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Nanocrystallization of LaF_3 in oxyfluoride glass

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Crystallization of LaF_3 in glasses from the SiO_2–Al_2O_3–Na_2O–LaF_3 system has been investigated. The structure of this compound makes it a good host for the rare earths. It has been found that the range of chemical compositions of glasses from which ultra-transparent glass-ceramics with LaF_3 nanocrystallites can be obtained is very limited. It is determined by crystalochemical factors, in particular by the position of Al and La in the glass structure. The optical proportions between Al_2O_3, Na_2O and LaF_3, leading to the effect of nanocrystallization of this fluoride, as well as the temperature and time of ceramization, have been determined. If these proportions are not maintained, the undesirable crystals of nepheline ($NaAlSiO_4$) and $LaAl_2O_3$ are formed. It has been found that the crystallization of LaF_3 is essentially affected by the kind of the compounds used to introduce La and F into the glass. In the obtained material the dimensions of LaF_3 crystallites varied from 20 to 100 nm.

Keywords: nanocrystallization, oxyfluoride glasses, nanotechnology.

1. Introduction

The fundamental problem with glass-ceramic systems is that optical scattering is much too large, even for devices with short (few centimeters) optical paths. In the 90s of XX century, a new kind of material – the so-called ultra-transparent glass-ceramics – has been developed for fotonic application [1], [2]. It can be obtained by crystallization of oxyfluoride glasses. Such glass-ceramics contains 10–30 vol% of Pb-, Zn-, Y- or La-fluorides in aluminosilicate glassy matrix. Glass-ceramic materials containing such fluorides demonstrate luminescence of a considerable quantum effectiveness at 1.3 μm [3]. Thus, they combine the advantages of optical glasses (low scattering losses, chemical resistivity, formability) with the spectroscopic properties of the crystals of fluorides doped with the rare earths [4].

In the paper preliminary investigations on the possibility of obtaining LaF_3 nanocrystallites in glasses from the Na_2O–Al_2O_3–SiO_2–LaF_3 system have been presented.

2. Experimental

Oxyfluoride glasses have been obtained by melting of the 25 g batches in platinum crucibles in an electric furnace at the temperature of 1450 °C in air atmosphere. The melts were poured out onto a steel plate forming a layer about 2 to 5 mm thick. The obtained glasses were annealed.

The following raw materials were used to prepare the batches: SiO_2, Al_2O_3, Na_2CO_3, NaF, Na_3AlF_6, La_2O_3 and LaF_3. In all the melted glasses a constant amount of SiO_2 equal to 55.6 mol% was maintained. The compositions of the glasses are listed in the Table.

T a b l e. Composition of the glasses obtained from the SiO_2–Al_2O_3–Na_2O–LaF_3 system.

	Composition [mol%]			
Glass No.	SiO_2	Al_2O_3	Na_2O	La_2F_6
0	55.60	31.08	13.32	—
1	55.60	25.75	17.32	1.33
2	55.60	22.64	18.28	3.48
3	55.60	21.31	17.21	3.28
4	55.60	23.98	17.76	2.66
5	55.60	21.75	17.32	5.33
6	55.60	25.75	13.32	5.33
7	55.60	23.98	13.32	7.10
8	55.60	27.53	12.43	4.44
9	55.60	26.64	10.66	7.10

The ability of the obtained glasses to crystallize was determined by DTA investigations conducted on the derivatograph C MON, Budapest. The samples were heated in platinum crucibles at the rate 10 °C/min in air atmosphere to the temperature of 1000 °C. Glasses revealing the effect of ceramization (glasses No. 4 and 7) have been selected for further thermal treatment. They were subjected to heating for 17, 2 hrs and 20 min at the temperature of 750 °C in the case of glass No. 4 and at 690 °C for glass No. 7. The kind and the size of the formed crystallites were examined using the XRD and TEM methods, respectively.

3. Results and discussion

The effect of glass composition on the tendency to ceramization process is shown in Fig. 1. In order to obtain LaF_3 nanocrystallization, the LaF_3 and Na_2O contents must be carefully balanced with the Al_2O_3 content. Spontaneous LaF_3 crystallization occurs when the content of LaF_3 in glass increases. On the other hand, in Al_2O_3-rich glasses with deficiency of LaF_3 the effect of ceramization disappears and stable glass is

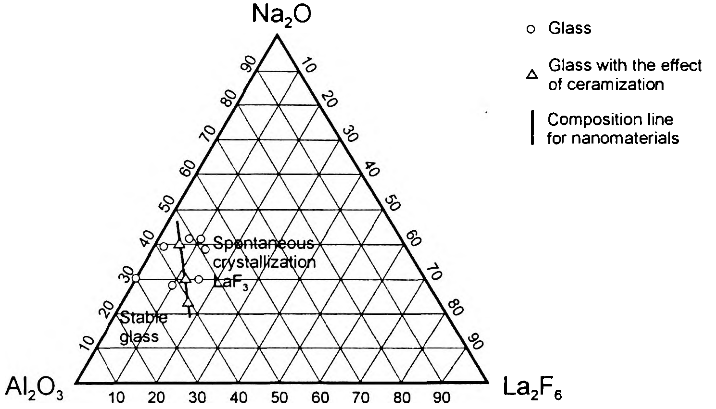

Fig. 1. Effect of glass composition on the tendency to ceramization process for glasses with 55.6 mol% SiO_2.

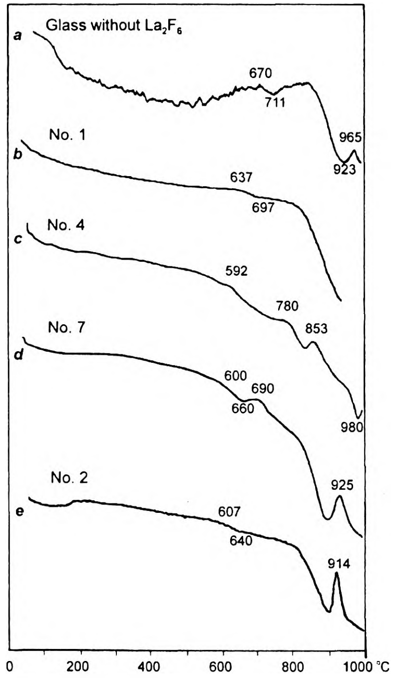

Fig. 2. DTA curves.

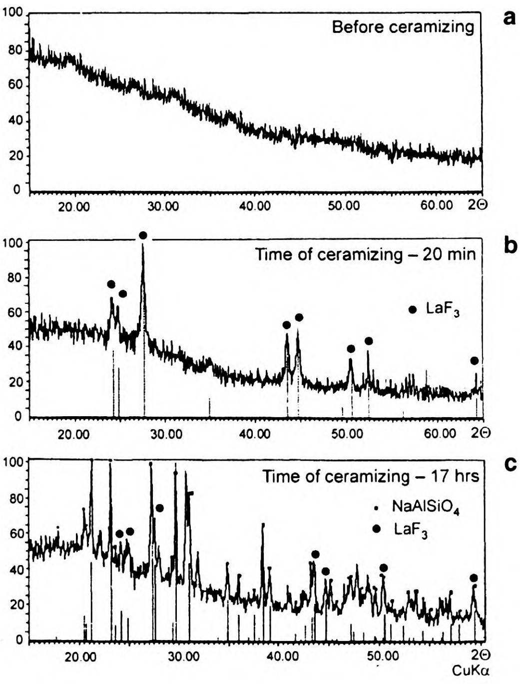

Fig. 3. XRD – glass No. 4.

obtained. It seems that glass-ceramics with nanocrystals can be produced only from glasses of the compositions shown along the solid line marked in Fig. 1.

Comparing the DTA curves (Fig. 2) of the parent glass (without lanthanum fluoride – glass No. 0) with the curves of glasses with LaF_3 addition, one can observe that the introduction of LaF_3 is responsible for the reduction of the transformation temperature and the softening point of the glass. Figure 2 shows the DTA curves for glasses with their chemical composition taken from the region of stable glass (Fig. 2, curve *b*), laying on the nanocrystalline line (Fig. 2, curves *c*, *d*), and taken from the region of spontaneous crystallization (Fig. 2, curve *e*). The effect of ceramization connected with nanocrystallization can be observed for glasses No. 4 and 7 as a rather small exothermic peak at the temperatures of 690 °C and 780 °C, respectively.

The X-ray diffraction (XRD) investigations of a sample of glass No. 4 after the DTA analysis have revealed crystallization of 3 phases: the expected LaF_3 phase and additional $NaAlSiO_4$ and $LaAlO_3$ phases.

In the case of glass No. 4 heated for 17 hrs the formation of LaF_3 and $NaAlSiO_4$ phases was observed (Fig. 3**c**). The presence of the second phase is not desired, as it causes the loss of transparency. Shortening of the heating time to 2 hrs resulted in the reduction of the contribution of the nepheline phase. In a sample in which the ceramization process lasted solely for 20 min, only the presence of LaF_3 was observed (Fig. 3**b**).

In the case of glass No. 7, for all heating times, LaF_3 was the only crystallizing phase. Here, only the increase in the intensity of reflexes with the prolongation of the

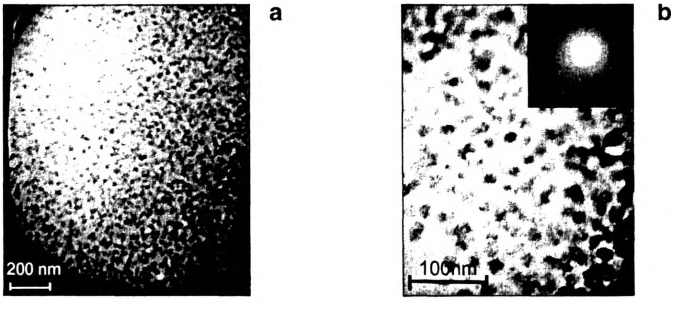

Fig. 4. TEM – glass No. 4 after 20 min ceramization.

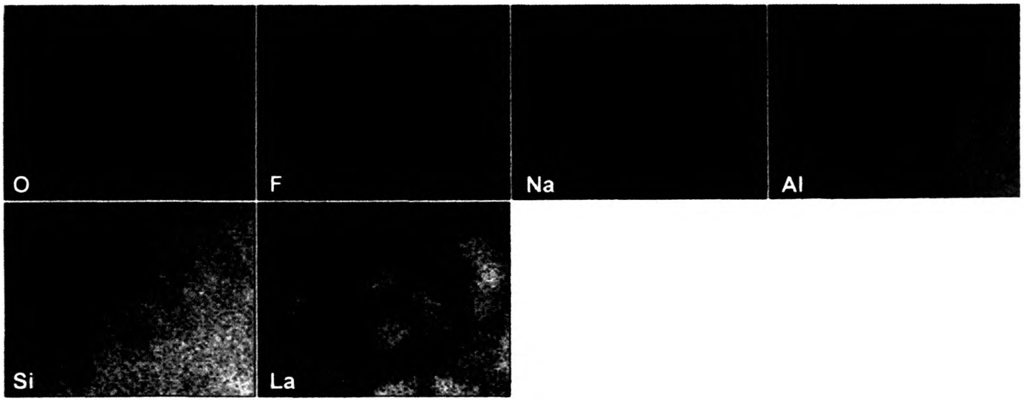

Fig. 5. Mapping – glass No. 4 after 20 min ceramization.

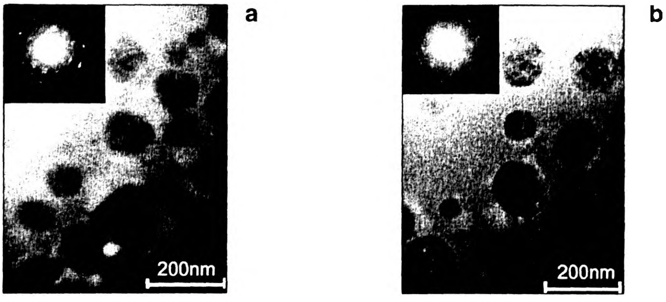

Fig. 6. TEM – glass No. 7 after 17 hrs ceramization.

time of termal treatment has been observed. Thus, it can be stated that in the case of this glass it is possible to control the size of the nanocrystallites that are being formed by controlling the time of the ceramization process.

Figure 4 shows the photographs of the nanostructure of sample No. 4 after 20 min of treatment at the temperature of 750 °C. There can be observed clearly visible, numerous crystallites, uniformly distributed in the glassy matrix, with their size not exceeding 50 nm. Mapping of this material has revealed that these crystallites show an increased concentration of fluoride and lanthanum atoms (Fig. 5). This observation is in agreement with the XRD results. Figure 6 shows the TEM investigations for the sample No. 7 subjected to the process of ceramization for 17 hrs. In this material the crystallites are greater, and their size varies from 50 to 100 nm.

4. Conclusions

The obtained results of our investigations allowed to conclude the following:

1. Glass-ceramic material with the size of LaF_3 crystallites smaller than 100 nm can be obtained in the system of oxyfluoride glasses Na_2O–Al_2O_3–SiO_2–LaF_3. To obtain this kind of material, however, it is necessary to select accurately the proportions of the particular components of the glasses whose compositions should lay along the solid line marked in Fig. 1.

2. The optimal temperature of the process of ceramization is 680–750 °C, depending on the amount of LaF_3 added.

3. To obtain LaF_3 crystallites with dimensions smaller than 50 nm, the time of the ceramization process should not be longer than 20–30 min.

4. For parameters different from those specified in above three items the additional crystalline phases $NaAlSiO_4$ and $LaAl_2O_3$ are formed.

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