

Influence of melting and annealing conditions on the optical spectra of a borosilicate glass doped with CoO and NiO

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In the high-viscosity borosilicate glass (NBS2) doped with 0.3 mol% CoO or NiO quenching resulted in a freeze-in snap-shot of the glass structure within the dopants' transformation process from their high-temperature tetrahedral coordination to the octahedral form normally present in this glass at room temperature. In this transitional state the octahedral, tetrahedral and a third pseudo-tetrahedral transitional coordination are simultaneously present. The optical spectra of the doped glasses are discussed in relation to the different melting and cooling conditions applied. Quenched glasses were also tempered on a heating table, which permitted to take the optical spectra at each temperature step.

In contrast to Co^{2+} , Ni^{2+} has a strong octahedral preference. Thus for NiO-doped NBS2 glass tempering or annealing always results in relaxation into the octahedral coordination. For Co^{2+} , which is also octahedrally coordinated in the annealed NBS2, tempering of the quenched glass leads to a relaxation into octahedrally and tetrahedrally coordinated Co^{2+} . These structural changes are especially strong when the applied temperatures lie 150 to 200 °C above T_g of the NBS2 glass where also the viscosity-temperature curve implies structural changes within the glass matrix.

1. Introduction

The origin of glasses is often ascribed to the process of supercooling melts. Accordingly, glasses are no longer present in a thermodynamic equilibrium and the glass structure is related to the preparation process of the glass as well as to the effective structure within the melt. Lower coordination numbers are thermodynamically preferred at high melting temperatures. This behaviour was already observed in crystals [1]. Quenching of a melt should therefore – at least partially – freeze in a structure, which is found during the transformation process from the thermodynamically preferred structure of the melt to the structure favoured by the glass at room temperature, a transformation which is kinetically prevented below T_g .

Cobalt and nickel are rarely seen in glasses in oxidation states other than +2. However, depending on the glass matrix Co^{2+} or Ni^{2+} are found to change their coordination from octahedral to tetrahedral and thus have early been used as indicators of structure. The coordination of Co^{2+} and Ni^{2+} is strongly related to the op-

tical basicity of a glass, a measure of the electron donor power of the glass matrix [2].

Studies, involving two borosilicate glasses, NBS1 and NBS2, of different optical basicities and different amounts of nonbridging oxygens, in which Co^{2+} and Ni^{2+} were either tetrahedrally or octahedrally coordinated, showed an interesting phenomenon: when the melt of the NiO-doped glass NBS2 was quenched by casting in water, the glass had an orange to brown colour. After remelting and annealing in a graphite mould the same glass had a green to yellow colour. The CoO-doped glasses showed a less impressive colour change, although the quenched glasses were visibly greyer than the blue-violet annealed glasses and the optical spectra revealed significant variations in their spectra. Systematic studies showed that all doped NBS2 glasses differed in their colouring from the annealed glasses when quenched, despite being either poured beforehand in a graphite mould or on a brass block. The observed colour change is probably due to a coordination change of the dopants illustrating different structures of the glasses due to their different thermal history.

Some articles which examine the coordination change of Co^{2+} and Ni^{2+} in connection with small changes of the glass composition display optical spectra similar to those found for the glasses studied in this paper after various temperature treatments [3 and 4].

Received 31 October 2001.

Presented in German at: 74th Annual Meeting of the German Society of Glass Technology (DGG) on 31 May 2000 in Ulm (Germany).

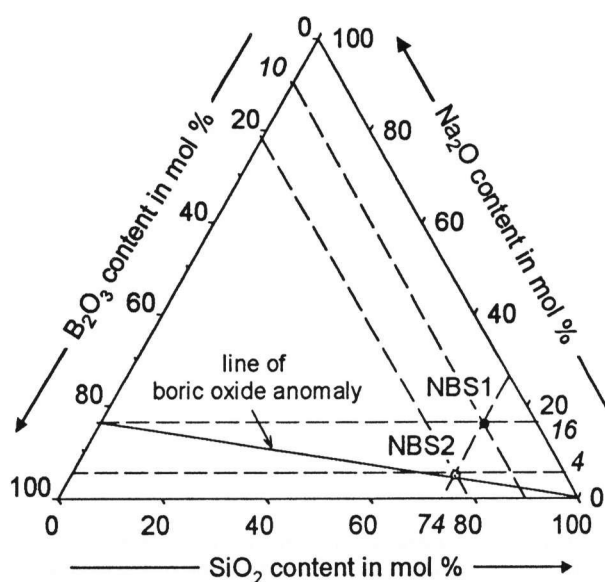


Figure 1. Ternary $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glass system, showing the sites of the glasses NBS1 and NBS2 and the lines of the boric oxide anomaly representing those glasses with a constant $\text{Na}_2\text{O}:\text{B}_2\text{O}_3$ ratio of 16:84 and an increasing SiO_2 content [9].

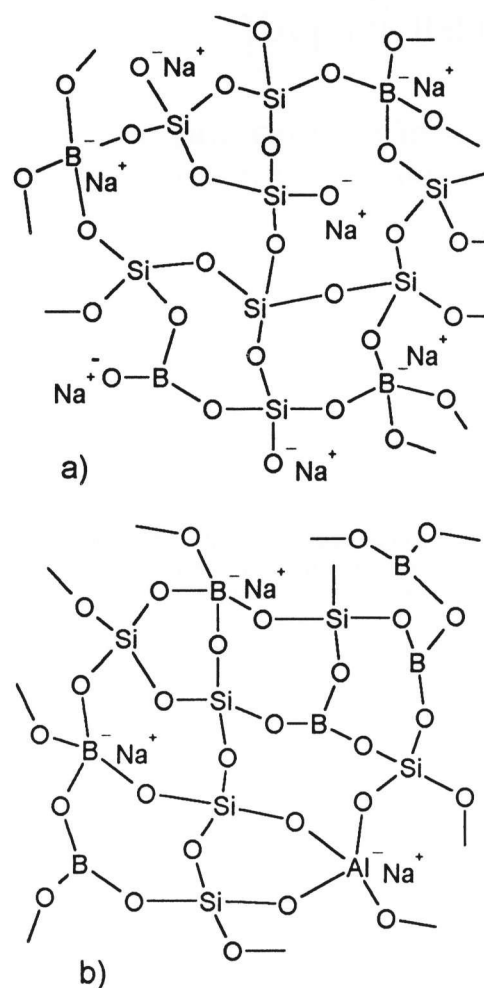
Other authors have also reported a temperature dependency. Already in 1933, Weyl mentioned the coordination change of Ni^{2+} in a sodium silicate glass, in which 2% of those ions octahedrally coordinated after annealing took on a tetrahedral coordination when the glass was quenched [5]. Kawatoe et al. also found a higher amount of octahedrally coordinated Ni^{2+} in an annealed sodium silicate glass than in a quenched one [6], and Blair and Duffy studied the changes in the optical spectra of doped phosphate glasses upon heating [7].

Compared to the NBS1 glass, the NBS2 glass contains hardly any nonbridging oxygens as B_2O_3 partly replaces Na_2O resulting in the ratio 1:5 of the boric oxide anomaly (figure 1). The structural model of this glass consists of a network of planar BO_3 units as well as BO_4 and SiO_4 tetrahedra (figures 2a and b). NBS2 is modelled on the technical glasses Duran® and Borofloat®, which like the former glass display an extremely low thermal coefficient of expansion and high resistance to thermal shock [8 and 9] (see also table 1).

The distinct change of colour between annealed and quenched NiO-doped NBS2 glasses was therefore investigated systematically. Additionally to experiments concerning the melting and cooling regimes, quenched samples were also tempered at a later time and the changes of the spectra during the heating process were followed by optical spectroscopy.

2. Coordination of Co^{2+} and Ni^{2+} in glasses

In glasses of high optical basicity Co^{2+} and Ni^{2+} are tetrahedrally coordinated, in other glasses the octa-



Figures 2a and b. Model of the glass structure of the borosilicate glasses: a) NBS1 and b) NBS2.

hedral coordination prevails. Next to the octahedral and tetrahedral coordinations, which are found simultaneously in glasses of medium optical basicity, a wide range of different transition coordinations are described in the literature. Examples postulated are the free ion [10], oxygen-bridged Ni^{2+} -ions ($\text{O}-\text{Ni}-\text{O}$) [11], square planar [12] or trigonal pyramidal [13 and 14] coordinated ions, as well as an eightfold coordination [15 to 23]. Gitter showed by matrix-range analysis in Co^{2+} - and Ni^{2+} -doped phosphate and borate glasses that a third coordination must exist. He ascribed this third coordination to a dodecahedral eightfold structure [19 to 21]. The dodecahedral coordination is not only the most widely discussed transition coordination in the literature, but also the one investigated with the widest range of analytical tools, including optical spectroscopy, magnetic susceptibility measurements, and an EPR saturation study by Warne [23]. Duffy showed the existence of an eightfold coordination of Co^{2+} in nitrate and acetate glasses by X-ray diffraction analysis [16 and 17]. In this pseudo-tetrahedral coordination of the bidentate ligands, four oxygen atoms were sited in a slightly shorter distance to the central atom than the other four. The

Table 1. Composition and some characteristics of the studied borosilicate glasses¹⁾

	composition in mol%	$A_{th}^{2)}$	ΣFe in ppm	$T_m^{3)}$ in °C	T_g in °C	α in $10^{-7} K^{-1}$	n_e	ν_e	ρ in g/cm^3
NBS2	$\left\{ \begin{array}{l} 74 SiO_2 \\ 21 B_2O_3 \\ 4 Na_2O \\ 1 Al_2O_3 \end{array} \right.$	0.48	5	1650 or 1700 or 1750	442	35	1.47	65	2.18
NBS1	$\left\{ \begin{array}{l} 74 SiO_2 \\ 10 B_2O_3 \\ 16 Na_2O \end{array} \right.$	0.53	6	1500	553	88	1.51	63	2.45

¹⁾ CoO and NiO were doped in concentrations of 0.3 mol% respectively.

²⁾ Optical basicity, calculated with the increment system according to Duffy [2].

³⁾ T_m refers to the final melting temperature of the oven, which was held for 1 h before the annealed or quenched samples were taken.

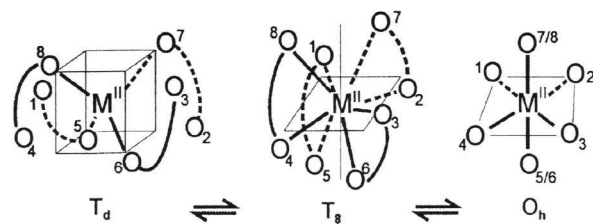


Figure 3. Schemata of the tetrahedral, pseudo-tetrahedral and octahedral coordination of Co^{2+} and Ni^{2+} in glass.

transition from the tetrahedral to the octahedral coordination via the pseudo-tetrahedral transition form is schematically shown in figure 3.

3. Experimental procedures

The composition and some characteristics of the borosilicate glasses studied are stated in table 1. The reagents SiO_2 , $CaCO_3$, Na_2CO_3 , H_3BO_3 and $Al(OH)_3$ at high-purity grade were used. As a result impurities were low. Iron as the main impurity was only present in the glasses at levels of about 5 ppm. Al_2O_3 had to be added to avoid phase separation, as the $Na_2O-B_2O_3-SiO_2$ composition of NBS2 shows a metastable immiscibility [8]. CoO and NiO were doped in concentrations of 0.3 mol%.

The glasses were melted in 250 g batches in Pt or Pt-Rh20 crucibles in a resistance-heated electric furnace. To ensure a sufficient homogeneity the melt was cast and quenched in water and later remelted. The NBS1 glass was melted at 1450 °C, for 3 h in the first melting process and another 2 h for the remelting process. The NBS2 glass was also quenched and remelted, however higher melting temperatures had to be employed: 1650 °C for the first melting step and up to 1750 °C for remelting. For the annealed glasses the melts were poured in a pre-heated graphite mould and cooled from 500 °C to room temperature with a cooling rate of about 30 K/h.

Quenched glasses were poured on a brass block, stamped with a brass plate and not annealed. Even though the T_g of the glass NBS2 is very low, high melting temperatures are needed for handling the melt. Because of the high temperature gradient between the crucible and the room temperature, the melt cools down very rapidly and in conjunction with its high viscosity this shortens the time available for pouring out the melt.

Experiments were conducted to investigate the influence of the melting temperature on the coordination of the dopants. Final melting temperatures, before either quenching the melt on a brass block or taking a sample for annealing, were set at 1650, 1700 and 1750 °C. The melt was kept at this temperature for 1 h before both samples were taken. Afterwards the same procedure was applied for the next higher melting temperature.

Due to the low thermal coefficient of expansion even quenched samples could be handled well mechanically. Therefore, sample plates of high quality were available for the optical spectroscopy studies. UV-VIS-NIR spectra were used to characterize the glasses. A double beam spectrophotometer (UV-3102, Shimadzu Tokyo (Japan)) was employed, recording the extinction $E = \lg(I_0/I)$ (error <1 %), which was later standardized to a nominal path length (d) of 1 cm.

Quenched samples were also subjected to a heating table, where the temperature was increased from room temperature to 725 °C in steps of 25 K. The changes in the optical spectra were recorded with a diode-array spectrometer. Even after the samples were subjected to temperatures almost twice as high as their T_g , they neither showed visible deformations, nor did the polished surface show any deterioration in spectroscopic qualities compared to its state at room temperature.

Viscosity studies were also performed. A rotational viscometer (BÄHR VIS 403, Hüllhorst (Germany)), working in a viscosity range from $10^{1.5}$ to 10^5 dPa s, and a 3-point-bending viscometer (BÄHR VIS 401), working in a viscosity range of 10^9 to 10^{13} dPa s, were employed.

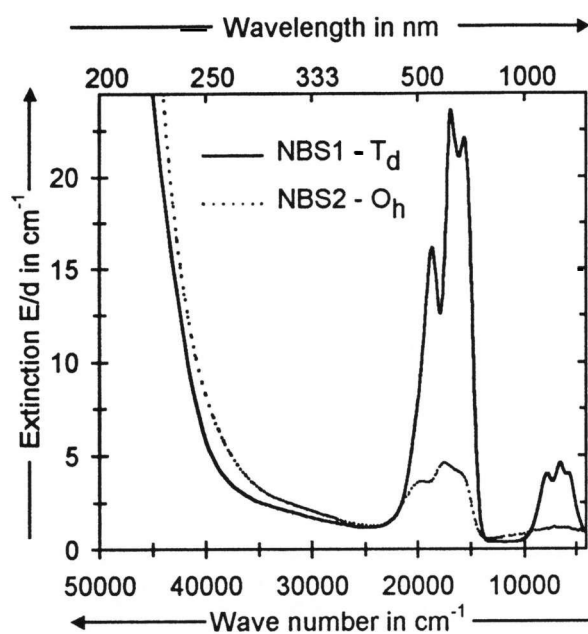


Figure 4. Typical optical spectra of tetrahedrally and octahedrally coordinated Co^{2+} in the borosilicate glasses NBS1 and NBS2 doped with 0.3 mol% CoO .

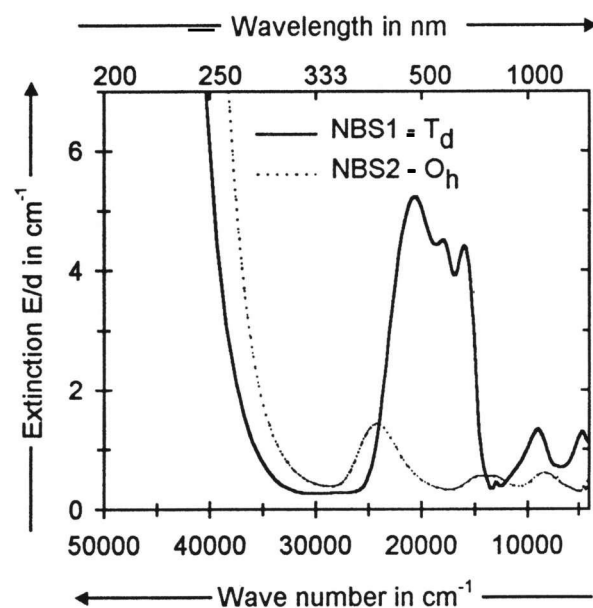


Figure 5. Typical optical spectra of tetrahedrally and octahedrally coordinated Ni^{2+} in the borosilicate glasses NBS1 and NBS2 doped with 0.3 mol% NiO .

4. Results and discussion

4.1 The optical spectra

Figures 4 and 5 show the optical spectra of the differently coordinated Co^{2+} and Ni^{2+} ions in the two borosilicate glasses. Co^{2+} and Ni^{2+} are mainly tetrahedrally coordinated in the NBS1 glass, which has the higher optical basicity with $A = 0.53$. In the NBS2 glass, which has a lower optical basicity with $A = 0.48$, both ions

show spectra typical of octahedral coordination. The octahedrally coordinated ions have a center of symmetry and thus are Laport forbidden. They have a much lower transition probability for the d-electrons and therefore a lower specific extinction coefficient ϵ_{λ} than the tetrahedrally coordinated ions.

The ligand field stabilization energy of octahedrally coordinated Ni^{2+} is greater than that of the tetrahedral coordination by as much as 80 kJ/mol. Therefore the spectrum of Ni^{2+} -doped NBS1 still includes a significant amount of octahedrally coordinated Ni^{2+} , whereas the spectrum of Co^{2+} , for which both coordinations are energetically equivalent, arises mainly from the tetrahedrally coordinated ion [1 and 24]. A band separation of the optical spectra of the Ni^{2+} -doped borosilicate glasses can be seen in figures 6a to c. These fits are based on earlier studies by Gitter, who resolved the Ni-related bands in the optical spectra of several series of glasses [19 to 21]. Bands of octahedrally, tetrahedrally and pseudo-tetrahedrally coordinated Ni^{2+} can be distinguished in the spectra.

4.2 Influence of the melting and cooling regimes

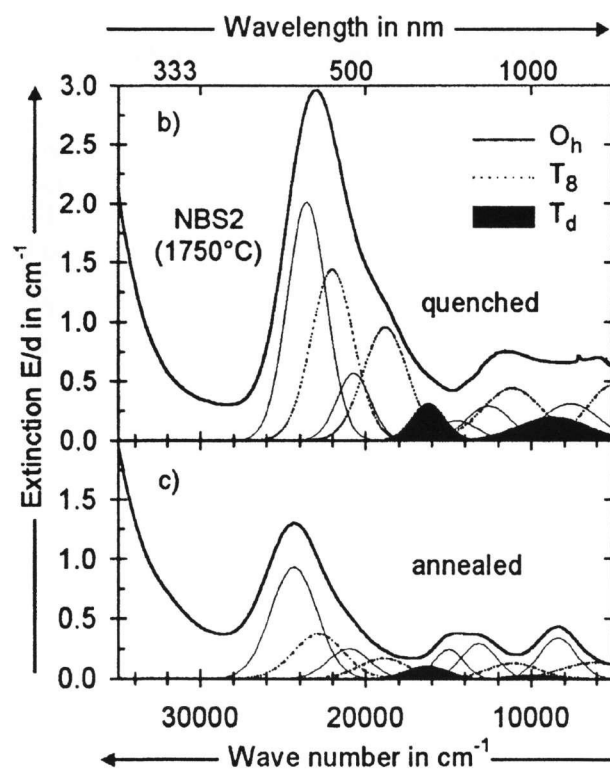
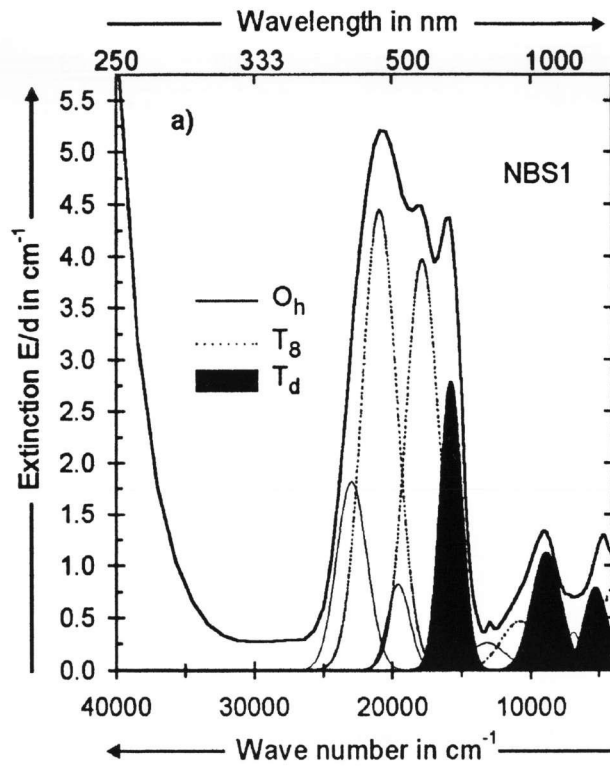
Figure 7 displays the spectra of NiO -doped NBS2 glasses melted at different temperatures. The curves 1 to 3 all arise from quenched glasses and display a significant dependence on the final melting temperature. Curve 4 is from an annealed sample, for which no dependence on the final melting temperature was observed.

The analogous spectra for CoO -doped glasses are shown in figure 8. Contrary to the NiO -doped glasses the spectra of the quenched glasses are now in such good agreement that only the spectrum of one glass is displayed as an example for all quenched glasses. The structure of the melt does not seem to change significantly in the temperature range between 1650 and 1750 °C. Curve 1 stems from a quenched glass with a final melting temperature of 1700 °C. On the other hand, in the case of the annealed CoO -doped glasses a stronger dependence on the final melting temperature can be observed in the spectra shown in curves 2 to 3.

To answer the question of why such different temperature dependencies are found for the NiO - and the CoO -doped glasses, the interpretation of these spectra has to be discussed in some detail.

4.2.1 Nickel

Increasing melting temperatures leads, in the spectra of the NiO -doped glasses, to an increase of the intensity of the main band at 420 nm. Further comparison of the spectra of the annealed and the quenched samples also show significant changes in the position and form of the



Figures 6a to c. Optical spectra including band separation of the NiO-doped borosilicate glasses: a) NBS1, b) quenched NBS2 and c) annealed NBS2.

bands at higher wavelengths. Figures 6b and c show the band separation for the spectra of an annealed and a quenched NiO-doped NBS2 glass. The position of the bands is based on data from Gitter [19 to 21], who ascribed these bands in a study of NiO-doped borate and phosphate glasses to octahedrally, tetrahedrally and the

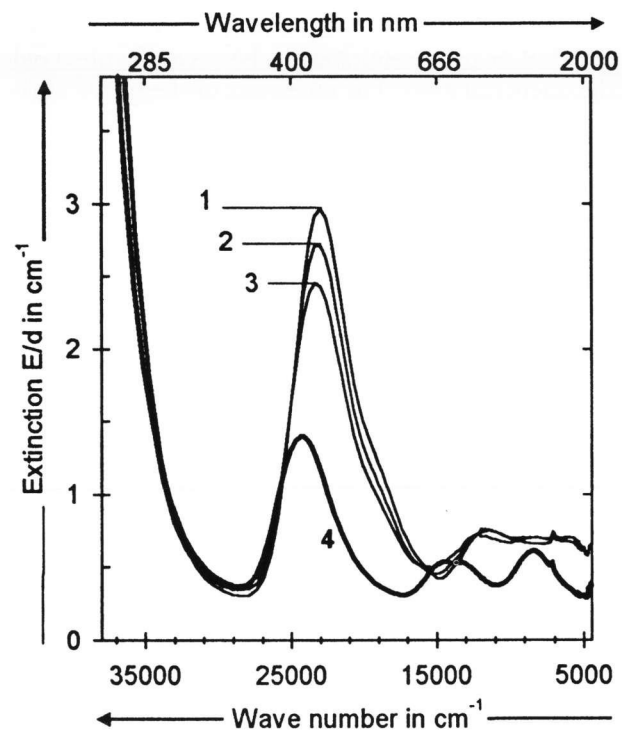


Figure 7. Optical spectra of NiO-doped NBS2 glasses; samples quenched at final melting temperatures of: curve 1 = 1750°C, curve 2 = 1700°C, curve 3 = 1650°C, curve 4 = annealed sample.

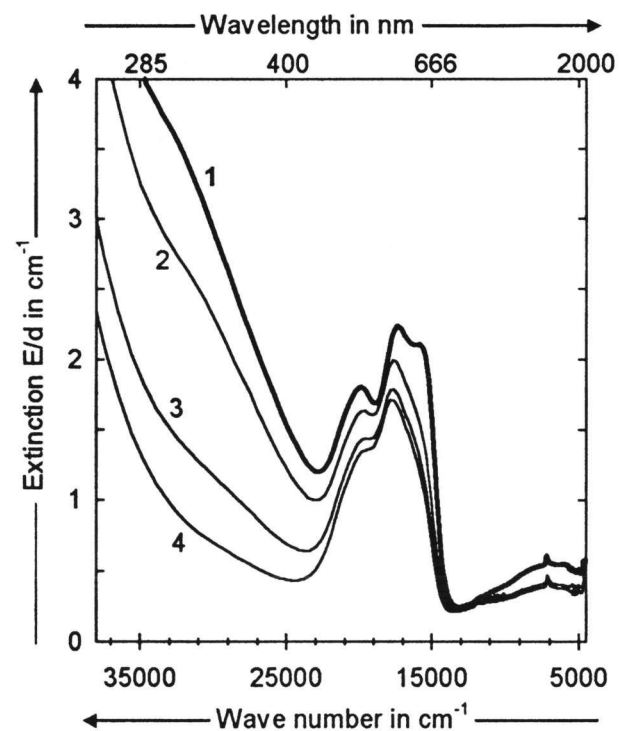


Figure 8. Optical spectra of CoO-doped NBS2 glasses; curve 1 = quenched glass; annealed samples with final melting temperatures of: curve 2 = 1750°C, curve 3 = 1700°C, curve 4 = 1650°C.

eightfold dodecahedral coordinated ions. While the main bands in the annealed glass arise from octahedral Ni²⁺ and only minor levels of tetrahedrally or eightfold coor-

ordinated Ni^{2+} are found, a significant increase of the dodecahedral or pseudo-tetrahedral Ni^{2+} can be observed in the quenched glass. The intensities of the bands attributed to tetrahedral Ni^{2+} are very low for all glasses. However, the absolute intensity of some of the stronger octahedral bands does nevertheless increase in the quenched compared to the annealed glass. One explanation for this uneven change in the extinction coefficients of the octahedral bands might be explained as presented by Blair and Duffy [7]. Discussing similar changes in the spectra of Ni^{2+} -doped phosphate glasses upon heating, they propose that the spectral changes are caused either by a decrease in the energy separation of the vibrational states as the glass structure becomes more relaxed upon higher temperatures, or by an increase of the optical basicity, which would in turn enhance the covalency and thus relax the mechanism for electronic transitions. Upon quenching the NBS2 glass freezes in a structure of higher basicity, this might result in a higher extinction coefficient for some of the otherwise electronically forbidden octahedral bands.

4.2.2 Cobalt

The spectra of the quenched CoO-doped glasses show a hint of the band characteristic of tetrahedral Co^{2+} . However, the overall intensity is more similar to that of octahedrally coordinated Co^{2+} and therefore the content of tetrahedrally coordinated Co^{2+} must be rather low, as the bands are only visible due to their high extinction coefficient. On the other hand these bands might also be attributed to pseudo-tetrahedrally coordinated Co^{2+} . According to Warne et al. the spectrum of pseudo-tetrahedral Co^{2+} should resemble that of octahedral Co^{2+} in its intensity and that of tetrahedral Co^{2+} in its band positions [23].

Another important feature is the absorption around 280 to 350 nm, which is most pronounced in the quenched glasses, but can be found in all CoO-doped glasses of high final melting temperatures. This band, which is fully absent in the NiO-doped glasses, is also smaller in the annealed CoO-doped glasses than in the quenched glasses of the same melt. This is also true when the quenched glass sample was prepared just before the corresponding annealed sample, therefore this band cannot be caused by an impurity but must be due to a Co-related transition. One possible origin would be the CT transition of Co^{3+} , which is known to exhibit a strong and broad absorption below 400 nm [25 to 27]. Even though only very small amounts of Co^{3+} would be sufficient for this absorption, studies on the temperature dependence of redox equilibria generally tend to show that the lower and not the higher oxidation states are favoured at higher melting temperatures [28 and 29]. The origin of the 280 to 350 nm band may also be due to a transition of the pseudo-tetrahedral transition coordination of Co^{2+} . This interpretation may be supported

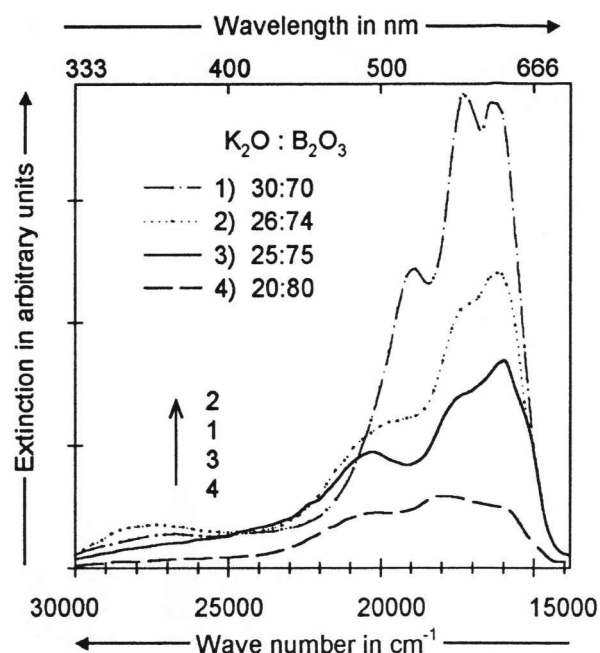


Figure 9. Optical spectra of a series of CoO-doped alkali borate glasses with increasing alkali content; according to Gitter [21].

by the analysis of the spectra recorded by Gitter, which are displayed in figure 9 [21]. This figure consists of a series of optical spectra from CoO-doped alkaline-borate glasses with increasing alkaline content. This series shows the typical tetrahedral spectrum, several mixed spectra and a typical octahedral spectrum. Curves 1 to 4 display the transition from a typical octahedral (1) to a typical tetrahedral coordination (4), as would be expected with increasing alkali content of the glasses. This transformation is accompanied by an increase of a band at about 350 nm. This band reaches a maximum in glass 3. In sample 4, where the spectrum is dominated by transitions of the tetrahedral coordination, the 350 nm band does already decrease. Gitter did not further refer to this band, but as this band is especially strong in those glasses of mixed coordination it might well be due to a transitional coordination, either a distortion of the two known coordinations or an additional third coordination.

Despite the many similarities in the chemistry of Co^{2+} and Ni^{2+} in glass, there is at least one important difference of interest from the aspect of this study. The octahedral site preference energy of Ni^{2+} , with 80 kJ/mol is quite high, while both coordinations are energetically equivalent in the case of Co^{2+} [1 and 24]. The different behaviour of CoO- and NiO-doped NBS2 glasses under varying melting and cooling conditions might well arise from these different coordination preferences.

Ni^{2+} is found in all annealed NBS2 glasses in an octahedral coordination, no matter what final melting temperature was applied. At the high temperatures in the melt octahedral Ni^{2+} is partly transformed to tetrahedral and pseudo-tetrahedral Ni^{2+} . Because of the high

octahedral preference only a small portion of the Ni^{2+} takes part in this transformation. An increase of the final melting temperature by 50 K also increases the tetrahedral and pseudo-tetrahedral content in the melt, which can be partly frozen in by quenching. The scenario for Co^{2+} is slightly different. As both, the tetrahedral as well as the octahedral coordination are energetically nearly equivalent, the coordination ratios in the melt have reached a state more or less independent of the final melting temperatures studied. While hardly any changes were found in the optical spectra of the quenched glasses, a dependency of the spectra of the annealed glasses on the melting temperature was nevertheless found. A sample taken at 1750 °C still shows a spectrum with a high intensity band around 280 to 350 nm, indicating a high content of pseudo-tetrahedral Co^{2+} . The spectrum of a sample taken at 1650 °C resembles more that of octahedrally coordinated Co^{2+} and hardly any traces of the band around 280 to 350 nm are found. These variations might be due to the difference between the final melting temperature and the annealing temperature. The higher this temperature difference is, the higher is the amount of transitional structures still present at the time when the viscosity of the sample becomes too high for any further transformations.

4.3 Subsequent tempering experiments

In order to study the influence of cooling in more detail, additional tempering experiments were carried out on a heating table. Quenched samples were heated from room temperature to 725 °C in steps of 25 K and the optical spectra were recorded over the process. Figures 10 and 11 show selected spectra of this series for the CoO- and NiO-doped quenched glasses over the heating process.

For CoO-doped glass a decrease in the absorption around 280 to 350 nm can be found with increasing heating temperatures (figure 10). Major changes can be observed in the intensities of the Co^{2+} main bands, until the spectra resemble the mixed spectra of the glasses 2 and 3 as found by Gitter in figure 9, which are mainly due to octahedral and tetrahedral transitions. Therefore, a disproportioning of the frozen-in transitional pseudo-tetrahedral coordination into octahedral and tetrahedral units might cause the observed changes.

For the NiO-doped glass a shift of the UV absorption edge to longer wavelengths is observed (figure 11). Additionally the main absorption band at ≈ 450 nm begins to decrease at temperatures higher than T_g . This decrease becomes quite significant at temperatures 150 to 200 °C above the T_g of the NBS2 glass.

Figure 12 shows the optical spectra of NiO-doped NBS2 in the course of different thermal treatments. The first two spectra were taken at room temperature of the quenched glass, (1) with the double beam spectrometer over the whole range, and (2) with the diode-array spec-

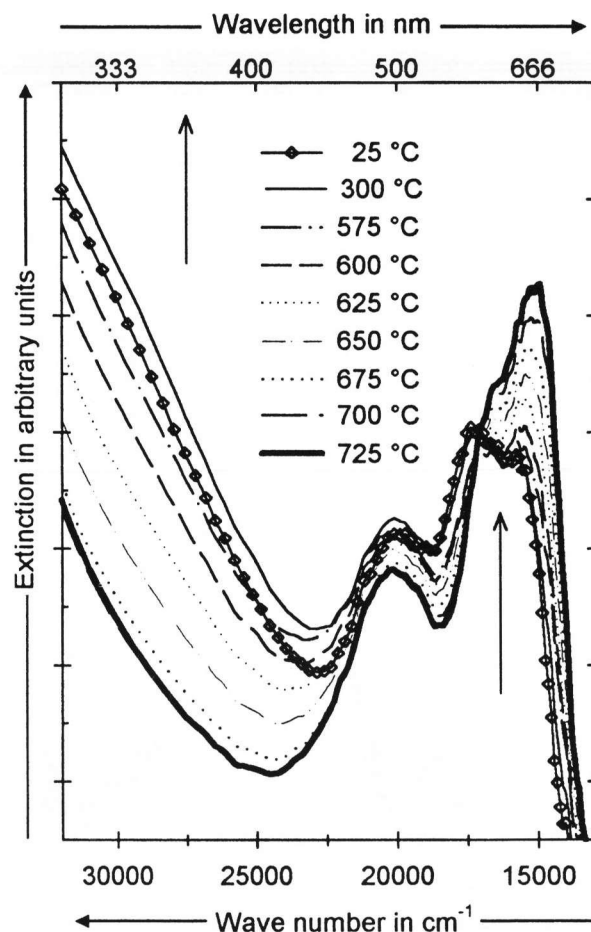


Figure 10. Optical spectra of a quenched CoO-doped NBS2 glass with increasing temperatures on the heating table.

trometer of the heating table. Heating the sample to 720 °C gives spectrum (3). As previously mentioned spectrum (3) differs from (1) and (2) in the UV absorption edge, which is now shifted to longer wavelengths, and in the decreased height of its main band. After room temperature was reached again by sample (3), spectrum (4) of the thus tempered glass was taken over the whole range with the double-beam spectrometer. In this spectrum the position of the absorption edge recovered its initial value, an effect that can be attributed to the temperature dependency of the absorption edge, and which has already been described in other undoped glasses [30]. The decrease of the main absorption band in the spectrum taken at room temperature is even more pronounced than in the spectrum taken at 720 °C. The spectrum of the quenched and subsequently tempered glass is in very good agreement with spectrum (5). This last spectrum belongs to an NiO-doped glass initially annealed after melting.

The differences in the heating table experiments for the CoO- and NiO-doped glasses can be attributed as before to the different coordination preferences of Co^{2+} and Ni^{2+} . Both ions are in part pseudo-tetrahedrally coordinated in the quenched glass samples. Heating the

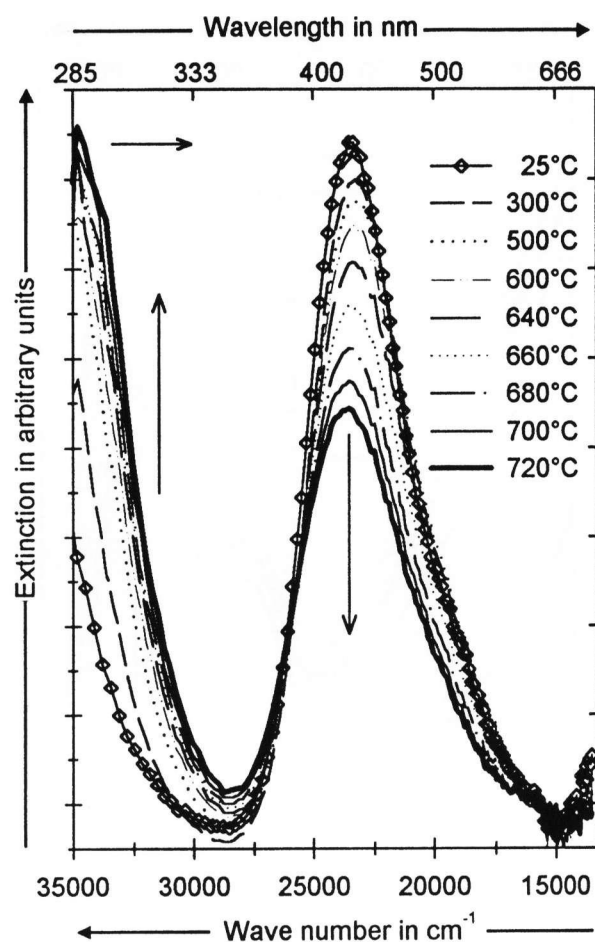


Figure 11. Optical spectra of a quenched NiO-doped NBS2 glass with increasing temperatures on the heating table.

glasses above T_g allows for a relaxation of the glass matrix. While pseudo-tetrahedral Ni^{2+} will be transformed primarily into the favoured octahedral coordination, pseudo-tetrahedral Co^{2+} will adapt not only the octahedral but also the energetically equivalent tetrahedral coordination.

4.4 Discussion

The spectra show that not only Ni^{2+} but also Co^{2+} are ordinarily found in an octahedral coordination in the annealed NBS2 glass. The quenched glasses on the other side contain a significant amount of pseudo-tetrahedral coordinated ions. This is caused by a coordination change of the dopants at the high melting temperatures, at which small coordination numbers are favoured. The transformation from octahedral to tetrahedral coordination includes an eightfold pseudo-tetrahedral transition step.

The reverse coordination change, which is found during the cooling or quenching process, normally takes place so rapidly that no evidence of the dopants' coordi-

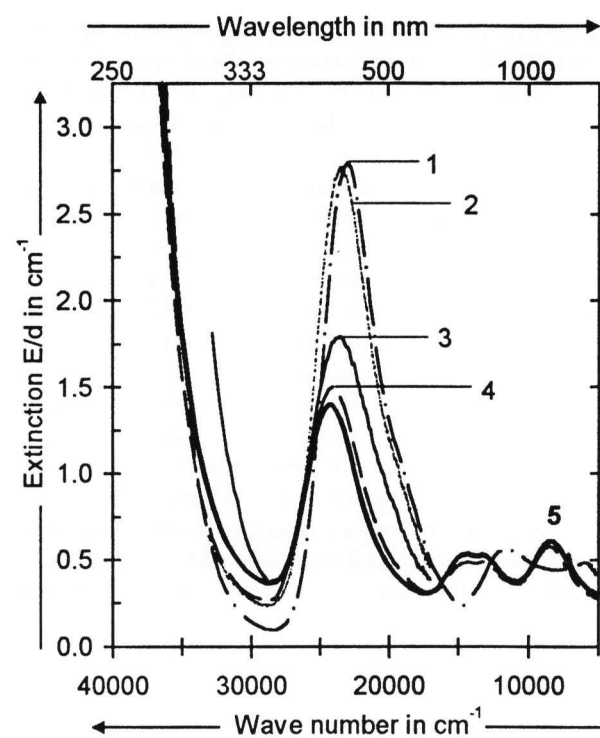


Figure 12. Optical spectra of NiO-doped NBS2: curve 1 = quenched, curve 2 = sample from curve 1 at 25°C (heating table), curve 3 = sample from curve 1 at 720°C (heating table), curve 4 = sample from curve 3, cooled down to room temperature, curve 5 = annealed reference sample (see also explanation in the text).

nation history during the melt is found afterwards in the optical spectra. However, in the NBS2 glass, differences in the coordination of Co^{2+} and Ni^{2+} are found in the optical spectra of annealed and quenched glasses. In the quenched glasses both ions adopt a coordination different from the dominating octahedral coordination normally found in the NBS2 glass. The pseudo-tetrahedral coordination is at room temperature a thermodynamically unfavoured coordination and is therefore normally not found in glasses in significant amounts. Even glasses of medium basicity show – at least at the concentration range studied for the dopants – mixed spectra of octahedral and tetrahedral coordinated ions rather than significant amounts of the pseudo-tetrahedral transition coordination.

4.4.1 Nickel

Octahedrally coordinated Ni^{2+} prevails in the NiO-doped glasses, due to the high octahedral preference of Ni^{2+} . A certain amount of octahedral Ni^{2+} is probably even present in the melts. After quenching the melt, a mixed coordination containing octahedrally as well as pseudo-tetrahedrally coordinated Ni^{2+} is found. The ratio of pseudo-tetrahedral Ni^{2+} increases with an increasing final melting temperature. Later tempering of a

quenched sample at temperatures exceeding T_g causes a relaxation of the glass matrix, which also allows the Ni^{2+} ion to enter a thermodynamically more favoured coordination. The tempering leads in the case of Ni^{2+} to a conversion of all ions into the octahedral coordination so that all NiO-doped NBS2 samples annealed initially or those quenched and later tempered show a pure octahedral coordination of the Ni^{2+} ions.

4.4.2 Cobalt

In the CoO-doped glasses the octahedral and the tetrahedral coordination are energetically equal. Compared to nickel a much higher content of pseudo-tetrahedral and tetrahedral Co^{2+} is formed in the melt. Because of the high viscosity of the NBS2 glass, quenching will result in a kinetical freezing of the pseudo-tetrahedral transition coordination through which the tetrahedral Co^{2+} has to pass during the cooling process. No significant changes are found in the coordination fractions for the CoO-doped glasses in dependence on the final melting temperature. Thus, Co^{2+} is present at similar coordination fractions at all melting temperatures studied between 1650 and 1750 °C. Tempering the quenched samples later on a heating table causes a relaxation of the glass matrix and Co^{2+} can take up a coordination thermodynamically preferred over the pseudo-tetrahedral transition coordination. Contrary to Ni^{2+} the crystal field makes no energetic distinction between octahedral and tetrahedral coordination for Co^{2+} and thus both forms are found in the tempered glass, although Co^{2+} is found in the initially annealed glasses predominantly in the octahedral form. In the quenched and tempered glasses relaxation of the pseudo-tetrahedral into a tetrahedral coordination seems to be just as likely, probably due to the stronger structural resemblance of these two coordinations. Thus, the tempering process leads to spectra similar to those of the mixed octahedral/tetrahedral spectra found in other glasses of medium-high basicity.

The dependence of the coordination fractions in the initially annealed CoO-doped glasses on the final melting temperature is probably connected to the difference between melting and annealing temperature of the cooling oven. The relatively slow cooling process from the melting temperatures around 1700 to 500 °C (the NBS2 glass has only a T_g of 442 °C) will bring about slightly different cooling curves for the different initial temperatures. In combination with the high viscosity of this glass, the transformation process will thus also take slightly different courses and will stop at different stages. Therefore, a higher amount of pseudo-tetrahedrally coordinated Co^{2+} is found in the annealed glasses prepared at higher melting temperatures. For the quenched glasses the cooling process happens so quickly, that for all initial melting temperatures the same transformational structure is frozen in.

5. Viscosity

The two different viscosity measurements covered a wide viscosity range. Therefore the viscosity-temperature curve could be extrapolated with some certainty for temperatures that were not experimentally analysed. These values were calculated with the Vogel-Fulcher-Tammann (VFT) equation:

$$\lg \eta = A + \frac{B}{T - T_0}$$

The parameters A , B and T_0 necessary for these calculations were determined from experimental values. The viscosity-temperature curves of the two glasses NBS1 and NBS2 are shown in figures 13a and b.

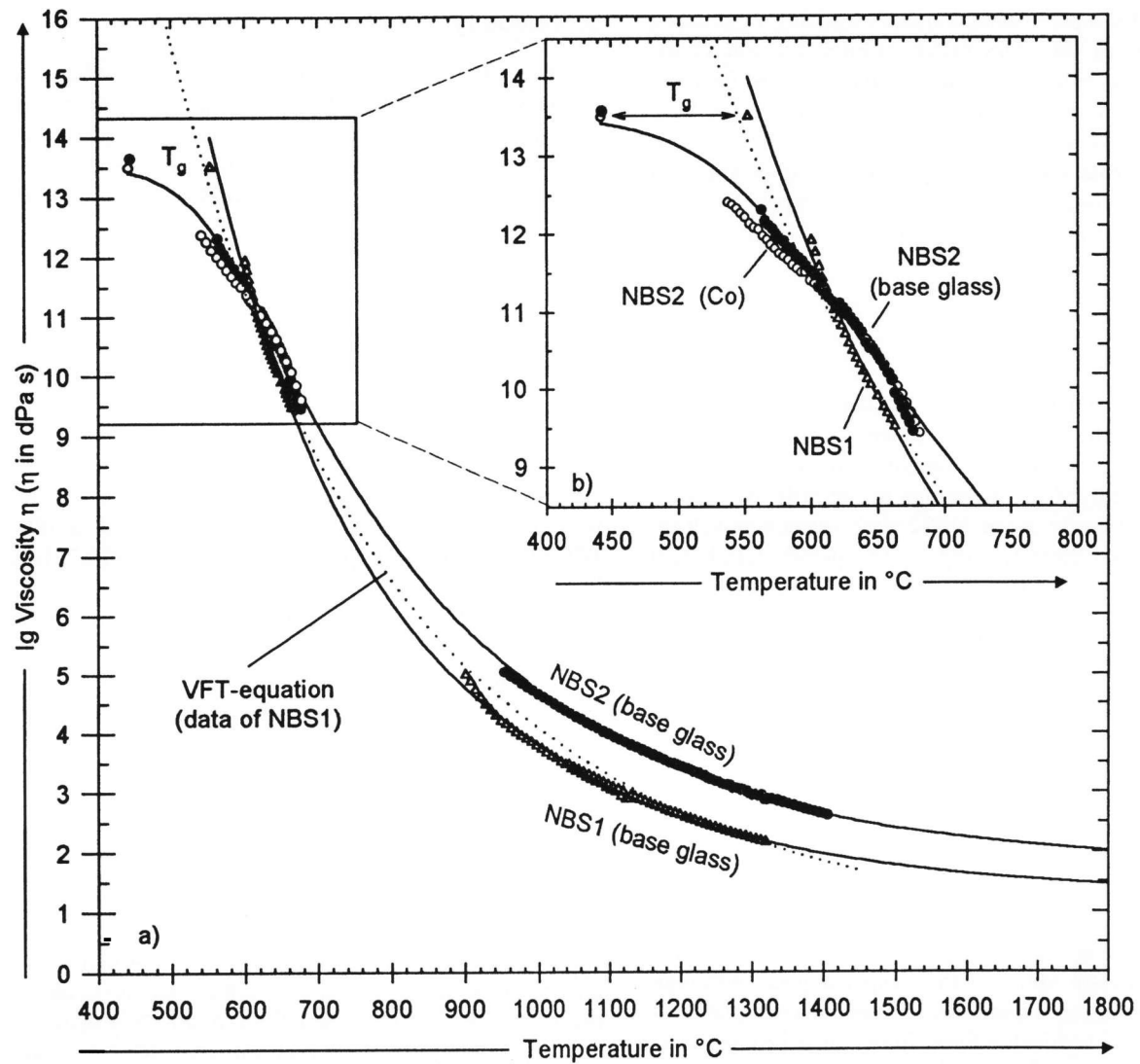
The VTF curve for the glass NBS1 is also shown and is in good agreement with the experimental results. While the viscosity-temperature curve of the NBS1 glass has the common form, the curve of the NBS2 glass shows with decreasing temperature – at about 150 °C above T_g – distinct deviations from the ideal Newtonian behavior and can not be modelled with the VFT equation. A similar curve to the one for the undoped NBS2 base glass was found for the CoO-doped glass. The NiO-doped glass was not measured separately. It can be seen from the displayed curves that the NBS2 glass has a higher melting temperature than the NBS1 glass, even though its T_g is lower. The viscosity of the NBS2 glass is also higher at higher temperatures.

Deviations from the ideal temperature-viscosity curve are often connected to crystallization or phase separation processes in the glasses. Neither was observed in the glass NBS2. These deviations might otherwise be due to a change in the structural units of the borate groups. More detailed studies on the glass structure of NBS2 could give important clues for this discussion.

Interestingly the most prominent changes in the tempering spectra of the quenched glasses were found when the temperature was raised up to 150 to 200 °C above T_g , a temperature range at which the inflection point of the temperature viscosity curve also happens to be. It might be that at these temperatures a slight change in the structure of the NBS2 glass takes place, like a coordination change of the borate groups, which in turn leads to the coordination change of the dopants. Duffy and Ingram determined the microscopic optical basicities for different borate groups, which are stated in figure 14 [31]. Duffy et al. also studied changes of the theoretical basicity A with increasing temperature in borate glasses and observed the expected increase of A while increasing the temperature from room temperature to 500 °C [32].

6. Conclusion

In the high-viscosity borosilicate glass NBS2 doped with CoO or NiO quenching resulted in a freeze-in snap-shot



Figures 13a and b. Viscosity-temperature curve of the borosilicate glasses NBS1 and NBS2; the experimentally derived values (Δ : NBS1, \circ : undoped NBS2 and \bullet : CoO-doped NBS2) are connected by a line (—) as guide for the eye, \cdots : VFT curve of NBS1; b) magnification of the section marked in a).

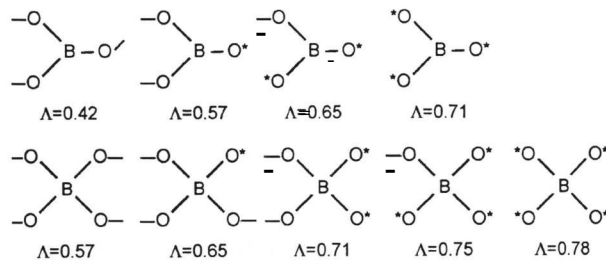


Figure 14. Schemata of different BO_3 and BO_4 units and their corresponding predicted microscopic optical basicities λ according to Duffy and Ingram [31]; (-O-: bridging oxygen; $^*\text{O}$: non-bridging oxygen).

of the glass structure within the transformation process from the high-temperature form containing a higher amount of tetrahedrally coordinated Co^{2+} and Ni^{2+} to the octahedral coordination thermodynamically favoured in the NBS2 glass at room temperature. In this

transitional state the octahedral, tetrahedral and pseudo-tetrahedral eightfold transitional coordinations are simultaneously present in the quenched glasses. Because of the octahedral preference of Ni^{2+} in the crystal field subsequent tempering or annealing of the NiO-doped glasses results in a relaxation into the octahedral coordination. For Co^{2+} , which does not energetically prefer the octahedral to the tetrahedral form, tempering of the quenched glasses leads to a relaxation into octahedral and tetrahedral coordinated ion. The relaxation into tetrahedra is enhanced due to the structural similarities to the energetically unfavoured pseudo-tetrahedral transition coordination. These structural changes induced by tempering of the quenched glasses are especially strong when the applied temperatures are 150 to 200 °C above T_g of the NBS2 glass where also the viscosity-temperature curve implies structural changes within the glass matrix. The exact nature of these changes within the glass structure of this borosilicate

glass NBS2 is certainly of interest and thus will be investigated in more detail in further studies.

7. References

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