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Crystallization behavior and properties of cordierite glass-ceramics with added boron oxide

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The glass forming behavior and glass-ceramic formation of cordierite compositions in the MAS (MgO-Al_2O_3-SiO_2) system with an added B_2O_3 content up to 3% were studied using glass samples prepared by melting the natural raw materials such as; talc, kaolin, alumina and boric acid as the source of MgO, SiO_2, Al_2O_3 and B_2O_3. XRD (X-Ray powder diffraction) analysis revealed glass formation and after heat treatment at various temperatures, the crystallization of the cordierite phase was observed at 950 °C for a 1 h heat treatment. Some physical properties, such as the hardness and thermal expansion coefficient of glass and glass-ceramics were measured and compared in order to see the effect of crystallization. Surface crystallization was observed and the addition of boron oxide reduced the crystalline surface layer thicknesses. The main crystalline phase was cordierite and a small amount of forsterite was also observed in MAS glass-ceramics.

Keywords: Crystallization, Cordierite glasses, Glass-ceramics, Heat treatment, Natural raw materials.

Introduction

The cordierite phase ($Mg_2Al_4Si_5O_{18}$) has long been a major phase in many ceramics and glass-ceramics. Cordierite ceramics have found applications in different branches of industry due to their electrical and thermal properties. Applications in multilayer ceramic packaging and ceramic-matrix composites, using stoichiometric or near stoichiometric cordierite glass-ceramics either from a melt-derived or from sol-gel derived glasses, recently have been implemented [1-3]. Beneficial properties in these applications include a thermal expansion coefficient close to that of silicon, a high chemical durability, a high volume resistivity, a low dielectric constant, a high refractoriness and a high mechanical strength.

The crystallization behavior of cordierite glasses with and without nucleating and fluxing agents (i.e. TiO_2, ZrO_2, CeO, V_2O_5, WO_3, CrO_3, NiO, CaF_2, B_2O_3, P_2O_5 and alkali oxides) has been studied extensively by many researchers [4-10].

A small amount of additives in glasses significantly affects the viscous behavior and the crystallization kinetics of the glass-ceramic system. B_2O_3 and P_2O_5 as additives to cordierite glasses have been studied extensively by researchers at IBM, who have developed cordierite glass-ceramics for use in ceramic packaging [1, 11]. However, relatively few fundamental studies have treated the crystallization process in such compositions and also there is not any study about the use of less pure natural raw materials in cordierite glass formation and in glass-ceramics.

Gregory and Veasey demonstrated the crystallization characteristics of a glass near the stoichiometric cordierite composition [8]. The devitrification of the base glass was studied by the DTA (Differential Thermal Analysis) method. The effects of the additions of vanadium pentoxide and tungsten oxide on the devitrification behavior of the base glass were also studied and discussed. As a result, no evidence of efficient catalysed crystallization was found using these additives.

Amista *et al*. prepared several glasses in the MgO-Al_2O_3-SiO_2 system with different compositions within the formation zone of cordierite [12]. The samples were examined after crystallization to investigate the influence of the composition on the phases formed by heat treating the glasses in the cordierite domain. Glass ceramics were obtained by heating the glasses at temperatures between 900 and 1200 °C. The thermal stability range of μ- and α-cordierite was strongly dependent on the excess components such as; MgO and Al_2O_3. It was reported that, excess MgO or Al_2O_3 induces the formation of forsterite and sillimanite, respectively.

Wu and Hwang demonstrated that the microstructural development and phase-transformation kinetics of stoichiometric cordierite glasses containing B_2O_3 and/or P_2O_5 additives were highly affected by the microstructural characteristics of the μ-cordierite and the type of additives [13]. The addition of B_2O_3 tended to cause the formation of spherulitic dendrites with thin dendritic arms, which promoted the formation of μ-cordierite, either from crystallization of the residual glass or from transformation of μ-cordierite. P_2O_5 had the opposite effect. Increasing the temperature increased the growth rate of μ-cordierite more than that of μ-cordierite.

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In the present study, the glass formation and the crystallization behavior of cordierite glasses with and without a boron oxide addition were studied by means of X-ray diffraction, DTA thermal analysis and microstructural development of glass samples during crystallization by SEM studies.

Experimental

Glass-forming procedure

The MgO-Al_2O_3-SiO_2 glass was melted from impure natural raw materials of talc, kaolin and alumina. A chemical analysis of the starting raw materials is shown in Table 1.

B_2O_3 was added in the form of H_3BO_3 to every 100 g of batch material. The calculated batch was melted in a platinum 2% rhodium crucible. The melting was carried out at 1520 °C for 2 h using an electric furnace (Protherm Elv160/8). Following this, the melt was cast into a preheated stainless steel rectangular mould with the dimensions of 5 cm × 5 cm and 0.5 cm. In order to remove thermal residual stresses of a glass sample, it was annealed in a regulated Carbolite HTF3 furnace at about 600 °C for 1 h. The muffle furnace was left to cool to room temperature at a rate of 30 K h^{-1}.

Chemical analysis of the resultant MAS-T-0 glass sample was determined using Philips PW2404 X-ray spectrometer and is shown in Table 2.

A fine powder was produced by crushing the glass pieces and XRD showed no traces of any crystalline phases. The crystallization behavior of glasses under non-isothermal conditions were determined by the DTA method which was performed in a Seiko 6300 thermo analyser using 20 mg powdered samples with a heating rate of 10 K·$minute^{-1}$ to 1200 °C. All DTA experiments were performed in a static air atmosphere with Al_2O_3 powder as a reference material. Heat treatments were carried out at temperatures of 900, 950 and 1000 °C for 1 h in a Nabertherm HT16/17 furnace to promote crystallization. The crystallization temperatures were selected from the DTA curves depending on the endothermic and exothermic reaction temperatures.

XRD analysis of the crystalline phases in the heat treated glass samples were determined by a PANalytical X'Pert Pro MPD diffractometer using Cu Ka radiation with a wavelength of 1.5418 Å. Data were collected in the 2θ range from 2 to 70°. The quantitative amounts of the crystalline phases in the glass-ceramic samples were determined using the full structure matching mode of the Rietveld refinement technique, using the X'Pert Highscore Plus program.

Table 2. Chemical analysis of the MAS-T-0 glass

Compound	Wt.%
MgO	22.403
Al_2O_3	28.136
SiO_2	47.357
CaO	0.935
Fe_2O_3	0.429

Some of the glass and glass-ceramic specimens were mounted in conductive resin, ground with 600, 1200 and 2500 grit silicon carbide and finally polished with a 1 μm diamond slurry to observe the microstructure using a Jeol JSM 6335F scanning electron microscope (SEM).

Thermal expansion coefficients of the glass and glass-ceramic samples were measured using a Netzsch DIL 402C dilatometer up to 500 °C with a heating rate of 10 K·$minute^{-1}$.

Vickers hardness measurements were carried out using a Zwick ZHV10 microhardness equipment on polished glass and glass-ceramics samples. The mean values, from 5 measurements, were reported. The applied load during the hardness measurements was 300 g.

Results and Discussions

Non-isothermal crystallization

The DTA curves were recorded at a heating rate of 10 K·$minute^{-1}$ for each cordierite glass. In all the DTA curves, the exothermic peaks indicating the crystallization of cordierite phases, are very clear and distinct in between 920-1040 °C and also, it can be clearly seen in that DTA curves that, there are shifts of the crystallization peaks to the right with increasing boron oxide content in the glasses. Also in all the DTA curves there are small second crystallization peaks which belong to the crystallization of the second crystalline phase forsterite. The T_g values of the glasses are also clear except for the MAS-T-0 glass and the T_g and T_p values (T_{p1} and T_{p2} values for cordierite and forsterite phase crystallizations, respectively) of the MAS-T glasses are given in Table 3 and the DTA curves are presented in Fig. 1.

As seen in the results that, with increasing boron oxide content in the glasses, the glass transition and crystallization temperatures were also increased. This behavior

Table 1. Chemical analysis of all the starting raw materials

	MgO	Al_2O_3	SiO_2	CaO	Fe_2O_3	TiO_2	Na_2O	K_2O	B_2O_3	LOI
Talc	34.4	0.78	62.1	1.36	0.36	-	-	-	-	1.0
Kaolin	-	36.92	47.80	0.31	0.62	0.31	0.01	0.73	-	13.3
Boric acid	-	-	-	-	-	-	-	-	56.25	43.75
Alumina	-	100.00	-	-	-	-	-	-	-	-

Table 3. DTA results of glass samples

MAS-T glasses	Peak temperatures (°C)		
	Tg	T_{p1}	T_{p2}
MAS-T-0	776	958	1001
MAS-T-1	780	985	1005
MAS-T-2	786	1000	1031
MAS-T-3	788	1015	1033

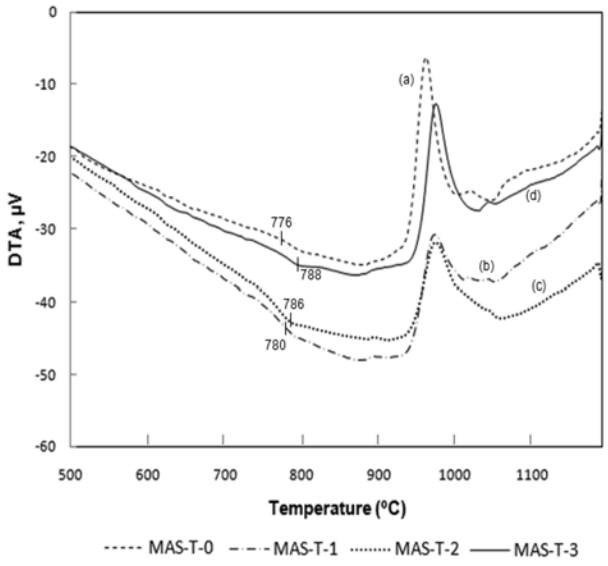

Fig. 1. The DTA curves of MAS-T-0 (a), MAS-T-1 (b), MAS-T-2 (c) and MAS-T-3 (d) cordierite glasses.

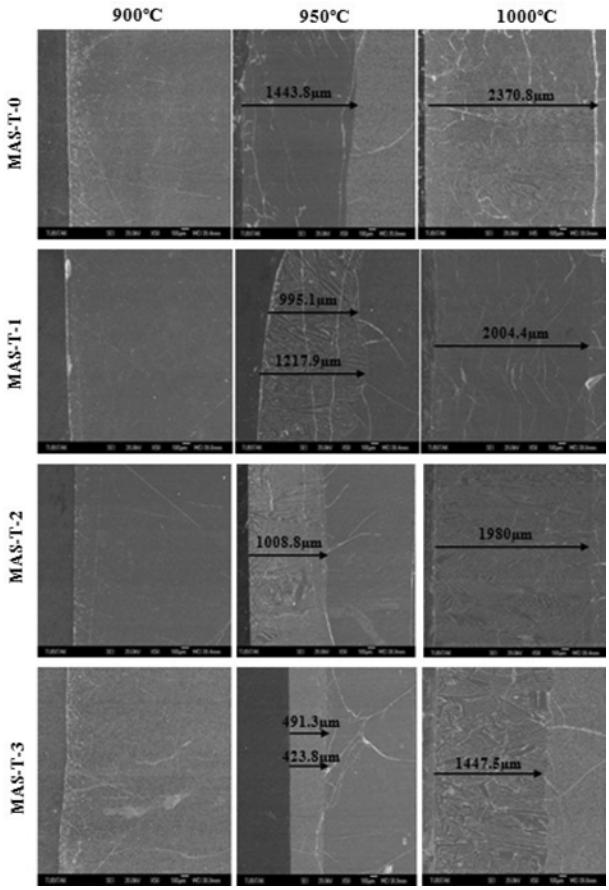

Fig. 2. SEM micrographs and thicknesses of crystalline surface layers of MAS-T glass-ceramics after various heat treatments.

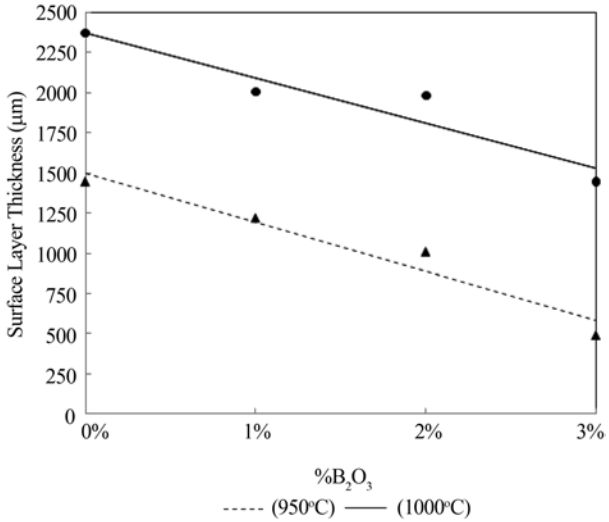

Fig. 3. Changes in the thickness of the surface layer with B_2O_3 content.

is attributed to the glass- forming ability of B_2O_3 and with increasing boron oxide in the glass composition, the bonds are stronger and as is very well known, glasses with stronger bonds are more resistant to crystallization on heat treatment. It has also been reported that B_2O_3 additions to the MAS glasses favors the crystallization of α-cordierite (indialite) [13]

Microstructural analysis by SEM

The microstructural examinations of the bulk glass and glass-ceramic samples, crystallized at different temperatures, were carried out by SEM using the polished and etched glass and glass ceramic surfaces. Some characteristic micrographs of the surface regions, are shown in Fig. 2.

In all samples, crystallization was not detected after the heat treatments at 900 °C for 1 h. At 950 and 1000 °C, the crystallization was detected and the crystallization mechanism was surface crystallization in all the samples. It was also observed that the thicknesses of the crystalline surface layers were changed with an increase in the B_2O_3 content in the MAS glasses. In order to see this more clearly, the values of the surface layer thicknesses are drawn on Fig. 3, with an increase in the B_2O_3 content. The decreases in the surface layer thicknesses with an increase in the B_2O_3 content was very clear. These results are consistent with the results and discussions given in the DTA and XRD sections that B_2O_3 in the MAS glasses retards the crystallization due to the formation of glass-forming bonds. In all the samples, crystallization was only observed on the surfaces. The crystalline surface layer grow towards the centre of the glass samples until covering all the glass samples.

Also, it was observed in the SEM micrographs that, with increasing B_2O_3 content in the MAS-T glasses, the structural

features of the resultant crystalline surface layer showed some differences as can be seen in Fig. 4(a) and (b), (both micrographs are larger versions of the micrographs given in Fig. 2) after crystallization at 1000 °C for 1 h. It can be seen that the dentritic arms are more visible and thicker in MAS-T-3 with a 3% B_2O_3 content. Similar observations and explanation were given by Wu and Hwang for MAS glasses in their study [13].

XRD analysis

The XRD analysis revealed that all the MAS-T glasses were amorphous after casting and annealing. These results indicates that, MAS compositions from natural raw materials can form glasses with a green color. Fig. 5 shows the XRD results of a MAS-T-0 annealed glass sample and a glass sample which was heat treated at 900 °C for 1 h. Fig. 6 shows the XRD results and the crystalline phases of MAS-T-0 glass-ceramic after heat treatment at 950 and 1000 °C for 1 h. The crystalline phases were determined as indialite (α-cordierite) ($Mg_2Al_4Si_5O_{18}$) (PDF number: 4-8-7865) and forsterite ($Mg_2(SiO_4)$ (PDF number: 4-8-8399). There was no crystallization in the annealed glass and after heat treatment at 900 °C for 1 h as seen in Fig. 5(a) and (b).

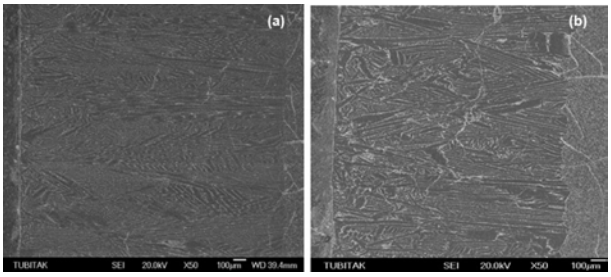

Fig. 4. SEM micrographs of the MAS-T glass-ceramic samples heat treated at 1000 °C for 1 h, MAS-T-2 (a) and MAS-T-3 (b).

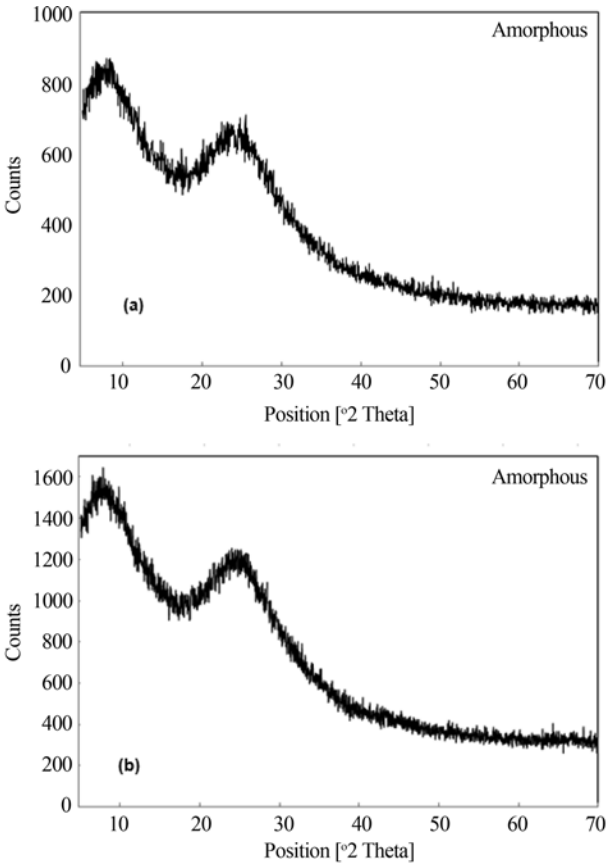

Fig. 5. XRD analysis of MAS-T-0 glass sample (a) and a glass sample which was heat treated at 900 °C for 1 h (b).

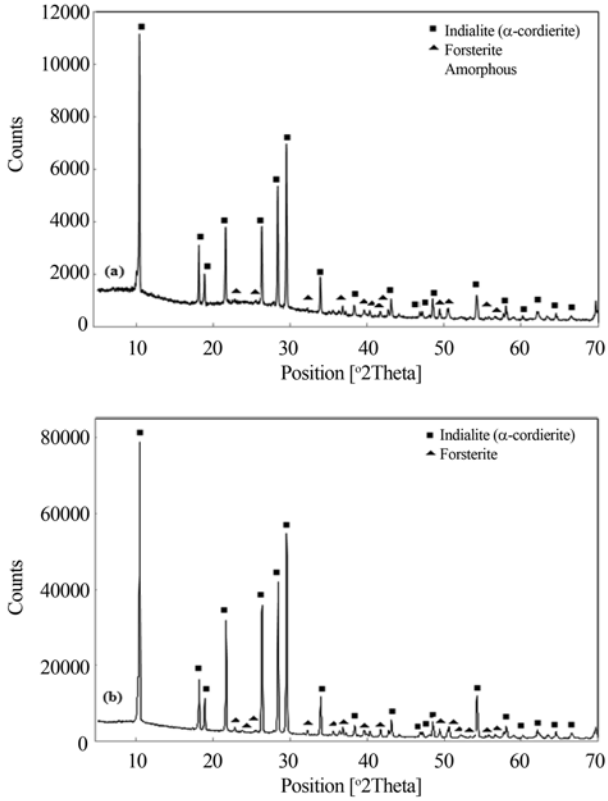

Fig. 6. XRD analysis of glass samples which were heat treated at 950 °C (a) and 1000 °C for 1 h (b).

It was observed that, the crystallization gets higher with increasing heat treatment temperatures. At 950 °C, some amorphous structure was observed but at 1000 °C there were only two distinct crystalline phases in the samples as seen in Fig. 6(a) and (b). The amounts of the crystalline phases were determined by Rietveld analysis and it was calculated as 78.82% indialite (α-cordierite), 15.68% forsterite and 5.5% amorphous at 950 °C, and 89.2% indialite (α-cordierite) and 10.8% forsterite at 1000 °C in MAS-T-0 glass-ceramics.

Thermal expansion coefficients

Thermal expansion coefficients (TEC) of MAS-T-0 glass and glass-ceramics were measured up to 500 °C and given in Table 4.

According to the results, crystallization of the base MAS-T-0 glass resulted with a decrease in TEC from 5.22×10^{-6} K^{-1} to around 2.7×10^{-6} K^{-1}. This is due to the formation of the cordierite phase in glasses and because

Table 4. Thermal expansion coefficients (TEC) of the glass and glass-ceramics

	TEC ($\times 10^{-6}$/°C)
MAS-T-0 annealed glass	5.2226
MAS-T-0 glass ceramic (950 °C)	2.7219
MAS-T-0 glass ceramic (1000 °C)	2.7917

Table 5. Vickers hardness for glass and glass-ceramic samples

	Vickers hardness HV, 300 g load (GPa)
MAS-T-0 annealed glass	803 (7.875)
MAS-T-0 glass ceramic (950 °C)	1401 (13.74)
MAS-T-0 glass ceramic (1000 °C)	1372 (13.46)

of the low TEC value of the cordierite phase (around 1.5×10^{-6} K^{-1}) [14]. In the present study the glass-ceramics also contained forsterite as a second crystalline phase and it was thought that the presence of forsterite to around 10 to 16% could be the reason for the TEC value of the MAS-T-0 glass-ceramics, being around 2.77×10^{-6} K^{-1}. These results showed that the crystallization of MAS-T glasses to glass-ceramics, reduces the TEC values as expected in glass-ceramics.

Vickers hardness

Vickers hardness results are given in Table 5. Vickers hardness values of the glass-ceramics for a 300 g load are much higher than that of the glass at around 1400 to 800 HV for the glass-ceramic and glass, respectively in Table 5. This is an expected result in the glass to glass-ceramics transition and the reason is that the crystalline phases in glass-ceramics are usually harder the glassy phases.

Conclusions

The crystallization behavior and some properties of the MAS-T glasses and glass-ceramics and also the effect of B_2O_3 additions to the glasses were studied. Surface crystallization was the only crystallization mechanism in the MAS-T glasses. In MAS-T glasses, crystallization started at 950 °C after a 1 h heat treatment and the crystalline phases were indialite (α-cordirite) and forsterite. Indialite ($Mg_2Al_4Si_5O_{18}$) was formed as the primary phase, followed by forsterite ($Mg_2(SiO_4)$) as the secondary one with contents of around 89.2 and 10.8% at 1000 °C, respectively. Increasing the B_2O_3 content in the MAS-T glasses, reduced the thicknesses of the crystalline surface layer. This could be attributed to the glass-forming ability of B_2O_3 which resulted in stronger bonds in the glasses and in turn reduced the crystallization tendencies of the glasses. Crystallization of the MAS-T glasses, resulted in an increase in the hardness and a decrease in the thermal expansion coefficient (TEC) as expected in glass to glass-ceramic transitions. The present study showed that, cordierite glasses and glass-ceramics, with useful properties, can be produced using impure natural raw materials.

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