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Mechanical Properties of α-Cordierite and β-Spodumene Glass-Ceramics Prepared by Sintering and Crystallization Heat Treatments

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Abstract: The α-cordierite and β-spodumene glass-ceramics containing B_2O_3, P_2O_5, and/or TiO_2 were produced in a bar shape by hot pressing and crystallization heat treatments of glass powders. Various physical properties of the glass-ceramics were examined. The α-cordierite glass-ceramics showed intrinsic high mechanical property values, whereas the β-spodumene glass-ceramics showed rather low ones. The relatively low density in β-spodumene glass-ceramics would lead to the low mechanical property values. This low density in the β-spodumene glass-ceramics would result from a possible premature crystallization which might hinder a completion of sintering of the matrix. The glass-ceramics without TiO_2 showed slightly higher mechanical properties than those with TiO_2. This difference would result from slightly higher density in the glass-ceramics without TiO_2. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Glass-ceramics are the crystalline materials which can be formed by controlled crystallization heat treatments of proper glasses. Most of them have unique properties such as translucency, high strength, and very low and uniform thermal expansion. They have very fine (~1 μm) and randomly oriented crystals with a few percent of the residual glass.[1] The recent applications of glass-ceramics are for matrix materials for ceramic fibre-reinforced composite materials,[2–6] substrate materials for semiconductor packaging,[7,8] heat exchangers,[1] telescope mirrors,[9] cooking wares,[10] and so on.

α-Cordierite ($2MgO–2Al_2O_3–5SiO_2$) and β-spodumene ($Li_2O–Al_2O_3–4SiO_2$) are glass-ceramics well-known for their good mechanical properties (strengths of ~250 and ~150 MPa, respectively; moduli of ~150 and ~100 GPa, respectively), low dielectric constants (~5 and ~6, respectively), and low thermal expansion coefficients (~2×10^{-6} and ~9×10^{-7} °C).[11,12]

A relatively new method of glass-ceramic preparation is the sintering of glass powders, followed by a nucleation heat treatment.[13–16] This technique gives cost benefits by reducing processing temperatures. Further, the formation of complex shapes can be obtained by using equipment common to a ceramic factory.[13]

The preparation of the glass-ceramics by sintering glass powders followed by crystallization heat treatments has been studied previously. Rabinovich[15] examined the sinterability of the cordierite glasses. All of the glasses containing TiO_2 as a nucleating agent, crystallized prematurely and showed poor sintering except those glasses containing Na_2O. Knickerbocker *et al.*[8] studied the sintering behaviour of the cordierite glass-ceramics with and without B_2O_3 and P_2O_5 addition. They found that off-stoichiometric cordierite glasses have lower viscosity and slow crystal growth rate, resulting in good sinterability. Also, they found that even a small amount of B_2O_3 and P_2O_5

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addition is effective to control sintering and crystallization of a cordierite glass. Knickerbocker *et al.*[16] also studied the effect of various oxide addition on the sintering behaviour of β-spodumene glass-ceramics. They reported that the addition of 3 wt% B_2O_3 or P_2O_5 to the stoichiometric β-spodumene glass-ceramic can enhance sintering. By addition of 3 wt% of P_2O_5 and B_2O_3 the shrinkage of the glass pellets during sintering increased by 4.2% and 0.5%, respectively.

The introduction of TiO_2 as a nucleating agent both in the MgO–Al_2O_3–SiO_2 and Li_2O–Al_2O_3–SiO_2 systems has been reported to lead to titanate formation and phase separation. Barry *et al.*[17] reported the formation of precursor nuclei of small crystallites, consisting of a titanium-containing compound in the heat-treated Li_2O–Al_2O_3–SiO_2 glasses. Doherty *et al.*[18] reported that $Al_2Ti_2O_7$ crystals were precipitated and that these crystals act as nuclei for crystallization in a Li_2O–Al_2O_3–SiO_2–TiO_2 system.

Maurer[19] studied the mechanism of crystallization in MgO–Al_2O_3–SiO_2–TiO_2 glass using light scattering and explained the role of TiO_2. He found the crystallization of TiO_2-rich regions to be caused by an emulsion within the vitreous body. Knodrat'ev and coworkers[20] investigated the crystallization of the glasses of the Li_2O–Al_2O_3–SiO_2 system and also observed the formation of liquids of Al_2O_3–TiO_2 type already in the melt, which can serve as nuclei. Beall and Duke[1] indicated that the addition of cations such as Ti^{4+}, Zr^{4+}, Hf^{4+}, Nb^{5+}, Mo^{6+}, W^{6+} and Cr^{3+} can cause the homogeneous glass melt to become immiscible. They observed the amorphous phase separation that develops on cooling of Li_2O–Al_2O_3–SiO_2–TiO_2 glass by transmission electron microscopy (TEM).

Sung *et al.*[21,22] reported the combined effects of B_2O_3 and TiO_2 additions on the sintering and crystallization behaviour of the α-cordierite and β-spodumene glass-ceramic systems. They found that the glass-ceramics containing both B_2O_3 and TiO_2 had approximately the same degree of sintering compared with the glass-ceramics containing only B_2O_3. The glass-ceramics containing B_2O_3 and TiO_2 showed much lowered crystallization temperatures than the glass-ceramics with only B_2O_3.

The purpose of this research is to examine mechanical properties of the α-cordierite and β-spodumene glass-ceramics containing B_2O_3, P_2O_5, and/or TiO_2 which were prepared by sintering followed by crystallization heat treatments. Four-point bending and micro-indentation were used to investigate the mechanical properties.

2 EXPERIMENTAL PROCEDURE

High purity powders of MgO, Li_2CO_3, Al_2O_3, SiO_2, B_2O_3, P_2O_5 and TiO_2 were used to produce cordierite and spodumene glasses. The chemical compositions of each glass are listed in Table 1. B_2O_3, P_2O_5 and TiO_2 were added to the stoichiometric cordierite and spodumene glasses in order to enhance sinterability and decrease the crystallization temperature as well. The chemicals were well mixed by zirconia-ball milling (YTZ Zirconia-Ball Media, Tosoh USA Inc., Atlanta, GA, USA). The glasses were prepared in a 50 ml platinum crucible using an electrical resistance furnace (DT-31-HT, Deltech Inc., Denver, CO, USA) in an air atmosphere. To homogenize the melt the mixture of chemicals were held at 1600 °C for 2 h. The platinum crucible containing the glass melt was removed from the furnace and quenched in distilled water to obtain a clear glass. Pouring the glass melt from the crucible was impossible due to the high viscosity and difficulty in temperature control. The glass fragments well dried in the oven were hand-ground using an alumina mortar and pestle. The ground powders were screened by a 325 mesh sieve and then ball-milled in a rotating milling machine with the same zirconia balls in methyl alcohol. After 6 h mill with a ball-milling speed of approximately 180 rpm the size of the glass particles ranged from 5 to 10 mm. No zirconia contamination was detected by using energy dispersive X-ray spectroscopy (EDS: TN-55000, Noran Co., Middleton, WI, USA) analysis.

A pyrolitic graphite die consisting of a main cylinder, and top and bottom pistons was designed to fabricate glass-ceramic bars. Figure 1 shows a schematic diagram of the graphite die. Inside edges of the die were rounded to avoid any breakage

Table 1. Compositions of the glasses prepared for present study

Glasses	Elements (wt%)						
	MgO	Li_2O	Al_2O_3	SiO_2	B_2O_3	P_2O_5	TiO_2
MASBP	22.00	—	20.00	52.00	3.00	3.00	—
MASBP	22.00	—	20.00	52.00	2.00	2.00	2.00
LASB	—	7.80	26.60	62.70	2.92	—	—
LASBT	—	7.50	25.60	60.35	2.80	—	3.73

during releasing the samples. Paper filters were cut into an exact dimension of the bottom piston and inserted into the bottom of the die. The glass powders were mixed with ethyl alcohol (70 vol% of ethyl alcohol) in a glass beaker and stirred well using a magnetic bar. The glass solution was poured into the graphite die and the glass powders were settled on the paper filters and formed precursor glass bars. After 24 h drying in a vacuum glove box the precursor glass sample with the graphite die was brought into a hot press machine (Physical Science Lab. at the University of Wisconsin-Madison, USA) which had a tungsten heating element and a diffusion pump for maintaining a high vacuum ($\sim 1.3\times10^{-9}$ atm). Applied load was 20.7 MPa. The sample was rate-heated (30 °C/min) to sintering temperatures, 890 °C for α-cordierite and 715 °C for β-spodumene. The temperatures were maintained for 4 h for sintering and then increased to 1050 °C for α-cordierite and 865 °C for β-spodumene. The temperatures were held for 4 h to complete crystallization. The round shape edges of the glass-ceramic bars were cut to make a rectangular shape using a diamond saw and carefully polished using SiC paper (grid #600). The final dimension of the glass-ceramic bars was $11.0\times1.7\times30.0$ mm.

The Archimedes method was used to measure the density of each glass-ceramic bar. Four-point bending was used to obtain flexural strength (modulus of rupture: MOR) and elastic modulus values of the glass-ceramic bars. Ten flexure bars for each glass-ceramic were used for the bending tests. Figure 2 shows a photograph of the four-point bending jig and Instron^{R} machine. The lowest cross-head speed of 0.254 mm min was used for the bending tests.

The glass-ceramic bars were cut into small pieces and mounted by using epoxy. These mounted samples were polished using SiC paper (grid #600) and alumina powder (1.00 and 0.05 μm). Special care was taken to keep the top and bottom surfaces of the epoxy body parallel. Micro-indentation (Micromet II, Micro-hardness Tester, Buehler, Lake Bluff, IL, USA) was used to evaluate elastic modulus and toughness values of the glass-ceramics. The micro-hardness tester can be utilized for both the Knoop and Vickers indentations. The lengths of two diagonals of each Knoop indentation were measured using a special eye-piece that had movable line indicators whose positions were determined by instrument. Ten indentations were measured on each sample and the values of diagonal lengths (a′ and b′) were averaged. These modulus values were compared with those obtained from four-point bending tests.

Fracture toughness (K_{IC}) of each glass-ceramic was determined using the Vickers micro-hardness indentation method. A surface crack was introduced into the sample surface using the micro-hardness tester. Ten indentations were made on each glass-ceramic.

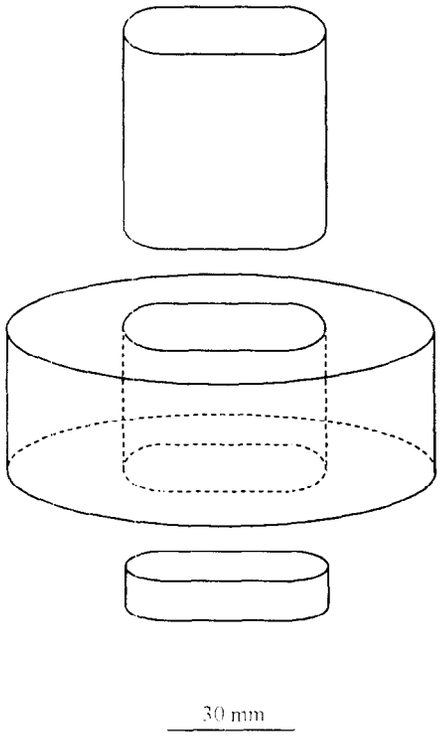

Fig. 1. A schematic diagram of the graphite die designed for glass-ceramic flexure bars preparation for present study.

3 RESULTS AND DISCUSSION

The α-cordierite and β-spodumene glass-ceramic flexure bars were successfully produced by hot

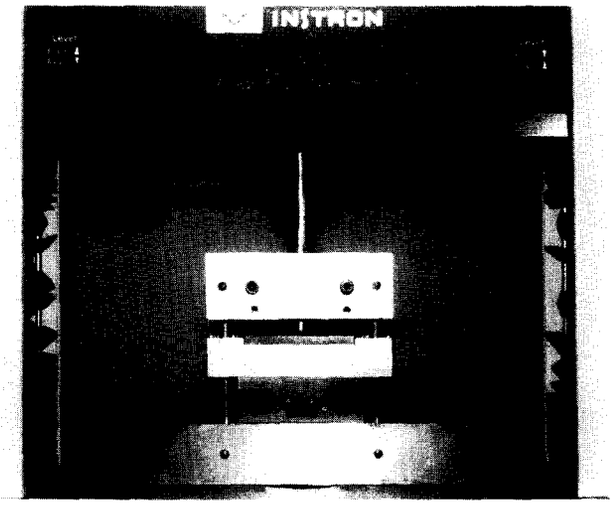

Fig. 2. A photograph of the four-point bending jig and Instron machine used for present study.

pressing. By using the Archimedes method the MASBP and MASBPT glass-ceramics showed 99.87 ± 0.08 and 99.70 ± 0.09% values of a theoretical density, whereas the LASB and LASBT glass-ceramics showed only 93.12 ± 0.07% and 92.55 ± 0.05% values of a theoretical density. The low density values of the LASB and LASBT glass-ceramics would result from a premature crystallization which might have occurred before completion of sintering of the glass bodies. The initiation of premature crystallization would increase the viscosity of glass body dramatically and hinder the sintering.

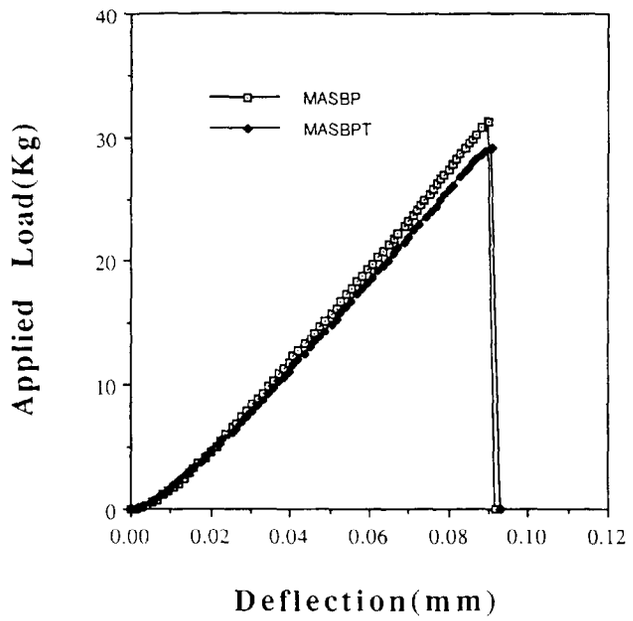

Fig. 3. The load vs deflection curves of the MASBP and MASBPT glass-ceramic bars prepared for present study.

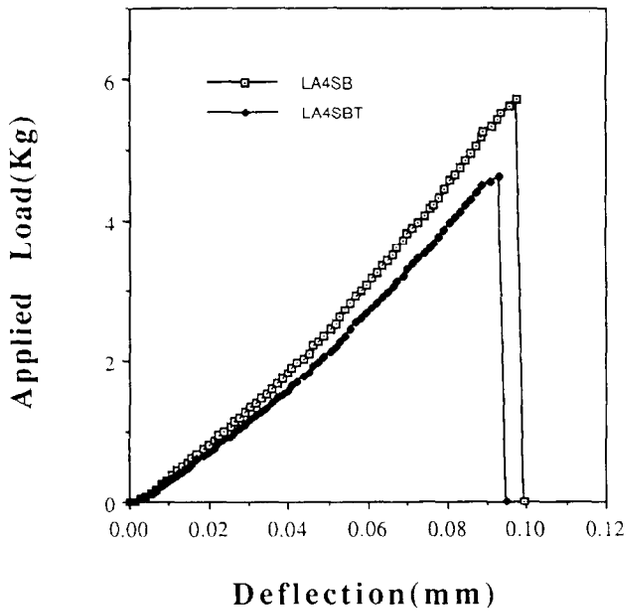

Fig. 4. The load vs deflection curves of the LASB and LASBT glass-ceramic bars prepared for present study.

Four-point bending tests were performed on the glass-ceramic bars. Figures 3 and 4 show typical load vs deflection curves of the MASBP and MASBPT, and the LASB and LASBT glass-ceramics, respectively. Flexural strength (modulus of rupture: MOR) values were calculated by using following equation:

$$MOR = 3P(L_o - L_I)/(2W T^2) \quad (1)$$

where P is the load at fracture (N), L_o and L_I are the outer (24.1 mm) and the inner (11.6 mm) span size, respectively, W is the width of the sample (11.0 mm) and T is the thickness of the sample (1.7 mm). Averaged flexural strengths of the MASBP and MASBPT glass-ceramics were determined as 174.4 and 163.0 MPa, respectively, whereas those of the LASB and LASBT glass-ceramics were determined as 31.7 and 25.4 MPa, respectively.

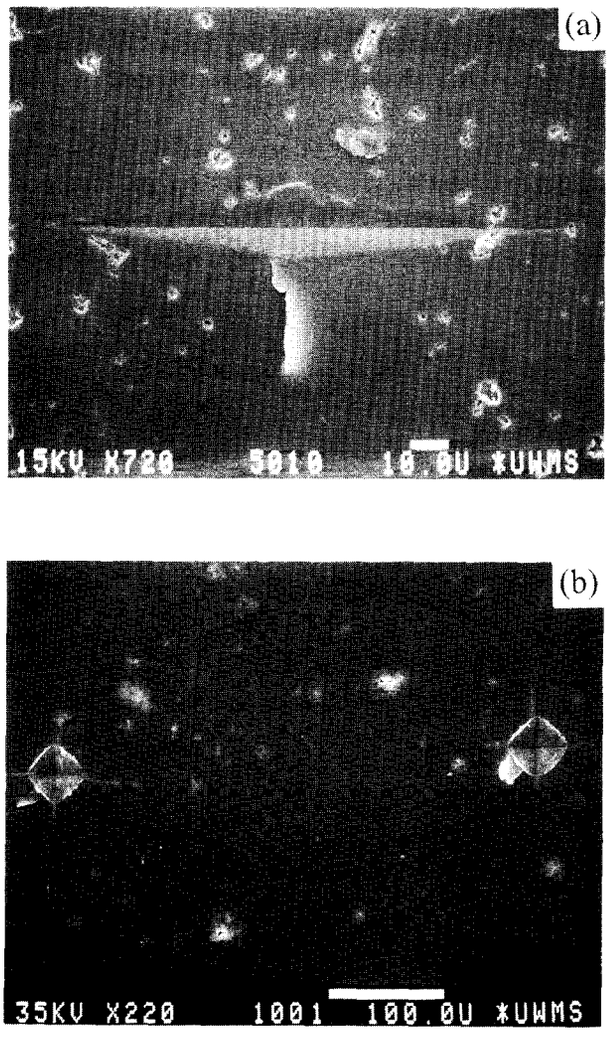

Fig. 5. The scanning electron micrograph (SEM) of Knoop (a) and Vickers (b) micro-indents of the MASBPT glass-ceramic prepared for present study.

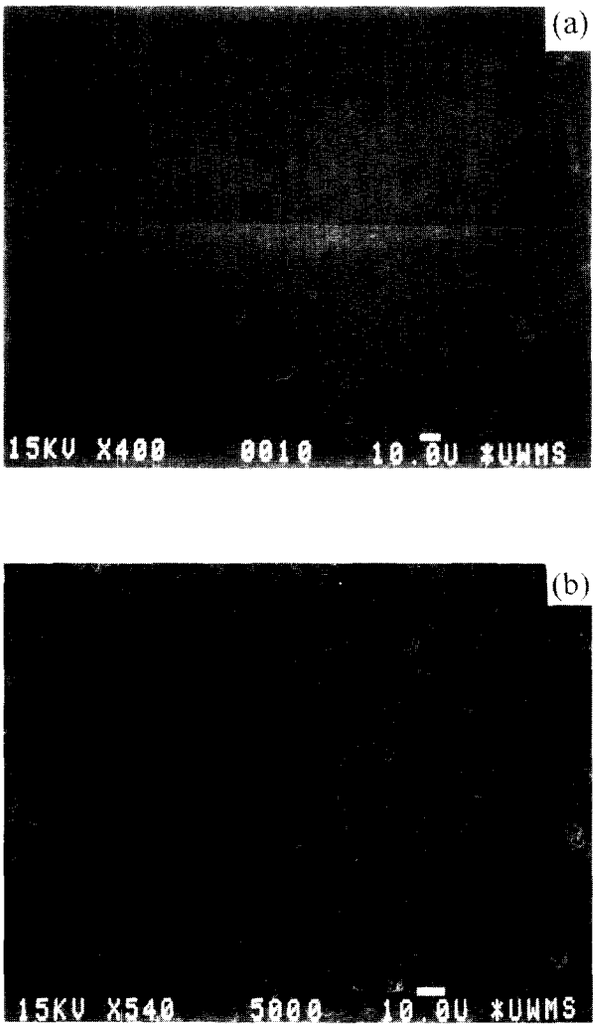

Fig. 6. The scanning electron micrograph (SEM) of Knoop (a) and Vickers (b) micro-indents of the LASBT glass-ceramic prepared for present study.

Elastic modulus values were calculated by using the following equation:

$$E = 11\ P\ L^3/(64\ W\ T^2 D) \qquad (2)$$

where P is the applied load, L is the outer span size, W is the width of the flexure bars (11.0 mm), T is the thickness of the sample (1.7 mm) and D is the deflection. The load (P) and deflection (D) values were taken from the linear portion of the load vs deflection curves in Figs 3 and 4. Averaged elastic modulus values of the MASBP and MASBPT glass-ceramics were determined as 140.8 and 134.3 GPa, respectively, whereas those of the LASB and LASBT glass-ceramics were determined as 26.1 and 22.7 GPa, respectively. The α-cordierite glass-ceramics (MASBP and MASBPT) showed intrinsic high strength and modulus values, whereas the β-spodumene glass-ceramics (LASB and LASBT) showed lower values than their intrinsic ones. These low mechanical properties of the β-spodumene glass-ceramics would result from the low density of the sintered bodies.

Knoop and Vickers micro-indentation was performed on the glass-ceramic samples which were mounted and polished. Figures 5 and 6 show SEM of the Knoop (a) and Vickers (b) micro-indents of the MASBPT and LASBT glass-ceramics. The modulus value of each sample was calculated using the following equation:[23]

$$b'/a' = b/a - \alpha H/E \qquad (3)$$

where b'/a' is the ratio of the indent diagonal dimension (a' is larger dimension), b/a is the ratio of the known Knoop indentor diagonal dimension (1/7.11), α is a constant (0.45), H is the Knoop hardness value measured from the indentations and E is the elastic modulus. Averaged hardness values of the MASBP and MASBPT glass-ceramics were primarily determined as 7.8 and 7.4 GPa, respectively, by using Vickers indentation for each sample, whereas those of the LASB and LASBT glass-ceramics were determined as 1.8 and 2.0 GPa, respectively. By using eqn (3) averaged elastic moduli of the MASBP and MASBPT glass-ceramics were determined as 152.0 and 140.8 GPa, respectively, whereas those of the LASB and LASBT were determined as 32.1 and 29.8 GPa, respectively. These elastic modulus values obtained from micro-indentation were slightly higher than those from the four-point bending tests.

Table 2. Summary of averaged physical properties of the glass-ceramics prepared for present study

Glass-ceramics	Physical properties				
	Density (g/cm^3)	Hardness (GPa)	Modulus (GPa)	Fracture toughness ($MPa \cdot m^{1/2}$)	Flexural strength (MPa)
MASBP	2.61	7.8	152.0[a] 140.8[b]	2.1	174.4
MASBPT	2.60	7.4	140.8[a] 134.3[b]	2.1	163.0
LASB	2.68	2.0	32.1[a] 26.1[b]	1.5	31.7
LASBT	2.62	7.4	29.8[a] 22.7[b]	1.6	25.4

[a]Elastic modulus from micro-indentation.
[b]Elastic modulus from four-point bending tests.

The K_{IC} values were calculated using the following equation:[24]

$$K_{IC} = 0.028H\, a^{1/2}(E/H)^{1/2}(c/a)^{-3/2}\text{MPa} \cdot \text{m}^{1/2} \quad (4)$$

where H is the Vickers hardness, E is the elastic modulus, a is the half size of the indentation diagonal, c is the radial crack size and P is the load on indenter (9.8 N). E values obtained from Knoop indentations were used for this calculation. Averaged fracture toughness value of both the MASBP and MASBPT glass-ceramics was determined as 2.1 ± 0.1 MPa·m$^{1/2}$, whereas those of the LASB and LASBT were determined as 1.5 ± 0.1 and 1.6 ± 0.1 MPa·m$^{1/2}$, respectively. A summary of physical properties of the α-cordierite and β-spodumene glass-ceramics prepared for present study is listed in Table 2.

4 CONCLUSIONS

α-Cordierite (MgO–Al_2O_3–SiO_2–B_2O_3–P_2O_5: MASBP and MgO–Al_2O_3–SiO_2–B_2O_3–P_2O_5–TiO_2: MASBPT) and β-spodumene (Li_2O–Al_2O_3–SiO_2–B_2O_3: LASB and Li_2O–Al_2O_3–SiO_2–B_2O_3–TiO_2: LASBT) glass-ceramic bars were produced by using hot pressing. The α-cordierite and β-spodumene glass-ceramic bars, respectively, showed ~99.8% and ~93.0% of their theoretical density values. The low density in β-spodumene glass-ceramics would result from a premature crystallization which might hinder a completion of sintering of the matrix. In four-point bending and microindentation (Knoop and Vickers) tests performed on the glass-ceramics the α-cordierite glass-ceramics showed their intrinsic high strength (~170 MPa) and modulus (~140 GPa) values, whereas the β-spodumene glass-ceramics showed low strength (~30 MPa) and modulus (~30 GPa) values. The low density would result in these low mechanical properties of the β-spodumene glass-ceramics. The glass-ceramics without TiO_2 (MASBP and LASB) showed slightly higher mechanical properties than those with TiO_2. This would come from slightly higher density in the glass-ceramics without TiO_2.

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