Nano crystallization of BaF_2 in a silicate glass system and the effect of viscosity and diffusion

SIXTH FRAMEWORK PROGRAMME

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The project

The study of nano crystallization of BaF_2 from silicate glasses is carried out within the scope of the EC-project **INTERCONY** (Interface Controlled Nucleation and Crystallization for Nanoparticle Synthesis). Transparent glass-ceramics in the system $Na_2O/K_2O/Al_2O_3/SiO_2/BaF_2$ are prepared and nano crystalline BaF_2 precipitated. If these materials are doped with rare earth ions, they will have a great potential for applications as upconversion materials in optical amplifiers or fiber lasers. Fundamental studies of the mechanism that leads to the formation of nano crystals will extend the knowledge on interfaces in multifunctional materials formed during nucleation and crystal growth. In order to simulate the crystallization process, experimental data for the viscosity of the residual glassy phase and diffusion of the crystal forming components are of great importance.

Preparation and analysis of the nano glass-ceramics

- Melting and casting the glass
- Crystallization of BaF_2 during heat treatment of the samples
- Studied glass compositions in mole %:

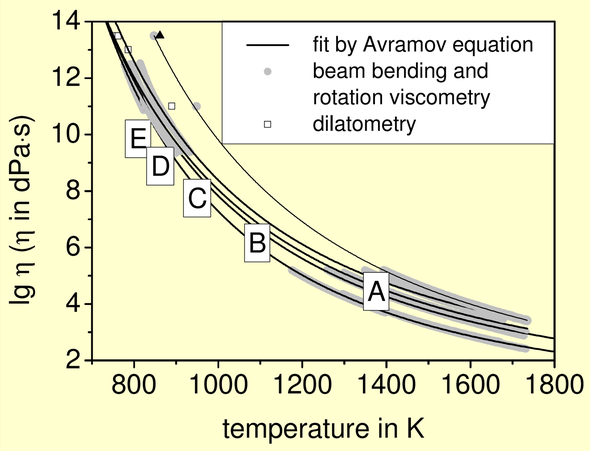
Sample	Al_2O_3	K_2O	Na_2O	SiO_2	BaF_2
A	8	16	2	74	**0**
B	7.92	15.84	1.98	73.26	**1**
C	7.84	15.68	1.96	72.52	**2**
D	7.76	15.52	1.94	71.78	**3**
E	7.52	15.04	1.88	69.56	**6**

Used equipment for viscosity and diffusion experiments:

- Rotation viscometer Bähr VIS 403
- Beam bending viscometer Bähr VIS 401
- Scanning electron microscope SEM Jeol 7001F FEM with EDX

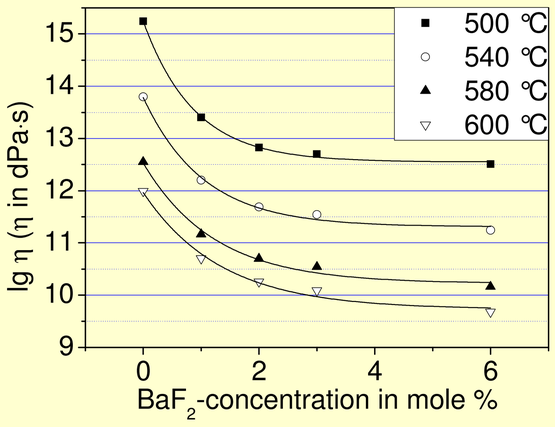
SEM Jeol 7001F

Viscosity



Experimentally obtained data of viscosity (grey circles) from glasses with different BaF_2-concentrations are fit by the **Avramov-equation:** (solid black line)

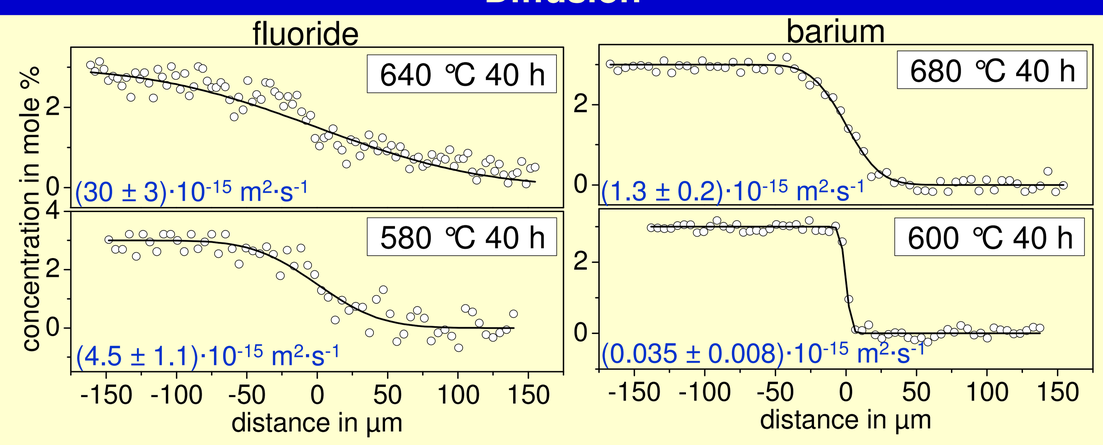
$$\eta = \eta_0 \cdot e^{2.3(13.5-\lg\eta_0)\left(\frac{T_g}{T}\right)^{\alpha}}$$

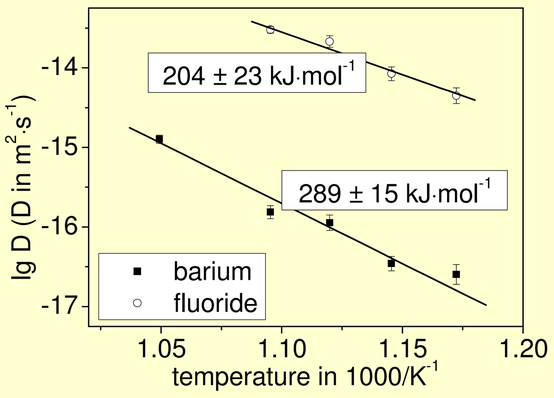


$$E_{\eta,A}(T) = 2.3(13.5-\lg\eta_0)\left(\frac{T_g}{T}\right)^{\alpha} RT$$

Therefore, the viscosity can be described as a function of BaF_2-concentration which represents the change of the viscosity of the residual glassy phase during the course of the crystallization.

Diffusion





Diffusion experiments are carried out by joining samples without BaF_2 and samples with 3 mole % BaF_2. Subsequently they are annealed in the range from 580 to 680 °C for 40 h. The concentration profiles of barium and fluoride are obtained by SEM-EDX technique.

The activation **enthalpy** is calculated from the Arrhenius-plot of diffusion coefficients as a function of temperature.

Activation energy

Sample	Activation enthalpy ΔH_D of **diffusion** in kJ·mol^{-1}		Activation energy ΔE_D of **diffusion** at T_g in kJ·mol^{-1}		Activation energy of **viscosity** at T_g in kJ·mol^{-1}	
	barium	fluoride	barium	fluoride	Avramov-equation	slope
A	289 ± 15	204 ± 23	170 ± 15	127 ± 23	217 ± 22	421 ± 42
D			**181 ± 15**	134 ± 23	**184 ± 18**	368 ± 37

The activation energy of diffusion is calculated from the enthalpy ΔH_D and entropy ΔS_D using the equation:

$$\Delta E_D = \Delta H_D - T\Delta S_D$$

and compared with the activation energy of viscosity obtained from the slope of the lgη(1/T)-curve as well as from the Avramov-equation.

Conclusions

- Diffusion coefficients of fluoride are approximately two orders of magnitude larger than those of barium.
- Activation energy of diffusion of barium is
  - around 85 kJ·mol^{-1} larger than that of fluoride and
  - in good agreement with the activation energy of viscosity at T_g (within the limits of error).
- An empirical equation for the viscosity as a function of BaF_2-concentration and temperature was obtained.