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LaF_3 nanocrystals as a host for Er^{3+} in oxyfluoride glass

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The paper presents new glass-ceramics as a material for up-conversion luminescence. Formation of the LaF_3 nanocrystals have been obtained as a low phonon host for rare earth active ions in oxide glassy matrix. The thermal conditions of LaF_3 nanocrystallization in the glass from the SiO_2–Al_2O_3–Na_2O–LaF_3 system have been presented. Transmittance and luminescence properties as a function of heat treatment have been investigated. The effect of incoming of Er^{3+} in LaF_3 crystals has been shown on the luminescence properties. AFM results have confirmed the growth of nano-scale crystals.

Keywords: nanocrystallization, oxyfluoride glasses, lanthanum fluoride, upconversion.

1. Introduction

Rare earth (RE) doped glasses are of great interest on account of their optical and fluorescence properties. One of the most important property for the development of fibre lasers and efficient amplifiers is a frequency upconversion phenomenon. To obtain RE upconversion material, the combination of high optical transparency and long fluorescence lifetimes characteristic of a low phonon energy environment is needed [1].

In silicate glasses, which are attractive because of their high degree of transparency and durability, phonon energy is too high (Tab. 1). On the other hand, fluoride glass is a desirable host for RE ions because it enables emission from RE energy levels and RE solubility in them is higher [2]. Unfortunately, fluoride glass is corrosive, unstable and not so easily prepared into fibers [3].

Oxyfluoride glass-ceramics has lower phonon energy than oxide glasses and ZrF_4–BaF_2–LaF_3–AlF_3–NaF (ZBLAN) [4], that is why they are desirable hosts for RE

T a b l e 1. Phonon energy of glasses and glass-ceramics [5].

Materials	The highest energy phonon [cm^{-1}]
Glasses:	
Borate	1250
Silicate	1100
Germanate	975
Tellurite	850
Fluoride	600
Chalcogenide	300
Oxyfluoride glass-ceramics:	
LaF_3	350
$Pb_{1-x}Cd_xF_2$	235
Heavy-metal oxide	800
Fluorozirconate	580
Fluoroindate	520

because they enable emission from RE energy levels that would otherwise be quenched in high-phonon energy glasses (Tab. 1).

The goal of the work was to explore the influence of the glass composition from the SiO_2–Al_2O_3–Na_2O–LaF_3 system as well as the heat treatment process on the tendency to the nanocrystallization of LaF_3, by comparing the luminescence properties.

2. Experimental

Oxyfluoride glasses have been obtained by melting 20 g batches in platinum crucibles in an electric furnace at the temperature range of 1400–1450°C in air atmosphere. The melts were poured out onto a steel plate forming a layer thickness of 2 to 5 mm. The following raw materials were used to prepare the batches: SiO_2, Al_2O_3, Na_2CO_3, AlF_3 and LaF_3. The compositions of the glasses are listed in Tab. 2.

The ability of the obtained glasses to crystallization was determined by DTA/DSC measurements conducted on the Perkin–Elmer DTA-7 System operating in the heat flux DSC mode. The samples (60 mg) were heated in platinum crucibles at a rate of 10°C/min in dry nitrogen atmosphere to the temperature of 1000°C. The glass transition temperature T_g was determined from the inflection point on the DSC curve.

T a b l e 2. Composition of melted oxyfluoride glasses.

Glass No.	Compositon [mol%]						
	SiO_2	Al_2O_3	Na_2O	La_2F_6	AlF_3	La_2O_3	Er_2O_3
R0noF	56.50	24.50	16.00	—	—	3.00	—
S3-Er	56.43	24.77	15.77	3.02	—	—	0.08
R0AlF-Er	59.47	22.63	11.58	3.16	3.16	—	0.08

Glasses revealing the effect of cerammization were selected for further thermal treatment. To obtain glass-ceramics with nanocrystallization of LaF_3 glasses S3-Er and R0AlF-Er were heated at 600°C/2h/12h/24h/96h and 565°C/2h/24h/96h, respectively.

The kind and the size of the formed crystallites were examined by XRD (Philips X'Pert Diffractometer) and AFM methods, respectively. The images were taken by a Nanoscope E AFM microscope (Digital Instruments) with A-head, which provides a maximum scanning range of 1 μm^2. Si_3N_4 tips were used with a spring constant of 0.06 Nm^{-1}. Fracture and AFM measurements were performed in air. The AFM images were measured in the height mode.

Upconversion fluorescence in Er^{3+}-doped samples was excited using a luminescence spectrophotometer FS 900 Edinburgh Instrument. The pumping light source used in the experiment was a 980 nm using POLAROID Laser Diode 4300. The laser was supplied from a power supply SDL 800, controlled by a pulses generator and it generated the pulses of 8 microseconds duration and frequency about 0.66 kHz. The irradiance was about 100 mW/cm^2. It worked with power of 1 W. The fluorescence spectra were recorded from a surface of the powder sample.

The double beam spectrophotometer Lambda 19 Perkin–Elmer has been used to measure the spectral dependences of transmittance $T(\lambda)$ over the wavelength range λ = 180–3200 nm. A monochromator has had a deuterium lamp as a source and a photomultiplier as a detector. Light scattering experiments have been carried out with an integrating sphere attached to the spectrophotometer. Total hemispherical transmittance as well as diffused transmittance has been measured relative to a Spectralon calibrated standard, which has 97–98% reflectance over the visible and in the near-infrared range.

3. Results and discussion

Glasses from the Na_2O–Al_2O_3–SiO_2 system doped with lanthanum fluoride during heating demonstrated, besides the thermal effects characteristic for typical phase

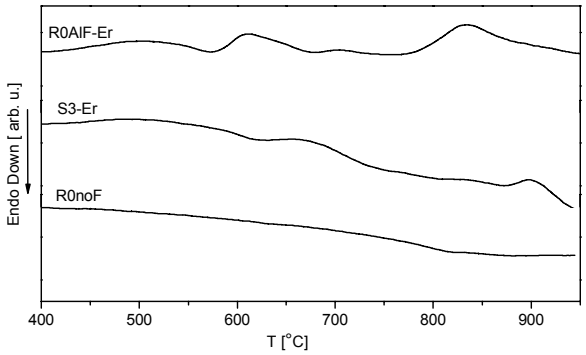

Fig. 1. DTA curves of glasses with the effect of LaF_3 cerammization.

T a b l e 3. Thermal characteristics of oxyfluoride glasses.

Glass No.	T_g [°C]	$T_{\text{beg. cer.}}$ [°C]	$T_{\text{beg. crys.}}$ [°C]	1st stage of crystallization	2nd stage of crystallization
R0noF	790	—	—	—	—
S3-Er	558	620	874	LaF_3	$NaAlSiO_4$
R0AlF-Er	533	577	770	LaF_3	$NaLa_9(SiO_4)_6O_2$

transitions occurring in a glassy material, an additional exothermal effect near the T_g temperature connected with LaF_3 crystallization. This effect is observed only for some definite chemical compositions of the examined glasses (see [6]). DTA/DSC curves indicate that the presence of a well visible effect of the glassy state transformation in the examined glasses is closely connected with the exothermic cerammization process (1st stage of crystallization) (Fig. 1). During the heat treatment at the 2nd stage of crystallization $NaAlSiO_4$ or $NaLa_9(SiO_4)_6O_2$ occurs. Generally, introducing of fluoride into the structure of the oxide glass causes decreasing in the thermal stablility and crystallization of LaF_3 at lower temperature and silicates at higher temperature (Fig. 1). The increase in fluoride content in glasses from the Na_2O–Al_2O_3–SiO_2 system causes a decrease in the transformation temperature T_g as well as in crystallization temperatures (Tab. 3).

Glasses were transparent up to 12 h of heat treatment at the temperature of the beginning of the first stage of crystallization. They showed the effect of slight opalescence with increasing time of ceramming up to 96 h. Figure 2 presents the total transmittance of unpolished R0AlF-Er sample at the range of 250–1500 nm before and after 96 h of treatment. The glass has absorption edge at ~300 nm. Crystallization of LaF_3 shifts the edge slightly (~50 nm) towards the longer wavelengths. The UV absorption edge, which limits the transparency at shorter wavelengths, is due to the

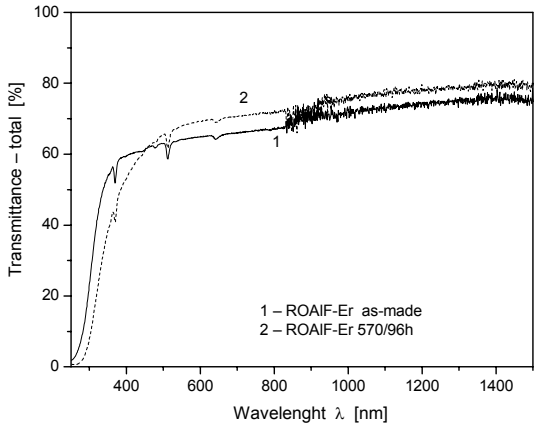

Fig. 2. Total transmittance of unpolished oxyfluoride glass samples: as-made (1) and 570°C/96h treated (2).

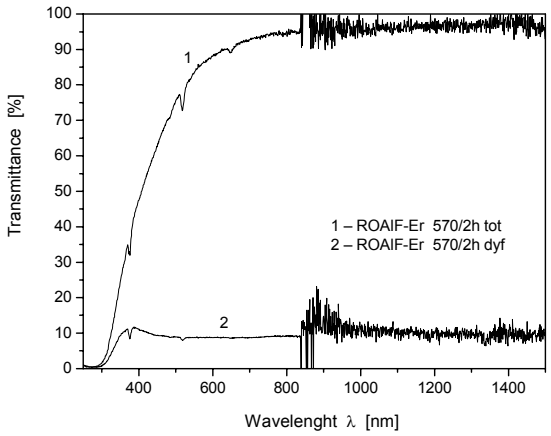

Fig. 3. Total (1) and diffused component (2) of transmittance of R0AlF-Er glass-ceramics after 2 h of cerammization.

electronic transitions in the glass, and its wavelength is related to the electronic band gap of the glass. When the band gap energy decreases, the UV edge shifts to longer wavelengths. Effect of cerammization causes also 5% increase in the total transmittance from 450 nm.

Figure 3 presents the diffused component of transmittance when compared to the total one of the polished sample R0AlF-Er after 2 h of heat treatment at 570°C. It can be seen that about 10% of light is scattering by the sample in the range of visible spectrum.

The energy level structure of Er^{3+} gives rich upconversion fluorescence lines, *i.e.*, 841 nm ($^4S_{3/2} \rightarrow {}^4I_{13/2}$), 799 nm ($^4I_{9/2} \rightarrow {}^4I_{15/2}$), 665 nm ($^4F_{9/2} \rightarrow {}^4I_{15/2}$), 549 nm ($^4S_{3/2} \rightarrow {}^4I_{15/2}$), 522 nm ($^2H_{11/2} \rightarrow {}^4I_{15/2}$), 406 nm (($^2G^4F^2H)_{9/2} \rightarrow {}^5I_{15/2}$) and 381 nm ($^4G_{11/2} \rightarrow {}^4I_{15/2}$). Er^{3+} ions in fluoride with a low phonon energy show intensive upconversion fluorescence at the range of 540–550 nm from $^4S_{3/2}$ level when pumped at a wavelength of ~980 nm. This is due to the mechanism of excited state absorption (ESA), which can be described as a two-step excitation process, whereby Er^{3+} ions are first excited from the ground state to the $^4I_{11/2}$ level by one photon, and then excited out of the $^4I_{11/2}$ level to the $^4S_{3/2}$ level by a second photon at some later time. Efficiency of the upconversion fluorescence depends on the high population in the $^4I_{11/2}$ level. This population can be achieved in LaF_3 phase with a low phonon energy. In silicate glass the fast non-radiative decay from $^4I_{11/2}$ level to the next lowest level $^4I_{13/2}$ causes quenching fluorescence at 550 nm wavelength. Fluorescence of the as-made glass is negligibly small (Fig. 4, curve *a*).

Figures 4 and 5 show changes in intensity of upconversion fluorescence with respect to the time of ceramming. It can be seen that the process of heat treatment makes the significant increase in efficiency of fluorescence, which is connected with the appearance of nano-crystallites LaF_3 with Er^{3+} ions into its structure. This effect was observed for our glass-ceramics only up to 12 h of ceramming. When the time of

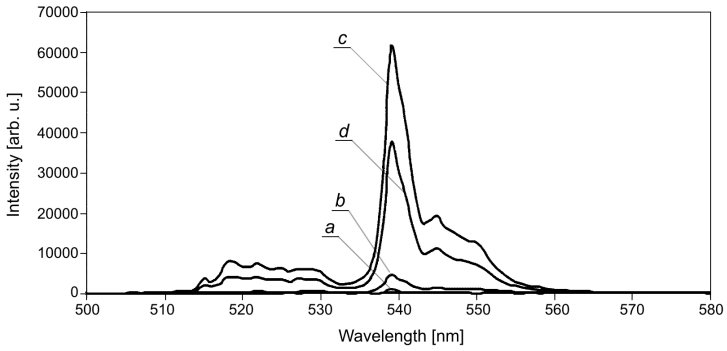

Fig. 4. Upconversion fluorescence spectra of $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition in Er^{3+}-doped glass-ceramics R0AlF-Er: as-made (*a*) and after 2 h (*b*), 12 h (*c*), 96 h (*d*) of heat treatment at 565°C.

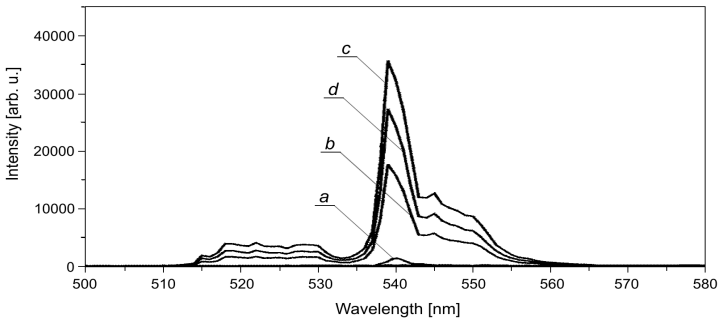

Fig. 5. Upconversion fluorescence spectra of $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition in Er^{3+}-doped glass-ceramics S3-Er: as-made (*a*) and after 2 h (*b*), 12 h (*c*), 96 h (*d*) of heat treatment at 600°C.

heat treatment was exceeding 24 h, the intensity of fluorescence spectra was decreasing. Thus, it indicates that for the highest upconversion luminescence LaF_3 crystals should be not more than 100 nm in size.

Figure 6**a** shows a fracture surface of the as-made glass. Figures 6**b** and 6**c** present AFM images of the glass after 2 and 96 h of heat treatment, respectively. After heat treatment at 565°C/2 h, AFM revealed the development of small crystals. When the time of heat treatment is increased, the grow of LaF_3 crystals up to 200 nm in size is observed.

4. Conclusions

In glasses from the SiO_2–Al_2O_3–Na_2O–LaF_3 system nanocrystallization of LaF_3 can be obtained by proper heat treatment near the transformation temperature. Crystals of LaF_3 can be a good host for Er^{3+} active ion because of low phonon energy. Obtained material shows the edge of absorption at 350 nm wavelength with the good transparency in visible and near infrared spectra.

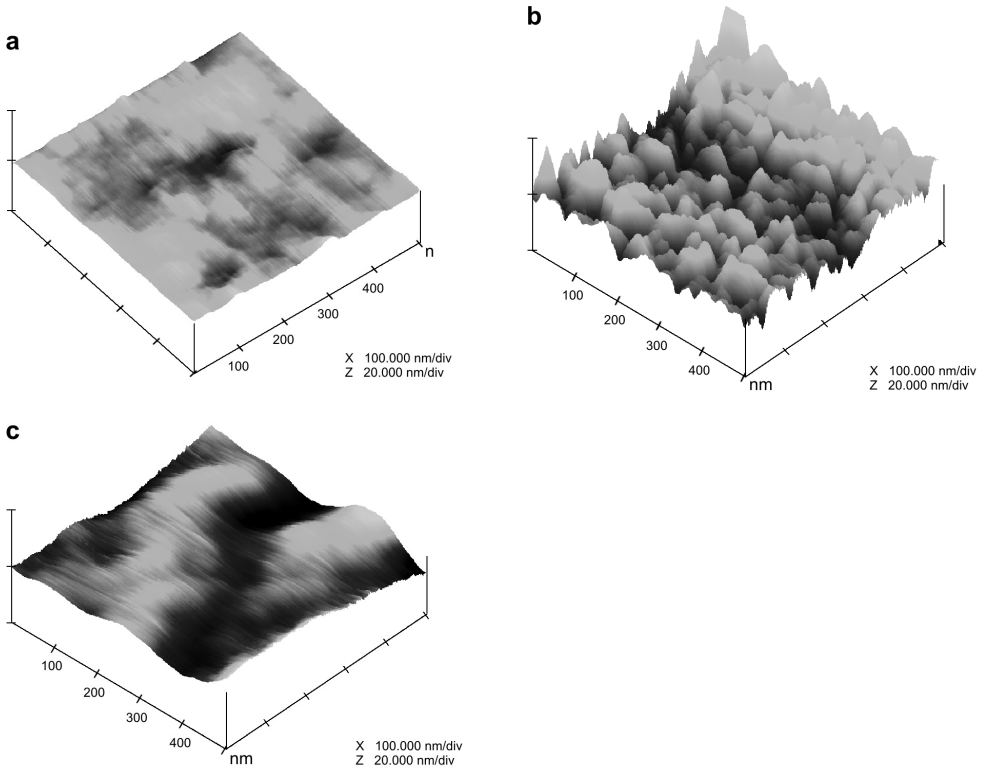

Fig. 6. AFM images of a fracture surface of glass R0AlF-Er: as-made (**a**), after 2 h (**b**) and 96 h (**c**) of the cerammization at 565°C.

It was found that the efficiency of upconversion luminescence is controlled by ceramming process. It means that the rare earth dopant preferentially segregates into the fluoride crystals during heat treatment.

Transparent glass-ceramics from SiO_2–Al_2O_3–Na_2O–LaF_3 system offers an alternative to other low phonon energy fluoride glasses as a host for Er^{3+} in 540 nm optoelectronic applications.

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