

Influence of Fluorine on Structure and Physical Properties of K₂O-CaO-SiO₂ Glasses

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1. Introduction

Fluorides in oxide glasses have been used for a long time as an opacifying [1, 2, 3] or as a crystallization agent [4, 5]. From investigations on different technical glasses it is known that fluorides strongly decrease the viscosity [6], the transformation temperature [7], the density and the refractive index [8]. Since most of these data were produced for industrial glasses, only relatively narrow fluoride concentration ranges have been investigated so far.

The structure of the F⁻-containing silicate glasses is discussed controversially. Some authors [9, 10] assume the formation of SiO_{4-x}F_x-tetrahedrons by replacing bridging O²⁻-ions by 2F⁻-ions. Other authors [11, 12] predict the bonding of the fluoride ions to network modifiers.

The aim of this work was to study the solubility of F⁻ in a model like K₂O-CaO-SiO₂ glass and to relate influences of F⁻ on physical glass properties and the microstructure of the glass to structural changes in consequence of the F⁻ incorporation.

2. Experimental

The basic composition of the investigated glasses was 74 mole% SiO₂, 16 mole% K₂O, 10 mole% CaO. Fluorine was introduced by replacing CaCO₃ and K₂CO₃ by CaF₂ and KF in the batch respectively. The glasses were melted in an inductively heated Pt-Rh(10) crucible at about 1500 °C. The melt was poured into a graphite mold after homogenization by stirring and waiting for the removal of the bubbles for two hours. The glass was annealed

at about 50 K above T_g for 30 minutes and the cooled to room temperature with 2 K/min.

The viscosity of the glasses was measured with a beam bending viscosimeter (heating rate 5 K/min) and a rotation viscosimeter (cooling rate 5 K/min). The transformation temperature and the coefficient of thermal expansion were determined by dilatometry with a heating rate of 5 K/min. The refractive index (n_D) was measured by a Pulfrich refractometer at a wavelength of 546,1 nm. The density of the glasses was determined by Archimedes method. The microstructure of the polished and HF-etched glass surfaces was investigated by a high resolution scanning electron microscope with a field emission gun (FEG-HRSEM) in combination with EDX.

3. Results

The glasses lost about 10 % of fluorine during the melting as shown in Figure 1.

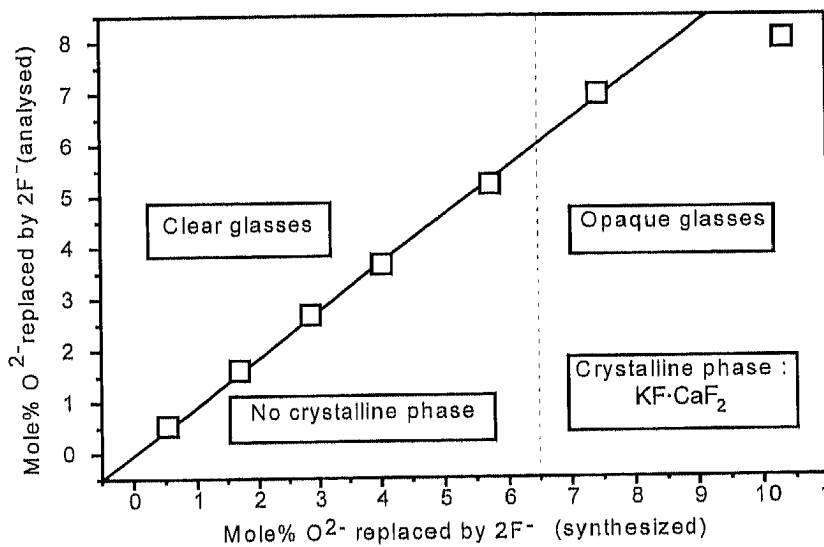


Figure 1: Fluorine concentration of the glasses as synthesized versus fluorine concentration, analyzed by potentiometry

Clear glasses were obtained for F⁻ concentrations up to 6 mole% O²⁻ replaced by 2 F⁻. At higher concentrations they became opaque, and a phase separation could be observed by FEG-HRSEM as shown in Figure 2.

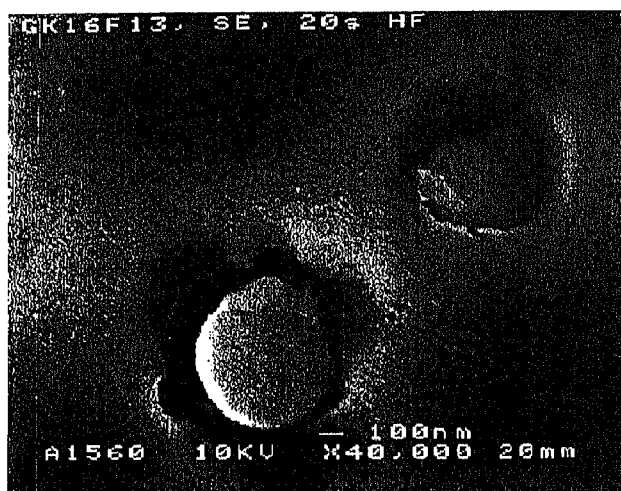


Figure 2: FEG-HRSEM-photo of the glass with 6,98 mole% 2F; etching: 20 s in 5 % HF-solution; acceleration voltage: 10 kV

EDX analysis pointed out, that the concentration of Si and O was about 40 % lower in the center of the spherical particles of about 500 nm in diameter than in the matrix. Since CaKF₃-crystallites of about 46 nm in size could be detected in these glasses by XRD, it is concluded that polycrystalline KF₂CaF₂ particles have grown under the given melting and cooling conditions. It is assumed that Ca-, K- and F-ions diffused towards the crystals from their interfacial region during the crystal growth, since this region has been removed completely by the etching process (Figure 2). Since all the glasses with lower F-content were homogeneous and amorphous it is concluded that a F-concentration of about 6 mole% 2F is the limit for the nucleation of KF₂CaF₂ under the chosen conditions.

After homogeneous glasses with remarkable F contents had been obtained, it was interesting to investigate the influence of F on the viscosity, as shown in Figure 3.

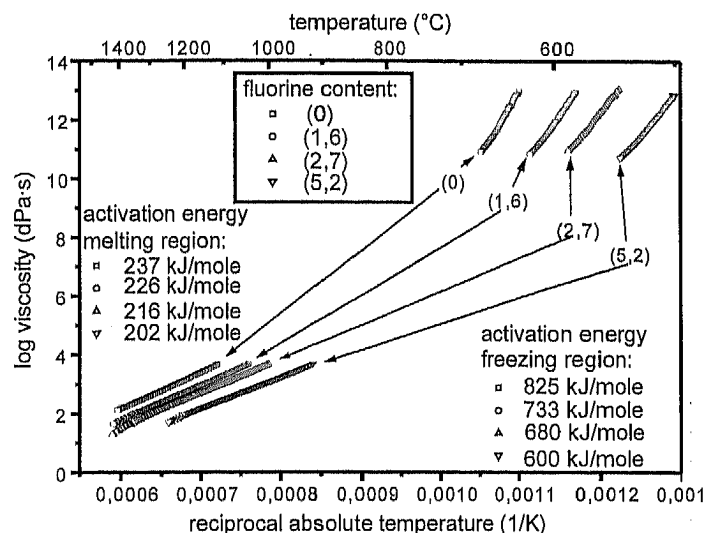


Figure 3: Viscosity versus reciprocal absolute temperature plot of $16\text{K}_2\text{O}\cdot 10\text{CaO}\cdot 74\text{SiO}_2$ glasses with different F concentrations. (mole% O^{2-} -ions replaced by 2 F⁻ions).

It shows that the viscosity decreases continuously with increasing F, and according to [13], that the dependence of the viscosity on the temperature can be described by an Arrhenius function in the melting and the freezing region with rather good approximation, since linear functions with correlation coefficients > 0.99 are obtained from Figure 3. As one can see the activation energy for the viscous flow decreases with increasing F content, but the decrease is much stronger in the freezing region than in the melting region. This may lead to the conclusion that the average size of the structural units involved in the viscous flow is decreasing in both regions and that the glass structure in the freezing region gets weaker with increasing F content. The weakening of the network should also affect the physical properties of the glass at room temperature. It was found, that the transformation temperature decreased from $615\text{ }^\circ\text{C}$ to $474\text{ }^\circ\text{C}$ and the density was reduced from 2.47 g/cm^3 to 2.44 g/cm^3 with a F content increasing from 0 to 5.2 mole%. Simultaneously the refractive index n_o is decreasing from 1.5161 to 1.4890 and calculations of the molar refraction with the Lorentz-Lorenz equation clearly show that this strong effect cannot only attributed to the decreasing

density but has to be related to the substitution of O^{2-} ions by F^- ions, having a much lower electronic polarizability.

From the investigation of the viscosity, the density and the T_g of the glasses it has to be concluded that bridging oxygen ions are replaced by Si-F-bonds.

Investigations with ^{29}Si -MAS-NMR show in the spectra an increasing Q^4 signal and a decreasing Q^3 signal with increasing F-content. An increased amount of crosslinked Q^4 Si atoms cannot be understood with respect to the remarkable decrease of viscosity and thus it has to be assumed that the increased Q^4 signal may be due to Q^3 units from $\text{Si}(\text{O}_{0.5})_3\text{F}$ tetrahedrons that is shifted to higher magnetic field strengths compared to the Q^3 units of $\text{Si}(\text{O}_{0.5})_3\text{O}^-$ with alkaline or earth-alkaline atoms, but this has to be confirmed by further investigations.

4. Conclusion

In the model system $74\text{SiO}_2 \cdot 16\text{K}_2\text{O} \cdot 10\text{CaO}$ homogeneous glasses can be obtained from pure batch substances and under melting and cooling conditions that are comparable to those of technical glasses, where up to 8 mole% of O^{2-} ions are replaced by $2F^-$ ions.

They are replacing bridging oxygens partially, since the F incorporation leads to a weakening of the glass network. But it has to be assumed that a part of the F ions are linked to Ca^{2+} and K^+ , since for F concentrations ≥ 6 mole% CaF_2 crystallites can nucleate and grow during cooling.

It has been shown that FEG-SEM in combination with EDX can be very useful tools for determination of structure property relationships.

5. Acknowledgment

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6. References

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