



# The effect of viscosity on nanocrystallization of strontium fluoride from a silicate glass



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## ABSTRACT

This paper describes the importance of the viscosity development in the glass-ceramics process with respect to the mechanism of nano crystallization in oxyfluoride glasses. In the glass system under investigation nano crystalline  $\text{SrF}_2$  is formed from a silicate glass  $\text{Na}_2\text{O}/\text{K}_2\text{O}/\text{SrF}_2/\text{Al}_2\text{O}_3/\text{SiO}_2$ . The occurring crystallization mechanism is clarified by the variation of the  $\text{SrF}_2$  concentration and the resulting structures. As expected, the mechanism shows similarities to other recently described oxyfluoride systems. The feature of the present system is that during cooling of the melt a liquid/liquid phase separation occurs which is not the case in similar systems containing  $\text{BaF}_2$ . A droplet phase enriched in strontium and fluoride is formed which is embedded in a silicate rich matrix phase. During thermal annealing, nano crystalline cubic  $\text{SrF}_2$  is precipitated inside the droplet phase. As a result, the viscosity of the residual glassy phase increases during the course of the crystallization. The crystal sizes do not exceed 8 nm, neither if the annealing time nor if the temperature is increased.

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## 1. Introduction

In the past few years, numerous studies were carried out on the precipitation of crystalline metal fluorides such as alkaline earth fluorides [1] and rare earth fluorides  $\text{LaF}_3$  [2] as well as ternary fluorides such as  $(\text{Pb}, \text{Yb})\text{F}_{2+x}$  [3] or  $\text{NaREF}_4$  (e.g. with  $\text{RE} = \text{Gd}$  or  $\text{La}$  [4,5]). In many systems, the crystallite sizes were in the range from 5 to 100 nm and hence notable smaller than the wavelength of visible light. Furthermore, the crystallite size distribution is fairly small. Hence, the partially crystalline materials are considered for numerous photonic applications [2,6–8]. The crystal lattices of the fluorides mentioned above are suitable host materials for rare earth elements. These glass-ceramics are candidates as laser materials combining advantageous properties of glasses (ability to fibre drawing) and of crystals (long fluorescence life time) and might e.g. be suitable as fibre amplifiers. Besides, the glass-ceramics have great potential as up-conversion materials if doped with  $\text{YbF}_3$  and  $\text{ErF}_3$  [9–11] and the ability of transforming the blue light of light emitting diodes (LED) into white light are to be mentioned [12].

Up to now, partially crystalline materials are not widely used in photonic technology. The reason is the general problem of materials composed by more than one phase. In these materials usually

light scattering occurs which can only be avoided, if either the refractive indices of the occurring phases are the same at all relevant wavelengths and temperatures or the sizes of the crystals are smaller than half of the wavelength of the used light. Since the different phases usually possess different refractive indices and furthermore the crystals usually do not have a unique size, the crystallite size distribution must be narrow in order to avoid light scattering. To achieve good fluorescence or up-conversion properties, the volume concentration should be at least some percentage.

The precipitation of comparatively large quantities of nano particles (at least some percentage) from glasses has only been reported from non-isochemical systems, i.e. such systems, the crystals precipitated possess another composition than the glass.

In principle, two different mechanisms may lead to nano crystalline glass-ceramics. In one of these two mechanisms, the first step is the formation of a liquid/liquid phase separated microstructure. The size of the phase separated droplets can be adjusted by the temperature/time schedule, e.g. the cooling rate from melt temperatures and, of course, by the chemical composition. In the past few years, another mechanism has been reported, which does not go via liquid/liquid phase separation, but via homogeneous nucleation. After initial nucleation, a diffusion layer is formed which is depleted in the components, the crystal is formed from. If a metal fluoride crystal is precipitated from a silicate glass, the layer is depleted in fluorine and enriched in the glass forming components, i.e. in  $\text{SiO}_2$ . This leads to an increase in viscosity [13,14], and

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hence, the layer acts as diffusion barrier. The existence of such a diffusion barrier has been proved using advanced transmission electron microscopic techniques [15] as well as recently by anomalous small angle X-ray scattering (ASAXS) [16].

This paper presents a fundamental study on the crystallization of SrF<sub>2</sub> from a glass in the system Na<sub>2</sub>O/K<sub>2</sub>O/SrF<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> and the comparison to a barium containing glass with the same molar composition in order to clarify the crystallization mechanism for nano crystallization in this kind of glass systems.

## 2. Experimental

Glasses with the nominal mol% compositions (100 - x) (8Al<sub>2</sub>O<sub>3</sub>·16K<sub>2</sub>O·2Na<sub>2</sub>O·74SiO<sub>2</sub>)·xSrF<sub>2</sub> (with x = 0, 1, 2, 3, 4, 5 and 6) were melted from reagent grade raw materials Al(OH)<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, SiO<sub>2</sub> (quartz) and SrF<sub>2</sub> in batches of 200 g in a platinum crucible at 1500 °C using an inductive furnace. The total amount of alkaline serves to decrease the melting point. The substitution of K<sub>2</sub>O for Na<sub>2</sub>O prevents the crystallization of NaF (KF crystals are not formed). The melt was stirred and held for 1.5 h. Then, the melts were cast on a brass block and transferred to a muffle furnace preheated to 480 °C. Subsequently, the furnace was switched off in order to cool the samples slowly (1–3 K min<sup>-1</sup>) to room temperature.

The fluorine concentration was analysed using wet chemical methods as well as by energy dispersive X-ray spectroscopy (EDS, EDAX Trident system) using a scanning electron microscope (SEM, JEOL JSM-7001F).

Thermal annealing of the sample was carried out using a muffle furnace and temperatures in the range from 520 to 600 °C for 20 or 100 h. In order to determine the glass transition temperature  $T_g$  and the crystallization temperature(s), the glasses were powdered and studied by differential scanning calorimetry (DSC, 822 Mettler Toledo) and differential thermal analysis (DTA, Shimadzu DTA 50) using a heating rate of 10 K min<sup>-1</sup>. X-ray diffraction (XRD) patterns were recorded from thermally annealed and subsequently powdered samples using a diffractometer Siemens D 5000 with CuK $\alpha$  radiation and Bragg–Brentano geometry. The density of the bulk samples was measured using a He-pycnometer (AccuPyc 1330). The viscosity was determined as a function of the temperature using beam bending viscometry (Bähr VIS 401) and rotation-viscometry (Bähr VIS 403).

The glass with the composition (in mol%) 7.6 Al<sub>2</sub>O<sub>3</sub>·15.2 K<sub>2</sub>O·1.9 Na<sub>2</sub>O·70.3 SiO<sub>2</sub>·5.0 SrF<sub>2</sub> was studied by transmission electron microscopy (TEM) (Hitachi H 8100) using a replica technique. For this purpose, the surface was etched by acid and the resulting surface shaped by a carbon/iridium layer. This layer is afterwards separated from the surface and studied in the TEM. A detailed description of this technique is reported in Ref. [17]. Some crystallized samples were additionally studied using scanning electron microscopy.

## 3. Results

The glass containing 6 mol% SrF<sub>2</sub> was opaque; XRD-patterns recorded from the powdered sample showed distinct lines attributable to cubic SrF<sub>2</sub>. Hence, the glass crystallized spontaneously during cooling of the melt. This could not be suppressed by casting the melt to a brass block and pressing it using a copper stamp. Glasses with SrF<sub>2</sub> concentrations of 5 mol% and less were visually transparent. Their XRD-patterns did not show any distinct lines and hence the samples were amorphous within the detection limit of XRD. The fluoride concentration in the glass was determined by wet chemically methods (method of Pietzka and Ehrlich [18,19]) and by EDS. After melting the glass, the fluoride concentration was in the average 26% smaller than that calculated from the batch

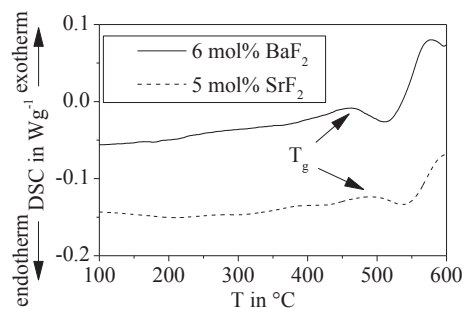


Fig. 1. The DSC-profiles of the samples containing BaF<sub>2</sub> and SrF<sub>2</sub>.

composition. Usually a fluoride loss occurs during melting oxy-fluoride glasses which can be attributed to the reaction with water (HF) or the formation of other volatile compounds (SiF<sub>4</sub> or AlF<sub>3</sub>).

In the DSC-profiles, the glass transition temperature,  $T_g$ , is clearly visible. In Fig. 1 an exothermic peak attributable to the crystallization of the sample is observed for the sample with 5 mol% SrF<sub>2</sub> around 600 °C which is close to the detection limit of the DSC. By comparison the sample with 6 mol% BaF<sub>2</sub> shows a similar crystallization peak around 580 °C.

As shown in Fig. 2, the glass transition temperature decreases with increasing SrF<sub>2</sub> concentration of the glass. The glass without SrF<sub>2</sub> has a glass transition temperature of 574 °C, which shows an approximately exponential decrease with increasing SrF<sub>2</sub> concentration until for 5 mol% a temperature of 508 °C is reached.

Fig. 3 shows a TEM-replica micrograph of a sample with 5 mol% SrF<sub>2</sub>. Small phase separation droplets with sizes in the range from 10 to 20 nm and isolated droplets with sizes of around 30 nm were observed (see Fig. 3).

The following heat treatments were carried out on the sample containing 5 mol% SrF<sub>2</sub>. In Fig. 4a, XRD-patterns are shown for the as melted sample and samples annealed at different temperatures in the range from 510 to 600 °C for 20 h. While the as melted sample is amorphous and does not show any distinct line, the samples annealed at temperatures of  $\geq 520$  °C show notably broadened lines all attributable to crystalline SrF<sub>2</sub> (JCPDS Nr. 6-0262). The sample annealed at 510 °C shows in principle the same lines, however, the broadening is even more pronounced. From the broadening of the XRD lines, the mean size of the crystallites was calculated using the Scherrer equation [20]. Therefore the peak at 44° was fitted by a Gaussian curve and the fitting error is included in the error bars in Fig. 4b. Here, the mean crystallite size is shown as a function of the annealing temperature for an annealing time of

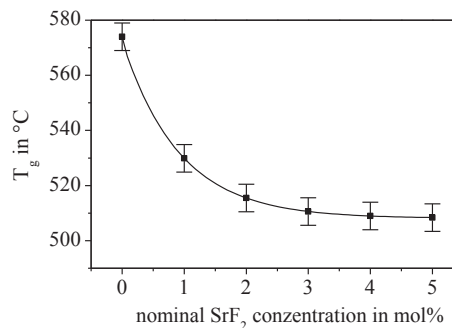


Fig. 2. The glass transition temperature of the prepared glasses as a function of the nominal (as weighed) SrF<sub>2</sub> concentration. The solid line represents the first order exponential fit.

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