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Immiscibility, nucleation and mechanical properties in the lithia-baria-silica system

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The current work investigates the effects of nucleation heat treatments, on the microstructure and mechanical properties of a novel silicate glass in Li_2O-BaO-SiO_2 system with 1 mol% P_2O_5 as nucleating agent. As-cast glass was exposed to nucleation heat treatments at 490-550 °C for 1-3 h. The microstructural examination was performed by SEM/EDS. The highest Vickers microhardness was determined to be 650 Hv for the sample heat treated at 550 °C for 1 h. The increase in the nucleation time also affected Vickers microhardness and the highest one was determined to be 600 Hv after nucleation for 3 h. The fracture toughness, K_{IC} reached 2.51 MPa.$m^{1/2}$ after nucleation at 550 °C for 1 h. The nucleation temperatures had a more pronounced effect on the fracture toughnesses in comparison to nucleation times. The indentation toughness data was used to determine Weibull parameters from Ln ln [1/(1-P)]- lnK_{IC} plots. Weibull modulus, m of the samples nucleated at 500, 510, 530, 550 °C for 1h. and 540 °C for 2 h. were determined similarly to be 3.8, 3.5, 4.7 and 3.9, respectively. The rest of the samples indicated higher Weibull moduli, which may be attributed to the formations of microcracks due to the mismatch in between newly formed crystals and remaining glassy matrix.

Key words: Silicate glass, Vickers hardness, Indentation toughness, Mechanical properties.

Introduction

Glass-ceramics are formed by melting, controlled nucleation and crystallization heat treatments starting from the glassy matrix [1]. The microstructure and properties of the glass-ceramics are affected by fabrication, glass composition, nucleating agents and the heat treatment [2]. For the controlled crystallization in glass ceramics, the nucleation is the key factor [1]. Stookey, McMillan, Höland and Beall measured experimentally the nucleation rate and crystal growth rate as a function of temperature [3-5]. Kingery et al., Weinberg et al., Zanotto and James reviewed the nucleation mechanisms [6-9].

The crystal nucleation was studied in baria-silica glasses during heat treatment with a liquid-liquid immiscibility effect where a composition change of the baria-rich matrix phase resulted in a rise of nucleation [10].

25.3 and 28.5% BaO glasses show immiscibility BaO-SiO_2 system. Near to BaO.$2SiO_2$ composition, the glasses do not phase separate where the nucleation increases with baria content. Towards both ends of the immiscibility region under the liquidus curve; at low or high BaO amount, spherical particles in a matrix were observed i.e, spherical barium-rich particles in a silica-rich matrix at low BaO contents. Near the immiscibility center, two phases were continuously interconnected for the bulk glass [13]. The immiscibility region was given in Li_2O-SiO_2 and BaO-SiO_2 phase diagrams [11, 12].

According to Kissinger method, the activation energy for BS_2 and LS_2 glasses are 495 ± 10 kJ/mol and 300 kJ/mol, respectively [14]. In addition to barium disilicate (BaO.$2SiO_2$) system, Li_2O is a suitable oxide to increase the rate of melting and facilitates the crystallization [15]. That is why we have chosen to examine this system.

In the present paper, a novel glass in Li_2O-BaO-SiO_2 system was produced by glass melting. After the nucleation heat treatments, Vickers microhardness and fracture toughness by the indentation method were measured. Weibull moduli, m of this particular glass was also calculated.

Experimental Procedure

The production of this particular glass in Li_2O-BaO-SiO_2 system was similar to that described in our previous study [16]. The commercially available SiO_2, $BaCO_3$, Li_2CO_3 and P_2O_5 were used as raw materials. The powder mixtures were subjected to ball-milling for short time. The melting was done inside a Pt crucible at 1400 °C temperature. After pouring into distilled water twice, the melts were refined for 14-16 h and then were cast into graphite moulds. Nucleation heat treatments were done on glass bulk samples between 490-550 °C for 1-3 h depending on the glass transition temperature

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obtained by differential thermal analysis (DTA). The bulk density of samples was determined using geometric dimensions. The optical microscopy images of the nucleated specimens were taken using Nikon Eclipse Optical Microscope at x1000 magnification. Scanning Electron Microscope (SEM) analysis using JEOL JSM-330 was done on nucleated samples after polishing and etching with diluted HF solution for 20-30 s. Vickers hardness (Hv) and Fracture toughness (K_{IC}) were determined on polished samples using the Schimadzu Vickers indenter under 200gr. and 500-1000gr., respectively.

Results and Discussion

The optimum nucleation temperature (540 ºC) was determined by Marotta method [11] as described in our previous study [16].

A phase separation was observed clearly as in Fig.1. However, according to Xia et al., the nucleation temperature is 660C to 770 ºC, with a maximum rate near 712 ºC [13]. Ramsden et al. investigated the nucleation kinetics of $BaO\text{-}SiO_2$ glasses between 673-807 ºC. The highest nucleation rates were close to the stoichiometric $BaO{\cdot}2SiO_2$ composition, not in the immiscibility region [17].

Table 1. Density Measurement Results vs Nucleation temperature and time.

T_N (°C) /t(h.)	Density (gr/cm^3)	%Relative Density	Theoretical Density (gr/cm^3)	Visual appearance
As-cast	2.52	72	3.51	Transparent
490/1	3.00	85	3.51	Transparent
500/1	2.68	76	3.51	Translucent
510/1	2.44	70	3.51	Transparent
520/1	2.88	82	3.51	Transparent
530/1	2.60	74	3.51	Transparent
540/1	3.10	88	3.51	Translucent
550/1	2.93	84	3.51	Transparent
540/2	3.00	85	3.51	Translucent
540/3	3.24	92	3.51	Transparent

Following the nucleation heat treatments which were performed on glass samples between 490-550 ºC for 1-3 h., the densities were measured using geometric dimensions as in Table 1. The visual appearances of the samples after the nucleation heat treatment were also indicated.

SEM images of the samples nucleated at 550 ºC/1 h., 540 ºC/1 h. and 540 ºC/3 h. were indicated in Fig. 2-6, respectively. The microstructures at high magnifications

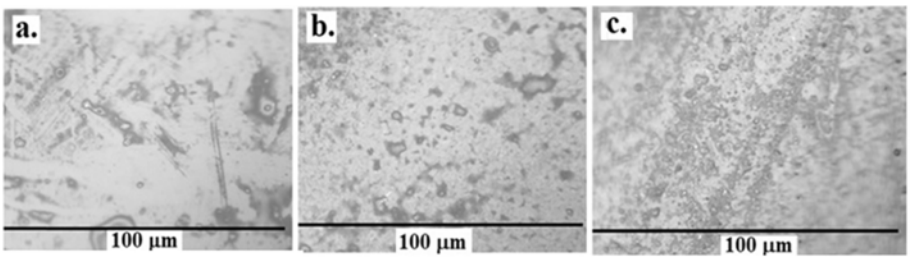

Fig. 1. Optical images of i. a. 510 ºC/ 1 h. x1000 b. 530 ºC/1 h. x1000 and c. 540 ºC/3 h. x1000.

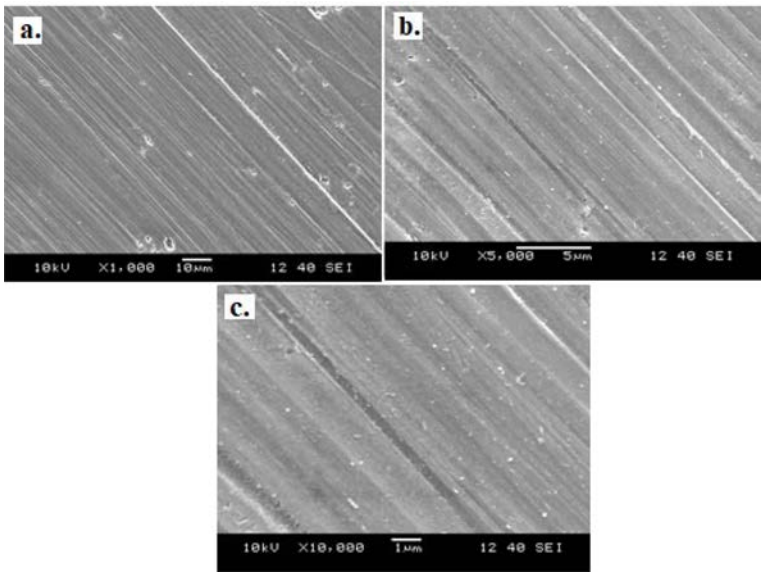

Fig. 2. SEM image after nucleation at 550 ºC/1 h., magnification a. 1000X, b. 5000X and c. 10000X.

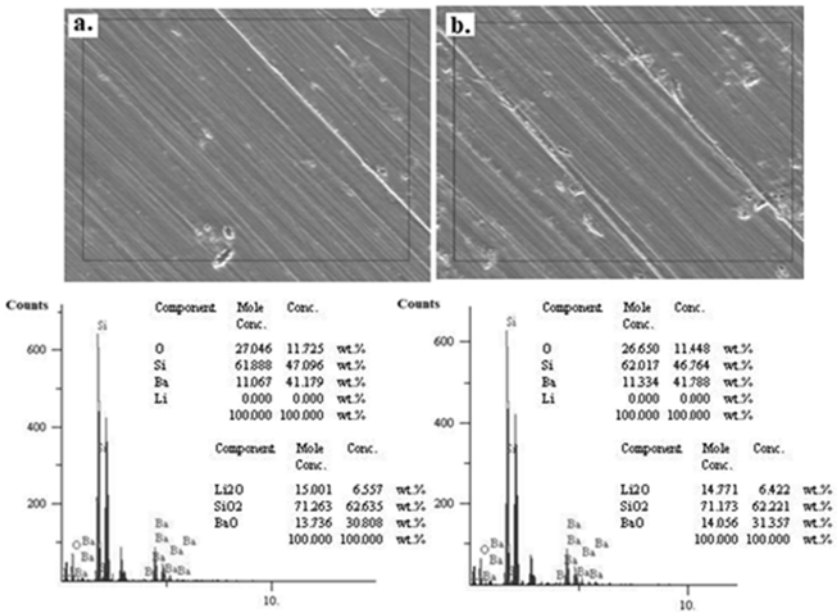

Fig. 3. EDS analysis after nucleation at 550 ºC/1 h., a. Region A, b. Region B.

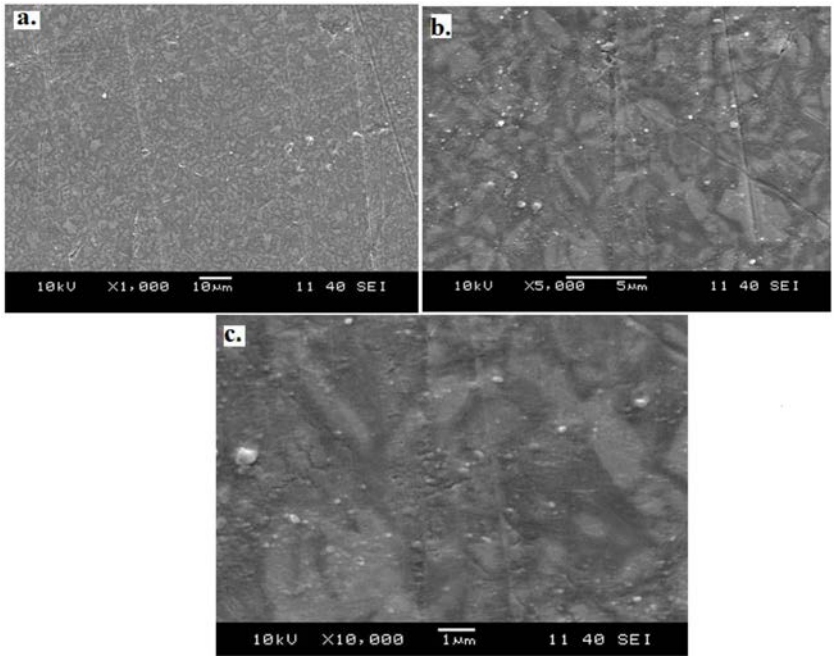

Fig. 4. SEM image after nucleation at 540 ºC/1 h., magnification a. 1000X, b. 5000X and c. 10000X.

showed the presence of a limited phase separation after the nucleation at 550 ºC/1h. However, phase separation became more evident after 540 ºC/3 h., which is the optimum nucleation temperature. The nucleation at 540 ºC/1 h. resulted in the onset of a spherulitic morphology, which is clearly observed at x5000 and x10000. EDS analysis results as in Fig. 3-7, showed that there is a homogeneous composition throughout the microstructure. Thus there was no compositional change between several points in the microstructure. Mole fraction of Li_2O, BaO and SiO_2 oxides in EDS analysis corresponds to $0.25[Li_2O.2SiO_2]$ $-0.75[BaO.2SiO_2]$ binary compound.

In order to determine the effect of nucleation heat treatment on the mechanical properties of the particular glass, Vickers hardness, H_v and indentation fracture toughness, K_{IC} of several nucleated samples for 1-3h. were measured.

Vickers hardness versus nucleation temperature was given is Fig. 8.a. The trend shows an increase up to highest hardness at a nucleation temperature of 550 ºC, which is 683.7 Hv (6.7 GPa). The increase in hardness can be attributed to partial increase of crystallinity due to heat treatment. Vickers hardness versus nucleation

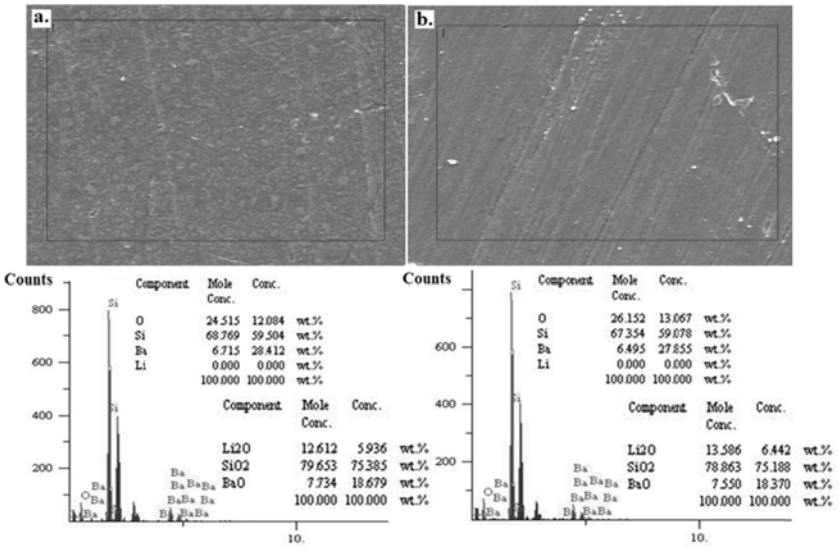

Fig.5. EDS analysis after nucleation at 540 ºC/1 h., a. Region A, b. Region B.

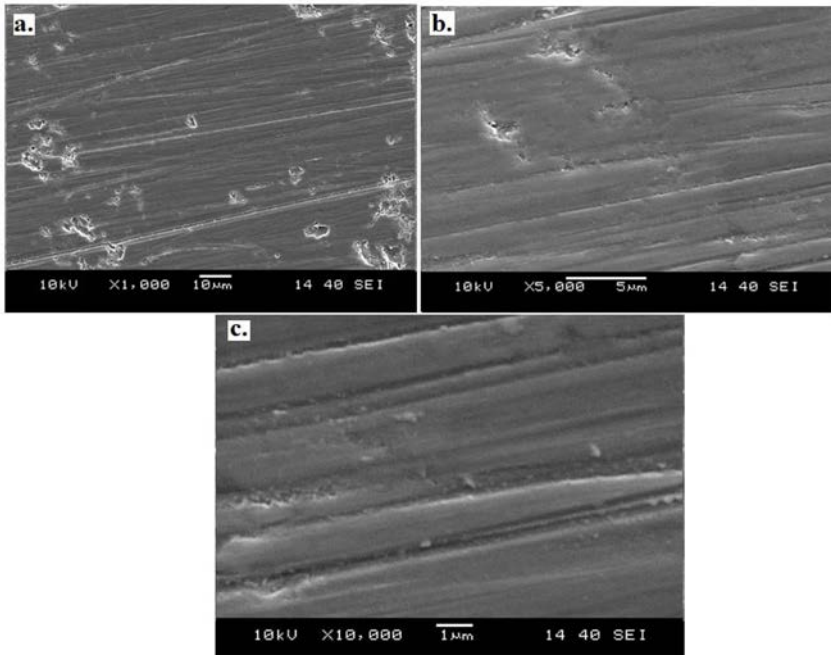

Fig.6. SEM image after nucleation at 540 ºC/3 h., magnification a. 1000X, b. 5000X and c. 10000X.

time was also given in Fig. 8.b. The increase in the nucleation time up to 3 h. resulted in a rise in hardness, particularly in between 2 and 3 h. which were 555.3 (5.5 GPa) and 607.7 Hv (~6 GPa) for 2 and 3 h. of nucleation treatment, respectively.

After Vickers hardness measurements depending on the nucleating parameters, fracture toughness of this particular glass has been determined using crack length (c) and indentation load (P) parameters according to Eq. [1] given in Gong and Chen's study [18].

where E is the Young modulus of silicate glasses and H is the Vickers hardness. E was chosen to be 99GPa as reported in the standard literature [19].

According to Fig. 9.a, as the nucleation temperature increased, fracture toughness increased gradually up to 540 ºC and reached 1.3MPa.m$^{1/2}$. After nucleation heat treatment at 550 ºC, toughness increased dramatically up to highest value of 2.51 MPa.m$^{1/2}$. A probable reason can be the high content of barium oxide in this particular glass. In Fig. 9.b, between 1 and 3 h. nucleation, fracture toughness changed from 1.3 to 1.45 MPa.m$^{1/2}$. Albakry et. al determined K_{IC} values for perpendicular and parallel faces, which are above 1 MPa.m$^{1/2}$ and 1.5 MPa.m$^{1/2}$, respectively [20]. It was concluded that the nucleation temperatures had a more pronounced effect on the fracture toughnesses in comparison to nucleation times.

The mean crack half-lengths, $\bar{c}$ for 15 indentations after the nucleation heat treatments were measured

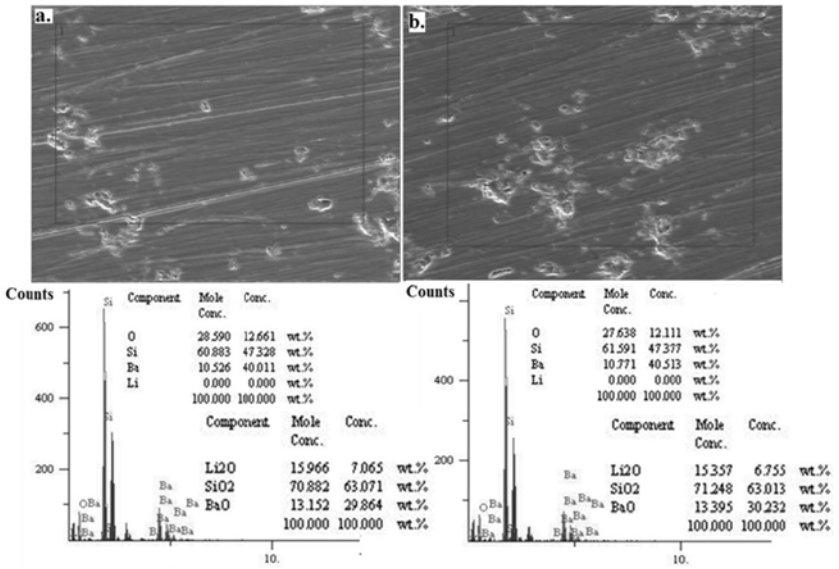

Fig. 7. EDS analysis after nucleation at 540 ºC/3 h., a. Region A, b. Region B.

Table 2. Crack half-length data for nucleation temperatures and times.

T_N(°C) / t(h.)	Mean, μm	*SD, μm	**C_V
490/1	41.60	1.4	0.04
500/1	41.64	8.6	0.04
510/1	40.96	8.5	0.02
520/1	38.58	2.1	0.00
530/1	32.08	4.0	0.15
540/1	34.46	3.8	0.06
550/1	39.72	7.5	0.01
540/2	37.27	6.7	0.07
540/3	36.85	3.0	0.09

*SD = Crack half-length standard deviation, **C_V = Coefficient of variation.

Table 3. Weibull moduli, m and scale parameters, K_0 for nucleation temperatures and times.

T_N (ºC) / t(h.)	m	K_0 (MPa. $m^{1/2}$)
490/1	22.9	0.25
500/1	3.8	0.39
510/1	3.5	0.45
520/1	21.1	0.37
530/1	4.7	0.41
540/1	14.6	0.51
550/1	3.9	1.02
540/2	4.2	0.53
540/3	9.4	0.42

were given in Table 2.

The nucleation heat treatment temperatures decreased the crack half-lengths mostly at 530 and 540 ºC, i.e at the optimum nucleation temperature. The crack half-length changed from 41.6mm at 490 ºC to 39.72 μm at 550 ºC. The nucleation time for 1-3h. did not change

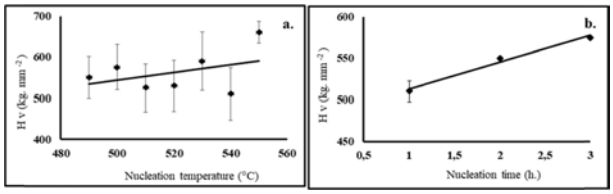

Fig. 8. Vickers indentation data versus a. nucleation temperature, b. nucleation time.

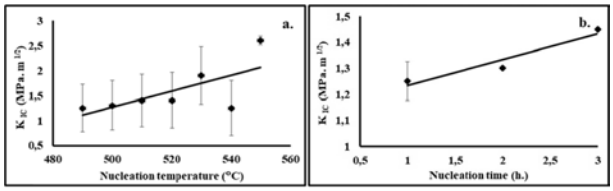

Fig. 9. Indentation fracture toughness versus a. nucleation temperature, b. nucleation time.

the crack half-length significantly. As shown in Fig. 10, Ln ln [1/(1-P)]- lnK_{IC} plots indicated a linear relationship. Besides, Weibull moduli, m and scale parameters, K_0 obtained from Ln ln [1/(1-P)]- lnK_{IC} plots were given in Table 3.

As in Table 3, the sample nucleated at 540 ºC for 1 h. had a Weibull modulus, m of 14.6, which exhibited a great amount of crystallization in the microstructure since this is the optimum nucleation temperature determined by DTA analysis. Since m is a parameter related to the scatter of measured values, i.e fracture toughness, a better homogeneity was observed in the mechanical properties in the less crystallized samples. However, when the nucleation temperature increased, some of the glassy matrix started to crystallize and a heterogeneous microstructure occurred.Thus the uniformity of the mechanical properties diminished. Since the optimum nucleation temperature for this

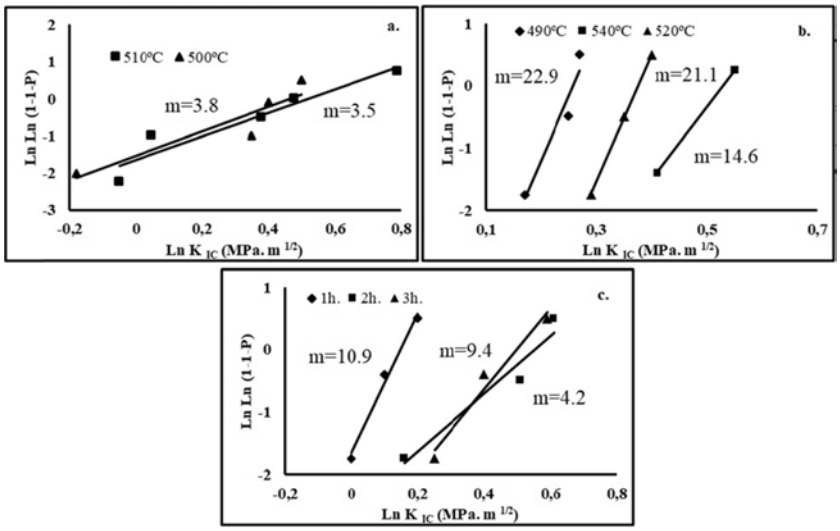

Fig.10. Ln ln [1/(1-P)]- lnK_{IC} plots for a. and b. nucleation temperatures, and c. nucleation times.

particular glass was 540 ºC, more crystals in the microstructure are expected to form in this sample, which in turn decreased Weibull modulus.This may be attributed to the formations of microcracks due to the mismatch in between newly formed crystals and remaining glassy matrix.The samples nucleated at 490 and 520 ºC had Weibull moduli of 22.9 and 21.1, respectively.

Conclusions

In the present study, the mechanical properties of a novel glass in Li_2O-BaO-SiO_2 system, which was produced by casting were investigated. As-cast samples were exposed to several nucleation heat treatments between 490 and 550 ºC for 1-3 h. Following the nucleation heat treatments, optical images of the samples were taken to reveal phase seperation. The most clear evidence of phase seperation was observed in the sample nucleated at 540 ºC for 3 h. Visual apperances of most samples indicated transparency whereas others such as nucleated at 540 ºC/1 h. and 540 ºC/2 h., showed translucency. The highest Vickers microhardness was obtained at a nucleation temperature of 550 ºC, which is 683.7 Hv (6.7 GPa). The possible reason is the partial increase of crystallinity due to heat treatment. After nucleation heat treatment at 550 ºC, indentation fracture toughness, K_{IC} increased dramatically up to highest value of 2.51 MPa.$m^{1/2}$. Also, Ln ln [1/(1-P)]- lnK_{IC} plots were drawn to determine Weibull moduli, m and scale parameters, K_0 for nucleated samples. Weibull modulus, m of the samples nucleated at 500, 510, 530, 550 ºC for 1 h. and 540 ºC for 2 h. were determined similarly to be 3.8, 3.5, 4.7 and 3.9, respectively. Higher Weibull moduli were calculated from the other samples due to microcracks formed by mismatch in between newly formed crystals and remaining glassy matrix.

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