

EFFECT OF LaF₃ ADMIXTURE ON THERMAL STABILITY OF BOROSILICATE GLASSES

M. Środa*

AGH – University of Science and Technology, Faculty of Materials Science and Ceramics, A. Mickiewicza 30, 30-059 Cracow, Poland

Oxyfluoride glass-ceramics based on the aluminosilicate glass-matrix with the nano-phase of fluoride is an interesting material for optoelectronics. A new glass from the SiO₂–B₂O₃–Na₂O–LaF₃ system in which nanocrystallization of LaF₃ could be obtained as well is presented.

Thermal stability of glass and the crystalline phases formed upon heat treatment were determined by DTA/DSC and XRD methods, respectively. The effect of the glass composition on thermal stability was investigated by the SEM method.

It has been found that the addition of LaF₃ increases the tendency to decomposition of the borosilicate glass. In glasses with the ratio B₂O₃/(Na₂O+3La₂F₆) < 1 it is possible to obtain the immersed crystallization of LaF₃ in transparent glassy matrix. The process is preceded by LaOF formation. Glasses with the composition B₂O₃/(Na₂O+3La₂F₆) ≥ 1 revealed the tendency to La(BSiO₅) crystallization.

Keywords: borosilicate glass, lanthanum fluoride, oxyfluoride glass, thermal analysis

Introduction

Oxyfluoride glass ceramics based on the aluminosilicate glass-matrix has been developed since it was first reported in 1993 [1]. In this material, the low phonon energy lanthanum fluoride phase could be immersed in oxide glassy matrix by appropriate thermal treatment in low range of the composition [2, 3]. Because rare earth ions can selectively concentrate into fluoride crystals, the glass ceramics can offer excellent optical properties. As long as the crystals of LaF₃ do not exceed 100 nm in size, the material remains transparent and gives intensive upconversion luminescence [4].

Borosilicate glasses are commonly used as fibers, chemically and mechanically resistant containers as well as for encapsulation of radioactive wastes [5]. In recent years, glasses with B₂O₃ as a component have been investigated in searching materials with new optical properties [6, 7]. On account of the lower melting temperatures and easy formation of fibres these glasses might be an interesting material for optoelectronics; unfortunately, they have high phonon energy ~1300 cm⁻¹. Inducing in the borosilicate glasses the phenomenon of nanocrystallization of low phonon energy phase could eliminate the above disadvantage. Hence in the present study the glass compositions have been designed so as to make it possible to define the effect of the charge of the modifier ions on the thermal stability and the ability to crystallization. Two ratios B₂O₃/Na₂O for the model

glasses without LaF₃ and B₂O₃/(Na₂O+3La₂F₆) for LaF₃ doped glasses have been accepted.

Experimental

Twelve glasses, with the constant content of 15 mol% B₂O₃, were prepared in two series. The glass compositions are listed in Table 1. The first series contains borosilicate glasses without admixture of LaF₃. The ratio of B₂O₃/Na₂O has been varied from 0.4 to 1.4. The second one was melted with 3 mol% of La₂F₆ and the ratio B₂O₃/(Na₂O+3La₂F₆) has taken the same values.

Batches were prepared by mixing appropriate quantities of chemically pure reagents: SiO₂, H₃BO₃, Na₂CO₃ and LaF₃. Glasses have been obtained by melting 20 g batches in a covered platinum crucible in an electric furnace at the temperature 1300°C in air atmosphere. Each molten glass was poured out onto a stainless plate forming a layer of ca. 3 mm thickness.

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 of 60 mg in mass were heated in platinum crucibles at a rate of 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 and the enthalpy of

* msroda@agh.edu.pl

Table 1 Composition of prepared borosilicate glasses

Glass	Ratio		Composition/mol%				
	B ₂ O ₃ /Na ₂ O	B ₂ O ₃ /(Na ₂ O+3La ₂ F ₆)	SiO ₂	B ₂ O ₃	Na ₂ O	La ₂ F ₆	
Series I	0.4B ₂ O ₃	0.4	–	47.5	37.5	–	
	0.6B ₂ O ₃	0.6	–	60	25.0	–	
	0.8B ₂ O ₃	0.8	–	66.25	18.75	–	
	1.0B ₂ O ₃	1.0	–	70	15	–	
	1.2B ₂ O ₃	1.2	–	72.5	12.5	–	
	1.4B ₂ O ₃	1.4	–	74.29	10.71	–	
Series II	0.4B ₂ O ₃ ·LaF ₃	–	0.4	53.5	15	28.5	3.0
	0.6B ₂ O ₃ ·LaF ₃	–	0.6	66	16	16	3.0
	0.8B ₂ O ₃ ·LaF ₃	–	0.8	72.25	9.75	16	3.0
	1.0B ₂ O ₃ ·LaF ₃	–	1.0	76	6	16	3.0
	1.2B ₂ O ₃ ·LaF ₃	–	1.2	78.5	3.5	16	3.0
	1.4B ₂ O ₃ ·LaF ₃	–	1.4	80.29	1.71	16	3.0

ceramization (ΔH_{cryst}) of the 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 ($\Delta T = T_{\text{cryst}} - T_g$). Glasses revealing the effect of crystallization were selected for further thermal treatment.

The kind and the size of the formed crystallites were examined by XRD in the range 10–70° 2θ (Philips X'Pert Diffractometer) and SEM (FEI Nova200 NanoSEM) methods.

Results and discussion

Thermal stability

Glasses from the system Na₂O–B₂O₃–SiO₂ with the ratio B₂O₃/Na₂O from 0.4 to 1.4 were transparent and no opalescence was observed. The glasses demonstrated high thermal stability without effects of crystallisation on DTA curves (Fig. 1). Some small exothermal effects in the range 700–750°C are connected with the change of heat capacity caused by sintering of the powder sample [8]. The performed XRD investigations of glasses heated in this range of temperature have not revealed formation of the crystal phases. Glasses of the series I were characterized by the transformation temperature (T_g) in the range 550–600°C, and this temperature was lower for glasses with higher Na₂O: glasses 0.4B₂O₃ and 0.6B₂O₃ (Table 2).

Introduction of LaF₃ into the glass considerably changed its thermal stability. With increasing ratio B₂O₃/(Na₂O+3La₂F₆) increased tendency of the glass

for phase separation was observed. It was manifested by the reduction of transparency while the amorphous character of the sample was preserved, which was confirmed by XRD examination.

Addition of 6 mol% LaF₃ to the borosilicate glass (series II) resulted in lowering the transformation temperature (Fig. 1, Table 2). The greatest decrease of T_g was observed in glasses with the ratio B₂O₃/(Na₂O+3La₂F₆) equal to 0.8. The change of this ratio in both directions resulted in the reduction of the difference in T_g between the glasses of both series. Simultaneously, glasses with LaF₃ additions demonstrated increased ability for crystallization. In the case of the glass 0.4B₂O₃·LaF₃ the observed exothermal effect at 640°C was rather small, whereas on the DTA curve of the 0.6B₂O₃·LaF₃ glass two peaks were visible, with the maxima at 686 and 765°C. The performed XRD analysis has shown that the crystallization products were LaOF and LaF₃, respectively.

In the case of 0.8B₂O₃·LaF₃ sample, on the DTA curves near the transformation temperature, the effect of ceramization was clearly visible. X-ray examinations have confirmed the formation of lanthanum fluoride in the range 500–600°C. Simultaneously, the second effect of the crystallization of La(BSiO₅) was shifted towards higher temperatures.

Attaining the value 1.0 of the ratio B₂O₃/(Na₂O+3La₂F₆) resulted in the increase of the maximum temperature of LaF₃ formation and reduction of the crystallization temperature of La(BSiO₅). It is induced by the strong influence of phase separation in this glass. A distinct crystallization peak with the maximum at about 700°C characterized the glass 1.2B₂O₃·LaF₃. Formation in this temperature range of La(BSiO₅) phase was noticed. In the range 600–650°C a rather

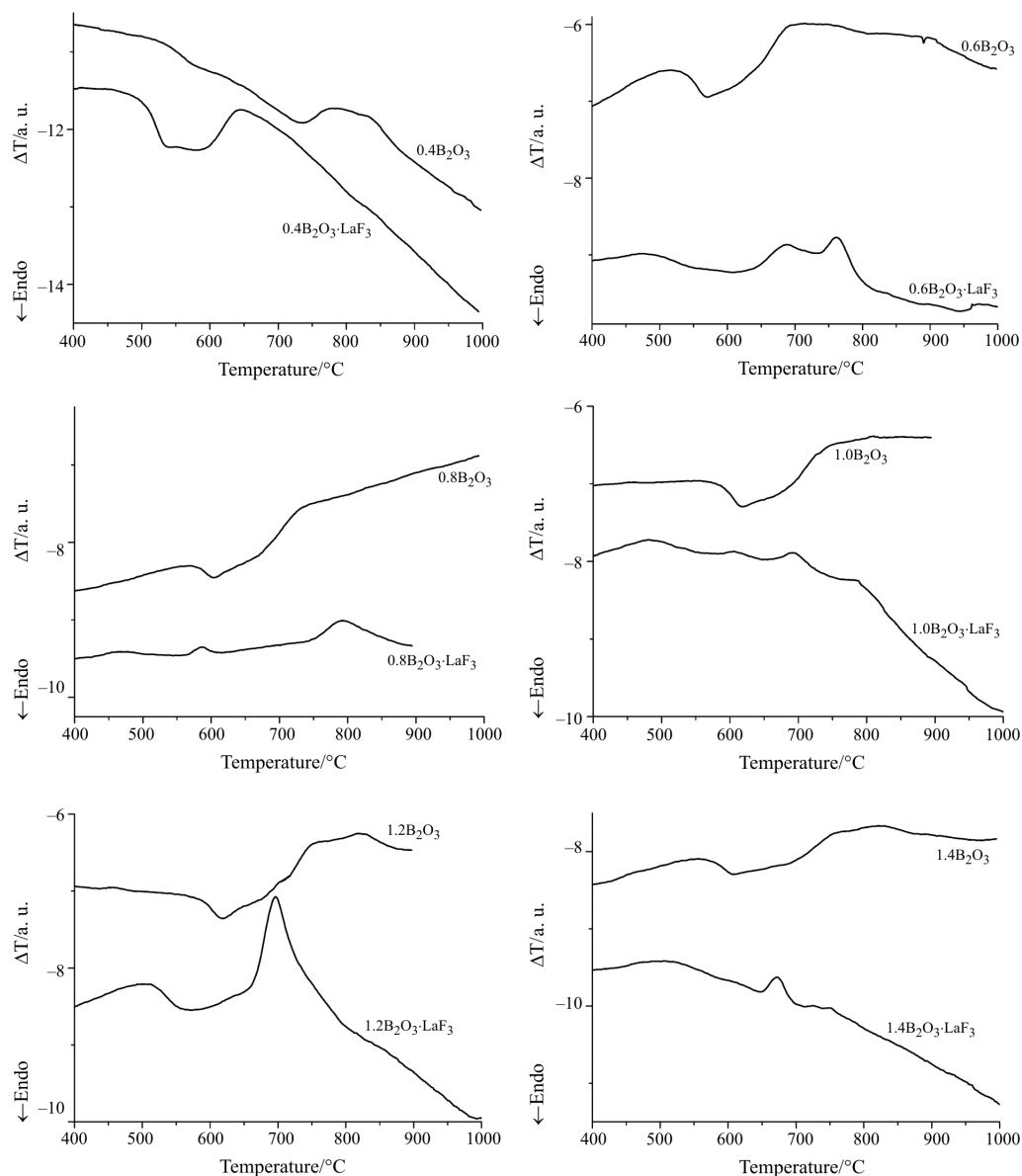


Fig. 1 DTA curves of series I (without LaF₃) and series II (LaF₃-doped) of borosilicate glasses

small effect of LaF₃ formation, partly masked by the main crystallization was also observed.

In the case of glass with the highest ratio $B_2O_3/(Na_2O+3La_2F_6)=1.4$ this effect is hardly visible because of strong phase separation. Thus, crystallization peak La(BSiO₅) is considerably reduced, whereas in the range 700–750°C there appears a successive small effect of crystalbite crystallization.

The Δc_p changes at transformation temperature as a function of the amount of the modifiers, although identical in both series of the glasses, are not linear. This is evidence of changes in the glass framework connected with the change within the borate groups, which can take various forms, e.g. tetraborate, diborate, pentaborate or even metaborate groups [9]. This causes a change in the properties of these

glasses, called boron anomaly [10]. The greatest Δc_p changes at T_g have been found in glasses with the highest amount of modifiers. It results from the fact that Δc_p , as the indicator of configuration entropy, is sensitive to the increase of the number of broken bonds within the range of transformation of the glassy state. Simultaneously, its higher value is evidence of lower flexibility of the glass framework. Reduction of the adopted ratio to 0.8 causes the reduction of Δc_p . However, for the glasses 1.0 and 1.2 a renewed increase in the change of specific heat is observed. Further reduction of the amount of the modifier leads again to the reduction of Δc_p value in both series of glasses what is induced by the change of boron groups in the framework. When comparing both series it can be noticed that glasses containing LaF₃ are character-

Table 2 Thermal characteristics of borosilicate oxyfluoride glasses

	Glass	$T_g/^\circ\text{C}$	$\Delta C_p/$ $\text{J g}^{-1} \text{ }^\circ\text{C}^{-1}$	$\Delta H_{\text{crys}}/\text{J g}^{-1}$ ($T_{\text{max cryst}}/^\circ\text{C}$)	$\Delta T=$ $T_{\text{max cryst}}-T_g/^\circ\text{C}$	Crystallizing phase
Series I	0.4B ₂ O ₃	554	0.812	–	–	–
	0.6B ₂ O ₃	553	0.804	–	–	–
	0.8B ₂ O ₃	590	0.415	–	–	–
	1.0B ₂ O ₃	600	0.633	–	–	–
	1.2B ₂ O ₃	600	0.798	–	–	–
	1.4B ₂ O ₃	590	0.462	–	–	–
	0.4B ₂ O ₃ ·LaF ₃	516	0.630	–	–	–
Series II	0.6B ₂ O ₃ ·LaF ₃	521	0.337	20.239 (686); 17.335 (765)	165	LaOF, LaF ₃
	0.8B ₂ O ₃ ·LaF ₃	495	0.124	2.276 (586); 34.685 (794)	91	LaF ₃ , La(BSiO ₅)
	1.0B ₂ O ₃ ·LaF ₃	540	0.521	2.088 (606); 48.207 (696)	66	LaF ₃ , La(BSiO ₅)
	1.2B ₂ O ₃ ·LaF ₃	535	0.690	129.493 (645) (697)*	110	LaF ₃ , La(BSiO ₅)
	1.4B ₂ O ₃ ·LaF ₃	562	0.447	12.085 (673)**	111	LaF ₃ , La(BSiO ₅), SiO ₂

*Two stages of crystallization have been combined into one exothermal effect; **glass with strong tendency to the phase separation

ized by lower Δc_p values. This is the result of the weakening of the glass structure through the introduction of F⁻ ions, whose charge is smaller by half than that of oxygen ions.

SEM investigation

Figures 2 and 3 show the microstructure of a fracture surface of 1.0B₂O₃·LaF₃ glass before and after thermal treatment at the temperature 750°C. This glass was characterized by small opacity after melting which was evidence of the separation of the B-rich and Si-rich glassy phases. In Fig. 2 the separated borate phase can be observed. The process of thermal treatment at the crystallization temperature leads to the appearance, besides the areas rich in the borate

phase, of smaller intrusions deriving from the crystal phase (Fig. 3), which has been confirmed by XRD investigations (Table 2).

Figure 4 shows the fracture of 0.6B₂O₃·LaF₃ sample, heated at the temperature 750°C, which did not reveal the phenomenon of phase separation during melting. Figure 5 shows the same sample after the process of etching in 35% hydrochloric acid solution at the ambient temperature which lasted for 30 min. The process of etching should lead to the dissolution of the borate phase and the appearance of voids in the silicate matrix as it occurs in the case of producing the Vycor glass. From Fig. 5 it follows that the intrusions did not disappear. This may be evidence that these are LaF₃ crystallites.

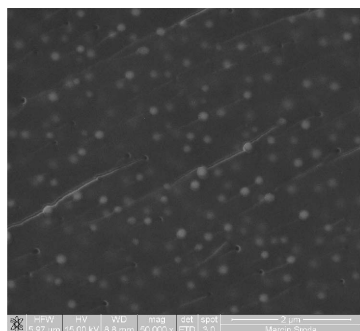


Fig. 2 SEM of as-made glass (1.0B₂O₃·LaF₃ sample); magnification=50000×

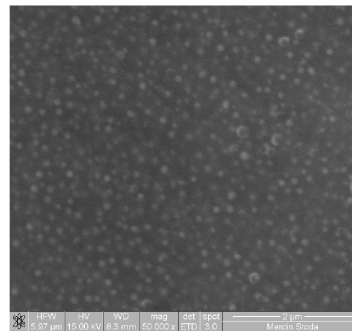


Fig. 3 SEM of 1.0B₂O₃·LaF₃ sample after thermal treatment for 30 min at 750°C; magnification=50000×

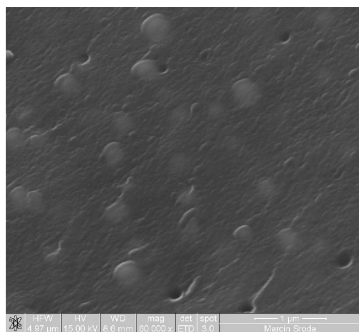


Fig. 4 SEM of sample 0.6B₂O₃·LaF₃ after thermal treatment for 30 min at 750°C; magnification=60000×

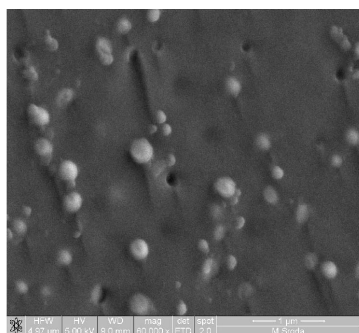


Fig. 5 SEM of sample 0.6B₂O₃·LaF₃ after thermal treatment for 30 min at 750°C and etching in HCl solution; magnification=60000×

Conclusions

Borosilicate glasses with the ratio B₂O₃/Na₂O from 0.4 to 1.4 are thermally stable. Introduction of 6 mol% LaF₃ to the glasses caused the lowering of the transformation temperature and reduction of thermal stability. With increasing ratio B₂O₃/(Na₂O+3La₂F₆) the glasses lost their transparency. This was due to separation of the borate and silicate phases. The process of separation depended on the amount of Na₂O. Sodium oxide had a stabilizing effect, and its absence induced the phenomenon of separation (glasses with the ratio B₂O₃/(Na₂O+3La₂F₆) ≥ 1).

The crystallization process of these glasses was also determined by the amount of Na₂O. The process of LaF₃ crystallization proceeded through the formation of intermediate LaOF phase in the case of the (0.4/0.8)B₂O₃·LaF₃ glasses. The increase in the value of the crystallization enthalpy was observed with increasing ratio B₂O₃/(Na₂O+3La₂F₆), which was connected

with formation of La(BSiO₃) phase. Simultaneously, the enthalpy of LaF₃ crystallization became reduced.

The performed investigations have shown that in the borosilicate glasses it is possible to obtain LaF₃ crystallization. However, to maintain the appropriate optical transparency, the compositions of these glasses must contain a sufficient amount of Na₂O for compensation the charge of trivalent boron and stabilize the boron ions in tetrahedral coordination as well as prevent the occurrence of separation.

The obtained materials, demonstrating the phenomenon of ceramization, on account of the fact of ease of manufacturing, i.e. low melting temperature, may be used as matrix to introduce elements from the lanthanide group. Studies intended to obtain in these glasses the luminescence effect induced by up-conversion are continued.

Acknowledgements

The author would like to thank Mrs. Barbara Trybalska for SEM figures.

The work was financially supported by the Polish Ministry of Education and Science, grant No. 3 T08D 048 29.

References

- 1 Y. Wang and J. Ohwaki, *Appl. Phys. Lett.*, 63 (1993) 3268.
- 2 M. J. Dejneka, *MRS Bulletin*, November (1998) 57.
- 3 M. Środa, I. Waclawska, L. Stoch and M. Reben, *J. Therm. Anal. Cal.*, 77 (2004) 193.
- 4 M. Środa, M. Reben, M. Kwaśny and I. Waclawska, *Optica Applicata*, XXXV, 4 (2005) 851.
- 5 E. W. Deeg, *Borate Glasses: Structure, Properties and Applications*, L. D. Pye, V. D. Frechette and N. J. Kreidl, Eds, Plenum, New York 1978, p. 587.
- 6 J. Sun, J. Zhang, Y. Luo, S. Lu, X. Ren, B. Chen and X. Wang, *Opt. Mater.*, 28 (2006) 306.
- 7 J. Sun, J. Zhang and S. Lu, *Proceedings of SPIE*, 5640 (2005) 455.
- 8 A. Yamamoto, *Japan Analyst*, (1965), p. 692.
- 9 M. Środa and Cz. Paluszkiwicz, *Proc. EUCMOS Istanbul 2006*, *J. Mol. Struct.*, (2006) in press.
- 10 A. C. Wright, S. A. Feller and A. C. Hannon, Eds, *Borate Glasses Crystals & Melts*, The Society of Glass Technology, Sheffield 1997.

DOI: 10.1007/s10973-006-8137-6