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Effect of Er_2O_3 on thermal stability of oxyfluoride glass

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Abstract Glasses have been synthesized in the system SiO_2–Al_2O_3–Na_2O–AlF_3–LaF_3–Er_2O_3. A base glass (in mol% $67SiO_2$–$9Al_2O_3$–$20Na_2O$–Al_2F_6–$3La_2F_6$) was modified by 0.5, 0.75, 1, 1.25, 1.5, 2 and 5 mol% Er_2O_3, respectively. Glasses were prepared by conventional fusion method from 20 g batches. The glass transition temperature (T_g), the jump-like changes of the specific heat (ΔC_p) accompanying the glass transition and the enthalpy of crystallization (ΔH) were calculated. DTA measurements clearly reveal that the increase of the Er_2O_3 content in the glass changes the effects of crystallization and diminishes the thermal stability of the glassy network. In the same time the changes in the transition temperature are observed. The formation of $NaLaF_4$ and $Na_{1.45}La_{9.31}(SiO_4)_6(F_{0.9}O_{1.1})$ as a main phase was confirmed. The diminishing of the thermal stability was connected with erbium which incorporated into $Na_{1.45}La_{9.31}(SiO_4)_6(F_{0.9}O_{1.1})$ structure.

Keywords Aluminosilicate glass · DTA/DSC · Erbium oxide · LaF_3 · Oxyfluoride glass · Thermal stability

Introduction

Glasses doped with lanthanide ions have been receiving more and more attention because of their luminescence properties. They have potential applications in optoelectronics as laser hosts, optical amplifiers and also they can be used in infrared to visible light conversion devices [1, 2]. Knowledge of the role of rare earth ions in multi-component glasses and their influence on the thermal stability is of great importance for the design of new glass ceramic compositions for photonics applications. The erbium is especially interesting because the $^{13}I_{3/2} \rightarrow {}^{15}I_{3/2}$ transition coincides with the lowest attenuation window of silica glass fibers [3, 4]. Thus, erbium doped glasses and glass ceramics can be used to amplify attenuated signals in optical fiber telecommunication systems.

The local structure of erbium ions in silica and sodium silicate glasses by EXAFS has been studied by Marcus and Polman [5]. They found that the local environment of erbium ions is different in the two glasses. It was stated that the more depolymerized network structure in sodium silicate glass allows erbium ions to adopt more optimal coordination environments.

Erbium oxide concentration can be as high as 10 mol% in sodium silicate glass [6]. Such amount of lanthanide has to induce the changes in the thermal stability and optical properties of glass. On the other hand, this makes the multicomponent silicate glasses potential hosts for waveguide lasers and amplifiers, in which a much higher rare earth doping level is required as a result of their limited dimension compared to fiber based devices [7].

To enhance the luminescence transitions Er^{3+} ions should be concentrated into a low phonon structure. To obtain this purpose lanthanides ions should be introduce to the low phonon glass, for example, chalcogenide glasses, i.e. fluoride glass [8] or glass ceramics with the low phonon nanocrystalites [9]. Thus, oxyfluoride glass ceramics based on the silicate glassy matrix and nanocrystalites of LaF_3 or PbF_3–CdF_3 have been developing for the last decade [10–12]. For the optical properties of glass ceramics, it is important to induce and control the crystallization of fluorides within the range of nanometers and to selectively

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build-in rare earth ions into low phonon crystallites. To my knowledge the influence of Er ions on the thermal stability of oxyfluoride glass has not been studied so far. Introduction of Er_2O_3 can influence the process of cerammization in the oxyfluoride glass changing its course of crystallization. Thus, the purpose of this work was to investigate the effect of Er_2O_3 on the thermal stability of oxyfluoride aluminosilicate glass.

Experiments

A base glass (in mol% $67SiO_2$–$9Al_2O_3$–$20Na_2O$–Al_2F_6–$3La_2F_6$) was modified by 0.5, 0.75, 1, 1.25, 1.5, 2 and 5 mol% Er_2O_3, respectively. Batches were prepared by mixing chemically pure reagents: SiO_2, Al_2O_3, AlF_3, Na_2CO_3, and LaF_3. Glasses have been obtained by melting 20 g batches in a covered platinum crucible in an electric furnace at the temperature 1450 °C in air atmosphere. Each molten glass was poured out onto a stainless plate forming a layer of ca. 3 mm thickness.

The effect of the thermal stability was investigated by DTA/DSC measurements conducted on the Perkin Elmer DTA-7 System operating in heat flux DSC mode. The samples of 60 mg in mass were heated in platinum crucibles at a rate of 10 °C min^{-1} in a dry nitrogen atmosphere to the temperature of 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 and the enthalpy of crystallization (ΔH_{cryst}) of the glass were calculated using the 7 Series Perkin Elmer Thermal Analysis Software Library. The ability of glasses to crystallize was measured by the values of the maximum crystallization temperature ($T_{max\ cryst}$), the enthalpy of crystallization and the values of the thermal stability parameter of glasses ($\Delta T = T_{onset\ cryst} - T_g$). The crystallizing phases were analyzed by the XRD method using the Philips X'Pert Diffractometer.

The Fourier transform infrared spectroscopy (FT-IR) studies of glasses were carried out on the Digilab FTS 60v spectrometers at a 4 cm^{-1} resolution in transmission mode.

Results and discussion

Thermal stability

The based glass and glasses doped Er_2O_3 from 0.5 to 2 mol% were transparent and X-ray amorphous. Glass with 5 mol% Er_2O_3 showed spontaneous partial crystallization during quenching. Figure 1 shows the DTA curves of oxyfluoride aluminosilicate glasses doped with different

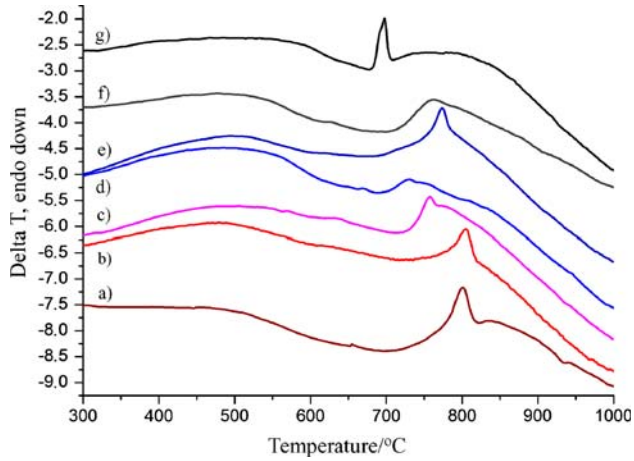

Fig. 1 DTA curves of oxyfluoride aluminosilicate glasses doped with: (a) 0, (b) 0.5, (c) 0.75, (d) 1, (e) 1.25, (f) 1.5, (g) 2 mol% Er_2O_3

amounts of Er_2O_3. DTA measurements clearly reveal that the increase of Er_2O_3 content in the glass changes the temperature of crystallization and diminishes the thermal stability of the glass. The main peak of crystallization shifted from 800 °C for based glass (curve a) to 700 °C for glass doped 2 mol% Er_2O_3 (curve g). The crystallization process of the based glass led to the formation of $NaLaF_4$ and $Na_{1.45}La_{8.55}(SiO_4)_6(F_{0.9}O_{1.1})$ up to the temperature 800 °C (Fig. 2). The thermal treatment of the glass at a higher temperature revealed the transformation of $Na_{1.45}La_{9.31}(SiO_4)_6(F_{0.9}O_{1.1})$ into $NaLa_9(SiO_4)_6O_2$, the wide exothermal peak at the range 830–930 °C (Fig. 1, curve a).

In the systematic classification of elements, lantanoids lie in close proximity to modifying elements with respect to their function in the structure of oxide glasses. They markedly decrease viscosity at a high temperature when present in glasses in large amounts [13]. For the investigated oxyfluoride glasses the increase of viscosity can be observed at a low temperature. The introduction of more and more of the Er_2O_3 to the base glass shifted the transformation temperature towards the higher temperature. The evolution of the T_g temperature showed Fig. 3. In my opinion, this change is caused by the extra anions provided by Er_2O_3. The additional O^{2-} ions increases the polymerization of the network and therefore results in the better stability of the glass which then induces the rise of T_g.

Effect of a trivalent ion Er^{3+} can be visible at a highertemperature on the DTA curves. Erbium can play a similar role as Al^{3+} in the glass but compared with the aluminium, the effective radius is more than double and it has a considerably lower bonding strength to oxygen. Thus, it diminishes the temperature of the main peak of crystallization (Fig. 1). For all obtained oxyfluoride glasses the main peak is due to the crystallization of $Na_{1.45}La_{8.55}(SiO_4)_6(F_{0.9}O_{1.1})$. But the pattern of the phase is

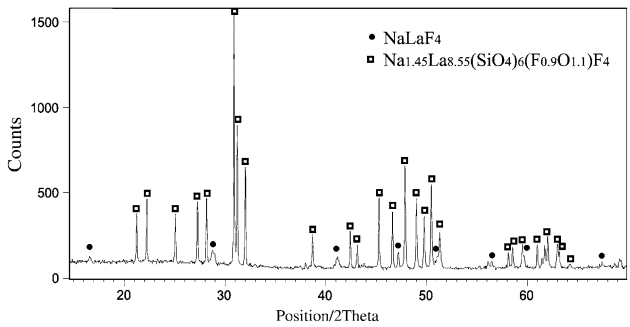

Fig. 2 XRD patern of $NaLaF_4$ and $Na_{1.45}La_{8.55}(SiO_4)_6(F_{0.9}O_{1.1})$ crystallization obtained after thermal treatment of the oxyfluoride glass up to 800 °C

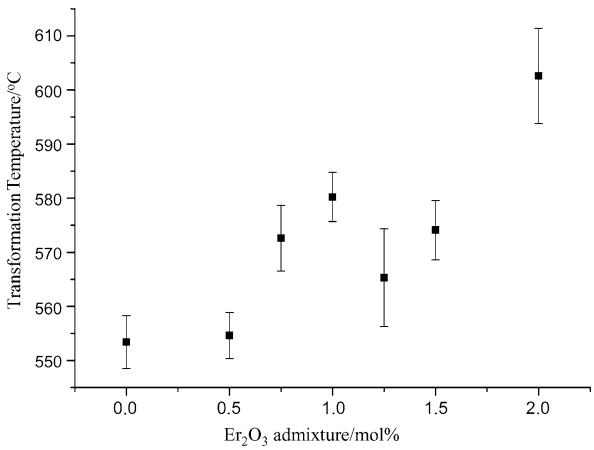

Fig. 3 The effect of Er_2O_3 admixture on transformation temperature (T_g) in oxyfuoride aluminosilicate glass

monotonously shifted to the higher values of the 2θ on the XRD plot. Figure 4 shows the lowering of the d-spacing for the most intensive peak $\{hkl = (3\,11)\}$. The observed effect can be explained by the phenomenon of the incorporation of Er^{3+} into the structure of $Na_{1.45}La_{8.55}(SiO_4)_6(F_{0.9}O_{1.1})$ and formation of $Na_{1.45}(La,Er)_{8.55}(SiO_4)_6(F_{0.9}O_{1.1})$. The effective radius of lanthanoids decreases with an increasing atomic number what is called the lanthanoid contraction. Thus, Er^{3+} ions replacing La^{3+} in the structure may diminish a distance of (*hkl*) planes. According to the references, the Er^{3+} ions act as a nucleating agent for the crystallization [14, 15]. Therefore, the lantanoids would affect the process of crystallization, and then induce the difference in the crystallinity.

The ΔC_p changes at the transformation temperature when the amount of Er^{3+} ions increased (Table 1). This is evidence of the changes in the glass framework. The greatest ΔC_p at T_g have been found in glasses with the lowest content of Er_2O_3. It results from the fact that ΔC_p, as the indicator of

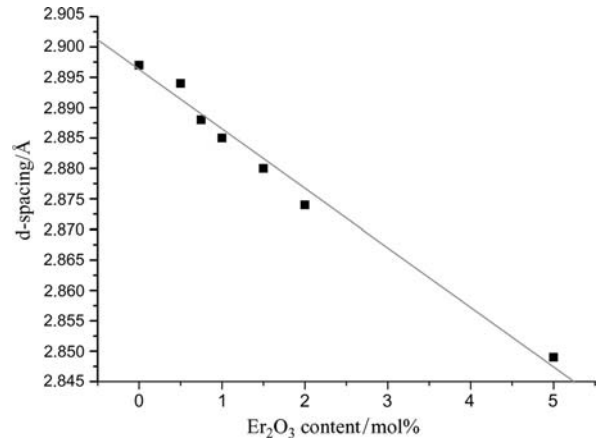

Fig. 4 The effect of the Er_2O_3 admixture on the lowering of the d-spacing for the most intensive peak $\{hkl = (3\,11)\}$ of $Na_{1.45}La_{8.55}(SiO_4)_6(F_{0.9}O_{1.1})$

configuration entropy, is sensitive to the increase of the number of broken bonds within the range of transformation of the glassy state. Its lower value with the increase of Er_2O_3 content is evidence of the more rigid of the glassy framework. Simultaneously, the increase of T_g and the lowering of the temperature of the main crystallization induces the diminishing of thermal stability of the glasses expressed by the formula $\Delta T = T_{\text{onset cryst}} - T_g$ (Table 1).

FT-IR study

The network of aluminosilicate glasses is formed by $[SiO_4]$ and $[AlO_4]$ tetrahedra [16]. Therefore, on the FTIR spectra of the glasses there can be observed bands connected with the Si–O–Si and Si–O–Al bridges. Figure 5 shows MIR spectra of the base and 2 mol% Er doped glasses. The spectra possess three main groups of bands with the maximum near 460, 710 and 1000 cm^{-1}. The strongest complex band 900–1150 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 [17]. The band in the region of 700 cm^{-1}, according to Tarte [16], is due to Al–O stretching modes in $[AlO_4]$ tetrahedron. The band at about 460 cm^{-1} is attributed to the bending vibrations of the tetrahedra $[SiO_4]$. According to Handke and Mozgawa, the bands at 800 and 470 cm^{-1} are due to the bending and rocking vibration of Si_2O units [18]. The positions of bands at 700 and 460 cm^{-1} are not sensitive to the introduction of Er_2O_3. Nevertheless, some broadening of the 713 cm^{-1} band is observed. It indicates the changes of the length and angles in the tetrahedra. In spite of the main band is shifted towards lower wavenumbers (1005 → 989 cm^{-1}) the broadening of the left shoulder of the band is observed and showed in Fig. 5. It indicates the increase of the number of the bridging oxygens and the

Table 1 Thermal characteristics of Er_2O_3-doped oxyfluoride glasses

Content of Er_2O_3 in the base glass (mol%)	ΔC_p (J/g K)	$T_{max\ cryst.}$ (°C)	ΔH (J/g)	Thermal stability $\Delta T = T_{onset\ cryst.} - T_g$ (°C)	Phases of crystallization
0	0.543	800, 835	47.5, 31.2	157	$NaLaF_4$, $Na_{1.45}La_{8.55}(SiO_4)_6(F_{0.9}O_{1.1})$, $NaLa_9(SiO_4)_6O_2$
0.5	0.509	802	68.9[a]	150	$Na(La,Er)F_4$, $Na_{1.45}(La,Er)_{8.55}(SiO_4)_6(F_{0.9}O_{1.1})$, $NaLa_9(SiO_4)_6O_2$
0.75	0.445	765	81.5[a]	142	
1	0.420	736	89.6[a]	116	
1.25	0.405	774	92.2[a]	110	
1.5	0.384	764	129.1[a]	115	
2	0.372	698, 765	22.2, 132.8	72	$Na_{1.45}(La,Er)_{8.55}(SiO_4)_6(F_{0.9}O_{1.1})$, $NaLa_9(SiO_4)_6O_2$

[a] Multi-stage of crystallization has been combined into one exothermal effect

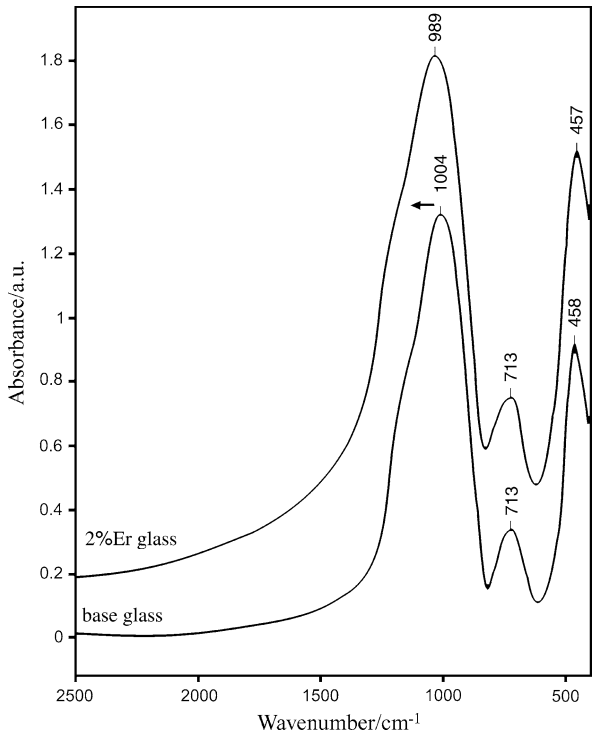

Fig. 5 FT-IR absorption spectra of oxyfluoride aluminasilicate glasses: the based glass and 2 mol% doped Er_2O_3 glass

polimerization of the glass framework. It corresponds to the increase of T_g temperature calculated from DTA/DSC curves. It can be stated that the admixture of Er_2O_3 up to 2 mol% increases the strength of the oxyfluoride aluminosilicate network in the range of high viscosity. This effect induces that the formation of $NaLaF_4$ is not observed for 2 and 5 mol% Er doped glasses. On the other hand, Er_2O_3 diminishes the thermal stability (ΔT) by lowering the temperature of the silicate crystallization $\{Na_{1.45}(La,Er)_{8.55}(SiO_4)_6(F_{0.9}O_{1.1})\}$ at the range of lower viscosity.

Conclusions

The effect of Er_2O_3 on the thermal stability of oxyfluoride aluminosilicate glass was studied by DTA/DSC analysis. Systematic studies have been done to reveal the influence of different erbium admixtures (form 0 to 5 mol%) on the thermal stability, structure and crystallization of oxyfluoride glass.

With the increase of Er_2O_3 content, the oxyfluoride glass network became more rigid what was observed by the higher transformation temperature. It was connected with the increase of the number of the bridging oxygen. The effect of the polymerization of the network was confirmed by the FT-IR study.

$Na(La,Er)F_4$ and $Na_{1.45}(La,Er)_{8.55}(SiO_4)_6(F_{0.9}O_{1.1})$ was formed during thermal treatment. The admixture of Er_2O_3 diminished the thermal stability (calculated as $\Delta T = T_{silicate\ cryst.} - T_g$) and increased ΔH what was due to the incorporating Er^{3+} ions to the $Na_{1.45}La_{8.55}(SiO_4)_6(F_{0.9}O_{1.1})$ structure.

Finally, it can be stated that the kind of the compound whose lantanoids are introduced to the batch must be taken into account at the stage of the designing of the oxyfluoride glass ceramics. It is of great importance for the transparent glass ceramics with the effect of luminescence.

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References

1. Mortier M, Bensalah A, Dantelle G, Patriarche G, Vivien D. Rare-earth doped oxyfluoride glass-ceramics and fluoride ceramics: synthesis and optical properties. Opt Mater. 2007; 29:1263–70.
2. Kam CH, Buddhudu S. Photoluminescence properties of Eu^{3+}:ZrF_4-BaF_2-LaF_3-YF_3-AlF_3-NaF glasses. Phys B: Phys Condens Matter. 2004;344(1–4):182–9.

3. Becker PC, Olsson NA, Simpson JR. Erbium-doped fiber amplifier: fundamentals and technology. San Diego, CA: Academic Press; 1999.
4. Miniscalco WJ. Erbium-doped glasses for fibre amplifiers at 1500 nm. J Lightwave Technol. 1991;9:234–50.
5. Marcus MA, Polman A. Local structure around Er in silica and sodium-silicate glasses. J Non-Cryst Solids. 1991;136:260–5.
6. Neeves AE, Bruce AJ, Reed WA, Rabinovich EM, Grodkiewicz WH, Kopylov NA, et al. Effect of concentration, host glass composition, and processing on the absorption and emission of Er^{+3} ions in sodium silicate glasses. In: Bruce AJ, Hiremath BV, editors. Solid state optical materials, vol. 28. Westerville, OH: American Ceramic Society; 1992. p. 353–67.
7. Du J, Cormack AN. The structure of erbium doped sodium silicate glasses. J Non-Cryst Solids. 2005;351:2263–76.
8. Delben RJ, Chaves DR, Candelorio PD, Delben AAST. Glass forming ability and thermal stability in the system $ZrF_{46}BaF_{26}PrF_3$. J Therm Anal Calorim. 2006;83:411–4.
9. Reben M, Wacławska I, Paluszkiewicz C, Środa M. Thermal and structural studies of nanocrystallization of oxyfluoride glasses. J Therm Anal Calorim. 2007;88:285–9.
10. Dejneka MJ, Transparent oxyfluoride glass ceramics. MRS Bulletin, November 1998, 57–62.
11. Tikhomirov K, Furniss D, Seddon AB, Reaney IM, Beggiora M, Ferrari M, et al. Fabrication and characterization of nanoscale, Er^{3+}-doped, ultratransparent oxyfluoride glass-ceramics. Appl Phys Lett. 2002;81(11):1937–9.
12. Środa M. Effect of LaF_3 admixture on thermal stability of borosilicate glasses. J Therm Anal Calorim. 2007;88:245–9.
13. Volf MB. Chemical approach to glass, glass science and technology, vol. 7. Elsevier, Amsterdam; 1984.
14. Mortier M, Patriarche G. Structural characterisation of transparent oxyfluoride glass-ceramics. J Mater Sci. 2000;35:4849–56.
15. Dantelle G, Mortier M, Vivien D, Patriarche G. Nucleation efficiency of erbium and ytterbium fluorides in transparent oxyfluoride glass-ceramics. J Mater Res. 2005;20(2):472–81.
16. Handke M, Mozgawa W. Vibrational spectroscopy of the amorphous silicates. Vibrat Spect. 1993;5:75–84.
17. Tarte P. Infrared spectra of inorganic aluminates and characteristic vibrational frequencies of AlO_4 tetrahedra and AlO_6 octahedra. Spectrochim Acta. 1967;A23:2127–43.
18. Handke M, Mozgawa W. Model quasi-molecule Si_2O as an approach in the IR spectra description glassy and crystalline framework silicates. J Mol Struct. 1995;348:341–4.