High temperature investigation of soda-lime-silicate glasses doped with manganese and chromium

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Introduction

The understanding of redox processes in glass forming melts has a significant importance in glass industry. Physical properties of glasses are not only affected by the type and concentrations of polyvalent elements present but also by their redox state. Absorption spectroscopy at room temperature is used, in general, to observe the different oxidation states of polyvalent elements in glasses. However, redox reactions are mainly running some hundred degrees above room temperature, starting in the region above Tg. For this reason, high temperature absorption spectroscopy was used to monitor these redox reactions and to detect a freezing-in temperature for the redox reactions.

Redox equilibria of polyvalent elements in glass melts are generally shifted to the oxidized species during cooling and hence the oxygen activity decreases. If only one polyvalent element occurs, the ratio $[A^{n+}]/[A^{(n-1)+}]$ remains constant during rapid cooling if the concentration of the reduced species is much larger than that of physically dissolved oxygen. In technical glass melts this is usually the case.

However, this situation changes if more than one polyvalent element is present. Here, redox reactions during cooling may play an important role: a melt containing solely the polyvalent element A and another melt containing two polyvalent elements A and B will usually not show the same redox ratios $[A^{n+}]/[A^{(n-z)+}]$ after cooling, although when equilibrated under the same conditions [1, 2, 3].

Experimental

Glasses with the base composition $16Na_2O \cdot 10CaO \cdot 74SiO_2$ doped solely with MnO or additionally with Cr_2O_3 or CrO_3 were prepared and investigated. UV-vis-NIR absorption spectra were recorded, first at room temperature, and then in the temperature range from 25 up to 800 °C using a specially constructed spectrometer:

the sample was placed inside the heating chamber of a microscope heating stage (TS 1500, LINCAM). For a detailed description of the apparatus see refs. [4, 5] The samples had a diameter of 6 mm and a thickness of 0.2 to 2 mm.

Results and discussion

Room temperature spectra of glass samples solely doped with MnO or with CrO_3 are given in Fig. 1, and samples doped with both MnO + CrO_3 in Fig. 2. Spectra of glasses solely doped with MnO or CrO_3 show the positions of the individual peaks of the different oxidation states and correlate with data from former works [6, 7, 8]. The absorption spectra of Mn^{3+},Cr^{3+} and Cr^{6+} in the range from 10,000 to 30,000 cm^{-1} were deconvoluted into a minimum number of Gaussian bands. Each band is described by three parameters: intensity, peak position and a full width at half maximum (FWHM). Peak position and FWHM do not remarkably change their values (if glass composition stays constant and the amount of the polyvalent element is < 1 mol %). The intensities of the individual bands depend on concentration of the respective oxidation stage.

During heating, the Cr^{6+} charge-transfer band at 365 nm decreases, and is completely vanished above 1.000 °C. The Cr^{3+} absorption bands at 450 and at 660 nm are shifted to larger wavelengths and become broader, intensity of the first one increases (due to a partial loosening of the LAPORTE role) whereas the intensity of the second one decreases.

Glasses doped with MnO show two absorption bands (probably due to JAHN-TELLER splitting) of Mn^{3+} ions at 500 and at 660 nm. With increasing temperature, bands are shifted towards higher wavelengths and become broader. It should be mentioned that above 700 °C, the JAHN-TELLER splitting is no longer visible and the two bands become a single band.

High-temperature absorption spectra recorded from glass doped with both $Mn^{2+/3+}$ and $Cr^{3+/6+}$ are shown in Fig. 3. Using band parameters of the glasses solely doped with $Mn^{2+/3+}$ or $Cr^{3+/6+}$, it is possible to deconvolute these high temperature spectra into Gaussian bands of the individual oxidation states of the polyvalent elements.

According to the redox reaction

$$3Mn^{2+} + Cr^{6+} \rightleftharpoons 3Mn^{3+} + Cr^{3+}$$

the intensity of the Mn^{3+} absorption band remains nearly constant up to 600 °C and is decreased at higher temperatures, but the band becomes broader. By contrast, the intensity of the Cr^{6+} absorption band decreases with increasing temperature up to 600 °C. It is assumed that with increasing temperature the Cr^{6+} peak is affected by the UV absorption edge. This effect is taken in account; however, still there is a decreasing curve. The intensity of the Cr^{6+} peak is increased at higher temperatures. At temperatures below 600 °C, the redox reaction is frozen in due to kinetical hindrance.

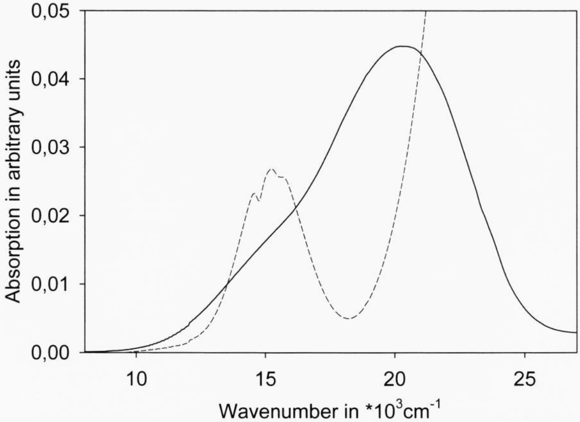

Fig. 1: Absorption spectra of glasses doped with 0.68 mole % MnO (solid) or 0.22 mole% CrO_3 (dashed) at room temperature.

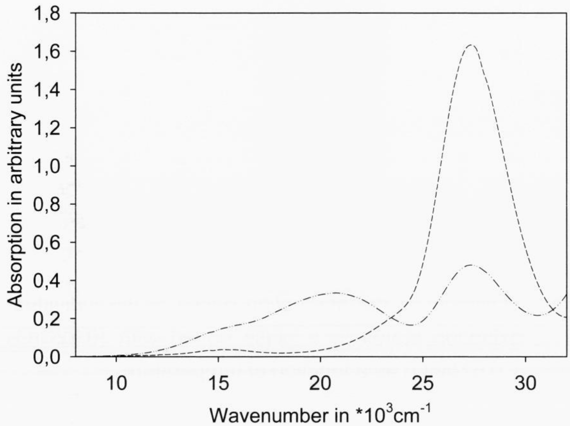

Fig. 2: Absorption spectra of glasses solely doped with 0.22 mole% CrO_3 (--) and with (0.22CrO_3 + 0.67MnO) (–··–) at room temperature.

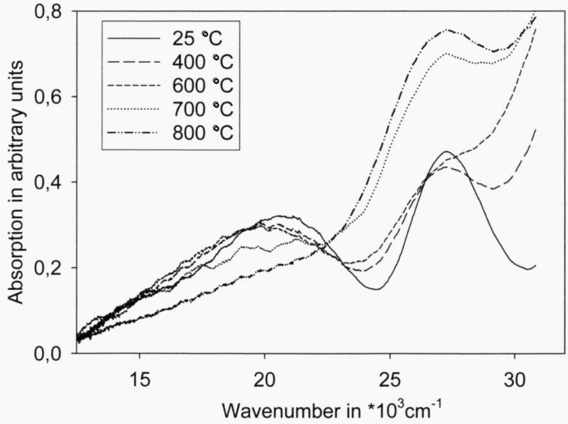

Fig. 3: Absorption spectra of a glass doped with (0.22 CrO_3 + 0.67 MnO) at different temperatures.

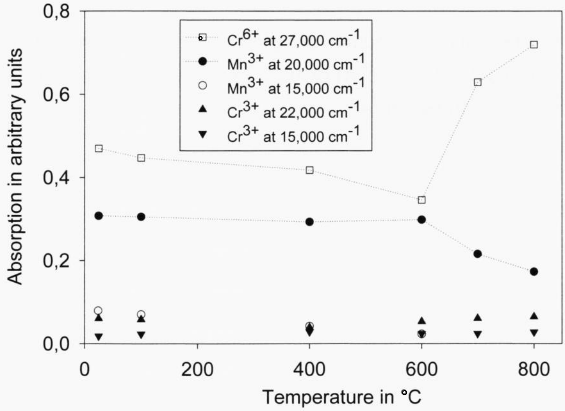

Fig. 4: Maximum of the absorption bands of the individual oxidation states in a glass doped with (0.22CrO_3 + 0.67MnO) as a function of temperature.

References

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