Multinuclear MAS NMR study of structural changes in LaF$_3$ doped borosilicate glasses for optoelectronics

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A new type of oxyfluoride glass-ceramics based on the silicate glassy matrix and the nano-phase of LaF$_3$ was developed for generating the up-conversion luminescence processes. In such material, the low-phonon energy crystals of LaF$_3$ are desirable host for the rare-earth elements. The effect of admixture of 3 mol% of La$_2$F$_6$ on the structural changes of glasses in the Na$_2$O–B$_2$O$_3$–SiO$_2$ system was investigated. The effect of LaF$_3$ additive was studied using ^{29}Si, ^{11}B, and ^{23}Na MAS NMR to learn more about the structural role of modifiers as well as fluorine in the glassy matrix. Glasses with compositions corresponding to different B$_2$O$_3$/Na$_2$O and B$_2$O$_3$/(Na$_2$O + 3La$_2$F$_6$) ratios in the 0.6–1.2 range were obtained by melt quenching. The ^{29}Si MAS NMR spectra indicated that the [SiO$_4$] units are more polymerized when the ratios and the fluorine admixture increase. The ^{11}B NMR spectra revealed the presence of both [BO$_4$] (Q^4) and [BO$_3$] (Q^3) units. The fraction of Q^3 increased with the decreasing sodium content. Glasses with the LaF$_3$ additive showed higher BO$_3$/BO$_4$ ratios. The effect of thermal treatment for glasses with the tendency towards LaF$_3$ crystallization was discussed in terms of structural changes.

Keywords: oxyfluoride glass, borosilicate glass, glass structure, MAS NMR, LaF$_3$.

1. Introduction

Borosilicate glasses are commercially used because of their good chemical and mechanical resistance [1]. They are also easy to fiberize (E-glass). The glasses have rather low refractive index and their phonon energy is high ($\sim$1300 cm^{-1}). Contrary to fluoride glasses, the low energy gaps between the excited states of lantanides and the phonon energy of the borosilicate matrix eliminate luminescence from higher energy levels. Thus, this hammers their application in optoelectronics. In order to

eliminate the above disadvantage, a nanocrystallization of low phonon energy phase could be induced in the borosilicate glass. Nanocrystals of LaF_3 immersed in the oxide glassy matrix could play a role of such phase. It has already been observed in aluminosilicate glasses [2–5]. Moreover, LaF_3 has good solubility of the rare earth (RE) ions in its structure without clustering.

The aim of the study was to determine changes in the framework of borosilicate glass caused by introduction of LaF_3. Furthermore, by changing the Na_2O content, the relation between the structure and the ability of LaF_3 phase to crystallize was also studied.

2. Experiments

Ten samples of glass, with the constant content of 15 mol% B_2O_3, were prepared in two series. The glass compositions are listed in the Table. The first series contained borosilicate glasses without admixture of LaF_3. The ratio of B_2O_3/Na_2O was varied from 0.6 to 1.4. The second series was melted with the addition of 3 mol% of La_2F_6, and the ratio $B_2O_3/(Na_2O + 3La_2F_6)$ was kept in the same range.

Batches were prepared by mixing appropriate quantities of chemically pure reagents: SiO_2, H_3BO_3, Na_2CO_3 and LaF_3. Glasses were obtained by melting 20 g batches in a covered platinum crucible in an electric furnace at a temperature of 1300 °C in the air atmosphere. Each molten glass was poured out onto a stainless plate forming a layer of *ca*. 3 mm in thickness.

The ability of the obtained glasses to crystallize was determined by DTA/DSC measurements conducted on the Perkin Elmer DTA-7 system operating in the heat flux DSC mode. The samples of 60 mg in weight were heated in platinum crucibles

T a b l e. Composition of borosilicate glasses prepared.

| | Glass | Ratio | | Composition [mol%] | | | |
		B_2O_3/Na_2O	$B_2O_3/(Na_2O + 3La_2F_6)$	SiO_2	B_2O_3	Na_2O	La_2F_6
Series I	$0.6\_B_2O_3$	0.6	—	60	15	25.0	—
	$0.8\_B_2O_3$	0.8	—	66.25	15	18.75	—
	$1.0\_B_2O_3$	1.0	—	70	15	15	—
	$1.2\_B_2O_3$	1.2	—	72.5	15	12.5	—
	$1.4\_B_2O_3$	1.4	—	74.29	15	10.71	—
Series II	$0.6\_B_2O_3\_LaF_3$	—	0.6	66	15	16	3.0
	$0.8\_B_2O_3\_LaF_3$	—	0.8	72.25	15	9.75	3.0
	$1.0\_B_2O_3\_LaF_3$	—	1.0	76	15	6	3.0
	$1.2\_B_2O_3\_LaF_3$	—	1.2	78.5	15	3.5	3.0
	$1.4\_B_2O_3\_LaF_3$	—	1.4	80.29	15	1.71	3.0

at the rate of $10\,°C\,min^{-1}$ in the dry nitrogen atmosphere up to $1000\,°C$. The kind of the crystallites formed was examined by XRD (Philips X'Pert Diffractometer).

High resolution, solid-state MAS NMR spectra were measured on the 7.05 Tesla/ 89 mm Magnex superconducting magnet, using the Bruker HP-WB MAS probe and the APOLLO pulse NMR spectrometer. A 4 mm diameter zirconia rotor equipped with the KEL-F turbine was filled with the powder sample and spinned under magic angle with the frequency ranging from 4 to 9 kHz. A free induction decay signal was recorded after application of a single, $2\,\mu s$ radio-frequency pulse, using sufficient power to excite all resonant nuclei in the sample.

The ^{29}Si MAS NMR spectra were measured at the resonance frequency of 59.517 MHz and 4 kHz spinning speed. The number of accumulations was equal to 128 and the repetition time 50 s. The ppm scale was referenced to the liquid sample of TMS (tetra-methyl-silane).

The ^{11}B MAS NMR spectra were measured at the resonance frequency of 96.119 MHz and 7 kHz spinning speed. The number of accumulations was equal to 128, and the repetition time 1 s. The ppm scale was determined by using 1 M solution of H_3BO_3.

The ^{23}Na MAS NMR spectra were measured at the resonance frequency of 79.250 MHz and 9 kHz spinning speed. The number of accumulations was equal to 256, and the repetition time 1 s. The ppm scale was referenced to 1 M solution of NaCl.

3. Results and discussion

3.1. Thermal stability

Glasses from the system Na_2O–B_2O_3–SiO_2 with the ratio B_2O_3/Na_2O ranging from 0.6 to 1.4 were transparent and no opalescence was observed. The glasses demonstrated high thermal stability without any crystallization effects visible on the DTA curves (Fig. 1). Some small exothermal effects in the range 700–750 °C are related to the change of heat capacity caused by sintering of the powder sample [6]. The XRD
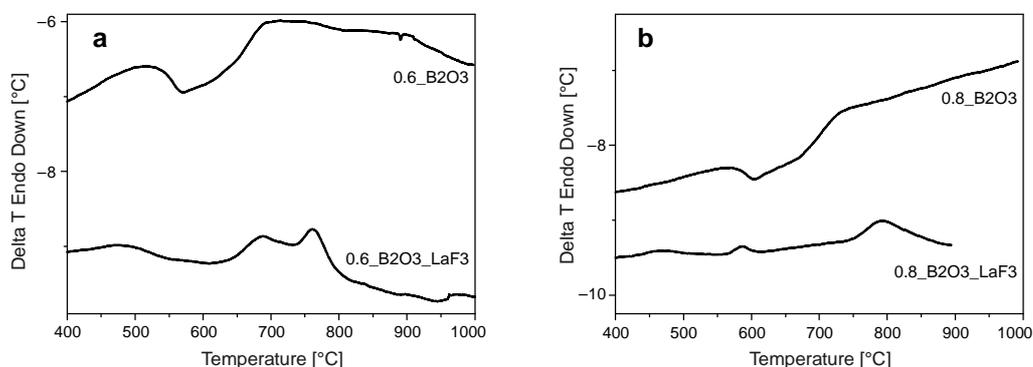

Fig. 1. Examples of DTA curves of 0.6 (**a**) and 0.8 (**b**) glasses of series I and II.

investigation of glasses heated in this range of temperature has not revealed any crystal phases. The introduction of LaF_3 into the glass changed its thermal stability considerably. At the ratio $B_2O_3/(Na_2O + 3La_2F_6) \geq 1$ an increased tendency of the glass to phase separation was observed. It was manifested by the reduction of transparency while the amorphous character of the sample was preserved.

Two peaks were visible on the DTA curve of the 0.6_B_2O_3_LaF_3 glass, with the maxima at 686 °C and 765 °C (Fig. 1**a**). The XRD analysis identified the crystallization products as LaOF and LaF_3, respectively.

In the case of 0.8_B_2O_3_LaF_3 sample (Fig. 1**b**), the transformation temperature (485 °C) and the effect of ceramization (590 °C) were clearly visible. X-ray examinations confirmed the formation of lanthanum fluoride in the range 550–600 °C. Simultaneously, the second effect of the crystallization of $La(BSiO_5)$ was detected at higher temperature. The thermal stability of these glasses was discussed in detail elsewhere [7].

3.2. MAS NMR

Figures 2**a** and 2**b** show ^{29}Si MAS NMR spectra of the glasses with (series I) and without LaF_3 (series II), respectively. Two overlapping peaks in the range from –80 to –120 ppm are observed, indicating that there are mainly two types of SiO_4 structural units: Q^3 (Si connected to three bridging oxygens (BO) and one non-bridging oxygen (NBO)) and Q^4 (having four BOs). According to literature, the peaks for Q^3 and Q^4 in borosilicate glasses should be in the ranges from –85 to –95 ppm, and from –102 to –115 ppm, respectively [8]. The deconvolution of the spectra of the series I gives the position of the peaks at –90 ppm for Q^3 and –104 ppm for Q^4 units. For glasses
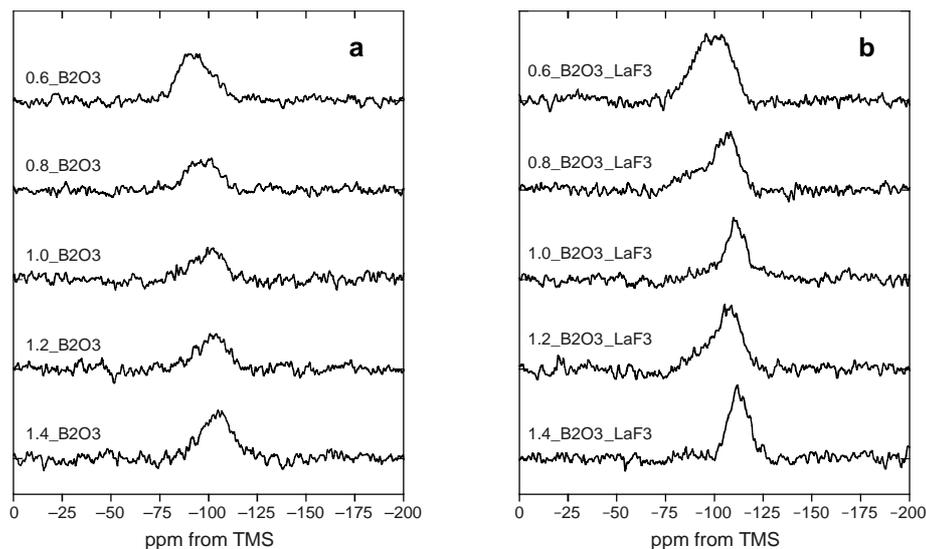

Fig. 2. ^{29}Si MAS NMR spectra of series I (**a**) and series II (**b**) glasses.
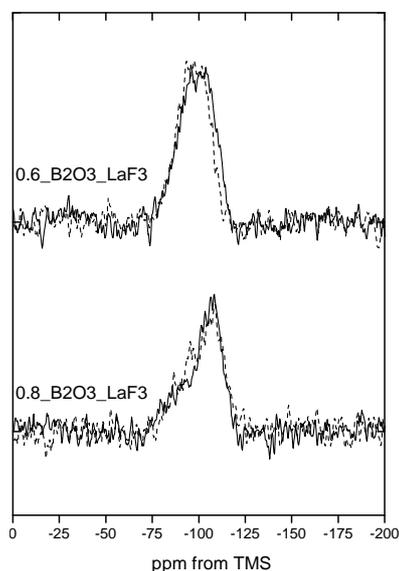
Fig. 3. Normalized ^{29}Si MAS NMR spectra of 0.6 and 0.8 glasses of series II. Solid and dashed lines correspond to samples before and after thermal treatment, respectively.

with the lower B_2O_3/Na_2O ratio, the Si atoms are located mainly in the Q^3 species (for the ratio value 0.6, $Q^3 = 72\%$ and $Q^4 = 28\%$). A decrease of Na_2O content increases the intensity of the Q^4 peak, which indicates the polymerization of the silica network.

The introduction of LaF_3 to the glass (series II) moves the ^{29}Si MAS NMR spectrum towards the more negative values of the chemical shift and the peak at -110 ppm becomes dominant. This effect can be caused by the phase separation process that occurs at higher values of the $B_2O_3/(Na_2O + 3La_2F_6)$ ratio. It is in agreement with the FTIR results obtained for those materials that were reported elsewhere [9].

The process of thermal treatment leading to the LaF_3 formation in the glassy matrix does not induce a significant change in the surroundings of silicon ions (Fig. 3).

Figure 4 shows the ^{11}B MAS NMR spectra collected for both series of glasses. The observed peaks corresponding to the BO_3 and BO_4 groups overlap. In ^{11}B MAS NMR spectra, a symmetric sharp peak is attributed to Q^4 in BO_4 tetrahedra, and the asymmetric broad peak is assigned to Q^3 in the trigonal BO_3 units [10].

A symmetric peak at about -20 ppm, which corresponds to BO_4 groups, dominates on the ^{11}B MAS NMR spectrum for the series I (glasses without LaF_3). An increase of the B_2O_3/Na_2O ratio does not cause any changes in the borate network. The deconvolution of the spectra gives the contribution of the Q^4 groups equal to 85% for the $0.6\_B_2O_3$ sample, which only slightly decreases to 81% for $1.4\_B_2O_3$.

The introduction of LaF_3 causes a significant growth of the broad, asymmetric line intensity in the range from -10 ppm to -40 ppm, which corresponds to BO_3 groups (for the $1.0\_B_2O_3\_LaF_3$ sample $Q^3/Q^4 = 1$). The addition of LaF_3 increases the tendency

towards separation of silica and borate phases, which results in the immiscibility process occurring when the ratio $B_2O_3/(Na_2O + 3La_2F_6) \geq 1$.

The process of thermal treatment leads to a small relative decrease of the asymmetric line as a result of decreased contribution of BO_3 units in the glass framework (Fig. 5).

Figure 6 shows the ^{23}Na MAS NMR spectra of the 0.6 and $0.8\_B_2O_3\_LaF_3$ glasses before and after thermal treatment. The ^{23}Na chemical shift can be correlated
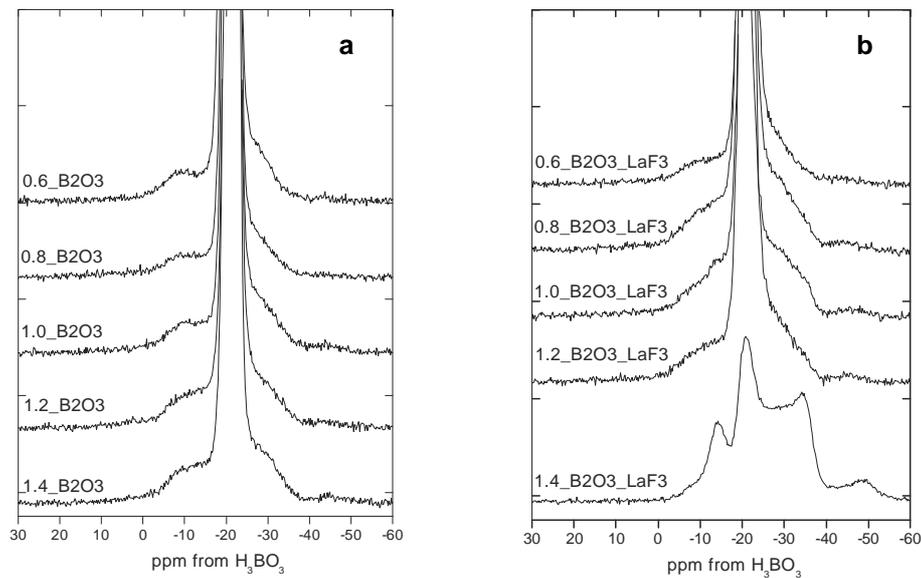

Fig. 4. ^{11}B MAS NMR spectra of series I (**a**) and series II (**b**) glasses.
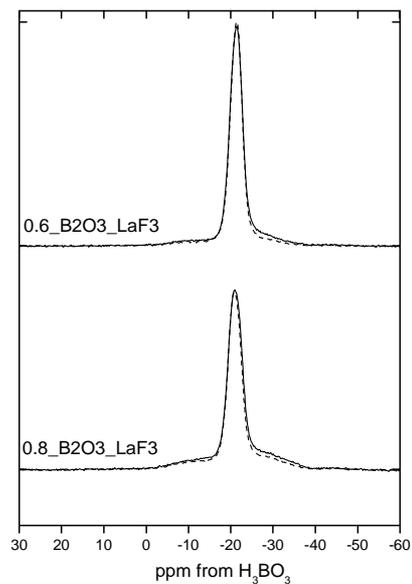

Fig. 5. Normalized ^{11}B MAS NMR spectra of 0.6 and 0.8 glasses of series II. Solid and dashed lines correspond to samples before and after thermal treatment, respectively.
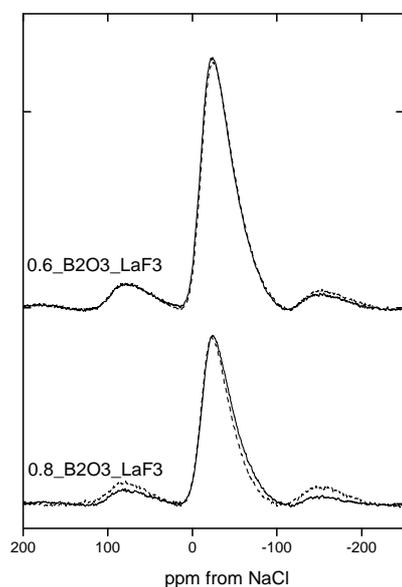
Fig. 6. Normalized ^{23}Na MAS NMR spectra of 0.6 and 0.8 glasses of series II. Solid and dashed lines correspond to samples before and after thermal treatment, respectively.

to the sodium oxygen distance [11]. It was shown by AGELI *et al.* [12] that the Na−O bond is longer when sodium acts as a charge compensating ion for BO_4 tetrahedra, as compared to the non-bridging oxygen bond (Si–O…Na) in the silicate network. No significant change in the line position or shape is observed after the annealing of the glasses. This indicates that the surroundings of Na^+ ions do not change.

4. Conclusions

The effect of LaF_3 introduction to borosilicate glass for different Na_2O contents was investigated by DTA and ^{29}Si, ^{11}B and ^{23}Na MAS NMR. Incorporation of LaF_3 into the glass matrix modifies its structure and thermal stability. It lowers the melting and the glass transition temperatures. The MAS NMR spectra showed an increased contribution of BO_3 units. Simultaneously, the polymerization of silica network was observed. It indicates that LaF_3 enhances the tendency towards phase separation in borosilicate glass.

The process of the thermal treatment producing nanocrystallization of lanthanum fluorine induced no change in the surroundings of Na^+ ions.

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