

## High-temperature UV-VIS-NIR spectroscopy of chromium-doped glasses

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Chromium-doped glasses with the basic composition (in mol%)  $16 \text{ Na}_2\text{O} \cdot 10 \text{ CaO} \cdot 74 \text{ SiO}_2$  were melted under different redox conditions. From these glasses, UV-VIS-NIR absorption spectra were recorded at temperatures up to  $1200^\circ\text{C}$ . While the intensity of the peak attributed to  $\text{Cr}^{6+}$  decreases, some of the peaks caused by  $\text{Cr}^{3+}$  increase in intensity at higher temperature. All peaks are slightly shifted to larger wavelengths and get broader with increasing temperature. Glasses melted under oxidizing conditions were slowly cooled as well as quenched. Using EPR spectroscopy, in the quenched sample,  $\text{Cr}^{5+}$  was detected in a larger concentration than in the slowly cooled sample. Otherwise, the  $\text{Cr}^{6+}$  concentration was larger in the slowly cooled sample. This is explained by a redox reaction, i.e. a disproportionation of  $\text{Cr}^{5+}$  to  $\text{Cr}^{6+}$  and  $\text{Cr}^{3+}$  during cooling. As shown by high-temperature spectroscopy of the quenched sample, this redox reaction is frozen in below  $550^\circ\text{C}$ .

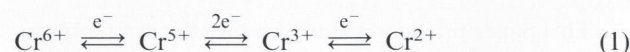
### Hochtemperatur-UV-VIS-NIR-Spektroskopie von chrom-dotierten Gläsern

Es wurden chrom-dotierte Gläser der Grundzusammensetzung (in Mol-%)  $16 \text{ Na}_2\text{O} \cdot 10 \text{ CaO} \cdot 74 \text{ SiO}_2$  unter verschiedenen Redoxbedingungen erschmolzen. Von diesen Gläsern wurden UV-VIS-NIR-Spektren bei Temperaturen bis  $1200^\circ\text{C}$  aufgenommen. Während bei höheren Temperaturen die Intensität des von  $\text{Cr}^{6+}$  hervorgerufenen Peaks abnahm, nahmen die Intensitäten einiger der  $\text{Cr}^{3+}$  zugeordneten Peaks zu. Alle Peaks wurden mit zunehmender Temperatur breiter und leicht zu größeren Wellenlängen hin verschoben. Unter oxidierenden Bedingungen erschmolzene Gläser wurden einerseits langsam gekühlt und andererseits abgeschreckt. Mit Hilfe der ESR-Spektroskopie wurde in der abgeschreckten Probe eine höhere  $\text{Cr}^{5+}$ -Konzentration gefunden als in der langsam abgekühlten Probe. Andererseits war die  $\text{Cr}^{6+}$ -Konzentration in der langsam abgekühlten Probe größer. Dies wurde durch eine Redoxreaktion, die Disproportionierung von  $\text{Cr}^{5+}$  zu  $\text{Cr}^{6+}$  und  $\text{Cr}^{3+}$ , beim Abkühlen erklärt. Wie durch Hochtemperaturspektroskopie einer abgeschreckten Probe gezeigt wurde, ist diese Redoxreaktion unterhalb von  $550^\circ\text{C}$  eingefroren.

### 1. Introduction

Chromium-doped glasses are widely manufactured in the glass industry and widely used as container glass. Another important application is that as green float glass. Chromium, in principle, may occur in glasses as  $\text{Cr}^{6+}$ ,  $\text{Cr}^{5+}$ ,  $\text{Cr}^{3+}$  and  $\text{Cr}^{2+}$  (e.g. [1 and 2]). Depending on the batch composition, the concentrations of the respective redox species may notably vary. Here, the addition of reducing species, such as carbon, or oxidizing species, such as  $\text{Na}_2\text{SO}_4$  or  $\text{NaNO}_3$ , is of major impor-

tance. Besides, however, other polyvalent species, such as iron, and the base glass composition may affect the chromium redox states [3 and 4]. At room temperature, the species  $\text{Cr}^{6+}$  and  $\text{Cr}^{3+}$  can clearly be distinguished using UV-vis-NIR spectroscopy [5 and 6]. The species  $\text{Cr}^{3+}$  and  $\text{Cr}^{5+}$  are paramagnetic and may quantitatively be determined by EPR spectroscopy. At high temperatures, voltammetric studies give evidence for the occurrence of three redox states:  $\text{Cr}^{6+}$ ,  $\text{Cr}^{3+}$  and  $\text{Cr}^{2+}$  [7 and 8], however, do not give any hint of the redox state  $\text{Cr}^{5+}$ .



Equation (1) gives an overview of all redox species occurring at room temperature. Redox equilibria are generally affected by the temperature and usually are shifted to the reduced species while increasing the temperature. At high temperatures, the redox species are in equilibrium with physically dissolved oxygen. Generally, the melt need not be in equilibrium with the surrounding

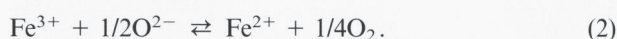
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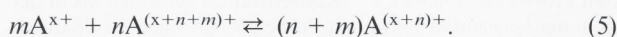
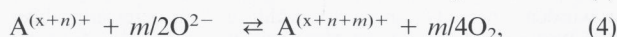
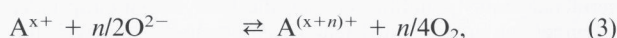
Der ausführliche Schlußbericht „Emissionsspektroskopie an Glasschmelzen zur quantitativen Bestimmung färbender Ionen“ (AiF-Nr. 12064 B) kann bei Bedarf über die Bibliothek der Deutschen Glastechnischen Gesellschaft (DGG) bestellt werden.



atmosphere, because diffusivity of oxygen in or out of a glass melt is a relatively slow process. In industrial glass tanks, usually this equilibrium is not reached and the redox states are primarily affected by the batch composition and not by the furnace atmosphere. During subsequent cooling of the melt, the redox ratios may change, however, further oxygen diffusion does usually not play an important part, if cooling rates typical of technical processes are supplied. This means, if only one polyvalent element is present, and such as iron occurs in only two oxidation states, the redox ratio (e.g.  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ) does not change in a noticeable manner during cooling of the melt, because in technical glass melts, the concentration of physically dissolved oxygen is much smaller than the iron concentration.



In melts of optical glasses, possessing iron concentrations as low as 0.001 wt%, this may not be valid. If a redox species occurs in more than one oxidation state, or more than one polyvalent elements are present, redox reactions may occur during cooling [4, 9 and 10]. If the temperature is further decreased, these redox reactions will get frozen in, and although thermodynamically possible will no longer occur [9 and 10]. For a polyvalent element which may occur in three different oxidation states, the redox reactions possible are syn- or disproportionation [11] (see equation 5).



The equilibria described by equations (3) and (4) each depend on temperature, but the attributed equilibrium constants usually are not affected by temperature to exactly the same extent. Thus, also the equilibrium described by equation (5) usually will depend upon temperature (e.g. [9 and 11]). Since this equilibrium is a homogeneous reaction (oxygen does not participate), diffusion of oxygen in or out of the melt is not necessary.

Spectroscopic studies of glasses and melts at high temperature have scarcely been reported [12 to 18]. For a quantitative interpretation of the spectra obtained, the temperature dependence of absorption coefficients as well as possible redox reactions have to be taken into account. It should be noted that the effect of temperature on the spectra is also of great importance for absorption and emission of light, and hence, for the temperature distribution in industrial glass tanks.

This paper provides a study on the effect of temperature on the absorption spectra of chromium-doped glasses.

## 2. Experimental procedure

Glasses with the basic composition (in mol%)  $16 \text{Na}_2\text{O} \cdot 10 \text{CaO} \cdot 74 \text{SiO}_2$  doped with chromium compounds

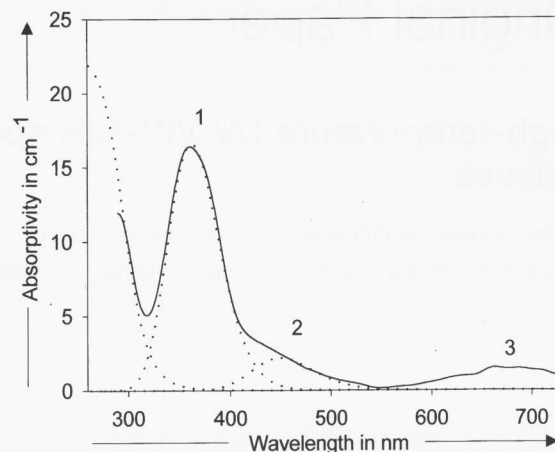


Figure 1. UV-VIS-NIR absorption spectrum from glass A recorded at room temperature (full line), dotted lines: absorption bands of the deconvoluted spectrum; 1:  $\text{Cr}^{6+}$  absorption band, 2 and 3:  $\text{Cr}^{3+}$  absorption band.

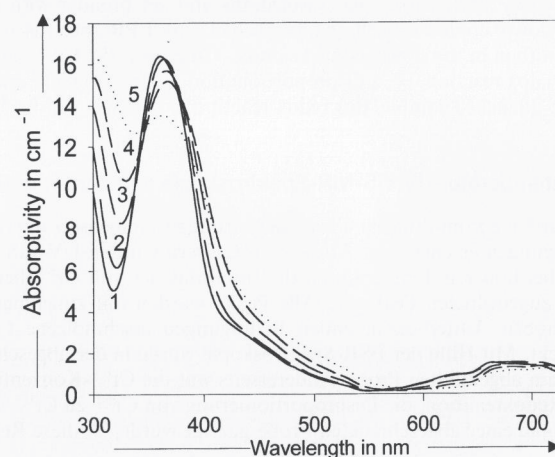


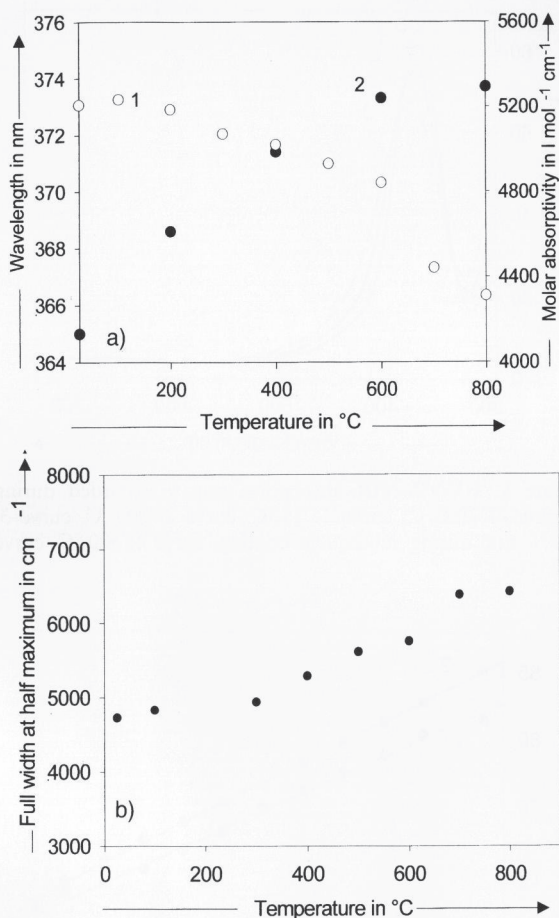
Figure 2. UV-VIS-NIR absorption spectra during heating of glass A recorded at the temperatures: curve 1: 25 °C, curve 2: 200 °C, curve 3: 400 °C, curve 4: 600 °C and curve 5: 800 °C.

were melted from the raw materials  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCO}_3$  and  $\text{SiO}_2$  in a platinum crucible at 1450 °C. The chromium compounds used were  $\text{Cr}_2\text{O}_3$  (1940 ppm Cr: glass A), and  $\text{Na}_2\text{CrO}_4$  (2000 ppm Cr: glass C). Glass B was prepared in silica crucibles using  $\text{Cr}_2\text{O}_3$  (3550 ppm Cr) and 1 wt% sugar as reducing agent. Spectra of the glasses were recorded at room temperature using a UV 3101 PC spectrometer (Shimadzu Inc., Kyoto (Japan)). High-temperature spectra were recorded using a diode array spectrometer (InstaSpecIIa, L. O. T., Darmstadt (Germany)). The glass samples were cut into small pieces (diameter: 6 mm, thickness: 0.2 to 4 mm) and heated using a microscope heating stage (LINKAM TS1500, Waterfield (UK)). The spectra were recorded in the wavelength range from 200 to 900 nm.

## 3. Results

Figure 1 shows UV-VIS-NIR-spectra of glass A at room temperature (full line). The UV cut occurs at approxi-





Figures 3a and b. Temperature dependency of the peak at around 365 nm; a) curve 1: molar absorptivity, and curve 2: wavelength of the absorption maximum; b) full width at half maximum.

mately 220 nm and the spectra show three distinct absorption bands, illustrated by the deconvoluted peaks (see dotted lines) at 365, 450 and 660 nm. The latter peak shows some splitting which is discussed later. Figure 2 shows spectra of glass A recorded during heating of the sample. The temperatures attributed to curves 1, 2, 3, 4 and 5 are 25, 200, 400, 600 and 800  $^{\circ}\text{C}$ , respectively. The effect of temperature is clearly seen: the intensities of the peaks at around 365 and 660 nm decrease, while the intensity of the peak at around 450 nm increases. The UV cut is shifted towards the visible range. Furthermore, the peak at around 365 nm is slightly shifted with temperature, as illustrated in figure 3a. Here, within the range from 25 to 800  $^{\circ}\text{C}$ , a shift from 365 to 373 nm is observed. This shift is small, but clearly significant and much larger than the error limits of the equipment used. The molar absorptivity decreases and the full width at half maximum of this peak increases (see figure 3b) with increasing temperature. Figure 4 shows UV-VIS-NIR spectra recorded during cooling of the composition A at the temperatures of 1200, 1000, 800, 600, 400 and 200  $^{\circ}\text{C}$ . By contrast to figure 2, here also the temperatures of 1000 and 1200  $^{\circ}\text{C}$  are included.

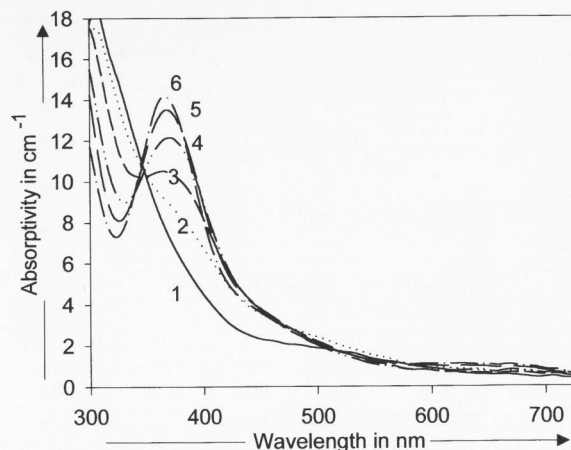


Figure 4. UV-VIS-NIR absorption spectra during cooling of glass A at the temperatures: curve 1: 1200  $^{\circ}\text{C}$ , curve 2: 1000  $^{\circ}\text{C}$ , curve 3: 800  $^{\circ}\text{C}$ , curve 4: 600  $^{\circ}\text{C}$ , curve 5: 400  $^{\circ}\text{C}$  and curve 6: 200  $^{\circ}\text{C}$ .

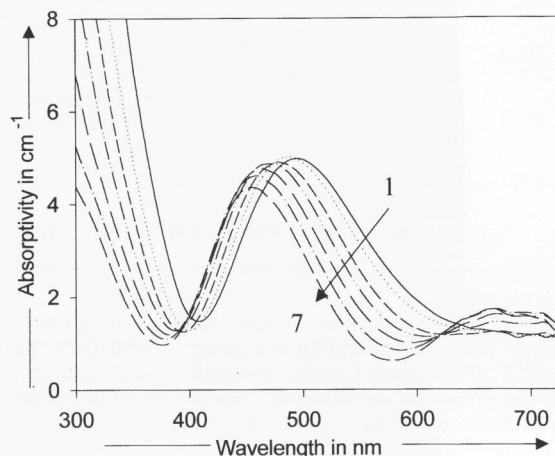
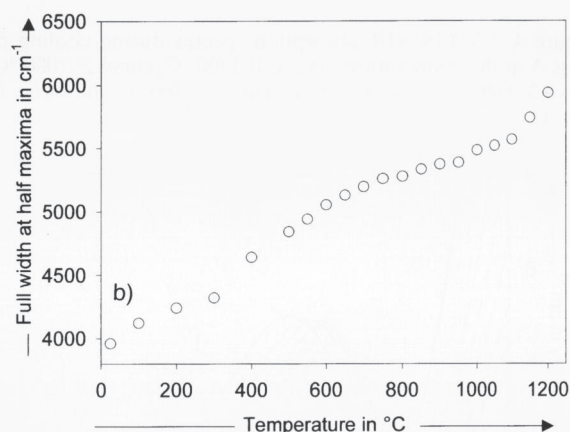
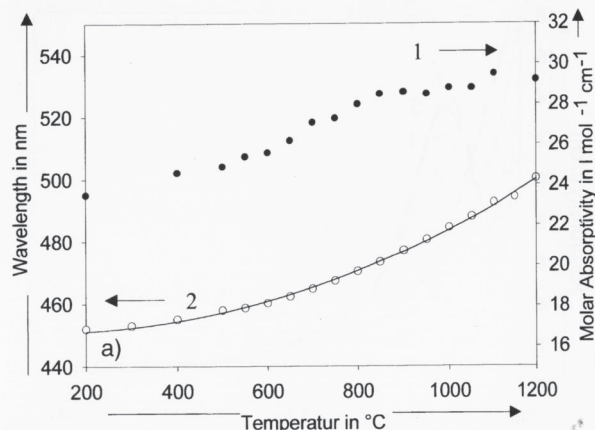


Figure 5. UV-VIS-NIR absorption spectra of glass B at the temperatures: curve 1: 1200  $^{\circ}\text{C}$ , curve 2: 1000  $^{\circ}\text{C}$ , curve 3: 900  $^{\circ}\text{C}$ , curve 4: 800  $^{\circ}\text{C}$ , curve 5: 700  $^{\circ}\text{C}$ , curve 6: 600  $^{\circ}\text{C}$  and curve 7: 500  $^{\circ}\text{C}$ .

At a first glance, curves attributed to the same temperatures possess similar shape. As also shown in figure 4, the spectra change notably at temperatures larger than 800  $^{\circ}\text{C}$ . The peak at around 365 nm decreases drastically and nearly disappears at 1200  $^{\circ}\text{C}$ .

UV-VIS-NIR spectra of glass B, which was prepared under reducing conditions, are shown in figure 5. The peak at around 365 nm is not observed, the two other peaks at around 450 and 660 nm are still seen. The peak at 450 nm increases in intensity with increasing temperature, is shifted to larger wavelengths (see figure 6a) and gets broader (see figure 6b). It is also clearly shown in figure 5 that the peak at around 660 nm is composed of several smaller peaks of different intensity. With increasing temperature, this absorption band changes its shape, the maximum absorptivity decreases and is shifted to larger wavelengths. Glass C was obtained using  $\text{Na}_2\text{CrO}_4$  as raw material. After melting the glass, it was either slowly cooled or, quenched as described above.



Figures 6a and b. Temperature dependency of the molar absorptivity and the absorption maximum of the Cr<sup>3+</sup> peak:  $^4A_{2g} \rightarrow ^4T_1(F)$ ; a) curve 1: molar absorptivity, and curve 2: shift of the wavelength of the absorption maximum; b) full width at half maximum of the Cr<sup>3+</sup> peak:  $^4A_{2g} \rightarrow ^4T_1(F)$ .

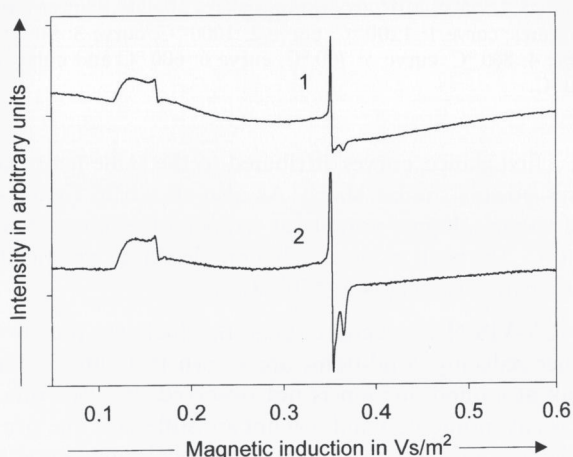


Figure 7. EPR spectra of glass C; curve 1: slowly cooled sample, curve 2: quenched sample.

The as-obtained glasses were investigated by electron paramagnetic resonance spectroscopy (EPR) at room temperature. Figure 7 shows spectra recorded from the slowly cooled glass (curve 1) and the quenched glass (curve 2). In both spectra, two signals are observed. The

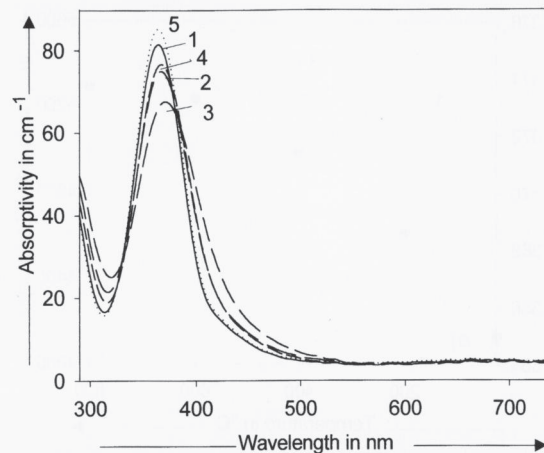


Figure 8. UV-VIS-NIR absorption spectra recorded during heating of glass C, curve 1: 25 °C, curve 2: 300 °C, curve 3: 590 °C and during subsequent cooling, curve 4: 300 °C, curve 5: 25 °C.

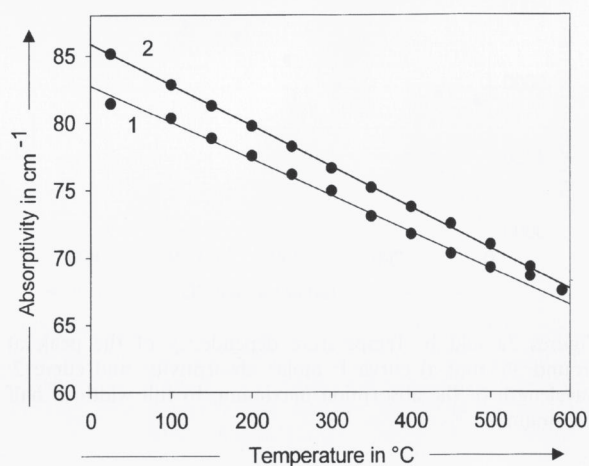


Figure 9. Absorptivity of the peak at around 365 nm during heating (curve 1) and during subsequent cooling (curve 2).

signal at around 0.15 Vs/m<sup>2</sup> is attributed to Cr<sup>3+</sup>, whereas the signal at 0.35 Vs/m<sup>2</sup> is caused by Cr<sup>5+</sup> [6]. The spectra were related to a standard (CuSO<sub>4</sub> · 5 H<sub>2</sub>O), which enabled a quantitative determination of the Cr<sup>5+</sup> concentration. The Cr<sup>5+</sup> concentrations were 20 and 35 ppm for the slowly cooled and the quenched glass, respectively.

Figure 8 shows UV-VIS-NIR spectra recorded from the quenched glass C, during heating (curves 1 to 3) and subsequent cooling (curves 4 to 5). Curves 1 and 5 were recorded at 25 °C, while curves 2 and 4 were both recorded at 300 °C. In both cases, the absorptivities at around 365 nm were smaller during heating. This behaviour is shown in figure 9 in more detail. Here, the absorptivities of the maximum at around 365 nm were plotted against the temperature. Curve 1 is attributed to the heating process while curve 2 describes the subsequent cooling process. During heating, the absorptivity decreases linearly up to a temperature of 500 °C. At larger temperatures, the absorptivities are somewhat higher than expected. During



subsequent cooling, a linear increase of the absorptivity with decreasing temperature is observed. In the range of 25 to 550 °C, all absorptivities measured were larger during cooling than during heating.

#### 4. Discussion

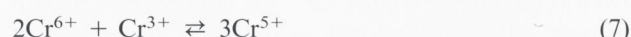
Spectra recorded at room temperature could be fitted assuming three absorption bands each of which has Gaussian shape (if the absorptivities were drawn against energy or wave number) within the limits of error of the measurement. Since in glass B, prepared under reducing conditions, the peak at around 365 nm does not appear in the spectrum, it can be concluded that this peak is caused by chromium in a higher valency state. As already frequently described in the literature, this peak is attributed to Cr<sup>6+</sup> which occurs in a tetrahedral coordination, i.e. CrO<sub>4</sub><sup>2-</sup>. While the Cr<sup>6+</sup> peak is still clearly visible at 800 °C, it is no longer detected at 1200 °C. In [13], Tilquin et al. reported on high-temperature spectra recorded from a Na<sub>2</sub>O · 1.2 SiO<sub>2</sub> · 1.2 B<sub>2</sub>O<sub>3</sub> melt at 1000 °C. They found that the peak attributed to Cr<sup>6+</sup> does not shift to larger wavelengths and the molar absorptivity remains constant at 1000 °C. This discrepancy can possibly be explained by the higher alkali concentration in this study which stabilize chromium in the hexavalent state. In our glass composition, it cannot be excluded that Cr<sup>6+</sup> occurs in a nontetrahedral coordination at high temperatures. According to the literature [19], the peak at around 450 nm is caused by the transition of Cr<sup>3+</sup> (<sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>1</sub>(F)). The absorptions at around 660 nm are split into three absorption bands. According to [20], the absorptions at 630, 650 and 680 nm are attributed to the <sup>4</sup>A<sub>2g</sub> → <sup>2</sup>T<sub>1</sub>, <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>2</sub>, and <sup>4</sup>A<sub>2g</sub> → <sup>2</sup>E transitions, respectively. From the latter, the <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>1</sub>(F) transition is spin-allowed [17]. The intensity of spin-allowed transitions should increase with temperature, as e.g. already observed in the case of Ni<sup>2+</sup> [21]. Concerning the <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>1</sub>(F) transitions, this is also observed in the case of Cr<sup>3+</sup> (see figure 5), since the absorption band at around 450 nm increases. From the shift of the absorption line at around 660 nm, the ligand field strength *D<sub>q</sub>* can be calculated for octahedrally coordinated Cr<sup>3+</sup>.

$$10 D_q = \tilde{\nu}({}^4A_{2g} \rightarrow {}^4T_2) \quad (6)$$

With increasing temperature, *D<sub>q</sub>* decreases from 1521 cm<sup>-1</sup> (for 25 °C) to 1490 cm<sup>-1</sup> for (600 °C). Since *D<sub>q</sub>* is proportional to *d*<sup>-5</sup> (*d* is the bond length Cr–O), a slight increase in *d* can be stated with increasing temperature. At all absorption bands, an increase in the full width at half maximum was observed with increasing temperature (see figures 3b and 6b). This should be caused by a broader distribution of the bond lengths at higher temperatures.

As shown in figure 7, the Cr<sup>5+</sup> concentration is an effect of the cooling rate. In the quenched sample, the Cr<sup>5+</sup>

concentration is larger than in the slowly cooled sample. This is in agreement with UV-VIS-NIR spectra of the respective samples. In the sample with the larger Cr<sup>5+</sup> concentration, the absorptivity of Cr<sup>6+</sup> is smaller. If this sample is thermally treated at temperatures of up to 590 °C and then cooled, the Cr<sup>6+</sup> concentration increases. In [22], the molar absorptivity (0.25 ppm<sup>-1</sup> cm<sup>-1</sup> or 5208 l mol<sup>-1</sup> cm<sup>-1</sup>) of Cr<sup>6+</sup> in a soda-lime-silica glass at room temperature was reported. The Cr<sup>6+</sup> concentrations calculated using this molar absorptivity are 352 and 337 ppm for the slowly cooled and the quenched sample, respectively. Hence, the Cr<sup>6+</sup> and Cr<sup>5+</sup> concentrations differ by 15 and 24 ppm, respectively. This can be explained assuming a redox reaction between Cr<sup>6+</sup> and Cr<sup>5+</sup>.



The redox reaction is shifted to the right side during heating. The species Cr<sup>5+</sup> should hence, preferably be formed at high temperatures. During cooling, a disproportionation of Cr<sup>5+</sup> to Cr<sup>6+</sup> and Cr<sup>3+</sup> is observed, which obviously is frozen in below a certain temperature. According to [9 and 10], the kinetics of redox reactions is controlled by diffusion of the respective species and hence should usually not be kinetically hindered at temperatures far above *T<sub>g</sub>*. However, at temperatures around *T<sub>g</sub>*, the cooling rate plays a certain part. When the cooling rate is larger, the freezing-in temperature should also be larger. During reheating of the quenched sample and subsequent slow cooling, the Cr<sup>6+</sup> concentration increases by 15 ppm, which according to equation (7) is attributed to a decrease of the Cr<sup>5+</sup> concentration by 23 ppm. This is in agreement with the difference of the Cr<sup>5+</sup> concentration of 24 ppm between the quenched and the slowly cooled sample. As shown in figure 9, the absorptivity of the quenched sample decreases with temperature. This is primarily due to the decrease in the molar absorptivity and not to a redox reaction. At temperatures ≥ 550 °C, there are slight deviations from linearity in figure 9. During cooling, absorptivities are larger than during heating at temperatures ≤ 550 °C. It should be noted that the ratios of absorptivities during heating and those during cooling remain approximately constant at temperatures ≤ 550 °C, while they change for larger temperatures. From this behaviour, it is concluded that the redox reaction according to equation (7) becomes frozen-in during quenching. During heating it is still frozen-in until a temperature > 500 °C is reached. Then, the reaction is no longer frozen-in and the Cr<sup>6+</sup> concentration approaches that of the slowly cooled glasses. Since *T<sub>g</sub>* of the glass studied is around 560 °C, also the freezing-in temperatures observed are in agreement with former theoretical treatments [10] as well as results from high-temperature EPR spectra obtained for the redox equilibria Fe<sup>2+</sup>/Fe<sup>3+</sup>/Mn<sup>2+</sup>/Mn<sup>3+</sup> and Fe<sup>2+</sup>/Fe<sup>3+</sup>/As<sup>3+</sup>/As<sup>5+</sup> [9].

Cr<sup>5+</sup> is a redox species observed in glasses using EPR spectroscopy. From UV-VIS-NIR spectroscopy, as pointed out above, there is an indirect evidence for the occurrence of Cr<sup>5+</sup>. Cr<sup>5+</sup> is a <sup>1</sup>*d* ion which in [23 and 24] is



described to occur in octahedral coordination. According to [23], absorptions are observed at around 350 and 440 nm in SiO<sub>2</sub> glasses prepared by a sol-gel route. In [24], careful deconvolution of absorption spectra recorded from soda-lime-silica glass led to the conclusion that minor quantities of Cr<sup>5+</sup> occur and give rise to an absorption at 462 nm. This band was attributed to the spin-allowed  ${}^2T_2 \rightarrow {}^2E$  transition which has a molar absorptivity of 140 l mol<sup>-1</sup> cm<sup>-1</sup>, i.e. in the same order as the absorption bands caused by Cr<sup>3+</sup>. Since both bands (350 and ≈ 450 nm) occur at wavelengths similar to peaks caused by Cr<sup>6+</sup> and Cr<sup>3+</sup>, respectively, it is not surprising that small quantities of Cr<sup>5+</sup> (24 ppm) are not detected in the UV-VIS-NIR spectra. It should be noted, however, that from voltammetric studies, Cr<sup>5+</sup> has not been reported up to now, although it should, as described above, be favoured at higher temperatures.

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