Vitrification and devitrification phenomena in the ternary MgO–Al$_2$O$_3$–B$_2$O$_3$ system

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Abstract

The ternary MgO–Al$_2$O$_3$–B$_2$O$_3$ system was studied with respect to the final product that either amorphous or devitrified glasses in the down middle region of the phase diagram. The developed phases in either the devitrified or the crystallized glasses were investigated. Magnesium borate (Mg$_2$B$_2$O$_5$) and a spinel (MgAl$_2$O$_4$) phases were developed in the devitrified samples during the cooling of the melts, whereas the crystallization of the formed glasses led to the development of magnesium borate (e.g. suanite (Mg$_2$B$_2$O$_5$) and kotoite (Mg$_3$B$_2$O$_6$)) and aluminium borate (Al$_4$B$_2$O$_9$) phases. The microstructures of the studied crystalline glasses were characterized by volume crystallization of either lath- or rounded-like crystals of suanite and Al-borate phases. The grain size of the formed crystals were increased from 10 μm to 500 nm with the domination of suanite or Al-borate phases. The coefficient of thermal expansion (CTE) changed from 69 to 59 $\times$ 10^{-7} °C^{-1} for glasses and from 81 to 56 $\times$ 10^{-7} °C^{-1} for the glass-ceramics, in the 20–500 °C range. The data of the glasses were correlated to the local structure changed induced by increasing of Al$_2$O$_3$/MgO and MgO/B$_2$O$_3$ ratios. The results of the glass-ceramics were explained on the basis of the nature and concentration of all phases formed including a residual glassy matrix.
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Keywords: MgO–B$_2$O$_3$–Al$_2$O$_3$ ternary glass system; Crystallization; Thermal expansion

1. Introduction

Glassy or devitrified phases developed within the MgO–Al$_2$O$_3$–B$_2$O$_3$ system, free of alkali oxide, are very important because it may have good electrical insulation. The possible crystalline phases developed in this system may belong to spinels and borates which are considered as important technical phases. The pre-mentioned phase diagram in this system shows different Mg-borate phases, comprised suanite (Mg$_2$B$_2$O$_5$) and kotoite (Mg$_3$B$_2$O$_6$). In the binary MgO–B$_2$O$_3$ sinhalite MgAlBO$_4$ was developed for glass of composition near 50MgO–30Al$_2$O$_3$–20B$_2$O$_3$ [1].

Glass-ceramic materials based on MgO–Al$_2$O$_3$–B$_2$O$_3$ system have been produced by combustion synthesis in a self-propagating mode. The results showed that a higher amount of devitrification occurs under both reduced and high gravity conditions [2]. MgAl$_2$O$_4$ was the most stable phase in the MgO–Al$_2$O$_3$–B$_2$O$_3$ system. 3MgO·B$_2$O$_3$ was first phase formed at 1200 °C, after the formation of MgAl$_2$O$_4$ phase [3].

In the MgO–SiO$_2$–Al$_2$O$_3$–B$_2$O$_3$ glass system, presence of Cr$_2$O$_3$ or Ni suppress the formation of cordierite, however, cristobalite was developed [4]. Through sol–gel route, substitution of B$_2$O$_3$ for Al$_2$O$_3$ was experimented in MgO–Al$_2$O$_3$–SiO$_2$ powder, cordierite crystallized in samples of B/Al ratio up to 1, while proto-enstatite predominated in samples of higher B/Al ratios [5].

Crystallization in the BaO–Al$_2$O$_3$–SiO$_2$ glass system exhibited large ionic conductivities with attributed activation energy as small as 0.45 eV [6]. Sintered glass-ceramic of low and zero thermal expansion was obtained in the later system [7,8]. In the Li$_2$O–Al$_2$O$_3$–B$_2$O$_3$ system, a Li$_3$AlB$_2$O$_6$ phase was developed with dielectric constant range from 4.2 to 5.4 and negative coefficient of thermal expansion, that is suitable for application in the multilayered microwave devices as a dielectric substrate [9].

The purpose of this work is to study, the possibility of preparing some magnesium aluminoborate compositions on the middle region of their oxide-composition triangle using melt

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quench route. The crystallization phenomena and characterization of glasses in the selected region of MgO–Al$_2$O$_3$–B$_2$O$_3$ system were investigated. The coefficient of thermal expansion (CTE) values of the studied glasses and their crystalline products are discussed.

2. Experimental techniques

Ten selected compositions were prepared within the ternary MgO–Al$_2$O$_3$–B$_2$O$_3$ system (Fig. 1). All these compositions are located in the region of Al$_2$O$_3$ (10–30), B$_2$O$_3$ (20–50) and MgO (20–50) mol% (Table 1). Reagent grade powders of MgCO$_3$, α-Al$_2$O$_3$, and H$_3$BO$_3$ were used. Before melting process, the batches were mixed and homogenized using ball mill mixer.

The glass batches were melted in Pt–2% Rh crucible, covered with Pt lid to minimize the evaporation, in an electric furnace with SiC heating elements at 1200–1500 °C for 4 h (Table 1). Melting was continued until clear homogeneous melt was obtained. This was achieved by swirling the melt several times at about 30 min intervals. All the formed glasses and devitrified one were cast into rods and discs, which were then annealed in a muffle furnace at 550 °C to minimize the strain of the glasses.

The crystalline phases were identified using X-ray diffractometry (XRD-model-Bruker AXS D8 advance, Cu Kα-radiation) with secondary monochromator settings in the 2θ ranges up to 70°. The glasses were nucleated at temperature near 650 °C and crystallization at near 800 °C, depending upon the composition, the desired phase assemblages and microstructure [10].

The microstructures of the crystallized glasses studied using scanning electron microscopy (SEM; Model Jeol JSM-T20) on the fresh fractured surface chemically etched by 1%HF + 1%HNO$_3$ solution.

The coefficients of thermal expansion (CTE) for the glass and crystallized glass samples (dimension 0.5 cm × 0.5 cm × 1.5 cm) were measured using Linseis dilatometer (model L76/1250, Germany) in a heating rate 5 °C/min.
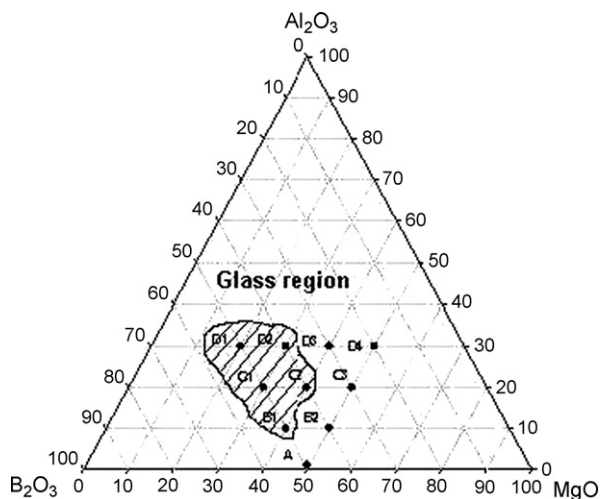
Table 1
The investigated compositions within the ternary MgO–Al$_2$O$_3$–B$_2$O$_3$ system

Sample no.	Batch composition (mol%)			Melting temperature (°C)
	Al$_2$O$_3$	B$_2$O$_3$	MgO	
A	–	50	50	1200
B1	**10**	**50**	**40**	1300
B2	10	40	50	1400
C1	**20**	**50**	**30**	1300
C2	**20**	**40**	**40**	1400
C3	20	30	50	1450
D1	**30**	**50**	**20**	1300
D2	**30**	**40**	**30**	1400
D3	30	30	40	1450
D4	30	20	50	1500

The bold letter compositions represent the formed glasses.

3. Results and discussion

3.1. X-ray diffraction analysis

The studied samples in the ternary MgO–Al$_2$O$_3$–B$_2$O$_3$ system e.g. B$_1$, C$_1$, C$_2$, D$_1$ and D$_2$ batches form glasses while the other samples in direction of increasing MgO and Al$_2$O$_3$ tend to be devitrified. Table 2 shows the summary of the final products from the melt-quenched processes of the present work.

The devitrified samples tend to form mainly a borate phase of Mg$_2$B$_2$O$_5$ formula; however, the increase of Al$_2$O$_3$ in the glasses enhanced the formation of a spinel phase of MgAl$_2$O$_4$ formula (Table 2).

From the melts, Fig. 1, the products of binary compositions (free from Al$_2$O$_3$) seem to be semi-devitrified with Mg$_2$B$_2$O$_5$ crystal phase. With the exception of B$_2$ sample, the samples containing the glass former B$_2$O$_3$ lower than 40 mol% gave either devitrified or semi-devitrified specimens. On the contrary, melts lead to be amorphous glass samples containing B$_2$O$_3$ ≥ 40 mol% (Fig. 1). This means that, the stabilization of the amorphous glassy state was increased by increasing the B$_2$O$_3$ as network former.

The crystallization trials of the present glasses take place in multi-stages heat-treatment at 675 °C/5 h to 800 °C/5 h. Table 3 and Fig. 2 show that the crystalline phases developed at the later

Table 2
The vitrification and devitrification products from ternary MgO–Al$_2$O$_3$–SiO$_2$ system

Sample no.	Sample state	Identified phase
A	Semi-devitrified	Mg$_2$B$_2$O$_5$
B$_1$	Glass	Amorphous
B$_2$	Semi-devitrified	Mg$_2$B$_2$O$_5$, AlBO$_3$
C$_1$	Glass	Amorphous
C$_2$	Glass	Amorphous
C$_3$	Devitrified	MgAl$_2$O$_4$, Mg$_2$B$_2$O$_5$
D$_1$	Glass	Amorphous
D$_2$	Glass	Amorphous
D$_3$	Devitrified	MgAl$_2$O$_4$
D$_4$	Devitrified	MgAl$_2$O$_4$, Mg$_2$B$_2$O$_5$

Glass (transparent), Semi-devitrified (glass + white crystals) and devitrified (white crystals).

Fig. 1. Ternary phase diagram (mol%) of the MgO–Al$_2$O$_3$–B$_2$O$_3$ system showed the batch compositions studied and glass region.

Table 3
Crystallization of the formed glasses at 550 °C/5 h to 800 °C/5 h

Sample no.	Developed phases
B_1	Suanite–Al-borate
C_2	Al-borate–Suanite
C_1	Al-borate–Suanite
D_2	Al-borate–Suanite
D_1	Al-borate–Kotoite

Suanite: $Mg_2B_2O_5$, PDF file No. 15-537; Al-borate: $Al_4B_2O_9$, PDF file No. 29-10; Kotoite: $Mg_3B_2O_6$, PDF file No. 38-1475.

temperatures. Only three borate phases were developed in the crystalline glasses, suanite, kotoite and Al-borate phases.

The present results revealed that, spinel $MgAl_2O_4$-phase was easily formed in devitrified glasses (i.e., C_3, D_3 and D_4), of high MgO and low B_2O_3 contents. However, Al-borate ($AlBO_3$) phase was developed in the semi devitrified glasses of high B_2O_3 (40 mol%) and low Al_2O_3 (10 mol%) contents (i.e., B_2). This may reflect the possible formation of separated phase in the present specimens. This means that during melt–quench–cooling process, the development of separated spinel phase may happen early. The late formation of separated spinel centers may concomitant with rapid epitaxial crystallization of borate or either growths of spinel, in the semi- or devitrified glass. During crystallization of the amorphous glasses a redistribution of the elements may take place, i.e., the spinel phase can react

with the boric oxide from the glassy matrix to form suanite and aluminium borate phases according to the following equation:

$$2MgAl_2O_4 + 3B_2O_3 \rightarrow Mg_2B_2O_5 + Al_4B_4O_9.$$
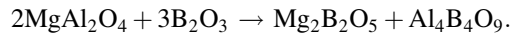
3.2. SEM analysis

Fig. 3 represents SEM micrographs of the fresh fractured surface of B_1, C_2 and D_2 samples, heat-treated at 550 °C/5 h to 800 °C/5 h. Volume crystallization were developed in the bulk samples with grain size range from 10 to 1 μm and 500 nm in
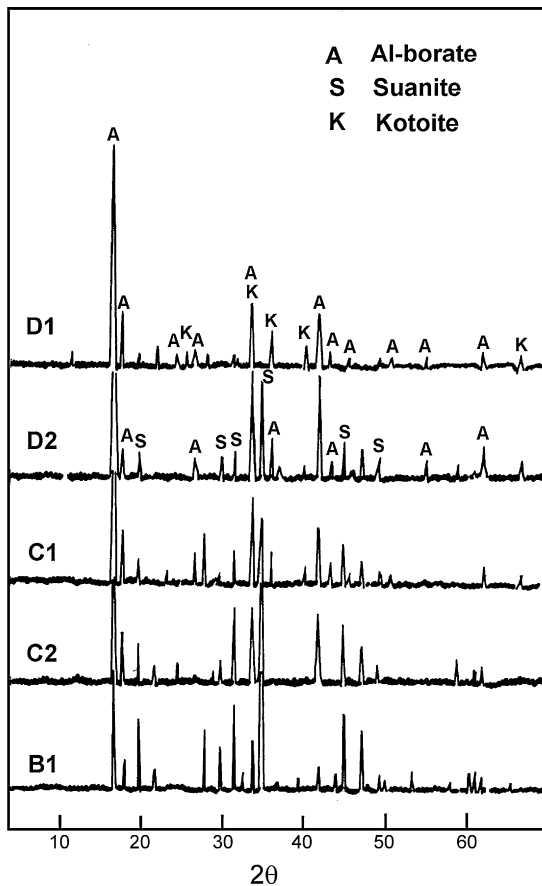

Fig. 2. X-ray diffraction patterns of the present glasses heat-treated at 675 °C/5 h to 800 °C/5 h.
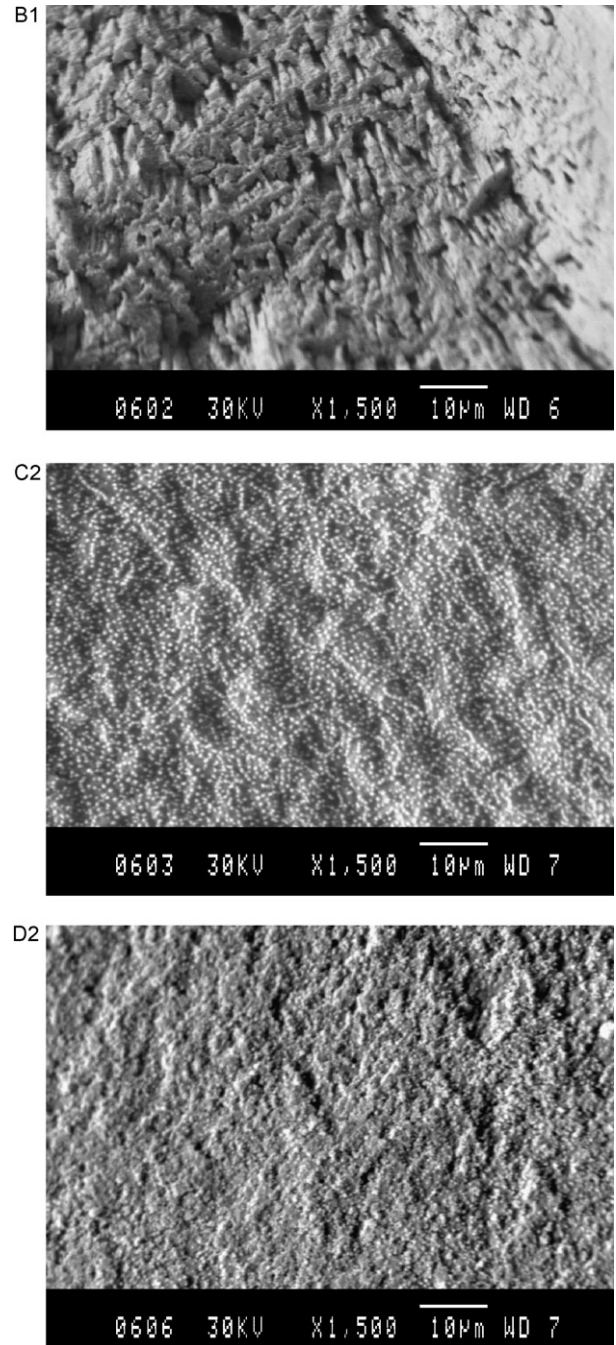

Fig. 3. SEM micrographs of B_1, C_2 and D_2 glasses heat-treated at 675 °C/5 h to 800 °C/5 h.
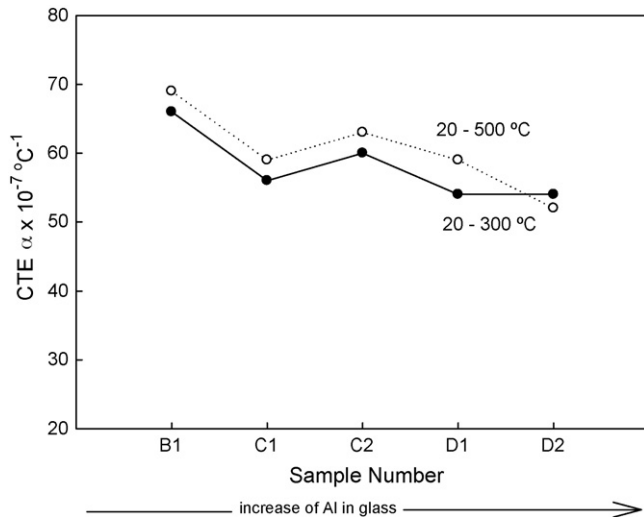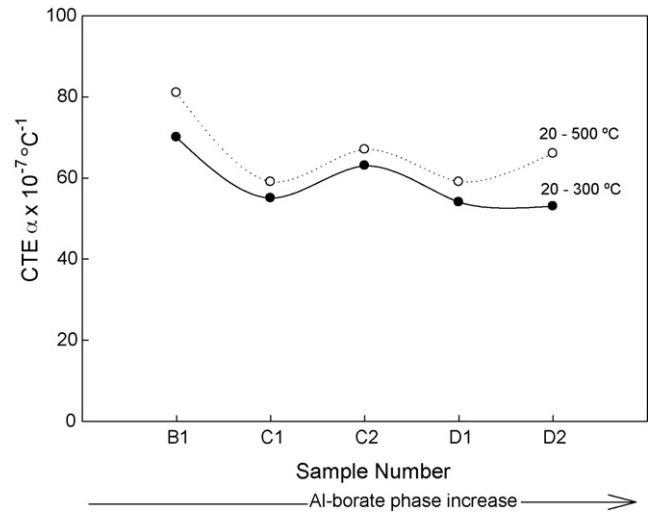
Fig. 4. CTE of the studied glasses.

Fig. 5. CTE of the studied glasses heat-treated at 675 °C/5 h to 800 °C/5 h.

size. The later formed crystals appear as small lath-like and rounded crystals.

It could be noted that, a relatively coarse material was developed in case of the crystallization of suanite as the major phase, however, near submicrometric particles are formed when Al-borate phase was crystallized alone. This means that, crystallization of Al-borate change the microstructure into more ultrafine microstructure.

3.3. CTE measurements

The coefficient of thermal expansion of the studied glasses and their respective crystalline materials are represented in Figs. 4 and 5 and Table 4. The dilatometric transformation (T_g) and softening (T_s) temperatures of the studied glasses are also reported in Table 4.

The data obtained clearly indicated that, a marked decrease in the CTE values and an increase in the T_g and T_s values were obtained by increasing Al_2O_3 content at the expense of MgO in glasses B_1, C_1 and D_1. This may be due to the fact that Al^{3+} coordination which seems to change to four coordination. This

Table 4
The coefficients of thermal expansion values of the studied glasses and glass-ceramics

Sample No.	CTE ($\times 10^{-7}$ °C^{-1})		T_g (°C)	T_s (°C)
	20–300	20–500		
B_1 (g)	66	69	590	611
B_1 (c)	70	81	–	–
C_1 (g)	56	59	605	634
C_1 (c)	55	59	–	–
C_2 (g)	60	63	602	623
C_2 (c)	63	67	–	–
D_1 (g)	54	59	607	636
D_1 (c)	52	56	–	–
D_2 (g)	60	62	599	610
D_2 (c)	63	76	–	–

g: glass; c: glass-ceramic.

is associated with a change in bonding character with simultaneous increase in the tightness of the structure, resulted in a decrease in the CTE values and an increase in both T_g °C and T_s °C values of the studied glasses [11].

However, the present results revealed also that the glass B_1 exhibited a higher CTE values than those of C_1 and D_1 glasses. A review of the structural units in each glass leads easily to a good understanding of this behaviour. Small addition of alumina to borate glass does not change the concentration of tetrahedral species, it merely increases the concentration of BO_3. Naturally, the CTE value increased and the T_g °C and T_s °C values decreased.

When the Al_2O_3 content >15%, both the BO_3 and the sum of $BO_4 + AlO_4$ increases by the same amounts but the non-bridging oxygens on boron drops to zero. This certainly should lead one to expect the decrease in the CTE values of C_1 and D_1 glasses and the increase in T_g °C and T_s °C values which is, in fact, observed [12].

In MgO-containing glasses (e.g. C_2 and D_2), the role of Mg^{2+} (single bond strength with oxygen of about 37 kcal/mol) replacing boron (single bond strength with oxygen is about 119 or 89 kcal/mol for B^{3+}) [13], is quite different. The ability of magnesium to be an intermediate oxide to form MgO_4 group or to be housed in octahedral coordination in the glass interstices is known [14].

Accordingly, the increase in the expansion coefficient of magnesium aluminium borate glasses as a result of increasing MgO at the expense of B_2O_3 can be attributed by considering that Mg^{2+} ion formed in these glasses exhibited in the interstitial position [15], so its binding to the network will be relatively small, leading to vibrations with larger amplitude [16]. Therefore, these vibrations have less resemblance with harmonic oscillators. The increased anharmonicity of the vibrations leads to higher CTE values.

Our results indicate that Mg^{2+} preferably exhibits an octahedral coordination in the glasses in which the MgO was added instead of B_2O_3 which can explain the increase in the CTE values and consequently the decrease in both the T_g and T_s

values. Therefore, it could be concluded that the data of the glasses were correlated to the local structure changes induced by increasing of Al_2O_3/MgO and MgO/B_2O_3 ratios.

The CTE values of the present crystalline solids were explained in relation to the nature and concentration of all phases including a residual glassy matrix. However, there are no data about the CTE values of magnesium or aluminium borate phases. The present results revealed that the CTE values of aluminium borate-containing glass-ceramics exhibited a lower CTE value than that of magnesium borate phases (i.e., suanite or kotoite phases).

Therefore, it could be concluded that the glass-ceramic B_1 exhibited the highest CTE value in the studied glasses. This may be due to the crystallization of suanite phase (as a major phase) of high CTE value than that of aluminium borate phase (as a secondary phase). While the samples C_1, C_2, D_1 and D_2 exhibited lower CTE values than that of sample B_1. This may be due to the development of aluminium borate phase (as a major phase) of lower CTE value than that of suanite or kotoite phase (as secondary phases).

4. Conclusions

Glass and glass-ceramic with homogeneous and medium coefficient of thermal expansion can be produced within the $MgO–Al_2O_3–B_2O_3$ system. Borate phase of $Mg_2B_2O_5$ and a spinel of $MgAl_2O_4$ formula were developed in the devitrified samples. Suanite, kotoite and Al-borate phases were formed in the prepared glass-ceramic. The increase of Al-borate at the expense of Mg-borate phases in the glass-ceramics, tend to form ultrafine microstructure. The thermal expansion coefficient of glasses and glass-ceramics were ranged from 69 to $59 \times 10^{-7}\,°C^{-1}$ and from 81 to $56 \times 10^{-7}\,°C^{-1}$, respectively (20–500 °C).

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