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DTA/DSC STUDY OF NANOCRYSTALLIZATION IN OXYFLUORIDE GLASSES

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Abstract

Crystallization of glasses of the Na_2O–Al_2O_3–SiO_2–LaF_3 system was studied by DTA/DSC, XRD and TEM methods. It has been found that the nanocrystallization of LaF_3 in the NAS-based glass strongly depends on ratio of $Na_2O/(SiO_2+Al_2O_3)$ and amount of doped LaF_3. Analysis of the local atomic interactions in the structure of oxyfluoride glasses has been used to explain the course of the crystallization.

Keywords: glass crystallization, nanoceramics, oxyfluoride glasses, phase transformation

Introduction

Glass-ceramic materials with the size of crystallites smaller than 100 nm (nanocrystallites) are still transparent like glass, and on the other hand, show unique properties. These materials, the so-called ultra-transparent glass-ceramics, can be obtained by way of nanocrystallization of glasses.

Rare earth-doped glasses are of great interest on account of their optical and fluorescence properties. These properties depend on the local environment of the rare earth (RE) ions and on the phonon energies [1, 2].

In silicate glasses, which are attractive because of their high degree of transparency and durability, phonon energy is too high. On the other hand, fluoride glasses are desirable hosts for rare earth ions because they enable emission from RE energy levels and their RE solubility is higher [3]. Unfortunately, fluoride glasses are corrosive, unstable, and not so easily prepared into fibers [4].

The alternative for silicate and fluoride glasses is oxyfluoride glass-ceramics, in which the active RE ion are incorporated into the low phonon energy fluoride crystals that form upon heat treatment.

Oxyfluorides have lower phonon energy than oxide glasses and ZrF_4–BaF_2–LaF_3–AlF_3–NaF (ZBLAN) [5], that is why they are desirable hosts for RE, because they enable emission from RE energy levels that would otherwise be quenched in high-phonon energy glasses. This kind of emission is of interest for fiber amplifiers, up-conversion lasers and etc. Materials, in which the fluoride crystals are

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protected by the oxide glass matrix, can offer mechanical and physical properties of an oxide glass, whereas the optical properties of the active ion are controlled by their fluoride crystals.

The processes of crystallization of rare earth fluorides in oxyfluoride glasses can be observed in the form of a distinct exothermal effect, a little above the glass transition temperature T_g (Fig. 1), whereas, for example, nanocrystallization of $Mg_{76}Ni_{19}V_5$ amorphous alloy takes place just in the beginning of the transformation [6]. This process is often termed ceramming process or ceramization [7].

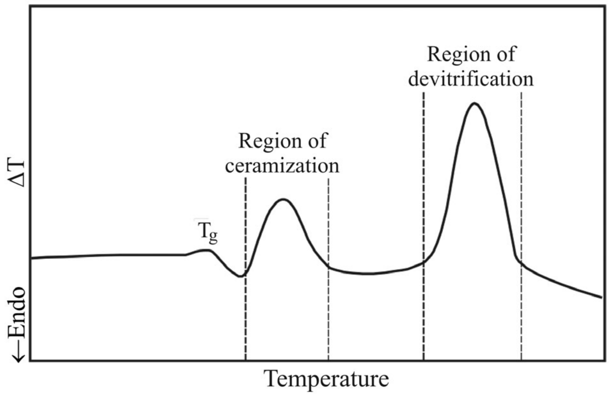

Fig. 1 DTA curve of an oxide glass with nanocrystallization of fluorides

The present study discusses the thermal effects occurring in glass from the SiO_2–Al_2O_3–Na_2O system with LaF_3 admixtures. The effect of the chemical composition of glass on the process of LaF_3 nanocrystallization was investigated.

Experimental

Oxyfluoride glasses have been obtained by melting 20 g batches in platinum crucibles in an electric furnace at the temperature 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 and LaF_3. The compositions of the glasses are listed in Table 1. The ability of the obtained glasses to 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 of ceramization of LaF_3 (ΔH_{cer}) 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 crystal-

Table 1 Composition of the oxyfluoride glasses with LaF_3 admixture

Glass No.	Composition/mol%				Ratio of components		
	SiO_2	Al_2O_3	Na_2O	La_2F_6	Na_2O/Al_2O_3	$Na_2O/(SiO_2+Al_2O_3)$	$La_2F_6/2(Al_2O_3+Na_2O)$
S0	53.29	23.48	21.82	1.42	0.929	0.284	0.016
$S1_{\text{less } SiO_2}$	51.11	26.19	20.22	2.48	0.772	0.262	0.027
S1	56.11	23.75	18.34	2.25	0.772	0.230	0.027
$S1_{\text{more } SiO_2}$	60.60	21.10	16.30	2.00	0.772	0.200	0.027
S2	56.24	24.25	17.10	2.41	0.705	0.213	0.029
$S3_{\text{least } Al_2O_3}$	55.60	21.46	18.50	4.44	0.862	0.240	0.056
$S3_{\text{less } Al_2O_3}$	55.60	21.96	19.00	3.44	0.865	0.245	0.042
S3	56.43	24.77	15.77	3.02	0.637	0.194	0.037
$S3_{\text{more } Al_2O_3}$	55.60	25.75	14.21	4.44	0.552	0.175	0.056
S4	56.61	25.32	14.46	3.62	0.571	0.176	0.046

lization (ΔH_{cryst}) and the values of the thermal stability parameter of glasses ($\Delta T = T_{cryst} - T_g$). Glasses revealing the effect of ceramization were selected for further thermal treatment. To obtain glass-ceramics with nanocrystallization of LaF_3, they were subjected to heating for 5, 10 and 20 min at the temperature of the maximum ceramming effect, respectively. The kind and the size of the formed crystallites were examined by XRD and TEM methods, respectively.

Results

Glasses from the system Na_2O–Al_2O_3–SiO_2 doped with lanthanum fluoride during heating demonstrated, besides the thermal effects characteristic for typical phase 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. Analysis of DTA/DSC curves indicates that the presence of a well visible effect of the glassy state transformation in the examined glasses is closely connected with the exothermic ceramization process (Fig. 2). Generally, the increase of LaF_3 content in glasses from the system Na_2O–Al_2O_3–SiO_2 causes a decrease of the transformation temperature (T_g) to 600°C, whereas the increase of SiO_2 content in the glass at stable ratios of $La_2F_6/2(Al_2O_3+Na_2O)$–(glasses: $S1_{\text{less } SiO_2}$, S1, $S1_{\text{more } SiO_2}$) causes the increase of T_g and the reduction of the specific heat change (ΔC_p) accompanying the glass transition region, which may be evidence of increased strength as well as flexibility of the glass network. Simultaneously, the temperature of the maximum effect of ceramization is shifted towards higher temperatures and its enthalpy (ΔH_{cer}) becomes reduced. This is evidence of a decreasing ability of the glass for ceramization, manifested by increasing value of the index of thermal stability of the glass ΔT (Table 2). In the case

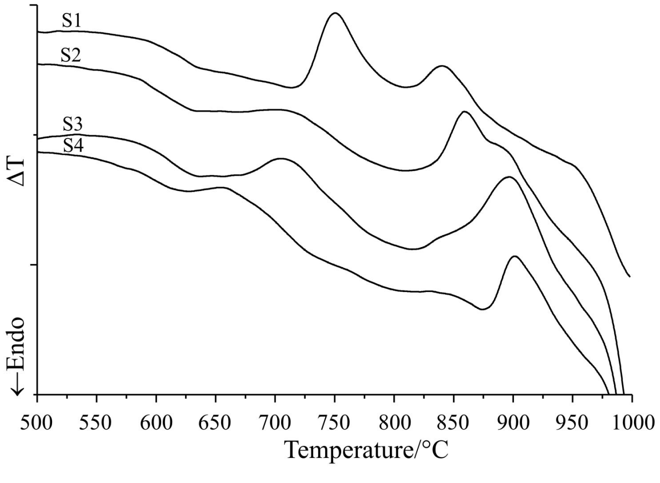

Fig. 2 DTA curves of glasses with ceramization effect

Table 2 Thermal characteristics of oxyfluoride glasses with LaF_3 admixture

Glass No.	T_g/°C	ΔC_p/J g^{-1} °C^{-1}	$T_{max\ cer.}$/°C	$\Delta H_{cer.}$/J g^{-1}	$T_{max\ cryst.}$/°C	$\Delta H_{cryst.}$/J g^{-1}	ΔT=$T_{max\ cer.}$–T_g/°C	Crystallizing phases
S0	627	0.487	–	–	870	43.35	–	sodium lanthanum silicate
$S1_{less\ SiO_2}$	617	0.548	713	53.65	802	12.17	95	LaF_3, sodium lanthanum silicate
S1	619	0.378	751	40.96	843	16.73	138	LaF_3, sodium lanthanum silicate
$S1_{more\ SiO_2}$	622	0.186	–	–	868	23.62	–	sodium lanthanum silicate
S2	609	0.473	719	20.51	861	44.36$^{1)}$	110	LaF_3 sodium lanthanum silicate, nepheline
$S3_{least\ Al_2O_3}$	615	0.5597	738	8.95	832	51.12	123	LaF_3, sodium lanthanum silicate
$S3_{less\ Al_2O_3}$	582	0.651	–	–	858	56.61	–	sodium lanthanum silicate
S3	608	0.726	708	14.15	891	98.87$^{1)}$	100	LaF_3, sodium lanthanum silicate, nepheline
$S3_{more\ Al_2O_3}$	584	1.260	662	37.16	902	67.02	78	LaF_3, nepheline
S4	597	0.431	662	26.71	902	41.93$^{1)}$	65	LaF_3, sodium lanthanum silicate

$T_{max\ cer.}$ – Temperature of maximum ceramization of LaF_3
$T_{max\ cryst.}$ – Temperature of maximum crystallization of aluminosilicate matrix
$^{1)}$double-stage crystallization

of glass containing the highest amount of silica (glass $S1_{\text{more } SiO_2}$) the specific heat change (ΔC_p) accompanying the glass transition attains the smallest value 0.186 J g^{-1} $°C^{-1}$, and the ceramization effect disappears completely (Table 2). This phenomenon is accompanied by the exothermal effect in the range 800–900°C, the maximum temperature of which is shifted towards higher temperatures and the enthalpy of crystallization (ΔH_{cryst}) increases. XRD investigations have shown that the crystallizing phase in this case is $NaLa_9(SiO)_6O_2$.

When Al_2O_3 content increases at the expense of Na_2O (glasses: S1, S2, S3, $S3_{\text{more } Al_2O_3}$) ΔC_p increases from the value 0.378 J g^{-1} $°C^{-1}$ (glass S1) to 1.260 J g^{-1} $°C^{-1}$ (glass $S3_{\text{more } Al_2O_3}$). This corresponds well with the regularities indicated in [8, 9] according to which ΔC_p is the indicator of the increase of configuration entropy caused by increased number of bound broken in the course of the transformation of the glassy state as a result of introducing Al^{3+} into the silicate framework of the glass. This phenomenon is accompanied by the decrease of the temperature of maximum ceramization ($T_{\text{max cer}}$) from the value 750 to 660°C (Table 2). At the same time there can be observed the reduction of the thermal stability parameter ΔT from the value 138°C (glass S1) to 65°C (glass S4). From the conducted investigations it follows that in order to obtain the ceramization effect the LaF_3 content in these glasses should be correlated with the amounts of Al_2O_3 and Na_2O. Increase in the value of $Na_2O/(SiO_2+Al_2O_3)$ ratio causes the decay of ceramization with simultaneous increase of the effect of crystallization ΔH_{cryst} in the temperature range ~850°C and formation of sodium–lanthanum silicate.

In glasses in which the $Na_2O/(SiO_2+Al_2O_3)$ ratio reaches the value <0.2 we can observe a second crystallization peak at the temperature ~900°C. This effect is connected with the host glass crystallization and formation of nepheline ($NaAlSiO_4$). The effect of $NaLa_9(SiO)_6O_2$ crystallization at the temperature ~850°C in this case disappears; simultaneously on the DTA curves the increase of the ceramization effect is observed.

The process of thermal treatment in the range of the ceramization effect results in obtaining the LaF_3 phase with the crystallites size <50 nm, as demonstrated by the results of investigations using the method of transmission electron microscopy (TEM). The volume fraction of the nanocrystal phase may be controlled by the temperature and duration of the thermal treatment as shown in Fig. 3.

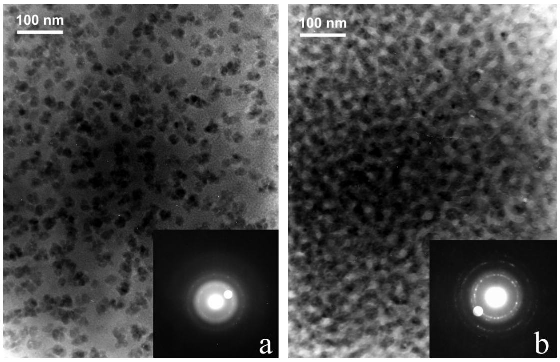

Fig. 3 TEM of S3 glass after a – 5 min and b – 20 min of the heat treatment at the maximum ceramization temperature

Discussion

Aluminium is an essential component of oxyfluoride glasses. It is indispensable if we want to introduce lanthanum in the amount of some mol% into the glass. Silicate glasses not containing aluminium accept in their structure only trace amount of lanthanum. In aluminosilicate glasses, sodium is a component supplementing the shortage of electric charge of tetrahedra $[AlO_4]$ in the framework, caused by the presence in them of the Al^{3+} in place of the Si^{4+}. Therefore they can replace in the framework the silica-oxygen tetrahedra in the accordance with the scheme: $(Na^{+}[Al^{3+}O_4])^{4-}\leftrightarrow[Si^{4+}O_4]^{4-}$.

Lanthanum, similarly as sodium, can participate in supplementing the tetrahedra $[AlO_4]$, although, as it is known from practice, in comparison with Na^+ only a limited amount of La^{3+} can be accepted in the composition of aluminosilicate glasses. It is located in these alumino-oxygen tetrahedra which have not been saturated by Na^+. Thus in the case of Na^+ shortage the amount of La^{3+} fixed with aluminium is increasing. For this reason the ability to crystallization of LaF_3 from the glass is characterized by the ratio $Na_2O/(SiO_2+Al_2O_3)$ as part of sodium can form bonds with SiO_2. Another important indicator is also the ratio Na_2O/Al_2O_3 which defines the degree of saturation of the tetrahedra $[AlO_4]$ by Na^+. Accordingly, the strongest effect of LaF_3 crystallization occurs on the DTA curve of S1 glass, while in the remaining glasses its intensity decreases in the sequence S2, S3, S4 (Fig. 2), i.e. in accordance with the change in the value of this indicator. In the case when lanthanum did not become crystallized as LaF_3 and remained in the glass, then at 850°C $NaLa_9(SiO_6)O_2$ crystallizes, while aluminium together with sodium forms the nepheline $NaAlSiO_4$, which crystallizes at about 950°C. When the amount of Na_2O in the glass is too small, lanthanum is retained by aluminium, LaF_3 crystallization is inhibited and the strongest thermal effect on the DTA curve is that derived from the crystallization of nepheline, similarly as in the S4 glass (Fig. 2). The effect of SiO_2 content on glass crystallization is the result of the increase of glass viscosity accompanying the increase in the amount of silica.

The influence of Al_2O_3 content is coupled with the total content of Na_2O+LaF_3. Reduction of Al_2O_3 content makes LaF_3 crystallization difficult, however, when it is accompanied by sufficiently great increase in the content of Na_2O and LaF_3 there takes place strong crystallization of this fluoride. A simultaneous increase in Al_2O_3, Na_2O and LaF_3 contents cause the crystallization of LaF_3 and its temperature becomes reduced even to 675°C.

The course of the crystallization of oxyfluoride glasses is determined by factors of crystallochemical nature in the particular by interactions between the atoms of the components. On account of the coexistence of two anions O^{2-} and F^- their character is particularly complex. To explain it, there has been carried out the analysis of the cation–anion interactions, expressed by the ionicity of their bonds (*i*) according to Göerlich, which is also a measure of the local chemical affinity of the elements bound with each other in the structure [10].

The ionicity of Na–O bond value is 0.807 and it is definitely greater than that of La–O ionicity (0.627). Thus La affinity to oxygen of the alumino-silicate framework and its combining with this framework is weaker in comparison with sodium [11]. This means also that the tetrahedra [AlO_4] will prefer Na^+ as a cation supplementing their electric charge in comparison with La^{3+}. The latter may saturate the charge of these tetrahedra in the case of sodium shortage, as it can be observed in the examined glasses. The ionicity of the bonds of the glass components with fluorine increases in the sequence Si–F (0.506), Al–F (0.608), La–F (0.678), Na–F (0.833). As sodium forms a bond with the tetrahedra [AlO_4], lanthanum is the next element of the highest affinity to fluorine and it should form a bond with it. The bonding of lanthanum with the alumino-silicate framework of glass proceeds through the oxygen bridge Al–O–La. Assuming as an indicator of the durability of the oxygen bridges in glass, the difference in ionicity of both bonds forming it (Δi), which is a measure of the acid–base interactions [12], it can be seen that the joining Al–O–La is much weaker (Δi=0.081) than Al–O–Na (Δi=0.261). This makes possible the separation of LaF_3 from the glass structure and crystallization as soon as the temperature T_g is exceeded, whereas for the crystallization of phases composed of the components of the alumino-silicate oxide framework, higher temperatures are needed.

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