



# The nano-crystallization and luminescence in the visible spectral range of thulium doped Na<sub>2</sub>O/K<sub>2</sub>O/CaO/Al<sub>2</sub>O<sub>3</sub>/CaF<sub>2</sub>/SiO<sub>2</sub> glasses



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## ABSTRACT

An oxyfluoride glass with the molar composition 59.3 SiO<sub>2</sub>·12.3 CaO·9.0 Na<sub>2</sub>O·5.3 K<sub>2</sub>O·3.7 Al<sub>2</sub>O<sub>3</sub>·10.4 CaF<sub>2</sub> was doped with Tm<sup>3+</sup> concentrations of  $2.5 \times 10^{18}$  and  $1 \times 10^{19}$  cm<sup>-3</sup>, which corresponds to about 0.005 and 0.02 mol% Tm<sub>2</sub>O<sub>3</sub> in the batch. The glasses were thermally treated in the temperature range from 530 to 600 °C, which resulted in the crystallization of CaF<sub>2</sub>. The XRD patterns showed extremely broadened lines attributed to mean crystallite sizes in the range of 6–11 nm. Scanning electron microscopy shows phase separation in the glass samples and crystallization within these phase separated droplets. Static luminescence spectra and luminescence decay curves were recorded for samples with different Tm<sub>2</sub>O<sub>3</sub> concentrations and after thermal treatment at different temperatures indicating that the Tm<sup>3+</sup> ions are located in a fluoride enriched environment.

## 1. Introduction

Glass ceramics containing nano-crystalline precipitations have extensively been studied in the past few decades due to their remarkable optical properties, which seem to be advantageous for numerous applications [1–4]. In the past few years many of those glass ceramic systems have been reported which contain crystals doped with rare earth ions, such as erbium, europium, neodymium, samarium, terbium, ytterbium, and thulium. In most cases these rare earth ions are embedded in alkaline earth, yttrium, lanthanum or gadolinium fluoride nanocrystals. This enables to combine several advantageous properties of glass; such as shaping by viscous flow and hence the suitability to draw fibers, and those of crystals, such as improved luminescence properties [1]. If the preparation of such materials is carefully optimized, new materials for various applications are possible, most notably fiber amplifiers [5].

The main problem that faces scientists in developing multi-phase optical materials is light scattering. It can be described as the scattering of light due to different refractive indices if the dimensions of these phase changes are not very small in comparison to the wavelengths used. In order to bypass such limitations in design, the refractive indices of the phases have to be the same at all operational wavelengths and temperatures, or the crystallite size must be much smaller than the wavelengths used. In previous reports [6–8], a generic method for the preparation of transparent glass-ceramics was presented. Here, nanometer scaled crystals with a narrow size distribution that are

homogeneously distributed within the glass matrix could be precipitated, which strongly reduces light scattering. This can be achieved by crystallizing fluoride crystals from highly viscous melts. Since components such as fluorides as well as network modifier ions are removed from the glass, the melt viscosity increases strongly during the course of the crystallization [8]. In a first step, a highly silica enriched layer is formed at the crystal surface, which in turn slows down further diffusion of fluorides to the crystal phase. Further growth of the crystallites increases this layer and finally results in the formation of a silica rich shell around the particles which acts as diffusion barrier that completely hinders any further crystal growth. The result is a strong decrease in the crystal growth velocity with time and hence mainly small crystals with a narrow size distribution are formed. The formation of such layers has been proved using anomalous X-ray scattering (ASAXS) and advanced transmission electron microscopic techniques [9,10].

The efficiency of the emission process of most rare earth ions depends strongly on the host material. Here, the phonon energy of the host plays a key role. In general fluoride glasses possess a much lower phonon energy (600 cm<sup>-1</sup>) than silica based glasses (1200 cm<sup>-1</sup>). Incorporating rare earth ions such as Yb<sup>3+</sup>, Er<sup>3+</sup>, and Tm<sup>3+</sup> into fluoride crystals reduces multi-phonon relaxation and enhances luminescence efficiency and lifetimes [11–14]. However, fluoride melts mostly have a poor glass forming ability, a high crystallization tendency, poor chemical durability and low mechanical stability. Therefore the precipitation of fluoride crystals from a silicate glass is a

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promising approach to produce new optical materials. However, it is difficult to prove that the rare earth ions are incorporated into the precipitated fluoride crystals. Incorporation of rare earth ions into lanthanide based crystal phases as e.g. LaF<sub>3</sub>, YF<sub>3</sub> or NaLaF<sub>4</sub> is self-evident and generally accepted, since it mostly results in strong changes in the absorption and emission spectra of these materials (see e.g. Refs. [11,15] for Tm<sup>3+</sup> doped materials). Incorporation into other fluoride nanocrystals is difficult to prove. In 2001 Hayashi et al. published an interesting study on Tm<sup>3+</sup> doped oxy-fluoride glass ceramics containing PbF<sub>2</sub> crystals. With precipitation of the PbF<sub>2</sub> crystals, the emission spectra of Tm<sup>3+</sup> showed a weak but notable substructure in comparison to the not annealed glass [16]. Furthermore, the luminescence lifetime increased notably with precipitation of the crystallites. A similar finding is reported by Mattarelli et al. [17] and Klimesz et al. [18]. In these cases changes in the Tm<sup>3+</sup> absorption spectra and increasing lifetimes were found for PbF<sub>2</sub> containing glass ceramics. In Ref. [19] a strong increase in the luminescence lifetime of Tm<sup>3+</sup> doped CaF<sub>2</sub> glass ceramics is reported. However, here no change in the shape of the excitation and emission spectra was observed and no SEM investigations were conducted. Therefore an incorporation of the Tm<sup>3+</sup> ions into the CaF<sub>2</sub> crystallites is not proved in this case. The increase in the luminescence lifetime might also be the result of phase separation of a rare earth containing fluoride enriched phase, which is likely to occur in the glass composition that was used here. In 2015, our group performed a detailed study concerning terbium doped oxyfluoride glass-ceramics containing CaF<sub>2</sub> nanocrystals, but incorporation of Tb<sup>3+</sup> into the CaF<sub>2</sub> crystals could also not be proved [20]. Therefore, while incorporation of Tm<sup>3+</sup> ions into lanthanide or lead containing fluoride crystals has been proved, it is still not clear if rare earth ions really enter the CaF<sub>2</sub> phase of transparent glass ceramics.

This work presents a study on the preparation and optical properties of oxyfluoride glasses doped with 0.005 and 0.02 mol% Tm<sub>2</sub>O<sub>3</sub> from which CaF<sub>2</sub> crystals can be precipitated. The crystallization behavior is investigated, the resulting microstructures characterized and the luminescence properties studied.

## 2. Experimental

Glasses with the mol% composition 59.3 SiO<sub>2</sub>:12.3 CaO:9.0 Na<sub>2</sub>O:5.3 K<sub>2</sub>O:3.7Al<sub>2</sub>O<sub>3</sub>:10.4 CaF<sub>2</sub> were melted from reagent grade raw materials Al(OH)<sub>3</sub> (Sumitomo Ltd.), CaCO<sub>3</sub> (Merck), K<sub>2</sub>CO<sub>3</sub> (Carl Roth) Na<sub>2</sub>CO<sub>3</sub> (Merck), SiO<sub>2</sub> (Carl Roth), and CaF<sub>2</sub> (VEB Chemiewerk Nünchritz) in batches of 200 g in a platinum crucible at 1400 °C for 90 min in an induction furnace. The glasses were doped with 2.5 × 10<sup>18</sup> and 1 × 10<sup>19</sup> Tm<sup>3+</sup> ions per cm<sup>3</sup>, which corresponds to about 0.005 and 0.02 mol% Tm<sub>2</sub>O<sub>3</sub> in the batch, respectively (see Table 1). Additionally, a CaF<sub>2</sub> sample doped with 1 × 10<sup>19</sup> Tm<sup>3+</sup>/cm<sup>3</sup> was prepared. For this few grams of CaF<sub>2</sub> powder (grain size < 40 μm) were doped with Tm<sub>2</sub>O<sub>3</sub>, pressed to a tablet and afterwards sintered at 1100 °C for 5 h.

The melts were cast on a copper block and placed in a furnace preheated to 520 °C. Then the furnace was switched off and the samples were allowed to cool to room temperature (cooling rate approximately 2 K/min).

The glass samples were thermally treated at temperatures in the range from 520 to 600 °C for 20–60 h. In order to determine T<sub>g</sub> and the

**Table 1**  
Chemical composition (mol%) of the prepared glasses.

Sample	SiO <sub>2</sub>	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	CaF <sub>2</sub>	Tm <sub>2</sub> O <sub>3</sub>
A	59.3	12.3	9.0	5.3	3.7	10.4	–
B	59.3	12.3	9.0	5.3	3.7	10.4	0.02 (1 × 10 <sup>19</sup> Tm <sup>3+</sup> /cm <sup>-3</sup> )
C	59.3	12.3	9.0	5.3	3.7	10.4	0.005 (2.5 × 10 <sup>18</sup> Tm <sup>3+</sup> /cm <sup>-3</sup> )

crystallization temperature(s), the samples were powdered and sieved to a grain-size of 250–315 μm and then studied by differential scanning calorimetry (Linseis DSC PT 1600) with a heating rate of 10 K min<sup>-1</sup>. X-ray powder diffraction (XRD) measurements were performed in a 2θ range from 10° to 60° from thermally annealed samples using a Rigaku miniFlex300 and CuKα radiation (λ = 1.541862 Å). From the XRD patterns the attributed mean crystallite size within the glass ceramics can be calculated using Scherrer's equation.

$$d = \frac{G \cdot \lambda}{B \cdot \cos \theta} \quad (1)$$

with G = 0.899 for a cubic system, λ = wavelength of the x-ray radiation (CuKα = 0.154 nm), B = full width at half maximum and θ the Bragg angle of the XRD-peak. In the present case, the crystal size was calculated from the full width at half maximum of the peaks at 2θ = 47° and 55°. The average of these 2 values was used for all samples. With respect to the peak broadening caused by the instrument, a silicon standard was measured and the respective full width at half maximum was subtracted from the samples peak.

Selected crystallized samples were studied by scanning electron microscopy (SEM; Jeol JSM7001F). For SEM imaging, the samples were broken and the fractured surface of the samples was etched for 20 s, using 10:1 NH<sub>4</sub>F:HCl. Subsequently the surface was coated with carbon by evaporation in high vacuum (10<sup>-3</sup> Pa). Etching of the sample surface is necessary to observe the exposed particles.

Luminescence spectra were recorded using the spectrometer (Shimadzu RF-5301 PC) in the wavelength range of 250–700 nm. For this measurement, polished samples with a thickness of 1 mm were used. For luminescence lifetime measurements, a high intensity pulsed InGaN-diode (LED 306-66-60–110, Roithner Lasertechnik GmbH, Wien, Austria) with an emission wavelength of 360 nm was used for excitation. The light emitted from the sample at a certain wavelength was amplified by a photomultiplier tube (R5929, Hamamatsu Photonics K.K., Japan) connected to a digital oscilloscope. This setup enables wavelength specific lifetime measurements. Luminescence lifetimes were measured for the strongest luminescence transition of Tm<sup>3+</sup> in the visible range at 453 nm.

## 3. Results

The as casted glasses were clear and visually transparent. The recorded DTA-profile of sample A showed a glass transition temperature of 520 °C, a broad exothermic peak at 628 °C and a narrow exothermic peak at 727 °C. The T<sub>g</sub> determined for sample B was 522 °C and the exothermic peaks occurred at 636 and 727 °C. T<sub>g</sub> of sample C is 521 °C. These values show that doping of small concentrations of Tm<sub>2</sub>O<sub>3</sub> have almost no notable effect on T<sub>g</sub> and the crystallization process of this glass composition. All samples annealed at 550 °C were still visually transparent. After annealing at 580 °C a whitish haze occurred and the samples that were annealed at 600 °C were completely opaque. The different doping concentrations had no observable effect on the appearance of the samples.

Fig. 1 shows the XRD patterns of samples A, B and C thermally treated at temperatures of 550, 580 and 600 °C for 20 h. While the as cast samples are amorphous and do not give any hint at crystallization, the thermally treated samples show notably broadened lines at 2θ values of 28°, 47°, and 55° that can all be attributed to CaF<sub>2</sub> (JCPDS no. 35-0816). Besides, in all samples, a broad halo is observed in the XRD patterns which is typical for a large concentration of amorphous phases.

The observed peak broadening is attributed to a crystallite size in the nanometer scale which can be calculated using Scherrer's equation. As shown in Fig. 2, the calculated mean crystallite sizes are all in the range from 6 to 11 nm. In general, the mean crystal size increases somewhat with increasing annealing temperature. It should be noted that this increase is comparatively small.

Fig. 3 shows SEM images of the glass samples A and B. It shows

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