Structure and Crystallization of Borate-Based Glasses for Machinable Material Applications

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Abstract—**This study investigated bulk crystallization at pre-set temperatures of B_2O_3-SiO_2-Al_2O_3-BaO-MgO glass system. Heat treatment at pre-set temperature was carried out between 900 and 1200°C on clear glasses to form non-transparent glass-ceramics. Structure of glasses were studied by Fourier transform infrared spectroscopy, phase evolution in the bulk crystallized samples was studied by x-ray diffraction, microstructures were observed by scanning electron microscope and micro-hardness was measured by Vickers method. Aluminum borate whiskers/rods were in the nano to micro sized regime and dispersed randomly within the remaining glass matrix. Whiskers had different sizes and morphologies depending on the heat treatment temperature. Increasing heat treatment temperature led to an increase in crystal size, length and the formation of hollow tubes. The surface hardness decreased when the morphology changed from fine rods into hollow tubes. The synthesized glass-ceramics in this study can be applied as machinable materials in various applications because their microstructures can resist microcracking.**

Index Terms—**Glass, crystallization, microstructure, whiskers, hardness.**

I. INTRODUCTION

Fibers and whiskers reinforced glasses and ceramics can lead to significant improvements in mechanical properties, such as increased fracture toughness, bending strength, hardness and thermal shock resistance [1]. The possibility of using whiskers is limited due to the health hazard posed by loose particles with a high aspect ratio shape [2]. Aluminum borate whisker ($9Al_2O_3 \cdot 2B_2O_3$) is a refractory compound (melting point 1440°C) possessing excellent physical properties, such as low density (2.94 g/cm^3), high hardness, high Young's modulus (400 GPa), high electrical resistivity and low coefficient of thermal expansion [3]. Such characteristics suggest that aluminum borate whisker could be used to reinforce ceramics to give ceramic–ceramic composites with increased fracture toughness and also reinforce light metals such as aluminum alloys. The metal matrix composites (MMCs) can be useful for the automobile and aerospace industries.

Aluminum borate whiskers have been synthesized by various methods such as vapor phase method, solid-state reactive firing and flux method using borates [4-5]. However, the product yields were found to be very low, 10% or less. The in-situ direct growth of whiskers in a glass to form glass-ceramic is an attractive alternative method. This is analogous to the creation of fluorcansite platelets in toughened glass–ceramics. Unfortunately, oxide systems that can be exploited are limited. Recently, the formation and crystallization behavior of glasses in the Al_2O_3–B_2O_3–SiO_2 system has been investigated [6], showing that whisker-shaped aluminum borate crystals can be obtained after thermal treatment.

This study investigated a specially formulated glass compositions based on a composition similar to that proposed by Lee et al. [7]. In this further compositional modification, both B_2O_3 and SiO_2 act as glass forming oxides. The effects of varying mole ratio between the two glass forming oxides on the materials properties were studied. The effect of varying B_2O_3/SiO_2 ratio on the crystallization of aluminum borate whisker glass-ceramics has never been investigated elsewhere. The in-situ crystallization of an aluminum borosilicate glass was carried out above glass transition temperature of the as-annealed glasses at pre-set tmperatures. Phase evolution, microstructures and their related microhardness values were investigated.

II. MATERIALS AND METHODS

Glass compositions according to Table I in the B_2O_3 – SiO_2 – Al_2O_3 – BaO – MgO glass system were prepared from high purity ($\geq$99%) raw materials: silica sand, B_2O_3, Al_2O_3, $BaCO_3$ and MgO. Melting was carried out in an alumina crucible at 1500°C for 1 h using electric furnace. The glass melt was cast onto a steel block and quickly transferred into a muffle furnace for annealing at 500°C for 2h then furnace cooled to room temperature. Glass block was cut into small pieces for further characterization. Fourier Transform Infrared (FT-IR) absorption spectra of the annealed glasses were obtained at room temperature in the wavenumber range of 4000–400 cm^{-1} using a Fourier transform infrared spectrometer (Vertex 70, Bruker). The samples were ground into fine powders (<180 μm) and then mixed with KBr powder in a very precise amounts using powder:KBr ratio of 1:9; subsequently, the mixtures were uniaxially pressed to form clear homogeneous discs. The FT-IR measurements were carried out immediately after preparing the discs to avoid moisture absorption. Chemical bonds in different environments will absorb varying intensities and at varying frequencies. The frequencies at which there are absorptions

of IR radiation can be correlated directly to bonds within the substance. Single-step heat treatment was used to crystallize glasses at temperature between 900 and 1200°C following the differential thermal analysis (DTA) data preliminarily performed on glass powders using a Perkin Elmer DTA7 with heating rate of 5°C/min. The isothermal crystallization was pre-set to the required temperature before inserting the samples into the furnace. The isothermal holding time was 4h after that the furnace was switched off and cooled to room temperature. X-ray Diffraction (XRD) was used to identify phases in crystallized samples. XRD study was performed on a Rigaku Miniflex II from 10° to 80° 2θ with a scan speed of 1°/min and step size 0.02° using Cu Kα radiation. Glass-ceramic samples were polished to mirror finish surfaces of 1μm using SiC papers and diamond paste. Chemical etching with 0.2%HF for 30 – 60 seconds was required to remove residual glass and discern microstructure. Microstructural study was performed by a Camscan MX2000 scanning electron microscope (SEM) at 10 – 20 kV. Samples were ultrasonically cleaned and gold-coated for conductive layer by a Cressington Sputter Coater 108. Hardness of glass-ceramics was obtained from a HV-1000B Vickers microhardness tester with a load of 1 kgf (9.81 N) on a mirror finish surface.

TABLE I: GLASS COMPOSITIONS MELTED IN MOL % OXIDE

Glass	Oxide (mol%)				
	B_2O_3	SiO_2	Al_2O_3	BaO	MgO
G1	50	23	17	5	5
G2	52	21	17	5	5
G3	54	19	17	5	5

III. RESULTS AND DISCUSSION

This study showed that different B_2O_3/SiO_2 ratio in the proposed glass compositions affected the structure and properties of glasses and also the crystallized glass samples. The preliminary investigation by differential thermal analysis of the as-annealed glasses indicated two distinct thermal transitions. The first endotherm was detected from the slope change of derivative curve and corresponds to the glass transition temperature, T_g. In bulk crystallized glass-ceramic, nucleation of crystals occurs above T_g. Exothermic peak was correlated with the crystallization of crystalline aluminum borate phase from the glass matrix. It was found that both the endotherm and exotherm shifted to lower temperatures with increasing in the B_2O_3/SiO_2 ratio. The glass transition temperatures were 646°C, 620°C and 598°C for glass G1, G2 and G3, respectively. The exothermic crystallization peaks were 825°C, 812°C and 800°C for glass G1, G2 and G3, respectively. The increase in B_2O_3 content leads to lower T_g and suggests that crystallization and crystal growth in the glass can be improved.

The Fourier transform infrared absorption spectra of as-annealed glass G1, G2 and G3 are shown in Fig.1. IR absorption peaks and vibration types of glasses G1, G2 and G3 were summarized in Table II. All annealed glasses showed four main absorption peaks which are related to different vibration types. It was found that increasing in the B_2O_3/SiO_2 ratio in the parent glass compositions resulted in broadening of B-O-B stretching vibration in [BO$_3$] triangles

and the peak slightly shifted to lower wavenumber from 1428 (for G1) to 1404 (for G3) cm^{-1}. The bending vibration of B-O-B in [BO$_3$] triangles shifted slightly to higher wavenumber from 687 (for G1) to 694 (for G3) cm^{-1}. The stretching vibration of B-O-B bond in [BO$_4$] tetrahedron shifted to lower wavenumber from G1 to G3 suggesting that this type of vibration was more likely in glass G1 as opposed to glass G3. The [BO$_4$] tetrahedra could dominate the glass structure in the glass composition with lower B_2O_3/SiO_2 ratio. In additions, the vibration of O-Si-O bond was easier for glass G3 compared to the other two compositions. The absorption peak shifted to higher wavenumber from 343 (for G1) to 436 (for G2) and 448 (for G3) cm^{-1}. This suggests that the structure of glass G3 was less rigid [6] and hence would lead to easier nucleation and growth of aluminum borate whiskers.
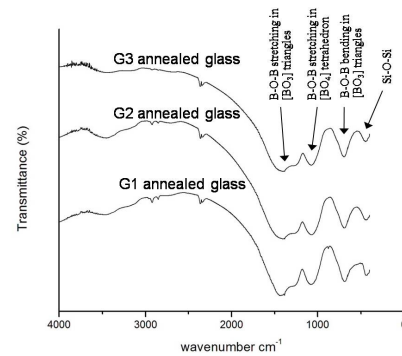

Fig. 1. FT-IR absorption peaks of as-annealed glasses G1, G2 and G3.

TABLE II: VIBRATION TYPES AND IR ABSORPTION OF GLASS G1, G2 AND G3

Glass	IR absorption band (cm^{-1})			
	B-O-B stretching in [BO$_3$] triangles	B-O-B stretching in [BO$_4$] tetrahedron	B-O-B bending in [BO$_3$] triangles	Si-O-Si
G1	1428	1079	687	434
G2	1404	1073	690	436
G3	1404	1070	694	448

At each heat treatment temperature, all glass compositions crystallized to give the same x-ray diffraction (XRD) peaks therefore only glass G3 data were reported. XRD analysis in Fig.2 showed example of a broad diffraction pattern of an as-annealed glass G3 confirming amorphous characteristic. Isothermal heat treatment revealed crystalline phases of $Al_4B_2O_9$, $Al_{18}B_4O_{33}$ and $BaAl_2B_4O_{10}$. The amount and type of crystalline phases formed depended on the heat treatment temperature. The glass crystallized significantly with increasing heating temperature to form crystalline aluminum borate crystals within glass matrix. At temperatures between 900 and 1000°C, $Al_4B_2O_9$ (JCPDS PDF#29-0010) was the only phase, while from above 1100°C, $Al_{18}B_4O_{33}$ (JCPDS, PDF#29-0009) was also present in addition to the $Al_4B_2O_9$ phase which decreased in diffraction peak heights possibly due to phase transformation into a more thermodynamically stable structure. In accordance with the phase diagram [8], the $Al_{18}B_4O_{33}$ phase is expected to form at about 1040°C from the decomposition or transformation of $Al_4B_2O_9$. The lower temperature phase of aluminum borate is retained to higher temperatures (in the glass-ceramic) because of limited mass transport between the glassy phase and the transforming

whiskers. In the case of the aluminum borate in the form of powders, boron oxide evolution can occur without such a kinetic limitation.
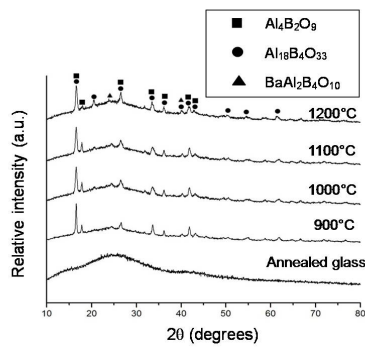

Fig. 2. XRD patterns of as-annealed glass G3 and its crystallized samples between 900 and 1200°C.
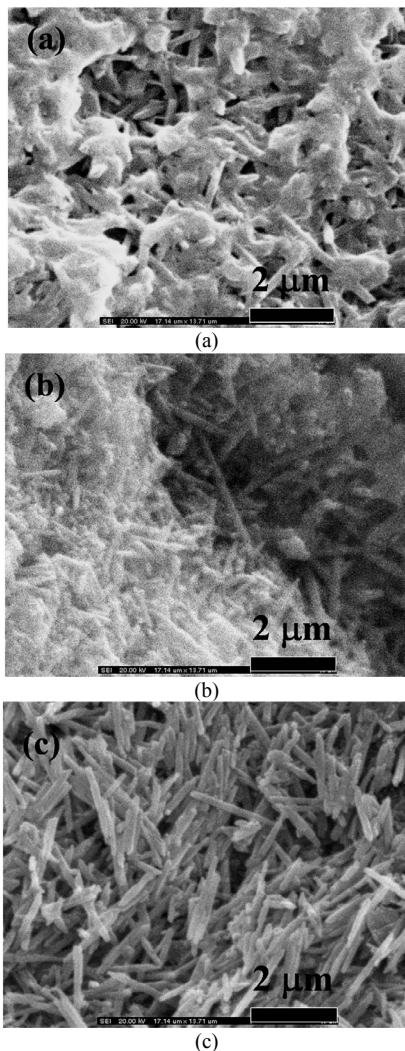

(a)

(b)

(c)

Fig. 3. Glass-ceramics prepared at 1000°C for 4 hours (a) glass G1 (b) glass G2 and (c) glass G3.

Microstructures of crystallized glass samples at 1000°C for 4h are shown in Fig.3. At this temperature the size of aluminum borate whiskers crystallized from G1, G2 and G3 (Figs.3a-c) seemed to be unaffected by the heat treatment temperature. The length of whiskers in crystallized glass sample at 1000°C was shorter than 2 μm and most of them were in sub-micron regime. The diameter of the rods/whiskers was less than 100 nm. At the same etching

conditions more residual glassy phase was observed in G1 composition. This could be related to the more rigid structure of the glass and hence difficulty for crystallization process. When the heat treatment temperature was increased to 1200°C the whiskers or rod-like crystals increase in size significantly. Microstructures for heat treated samples of G1, G2 and G3 at 1200°C are shown in Fig.4a-c. The length and diameter increased dramatically and varied from 5 – 10 μm in length. Whiskers in samples at 1000°C can be correlated with $Al_4B_2O_9$ phase according to XRD data. For samples heat treated at 1200°C, whiskers could be of either $Al_4B_2O_9$ or $Al_{18}B_4O_{33}$ or both. Interestingly, glass composition with higher B_2O_3/SiO_2 ratio led to the hollow tube morphology of the aluminum borate phase (Fig.4b). Some hollow tubes grew in expense of the others and they were surrounded by smaller whiskers which grew slower. The mechanism of formation is not yet known and has not been discussed in any related literature. Glass G3 with the highest B_2O_3/SiO_2 ratio (Fig.4c) showed partially melting of the large hollow tubes. This indicates that the composition of this phase may be slightly different from that in glass G1 and glass G2.
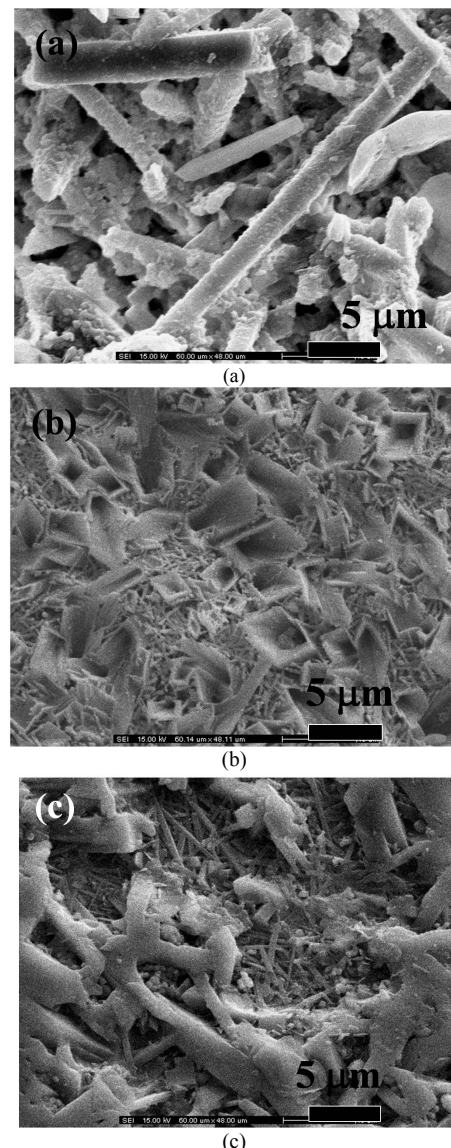

(a)

(b)

(c)

Fig. 4. Glass-ceramics prepared at 1200°C for 4 hours (a) glass G1 (b) glass G2 and (c) glass G3.

In terms of the mechanical properties, surface micro-hardness was measured and calculated from standard Vickers formula: $HV = 1.8544\ P/d^2$ where P is the indentation load and d is the diagonal of the indentation. The data are shown in Fig.5. The hardness values of the base glasses were reported at 25°C. It was found that the average values were highest at 25°C treat treatment. This was related to the fine aluminum borate whiskers in the microstructure. The dropping trend of the hardness value could be related to the larger crystal size. Especially the formation of hollow tubes may have generated large internal stresses and microcracks along the tubes upon indentation. This led to easy paths for crack propagation. Samples having smaller whisker crystals randomly oriented gave the interlocking microstructure which resulted in higher hardness [9].
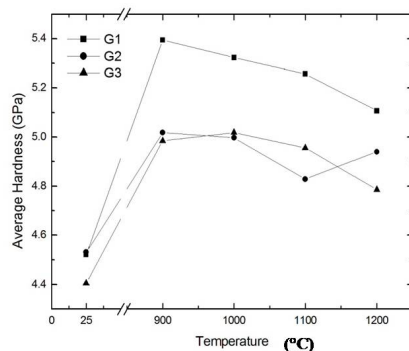

Fig. 5. Surface microhardness of the as annealed and the heat treated samples of G1, G2 and G3.

IV. CONCLUSIONS

The proposed aluminum borosilicate glass system crystallized via a bulk crystallization mechanism, resulting in an increasing amount of aluminum borate whiskers with increasing heating temperature. Different phases were found for samples heat treated at different temperatures. Microstructures and hardness values were effectively influenced by the ratio of B_2O_3/SiO_2 and the heat treatment temperature. All crystallized glass samples showed randomly oriented whisker crystals/rods with uniform microstructure.

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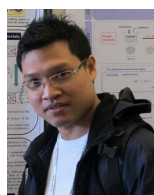
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