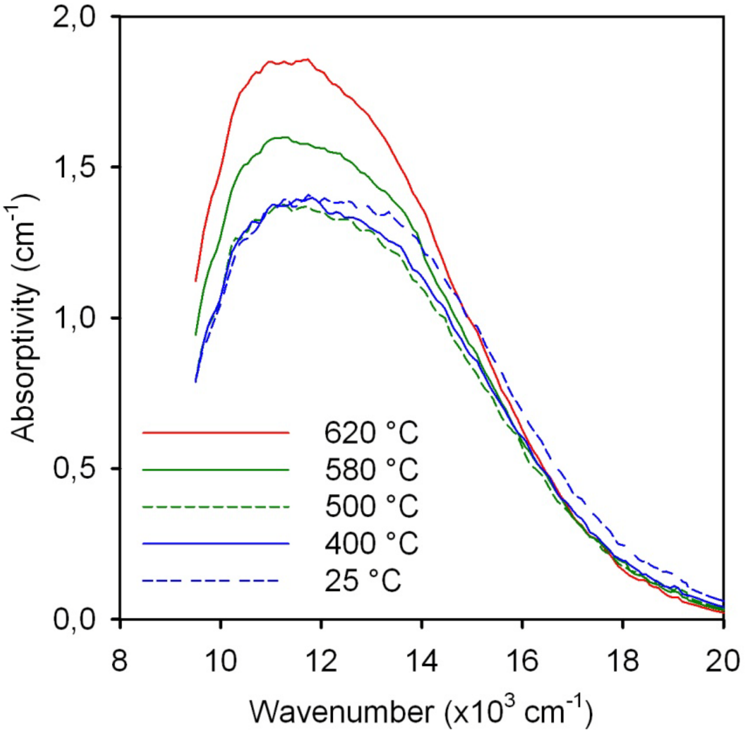


Figure 32: Absorption spectra of a glass doped with 1.2 mol% CuO and 1.2 mol% Sb_2O_3 at temperatures of 25, 400, 500, 580 and 600 °C during cooling using a rate of 0.5 $Kmin^{-1}$.

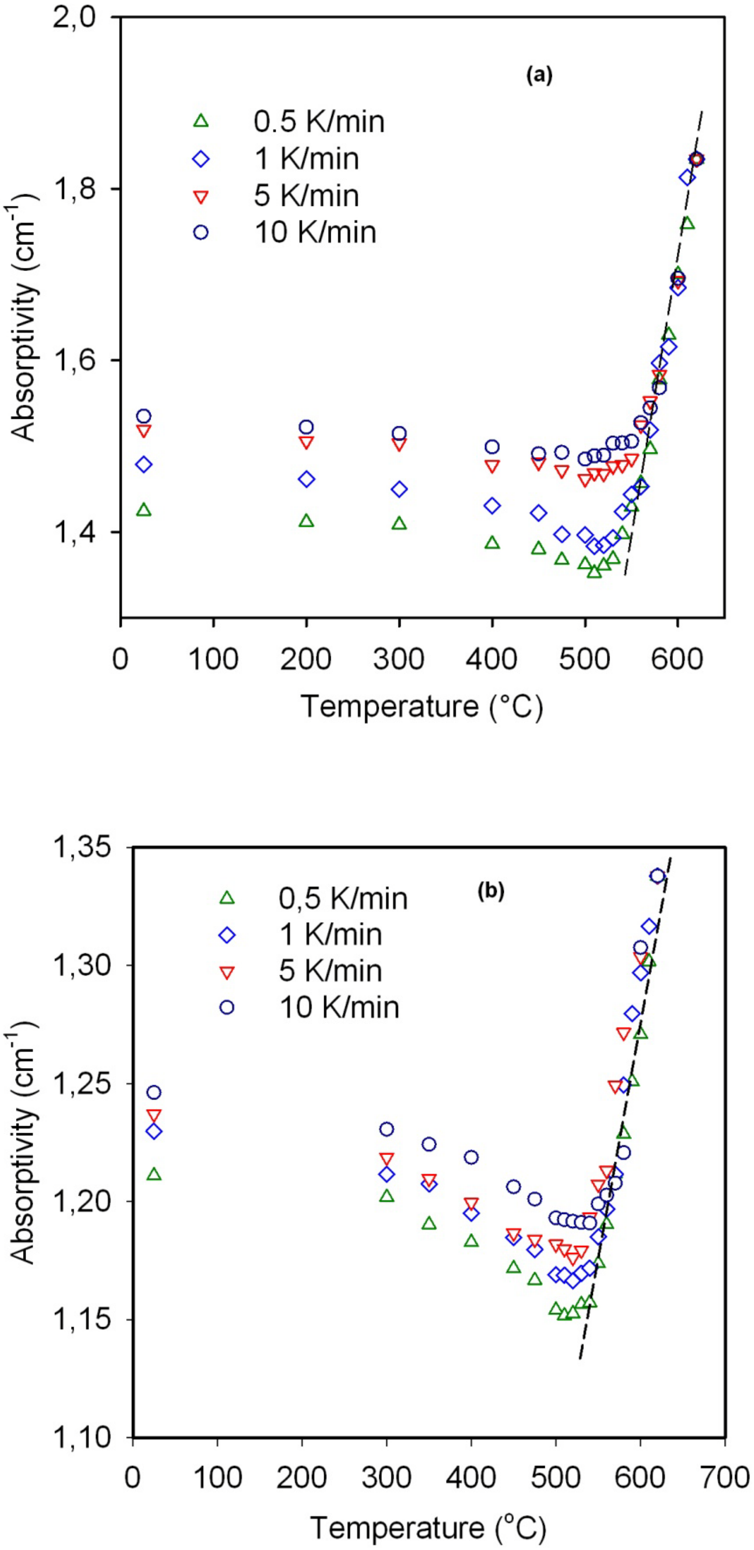


Figure 33: Absorptivity at maximum position of the Cu^{2+} band of glass doped with (a) 1.2 mol% CuO and 1.2 mol% Sb_2O_3 (b) 1.2 mol% CuO and 1.2 mol% As_2O_3 as a function of temperature using different cooling rates.

The temperature dependence of the absorptivity at the maximum position of the Cu^{2+} absorption band is shown in Figure 33 for the samples doped with 1.2 mol% CuO and 1.2 mol% Sb_2O_3 or 1.2 mol% As_2O_3 using different cooling rates of 0.5, 1, 5 and 10 $Kmin^{-1}$. In principle, it is the same which was already found in soda-lime-silica glasses doped with CuO and Sb_2O_3 or As_2O_3. It is obvious that the cooling rate has a strong effect on the Cu^{2+} absorptivity: While at temperatures above 570 °C the absorptivities were the same, at lower temperatures larger absorptivities are observed, if larger cooling rates were used. Also the resulting absorptivities at room temperature are larger, if higher cooling rates were supplied. The respective absorptivities are 1.42 (cooling rate 0.5 $Kmin^{-1}$), 1.48 (1 $Kmin^{-1}$), 1.52 (5 $Kmin^{-1}$), and 1.54 cm^{-1} (10 $Kmin^{-1}$) for the sample doped with copper and antimony, and 1.21 (cooling rate 0.5 $Kmin^{-1}$), 1.23 (1 $Kmin^{-1}$), 1.24 (5 $Kmin^{-1}$), and 1.25 cm^{-1} (10 $Kmin^{-1}$) for the sample doped with copper and arsenic [57].

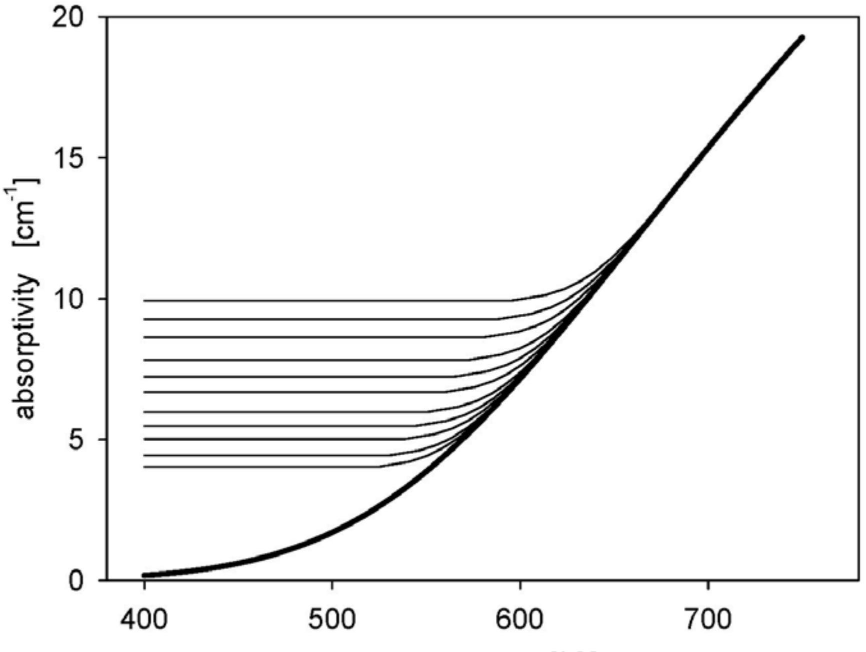


Figure 34: Theoretically calculate Cr^{6+} absorptivities (normalized to room temperature for different cooling rates) full lines: 2000, 1000, 500, 200, 100, 50, 20, 10, 5, 2, 1, 0.5, 0.2, 0.1 and 0.05 $Kmin^{-1}$ (from the top), thick line: equilibrium values.

The comparison with the glass doped with chromium and manganese during cooling (see Fig 34) [42] shows a similar behaviour like glasses containing Cu/Sb and Cu/As.

From the cooling curves given in Figure 33, fictive freezing temperatures for the redox reaction were derived and are given in Table 6.

Table 6: Fictive freezing temperatures T_f for the redox reaction in sodium borosilicate glass samples doped with 1.2 mol% CuO and 1.2 mol% As_2O_3 or Sb_2O_3 as a function of cooling rate

Cooling rate ($Kmin^{-1}$)	T_f (°C)	
	Cu/As	Cu/Sb
0.5	536	539
1	542	549
5	546	556
10	554	560

As shown in Figures 28 and 30, the absorptions both during heating and cooling increase strongly at temperatures larger than 550 °C in glasses doped with both copper and antimony or arsenic. This effect is not observed in the glass solely doped with copper or with copper and tin. It proves that in presence of antimony and/or arsenic, a redox reaction according to Eq. 47 takes place. As shown in Eq. 16, such a redox reaction should always take place if $2\Delta H^0_{Cu} \neq \Delta H^0_{As}$ (or ΔH^0_{Sb}). At temperatures smaller than 420 °C, the absorptivities did not change much with temperature and the redox reactions can be considered as frozen.

In the range between these two temperatures, Cu^{2+} absorptivities and, hence, the Cu^{2+} concentrations, depend on heating and cooling rates and, at a constant temperature, on time.

A redox relaxation behaviour like this was first proved experimentally in a soda-lime-silica glass doped with chromium and manganese [42]. From the relaxation times, rate constants of the redox reaction were calculated. The estimated activation energy calculated from these rate constants (535 ± 30 kJ·mol^{-1}) was (within the limits of error) in agreement with the activation energy for viscous flow (560 kJmol $^{-1}$) in this temperature range. It was concluded that in this case the rate determining step of the redox reaction is the re-arrangement of the coordination spheres around the polyvalent species since, during electron transfer, in the case of chromium the coordination spheres change: Cr^{3+} occurs in coordination number 6, whereas Cr^{6+} prefers the coordination number 4.

In contrast, the activation energy for the redox reaction $2Cu^{2+} + As^{3+} \rightleftharpoons 2Cu^{+} + As^{5+}$ obtained in a soda-lime-silica glass is only 210 kJmol^{-1} [58]. The coordination numbers for arsenic and copper remain the same ($As^{3+/5+}$: tetrahedral coordination, Cu^{2+}: with respect to c-axis, stretched octahedral coordination [3], Cu^{+}: with respect to c-axis, compressed octahedral coordination [59]) during the redox reaction. Thus, a change in the respective coordination number does not to occur. A redox reaction involves two consecutive steps, (i) the diffusion of the species and (ii) the electron transfer reaction. If during cooling, a reaction occurs between As^{3+} and Cu^{2+}, the diffusion of Cu^{2+} should be decisive. Unfortunately, experimentally determined copper diffusion coefficients are not available in literature for these temperatures. However, the calculated activation energy for the redox reaction was in the same order of magnitude as the activation energy of diffusion estimated for Ca^{2+} as another divalent ion [60]. Then, it can be assumed, that the diffusion of Cu^{2+} is the rate determining step of the redox reaction.

Cooling experiments with different cooling rates (from 10 to 0.5 Kmin^{-1}) from 620 °C to room temperature result in some new aspects, as shown in Figure 33: the Cu^{2+} concentrations at room temperature in the investigated samples depend on cooling rates. The higher the cooling rate, the higher is the Cu^{2+} concentration at room temperature. In principle, such a course of the cooling curves was already predicted for the soda-lime-silica glass doped with copper and different concentrations of arsenic [58] at cooling rate of 10 Kmin^{-1}. Also, fictive redox freezing temperatures were calculated. It was found that with using smaller cooling rates the fictive redox freezing temperatures are decreased.

The fictive freezing temperatures for the two sodium borosilicate glasses under investigation are given in Table 6. With increasing cooling rates, the fictive freezing temperature increases by about 20 K from 536 °C (0.5 K·min^{-1}) to 554 °C (10 K·min^{-1}) for the glass doped with copper and arsenic and from 539 °C to 560 °C for the glass with antimony. The fictive freezing temperature for the soda-lime silica glasses doped with copper and arsenic and for a cooling rate of 10 K·min^{-1} are 20 to 50 K higher.

The Bartenev equation [61] describes the dependence of the glass transition temperature T_g on the cooling rate q and quantitatively explains why glass-forming melts cooled with different rates exhibit different glass transition temperatures [35].

$$q = A \cdot \exp\left(\frac{E_q}{RT_g}\right) \tag{49}$$

E_q stands for the Bartenev activation energy and was found to be equal to the activation energy of the viscosity in the same temperature interval [35], [62], [63], [64]: in a narrow temperature range above T_g, the viscosity of glass-forming melts can be approximated by Arrhenius equation. The Bartenev equation enables to determine E_q from the dependency of the glass transition temperature on the cooling rate.

An equation similar to Bartenev equation also enables to describe the effect of cooling rate on the fictive redox temperature T_f [44]:

$$q = A \cdot \exp\left(\frac{E_q}{RT_f}\right) \tag{50}$$

For the $Mn^{2+}/Mn^{3+}/Cr^{3+}/Cr^{6+}$ redox reaction in soda-lime-silica glass, it was found that it is possible to estimate the activation energy of a redox reaction in a viscous medium by cooling the respective samples with different rates [44].

5.6.2 Mechanism of the redox reaction

The activation energy obtained from the relaxation experiments described in 5.5 is 210 kJmol^{-1}. This value is much smaller than that reported (530 kJ·mol^{-1}) for the $Mn^{2+}/Mn^{3+}/Cr^{3+}/Cr^{6+}$-redox reaction in a soda-lime-silica glass of the same base composition [42]. The activation energy in this system was close to that of the viscosity (550 kJ·mol^{-1}) [45] which gave rise to the assumption that the re-arrangement of the coordination spheres around the polyvalent species might be the rate determining step of the redox reaction. In the case of chromium, during electron transfer, the coordination sphere changes, since Cr^{3+} and Cr^{6+} occur in coordination numbers of 6 and 4, respectively. In the case of arsenic and copper, the coordination numbers remain the same (4 and 6, respectively), and hence a change in the coordination spheres does not occur.

Generally, a redox reaction is composed by a diffusion reaction and a subsequent electron transfer reaction.

$$\frac{1}{k_+} = \frac{1}{k_d} + \frac{1}{k_e} \tag{51}$$

with: k_d = rate constant of the diffusion process and k_e = rate constant of the electron transfer.

The rate constant k_d is directly related to the diffusivities and can be estimated by the Smoluchowsky equation:

$$k_d = C(D_A + D_B)(a_A + a_B) \tag{52}$$

with: D_A, D_B = diffusion coefficients, a_A, a_B = radii of the species A and B, respectively and C = $7.57 \cdot 10^{27}$ $m^{-3}M^{-1}$.

The electron transfer is an activated process, although the tunnelling of electrons is not. According to the quasi-classical theories of electron exchange [65], [66], [67], the electron transfer is governed by $\Delta G^{\#}$, the Gibbs energy of activation. According to these theories, the rate constant of the electron transfer reaction, k_e, is given by:

$$k_e = A \cdot \exp(-\Delta G^{\#} / RT) \tag{53}$$

The pre-exponential factor A is often approximated by the following expression (kinetic gas theory) [65]:

$$A = \kappa (RT / 2\pi m N_L)^{1/2} \tag{54}$$

where: N_L is Avogradro's constant, m is the mass of the species and κ is the transmission factor, generally taken as equal to 1. The Gibbs energy of activation, $\Delta G^{\#}$, is given by:

$$\Delta G^{\#} = \frac{\lambda}{4} = \frac{(\lambda_i - \lambda_o)}{4} \tag{55}$$

The reorganization energy λ is generally divided into the inner (λ_i) and the outer reorganization energy (λ_o). The latter is caused by the differences in the interaction of the oxidized and the reduced species with the dielectric continuum. It is given by:

$$\lambda_o = \frac{e_o^2}{8\pi\varepsilon_o}\left(\frac{1}{a}\right)\left(\frac{1}{n^2} - \frac{1}{\varepsilon}\right) \tag{56}$$

with: e_o is the unit charge, ε_o is the permittivity of the vacuum, ε is the static and n^2 the optical dielectric constant of the solvent. If the oxidized and the reduced species are metal ions which possess the same coordination numbers, the outer reorganization energy is given by:

$$\lambda_i = \sum_j \frac{f_j^R \cdot f_j^P}{f_j^R + f_j^P} \Delta q_j^2 \tag{57}$$

with: f_j is a force constant andΔq_j the difference in the bond lengths or angles (R stands for reactant and P stands for product). If the coordination number changes, the inner reorganization energy is much higher, because a complete rearrangement of the coordination sphere around each ion is necessary.

For the activation energy, the rate determining process of a chemical reaction is decisive. In principle, the rate determining step of the redox reaction might be the diffusion of the species involved in the mutual redox interaction or, however, the electron transfer reaction. By contrast to electron transfer reactions in solvents with high polarity, the outer reorganization energy plays a less important part. The term $(1/n^2-1/\varepsilon)$ (see Eq. 56) is 0.55 for water and around $(1/1.5^2-1/10) = 0.34$ for a typical glass (such as soda-lime silica) at elevated temperatures. Hence, outer reorganization energy, i. e. the changing interaction during the valence change of the polyvalent ion with the dielectric continuum during the course of the redox reaction should not be decisive. The inner reorganization energy is due to the structural rearrangement of the coordination around the polyvalent ions during the course of the redox reaction. In the simple case that the coordination number does not change (see Fig. 35a), only the alterations in the bond lengths and bond angles are decisive (see Eq. 57). However, in a glass melt, the incorporation of the reduced and the oxidized species are usually more different and, in the most cases, the coordination number changes (see Fig, 34b). In the case of the redox reaction between the species $Cr^{3+}/Cr^{6+}/Mn^{2+}/Mn^{3+}$, the coordination of chromium changes: whereas Cr^{3+} occurs in a silicate melt in octahedral coordination, Cr^{6+} is tetrahedrally coordinated. Then the structural rearrangement during the electron transfer reaction is much larger and also the activation energy should notably increase.

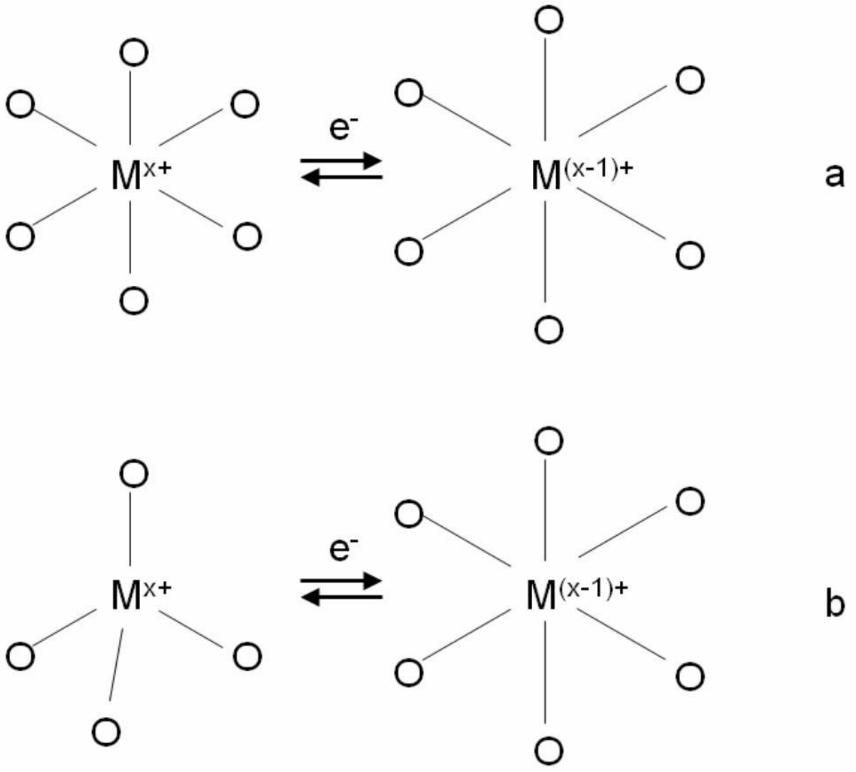


Figure 35: Schematic of a redox reaction without change in the coordination number (a) and with an increase of the coordination number during the reduction process (b)

Experimental values of diffusion coefficients in glass melts, measured by electrochemical methods, such as square-wave voltammetry at high temperatures (typical in the range from 800 to 1500 °C) are quite numerous. The diffusion coefficients of various polyvalent species differ up to six orders of magnitude at a temperature of 1300 ^{o}C [20]. At lower temperatures, the differences are even larger. For example the diffusion coefficients of Ag^{+}, a species highly mobile in glasses is large, while it is much smaller for ions such as Sb^{3+} which are incorporated much stronger into the glass network.

In comparison to the $Cr^{6+} + 3Mn^{2+} \rightleftharpoons Cr^{3+} + 3Mn^{3+}$ redox reaction, the reaction $2Cu^{+} + As^{5+} \rightleftharpoons 2Cu^{2+} + As^{3+}$ exhibits much smaller activation energies. In a glass with the composition $16Na_2O$-$10CaO$-$74SiO_2$, an activation energy of 210 kJ·mol^{-1} was determined from redox relaxation times [58]. It should be noted that in the case of the $Cr^{3+}/Cr^{6+}/Mn^{2+}/Mn^{3+}$ redox reaction, as described above, the coordination number of chromium changes while for the copper/arsenic reaction, the coordinations remain fairly similar. In the case of copper, Cu^{2+} has an octahedral coordination which is tetragonally distorted (one long axis) due to Jahn-Teller deformation, Cu^{+} possesses also a tetragonal distorted octahedral coordination, which, however, has two short bonds. In the case of arsenic, the coordination is fourfold for both As^{3+} and As^{5+}. Thus in the case of the redox reaction with copper and arsenic, the structural changes during the course of the redox reaction are not as pronounced as in the case of the $Cr^{3+}/Cr^{6+}/Mn^{2+}/Mn^{3+}$ redox reaction. Here only bond lengths and tetragonal distortions change. This is schematically illustrated in Figure 35a, while the changes in the coordination sphere as in the case of the $Cr^{3+}/Cr^{6+}/Mn^{2+}/Mn^{3+}$ system is shown in Figure 35b. In the latter case, the glass structure around the reacting chromium ions will drastically change and hence, the activation energy is much higher and approximately equal to that of the viscous flow at a temperature around the glass transition temperature. That means, the inner reorganization energy determines the activation energy and rate constants, while in the case of the $Cu^{+}/Cu^{2+}/As^{3+}/As^{5+}$ system, the diffusion is the rate determining step, which in the case of copper is attributed to an activation energy of approximately 200 $kJmol^{-1}$.

In the case of a fast electron transfer reaction, the diffusion should be the rate determining step. If during cooling, a reaction occurs between As^{3+} and Cu^{2+}, the diffusion of Cu^{2+} should be decisive. Unfortunately, in the literature, experimentally determined copper diffusion coefficients are only available for much higher temperatures. Ref. [15] reports on copper diffusion coefficients (mixed Cu^{+}/Cu^{2+}) determined electrochemically in soda-lime-silicate melts in the temperature range from 850 to 1100 °C.

The attributed activation energies were in the range from 134 to 141 $kJmol^{-1}$. Cu^{+} as a monovalent ion should show a smaller activation energy of diffusion than Cu^{2+} [56]. Hence, the activation energy of the Cu^{2+} diffusion should be larger than the mixed Cu^{+}/Cu^{2+} activation energy determined electrochemically. The activation energy of diffusion for Ca^{2+} (as another divalent ion) in a similar soda-lima-silica glass composition and comparable temperatures was reported to be 224 $kJmol^{-1}$ [60]. This value is in agreement with the activation energy determined in this paper. It should hence be assumed that the diffusion of copper is the rate determining step of the redox reaction. Although, the error in the activation energy is fairly high (±20 $kJmol^{-1}$), without any doubt, it is much smaller than that attributed to a viscosity controlled reaction. Therefore, this redox relaxation $2Cu^{2+} + As^{3+} \rightleftharpoons 2Cu^{+} + As^{5+}$ is the first example of a diffusion controlled homogeneous reaction in a glass [58].

It should be noted that relaxation processes in glasses at temperatures around the glass transition temperature are well-known. A recent discussion on relaxation in glass-forming liquids is given in [68]. Relaxation processes are differently related to the fundamental structural relaxation. The time scale of these processes decreases with increasing temperature. Qualitatively, the rate of recovery of a physical quantity following a small deviation from its equilibrium value can be described as a first order kinetic process [35]. Non-linearity in relaxation behaviour is often described by the Tool-Narayanaswamy model taking into account a non-linear parameter [69]. An empirical explanation of non-exponential decays is also given by Kohlrausch-Williams-Watts type stretched exponential functions [34], [70].

In the case of the mechanical relaxation (i. e. increase of density with time) in oxide glasses it is mainly the fundamental structure relaxation of the network formers whereas in case of the electrical relaxation (i. e. increase in the electrical conductivity with time) these processes are more affected by the network modifiers (see e. g. [70]).

6. Conclusions.

The redox reactions of copper with the redox agents arsenic, antimony and tin in two base glasses with the compositions i) $16Na_2O$-$10CaO$-$74SiO_2$ and ii) $25Na_2O$-$15B_2O_3$-$60SiO_2$ (compositions given in mol%) in a temperature range between 25 and 800 °C were studied by means of high temperature vis-NIR spectroscopy in the spectral range from 400 to 1100 nm (corresponds to wavenumbers from 25,000 to 9,000 cm^{-1}).

The soda-lime-silica glass i) is the most common model glass for many industrially produced glasses. It allows to study glass properties on the research level but also to apply the results for practical use. The sodium borosilicate glass ii) was chosen as a glass with a high activation energy of viscous flow in the temperature range above the transformation temperature and with a steeper (compared to base glass i)) course of viscosity vs. temperature.

The glass batches were prepared using raw materials for optical glasses (reagent grade materials): Na_2CO_3, $CaCO_3$, SiO_2, H_3BO_3 and CuO, As_2O_3, Sb_2O_3 and $Sn(COO)_2$. The glasses were melted in platinum crucibles in an induction furnace. Great store was set on glass quality (homogeneity, absence of bubbles).

High-temperature vis-NIR measurements were carried out using a modular spectrometer with chopper and lock-in amplifier in combination with a microscope heating stage. Light source was a halogen lamp, a grating monochromator was used for spectral dispersion and the intensity of the radiation was recorded by an Si detector. This spectrometer was used to investigate the spectral range between 400 and 1100 nm. In principle, it is possible to measure up to 5,000 nm if an additional PbSe detector in combination with a suited grating was used for a second measurement step. Though, the measuring time is much longer then, the time resolution of the experiments is decreased whereas the additional information on the Cu^{2+} band is comparatively low. The special arrangement (see Fig. 1) guaranties that the thermal radiation from heated sample, heating stage chamber and so on does not influence the absorption measurements of the samples under investigation.

The concentrations of the polyvalent elements added to the base glasses were always low enough and did not influence the optical basicity of the base glasses. Thus, the position and the bandwidth of the Cu^{2+} absorption band remain constant for different nominal copper concentrations added to the glass batch. In the investigated glass samples, the vis-NIR spectrum shows only one absorption band, the well known Cu^{2+} band at the border between the visible and the near Infrared region. At first glance, this band seems to be one single absorption band with Gaussian shape but a careful analysis reveals that the band is a superposition of three bands which is due to Jahn-Teller splitting. Nevertheless, the recorded Cu^{2+} absorption spectra were fitted by only one Gaussian band without errors scarcely worth mentioning. The additionally added redox agents arsenic, antimony and tin do not show absorption bands in the vis-NIR range. The respective bands are in the UV region superimposed by the absorption edge of the base glass. With increasing temperatures, this absorption edge shows the known behavior and is shifted towards longer wavelengths.

Glasses doped solely with copper

Spectra recorded from CuO doped glasses (soda-lime-silica and sodium borosilicate glasses) show the Cu^{2+} absorption band at around 12,500 cm^{-1} which results from the $^2E \rightarrow {}^2T_2$ transition. The bands exhibit almost Gaussian shape and results from sixfold (octahedral) coordinated Cu^{2+} ions. During heating, the position of the maximum of the band is shifted to smaller wavenumbers (from 12,650 cm^{-1} at room temperature to 11,500 cm^{-1} at 800 °C), the band becomes broader (from 7,200 to 7,600 cm^{-1}) and less intense, but only by about 5%. These changes are completely reversible with decreasing temperatures. The redox reaction according to $Cu^{2+}+\frac{1}{2}O^{2-} \rightleftharpoons Cu^{+}+\frac{1}{4}O_2$ is not shifted in these glasses during heating and cooling in a temperature range up to 800 °C because the diffusion of oxygen (O_2) into the melt is a very slow process even at higher temperatures.

But it is possible to adjust different $[Cu^{2+}]/[Cu^{+}]$ ratios in the glass samples by equilibrating the respective samples at high temperatures (T larger than 1250 °C). With increasing temperatures, the reaction $Cu^{2+} + \frac{1}{2}O^{2-} \rightleftharpoons Cu^{+} + \frac{1}{4}O_2$ is shifted to the right. This was used to determine experimentally the molar absorptivity ε of the Cu^{2+} in the soda-lime-silica: 25 $Lmol^{-1}cm^{-1}$. At temperatures used for the presented spectroscopic investigations, no further change of the $[Cu^{2+}]/[Cu^{+}]$ ratios adjusted at high temperatures was observed because the diffusion of oxygen (O_2) into the melt is a very slow process even at higher temperatures. This behavior was already known from soda-lime-silica base glass and is now confirmed for the sodium borosilicate glass.

Glasses doped with copper and tin

In principle, glasses doped with copper and tin show the same behavior during heating and cooling as glasses doped solely with copper. This was already shown for the soda-lime-silica base glass. The intensity of the Cu^{2+} absorption band is decreased by the addition of tin as $Sn(COO)_2$ (tin(II)-oxalate), compared to the intensity of the base glass solely doped with the same CuO concentration. This decrease is attributed to the reducing power of the oxalate during the glass melting process. In contrast to the effect of arsenic or antimony, no evidence for a temperature depending redox reaction according to $2Cu^{2+} + Sn^{2+} \rightleftharpoons 2Cu^{+} + Sn^{4+}$ was found. The intensity of the Cu^{2+} absorption band is slightly decreased during heating to 700 °C. The position of the maximum of this band is shifted to smaller wavenumbers and the band becomes broader during heating. These changes are completely reversible during cooling to room temperature. This behavior can be explained by the small standard reaction enthalpy $\Delta H^0_{Cu/Sn} = 6$ kJmol^{-1} of the reaction mentioned above.

Glasses doped with copper and arsenic or antimony

The addition of arsenic or antimony to either the soda-lime-silica or the sodium borosilicate glass doped with copper has a stronger effect on the [Cu^{2+}] and, hence, on the intensity of the Cu^{2+} absorption band, than the addition of tin. During heating, the Cu^{2+} absorptivity in the glasses doped with copper and antimony or arsenic is slightly decreased like in the glasses solely doped with copper or with copper and tin, but only until the temperature becomes larger than 400 °C. Then, the intensity of the Cu^{2+} band (and hence the [Cu^{2+}]) is decreased more strongly with increasing temperature and goes through a minimum. The smaller the heating rate, the more pronounced is the minimum and the lower is the attributed temperature. After passing the minimum, the intensity of the Cu^{2+} band is strongly increased again during further heating and the curves for different heating rates lie on the top of the other. The Cu^{2+} band intensity is then unaffected by the heating rate, but depends on temperature.

This can be explained by temperature dependent redox reactions according to $2Cu^{2+} + Sb^{3+} \rightleftharpoons 2Cu^{+} + Sb^{5+}$ and $2Cu^{2+} + As^{3+} \rightleftharpoons 2Cu^{+} + As^{5+}$, respectively. With increasing temperatures, the redox reaction is shifted to the left and hence, to an increase of the [Cu^{2+}]. The $\Delta H^0_{Cu/Sb}$ and $\Delta H^0_{Cu/As}$ values for these redox reactions are 102 kJmol^{-1} and 46 kJmol^{-1} and much higher than that of the redox reaction between copper and tin.

At temperatures higher than the corresponding minimum in the Cu^{2+} intensity curve, the redox reactions given above are in equilibrium. At temperatures smaller than 400 °C, these redox reactions are frozen in. Between these two ranges, kinetics plays an important part and hence, the influence of heating rate becomes obvious.

The appearance of the curves is different when the glasses were cooled from a temperature in the region where the redox reactions are in equilibrium (e.g. from 750 °C for soda-lime-silica base glass and from 650 °C for sodium borosilicate glass). First, the intensity of the Cu^{2+} band is decreased drastically and linearly with temperature according to the reverse behaviour during heating in this temperature range. At a certain temperature in this intermediate range, this decrease becomes much smaller before the Cu^{2+} absorptivity is slightly (and in principle linearly) increased again with decreasing temperature. Here, the redox reaction (and the corresponding $[Cu^{2+}]$) is frozen in and consequently, the $[Cu^{2+}]$ remains constant during further cooling. The lower the cooling rate, the lower is the resulting Cu^{2+} absorptivity and hence, the $[Cu^{2+}]$ in the glass samples at room temperature.

It is possible to estimate fictive redox freezing temperatures from this cooling investigations: the fictive freezing temperature T_f is the temperature under which the redox ratio (in the case discussed here: $[Cu^{2+}]/[Cu^{+}]$) does not change with temperature due to kinetic hindrance of the redox reaction. Fictive freezing temperature depends on cooling rate: the higher the cooling rate, the higher the redox freezing temperature. For cooling rates between 10 and 0.5 $Kmin^{-1}$, T_f varies from 554 to 536 °C for the sodium borosilicate base glass containing copper and arsenic and from 560 to 539 °C for the same base glass containing antimony instead of arsenic. The fictive redox freezing temperatures are by 20 to 50 K lower than the T_f estimated for the respective soda-lime-silica glasses.

The relaxation of redox reactions can be followed in this intermediate temperature range. Glass samples were heated up to (three) certain temperatures in this range and the decrease of the intensity of the Cu^{2+} band (and consequently of the $[Cu^{2+}]$) was recorded as a function of time. The relaxation times for the given temperatures were calculated from the decay curves. Using these relaxation times and the respective rate constants for the redox reactions, it is possible to calculate the activation energy of the redox reactions.

In soda-lime-silica glasses containing the redox pairs $Cr^{3+}/Cr^{6+}//Mn^{2+}/Mn^{3+}$, the relaxation of a redox reaction in glasses was proved for the first time. The activation energy for the redox reaction $3Mn^{3+}+Cr^{3+} \rightleftharpoons 3Mn^{2+}+Cr^{6+}$ was calculated to be 535 $kJmol^{-1}$. This is the same order of magnitude as the activation energy of viscous flow (560 $kJmol^{-1}$). The activation energy for the redox reaction $2Cu^{2+}+As^{3+} \rightleftharpoons 2Cu^{+}+As^{5+}$ in the soda-lime-silica glass is much lower: 210 $kJmol^{-1}$ (experimental activation energy of viscous flow: 560 $kJmol^{-1}$). In sodium borosilicate glasses, the activation energies for the corresponding redox reactions $2Cu^{2+}+As^{3+} \rightleftharpoons 2Cu^{+}+As^{5+}$ and $2Cu^{2+}+Sb^{3+} \rightleftharpoons 2Cu^{+}+Sb^{5+}$ are 270 $kJmol^{-1}$ and 265 $kJmol^{-1}$, respectively, (calculated activation energy of viscous flow: 850 $kJmol^{-1}$). Therefore, it can be assumed that for the redox pairs under investigation here the reaction rate depends on other mechanisms than the reaction rate in the chromium-manganese redox system. For the latter system, the structural re-arrangement is the rate determining step: Cr^{3+} is sixfold coordinated, whereas Cr^{6+} is fourfold coordinated (for Mn^{3+} and Mn^{2+}, the coordination number remains 6 or is changed from 6 to 4).

Such a re-arrangement is not necessary for the glasses containing copper and the other already mentioned redox partners: Cu^{2+} and Cu^{+} are octahedrally coordinated (though the first is stretched and the second compressed), $As^{3+/5+}$ and $Sb^{3+/5+}$ are tetrahedrally coordinated. Therefore, the rate determining step is the diffusion of Cu^{2+} ions. Unfortunately, there are no diffusion data available for Cu^{2+} in glasses in this temperature range. But the activation energy for diffusion of similar divalent cations (e.g. Ca^{2+}) in a soda-lime-silica glass is in the same order of magnitude as the activation energy for the redox reaction between copper and arsenic in this base glass. Therefore, the redox reaction $2Cu^{2+}+As^{3+} \rightleftharpoons 2Cu^{+}+As^{5+}$ is the first example of a diffusion controlled homogeneous reaction in a glass.

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Acknowledgments

I would like to express my gratitude and thank to:

Prof. Dr. Christian Rüssel for my occasion to have great research experience, supervision of the study and offering valuable insights on content of this research.

My advisor Dr. Matthias Müller for any support not only on my study but include my personal live in Germany.

HDoz. Dr. Doris Ehrt for discussion and additional information from the relate field.

Prof. Dr. Dörte Stachel for very nice glass industrial lecture.

Dr. Matthias Carl, Mr. Thomas Kittel, Ms. Gabriele Möller, Ms. Bettina Hartmann, Ms. Steffi Ebbinghouse, Mr. Lutz Preißer, Mr. Rainer Weiß, Ms. Corinna Seelheim and all colleagues in our institute for support my work, if I am work alone it impossible to finish this work.

Christian Bocker, Sandra Gerlach, Roman Wurth, Christian Worsch, Juliane Kaufmann and all friends in our institute for support my work and my live in Germany.

My German teacher and best friend Grit Matthias and all friends in German class for support my social live in Germany and help me to prove my language skill.

All Thai friend in jena (Por, Pok, Patt, Nui, P'Tai and Kwan) for delicious Thai food and make atmosphere like my live not far from my home.

Office of the Civil Service Commission Thailand, National Science and Technology Development agency Thailand, Department of Science Service Thailand and TSC for financial support.

My family father, mother, sister and Pat for never ending supply of faith, love and moral support.

Selbständigkeitserklärung

Ich erkläre, dass ich die vorliegende Arbeit selbständig und unter Verwendung der angegebenen Hilfsmittel, persönlichen Mitteilungen und Quellen angefertigt habe.

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