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THERMAL AND STRUCTURAL STUDIES OF NANOCRYSTALLIZATION OF OXYFLUORIDE GLASSES

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The influence of fluorine content on the structure and crystallization of oxyfluoride glasses from the Na_2O–Al_2O_3–SiO_2–LaF_3 system was studied by DTA/DSC, XRD, FTIR and SEM methods. It has been found that the increase in the fluorine content in the structure of oxyfluoride glasses causes the increase of the flexibility of their structure, which inhibits the process of crystallization of the silicate-aluminium matrix. Simultaneously the ability of the glass for LaF_3 crystallization, which shows a multistage character, is increasing. Analysis of the local atomic interactions in the structure of glasses has been used to explain the course of the crystallization.

Keywords: *oxyfluoride glass, nanocrystallization, phase transformation*

Introduction

Rare earth doped fluoride glasses are desirable materials for up-conversion lasers, optical amplifiers and display devices due to their low phonon energy environment for rare earths (RE) ions. However, fluoride glasses have some disadvantages such as poor chemical and mechanical stability. They are also very expensive, toxic, corrosive, unstable, and must be processed in a dry oxygen free atmosphere [1–3].

Rare earth doped oxyfluoride glass ceramics, in which the optically active ion selectively concentrates into a fluoride crystal phase immersed in an oxide glass matrix, can offer excellent optical properties because fluoride crystals possess good transparency. Oxyfluoride glass ceramics containing LaF_3 nanocrystals has been an attractive material in the continuous research for the novel optoelectronic devices since it was first reported in the 1995 by Dejneka. LaF_3 is a more suitable fluoride host for rare earth than PbF_2, since LaF_3 has better solid solubility for rare earth ions, a lower phonon energy (350 cm^{-1}) and adequate thermal and environmental stability [4, 5]. Earlier investigations [6] have shown that such materials can be obtained in a narrow range of the glass composition from the Na_2O–Al_2O_3–SiO_2–LaF_3 system. Nanocrystallization of LaF_3 takes place only when the proportions between the components of glass are accurately maintained. Ratios of the components $Na_2O/SiO_2+Al_2O_3$, Na_2O/Al_2O_3 and $La_2F_6/Al_2O_3+Na_2O$ are required for LaF_3 formation. These dependences were explained by acid–based interactions between components of the structure expressed by the ionicity of their bonds with oxygen.

The aim of the present paper was to explain the influence of fluorine content on the structure and crystallization of oxyfluoride glasses from the Na_2O–Al_2O_3–SiO_2–LaF_3 system.

Experimental

Oxyfluoride glasses have been obtained by melting 20 g batches in platinum crucibles in an electric furnace at the temperature range 1400–1450°C in air atmosphere. The melts were poured out onto a steel plate forming a layer of 2 to 5 mm thickness. The following raw materials were used to prepare the batches: SiO_2, Al_2O_3, Na_2CO_3, LaF_3, AlF_3 and NaF. The compositions of the glasses are listed in Table 1.

The ability of the obtained glasses for crystallization was determined by DTA/DSC measurements conducted on the Perkin-Elmer DTA-7 System operating in heat flux DSC mode. The samples (60 mg) were heated in platinum crucibles at a rate 10°C min^{-1} in dry nitrogen atmosphere to the temperature 1000°C. The glass transition temperature T_g was determined from the inflection point on the enthalpy curve; the jump – like changes of the specific heat ΔC_p accompanying the glass transition, enthalpy (ΔH_{cer}) of ceramization of LaF_3 and crystallization of the base glass were calculated using the 7 Series Perkin-Elmer Thermal Analysis Software Library. The ability of glasses for crystallization was measured by the values of the temperature (T_{cryst}), the enthalpy of crystallization (ΔH_{cryst}) and the values of the thermal stability parameter of glasses ($\Delta T=T_{ceram}-T_g$) (Table 2). To obtain the ceraming ef-

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Table 1 Composition of the oxyfluoride glasses with LaF_3 admixture with different amount of fluorine

Glass no.	Composition/mol%					
	SiO_2	Al_2O_3	Na_2O	La_2F_6	Na_2F_2	Al_2F_6
0	56.5	24.5	16.0	3.0	–	–
1	56.8	24.6	15.1	3.0	0.5	–
2	57.2	24.7	14.1	3.0	1.0	–
3	57.4	24.9	13.2	3.0	1.5	–
4	57.5	21.8	16.2	3.0	–	1.5
5	61.6	20.2	12.0	3.1	–	3.0
6	63.0	16.2	12.3	3.2	–	5.0

fect the glasses were heated for 20 min at the temperature of the beginning of the exothermal peak. Glasses revealing the second exothermal effect were heated for 1 h at the temperature of the maximum of the crystallization effect.

The kind and the size of the formed crystallites were examined by XRD (Philips X'Pert Diffractometer) and SEM (FEI Nora200 Nano SEM) methods.

The Fourier transform infrared spectroscopy (FTIR) studies of glasses and their crystallized forms were carried out on the Digilab FTS 60v spectrometers in FIR and MIR ranges (100–450 and 400–4000 cm^{-1}). All spectra were measured at 4 cm^{-1} resolution in transmission mode.

Results and discussion

Thermal stability

Results of the thermal investigations of glasses from the $Na_2O–Al_2O_3–SiO_2$ system doped with lanthanum fluoride have shown, besides the thermal effects characteristic for typical phase transitions occurring in a glassy material during heating, an additional exothermal effect near the T_g temperature connected with LaF_3 crystallization (Figs 1, 2). In all studied glasses we can observe a second crystallization peak at the temperature 750–900°C. This effect is also connected with formation of LaF_3 (Table 2). Increase of fluorine content, introduced into the structure of glasses by NaF or AlF_3, causes a decrease of the glass transition temperature T_g and a decrease of changes of the specific heat (ΔC_p) accompanying the glass transition region. This has been explained on the basis of the strength of the chemical bonds between the components of the considered glass structure, according to Göerlich [7]. Introduction of increasing amounts of Na–F (i_a=0.833), Al–F (i_G=0.608), Si–F (i_G=0.506) bonds, characterized by considerable ionicity, into the structure of glasses at simultaneous reduction of Na–O (i_G=0.809), Al–O (i_G=0.546), Si–O (i_G=0.428) and La–O (i_G=0.627) bonds of lower ionicity increases the flexibility of the structure of the examined glasses. In a consequence, the number of structural strains, the relaxation of which requires a small amount of energy, is decreasing. The glass transition effect occurs thus at lower temperature and is accompanied by a small change of the specific heat.

The introduction of fluorine ions, replacing oxygen ions in the glass structure, increases the tendency

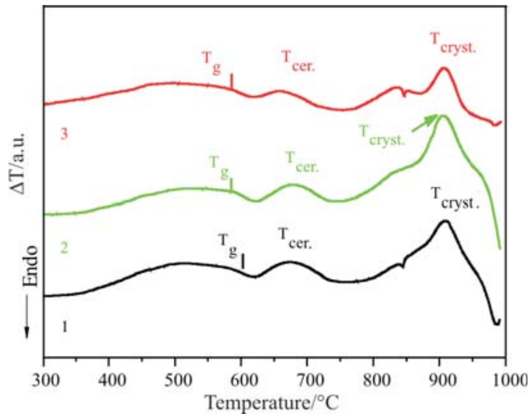

Fig. 1 DTA curves of glasses with ceramization effect – Glasses 1, 2, 3

Table 2 Thermal characteristics of oxyfluoride glasses with LaF_3 admixture

Glass No.	T_g/ °C	ΔC_p/ J g^{-1} $°C^{-1}$	$T_{b.\,cer}$/ °C	ΔH_{cer}/ J g^{-1}	$T_{max.cryst}$/ °C	ΔH_{cryst}/ J g^{-1}	ΔT_{cer}= $T_{b.cer}$–T_g	Crystallizing phases	
								$T_{b.cer}$	$T_{max.cryst}$
0	608	0.726	708	14.15	891	98.87	100	LaF_3	$(NaAlSiO_4)$, $NaLa_9(SiO_4)_6O_2$
1	571	1.41	677	31.08	910	49.90	105	LaF_3	LaF_3
2	577	1.03	627	30.23	905	55.33	50	LaF_3	LaF_3
3	576	0.81	664	18.04	908	41.15	88	LaF_3	LaF_3
4	545	1.18	587	25.04	870	27.20	42	LaF_3	LaF_3
5	538	0.71	570	13.72	749	34.19	32	LaF_3	LaF_3
6	547	0.72	577	36.46	742	49.20	30	LaF_3	LaF_3

$T_{b.\,cer.}$ – Temperature of beginning of ceramization of LaF_3, $T_{max\ cryst}$. – Temperature of maximum crystallization

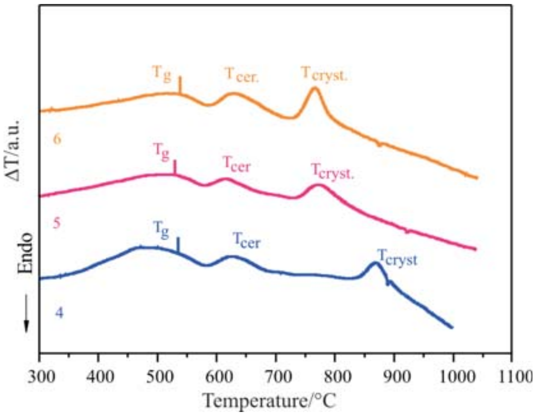

Fig. 2 DTA curves of glasses with ceramization effect – Glasses 3, 4, 5

of glass to LaF_3 crystallization. The temperature of the beginning effect of ceramization is shifted towards lower temperatures and its enthalpy (ΔH_{cer}) becomes increased (Table 2). This is evidence of the increasing ability of the glass for ceramization, manifested by decreased values of the index of thermal stability of the glass ΔT. Increase of fluorine content added by NaF causes a slight increase of the temperature of the second stage of crystallization, whereas the increase of fluorine content added by AlF_3 decreases the temperature of the second stage of crystallization. Values of enthalpy of the crystallization effect are lower in comparison with the values of enthalpy accompanying the crystallization of aluminosilicate matrix for the both glass types.

Because of LaF_3 formation at the first and the second stage of crystallization, increasing amount of fluorine in the glass structure causes a break of crystallization of the aluminosilicate matrix. The crystallization process usually starts in those components of the glass structure whose bonds can be easier broken. The smallest difference in the ionicity of the chemical bonds is demonstrated by the bridges of Al–F–La (Δi=0.070) type, and consequently they have been broken more easily in comparison with the bridges of Al–F–Na (Δi=0.225) or Si–O–Na (Δi=0.379) and Al–O–Na (Δi=0.261) type.

Structural study

The network of aluminosilicate glasses is formed by $[SiO_4]$ and $[AlO_4]$ tetrahedra [8]. Hence, in the IR spectra, the bands corresponding to vibrations of the oxygen bridges Si–O–Si and Si–O–Al should be visible. Figure 3 shows MIR spectra of the green glasses. The spectra possess three main groups of bands with the maximum near 450, 720 and 1020 cm^{-1}. The strongest complex band with the maximum at 991–1017 cm^{-1} is assigned to tetrahedral stretching modes of two types of bridges: Si–O(Si) and Si–O(Al) at about 1100 and 1000 cm^{-1}, respectively [9]. Complex of bands in the region of 720 cm^{-1} is due to Al–O stretching modes in $[AlO_4]$ tetrahedron, according to Tarte [10]. Comparing the spectra of green glass with the spectra of glass with increasing amount of fluorine ions, (glass No. 1–6), the edge of the band in the region of 708 cm^{-1} is shifted towards higher values up to 732 cm^{-1}. In the strongest complex of bands the edge of the band is also shifted towards higher value, from 991 to 1017 cm^{-1}, for glass in which the additional fluorine content increases. This is evidence of the influence of fluorine ions on the $[AlO_4]$ and $[SiO_4]$ tetrahedra.

The crystallization process of LaF_3 from the glass with increased amount of fluorine ions added by NaF does not cause any change of the spectra in the middle infrared region (Fig. 4), because the spectrum of LaF_3 does not occur in this region. X-ray diffraction investigations confirmed LaF_3 formation at the first and the

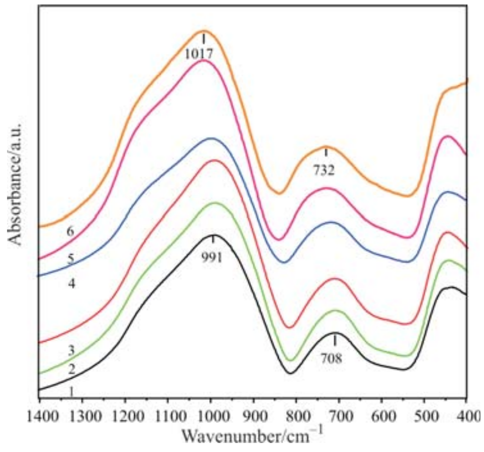

Fig. 3 Comparison of MIR absorption spectra of green glasses with additional amount of fluorine added by NaF, glass – 1, 2, 3, added by AlF_3 – glass 4, 5, 6

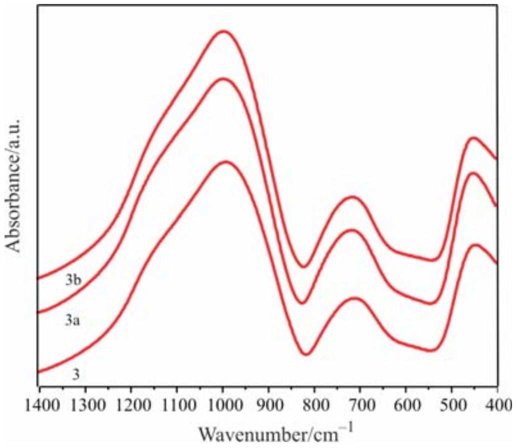

Fig. 4 Comparison of MIR absorption spectra of glasses with additional amount of fluoride added by NaF, 3 – green glass, 3a – glass after first stage of crystallization, 3b – glass after second stage of crystallization

second stage of crystallization. At the second stage of crystallization of glass with increased amount of fluorine ions added by AlF_3 there appear additional bands at 595 and 566 cm^{-1} in the middle infrared (glass 4, Fig. 5), where the band at 566 cm^{-1} appears after the first stage of crystallization of glasses with increasing fluorine content (glass 5, 6, Fig. 6). The presence of these absorption bands may be connected with formation of Al–F bonds which occur during LaF_3 crystallization in glasses with increasing amount of fluorine content. Figures 7 and 8 show FIR spectra, recorded for green glass and after first and second stage of crystallization of LaF_3. In the far infrared absorption spectrum of the LaF_3 the bands at 350, 270, 255, 206, 166,130 and 100 cm^{-1} are observed (Fig. 7).

The heat treatment of the glass containing fluorine ions added by NaF after the second stage of crystallization causes a reduction of the LaF_3 band intensity compared with that observed after the second stage of crystallization of glass, where additional amount of fluorine is added by AlF_3. The lower intensity of LaF_3 phase patterns was detected by XRD methods, as well. When the fluorine ions content increases and is added by AlF_3, the bands in the FIR spectra after the second stage of crystallization are sharp and very well fit the bands for the LaF_3 phase.

The process of thermal treatment in the range of the ceramization and crystallization effect results in obtaining the LaF_3 phase with the crystallites size <100 nm, as demonstrated by the results of investigations carried out using SEM.

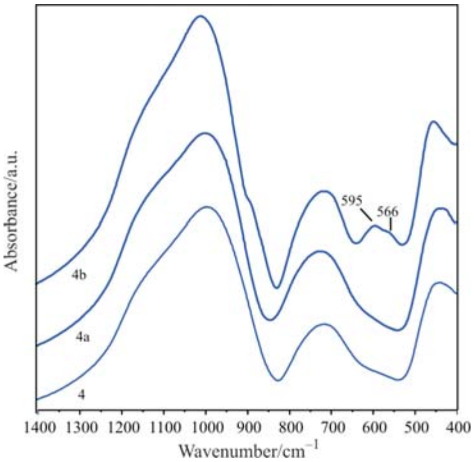

Fig. 5 Comparison of MIR absorption spectra of glasses with additional amount of fluoride added by AlF_3, 4 – green glass, 4a – glass after first stage of crystallization, 4b – glass after second stage of crystallization

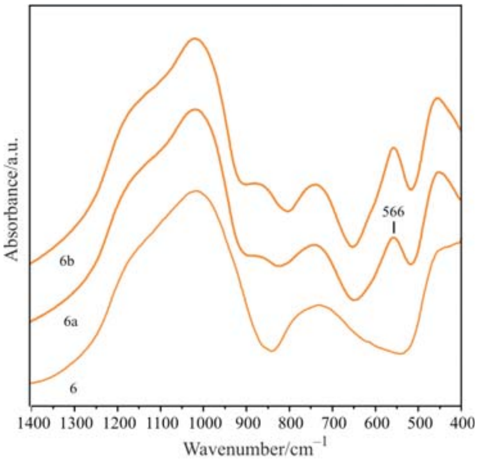

Fig. 6 Comparison of MIR absorption spectra of glasses with additional amount of fluoride added by AlF_3, 6 – green glass, 6a – glass after first stage of crystallization, 6b – glass after second stage of crystallization

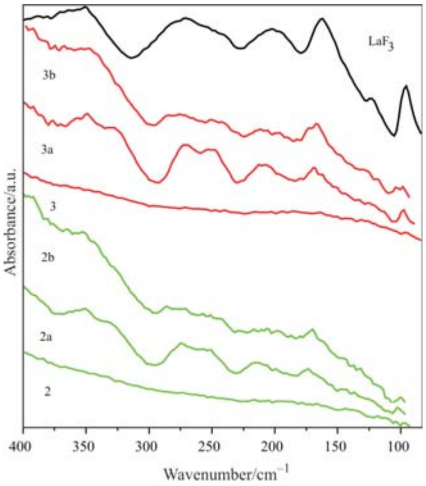

Fig. 7 Comparison of FIR absorption spectra of glasses with additional amount of fluoride added by NaF, 2,3 – green glass, 2a,3a – glass after first stage of crystallization, 2b,3b – glass after second stage of crystallization

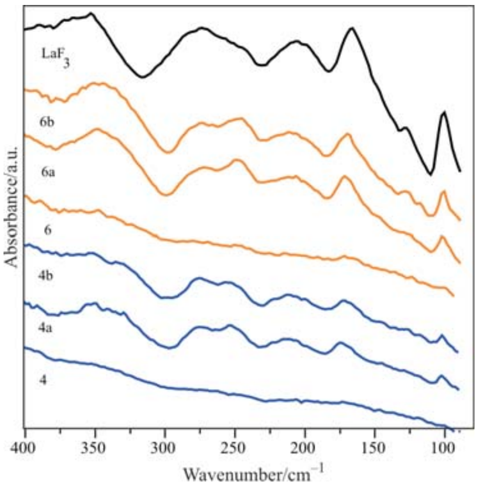

Fig. 8 Comparison of FIR absorption spectra of glasses with additional amount of fluoride added by AlF_3, 4,6 – green glass, 4a,6a – glass after first stage of crystallization, 4b,6b – glass after second stage of crystallization

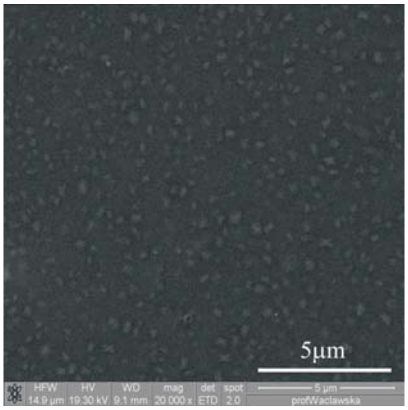

Fig. 9 SEM of glass 6 after the first stage of crystallization

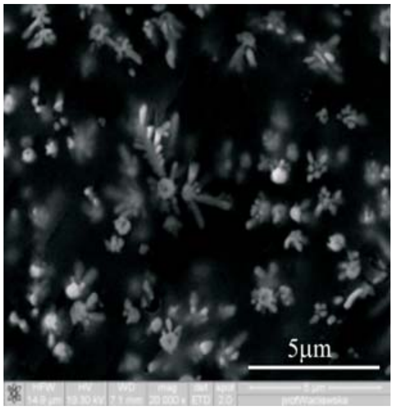

Fig. 10 SEM of glass 6 after the second stage of crystallization

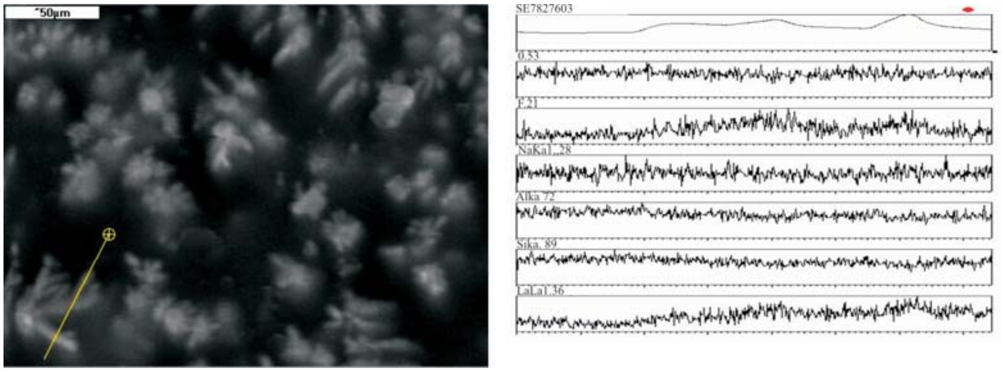

Fig. 11 EDS of glass 6 after the second stage of crystallization

Figure 9 shows a fracture surface of the glass with extended fluorine content after the first stage of crystallization. The effect of LaF_3 crystallization can be visible as crystallites of average size about 100 nm. Figure 10 presents columnar crystals of LaF_3 grown in the glass after the second stage of crystallization. The presence of LaF_3 was confirmed by EDS analysis (Fig. 11).

Conclusions

The increases of fluorine content in the structure of oxyfluoride glasses from the Na_2O–Al_2O_3–SiO_2–LaF_3 system causes the increase of the flexibility of their structure, inhibiting the process of crystallization of the silicate-aluminium matrix. Simultaneously there increases the ability of the glass for LaF_3 crystallization, which has a multi-stage character. At its first stage (ceramization) LaF_3 crystals of nanometric dimensions are formed, which are indispensable from the point of view of optoeletronics. In the course of the second stage of the crystallization of glasses, LaF_3 undergoes recrystallization, in the course of which there takes place the growth of grains and the change of their shape. This stage of crystallization is responsible for the loss of transparency of the examined glasses.

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