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Development and Crystallization Study of Li_2O-B_2O_3-SiO_2 Glass Ceramic Rich with ZrO_2

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GLASS ceramic in the system Li_2O-B_2O_3-SiO_2 was prepared by adding different amounts of ZrO_2 up to maximum saturation. DTA, XRD and SEM were used to study the crystallization behavior of these glass samples. Tetragonal and monoclinic zirconia, are the only crystallized phases obtained after different heat treatment schedules. Fraction of transformed ZrO_2 and total intensity of ZrO_2 were calculated. Microhardness was measured for different samples, and it was found to be depending on the amount of ZrO_2 added and the heat treatment parameters. Sample contains 20 g ZrO_2 and treated at 650ºC for 10 hr showed higher microhardness value (14.99GPa).

Keywords: Hardness, Glass-ceramic, Borosilicate, Zirconia and Martensitic transformation.

Modern science and technology constantly require new materials with special properties to achieve breathtaking innovations. This development centers on the improvement of scientific and technological fabrication and working procedures. That means rendering them faster, economically more favorable, and better in quality. At the same time, new material is introduced to improve our general quality of life, especially in daily life. Among these new materials, one group plays a very special role; glass-ceramic materials(1) .

Glass-Ceramics offer the possibility of combining the special properties of conventional sintered ceramics with the distinctive characteristics of glasses. So developing glass-ceramics demonstrates the advantage of combining various remarkable properties in one material.

Greater toughness is desired for glass-ceramics and many efforts are being made, including the formation of surface compressive stresses through ion exchange, (2-4) fiber reinforcement using both brittle (5,6) and ductile (7) fibers, and the addition of titanium (Ti) particles to bioactive glass-ceramics.(8)

Alternatively, there are methods to achieve glass-ceramics with higher toughness by modifying the microstructure of glass-ceramics primarily through crystallization. Chain silicate formation and zirconia (ZrO_2) precipitation are such methods (9-14). In this process, usually metastable, tetragonal ZrO_2 (t-ZrO_2)

particles are dispersed in a glass or glass-ceramic matrix. T-ZrO_2 phase particles transform to stable monoclinic ZrO_2 (m-ZrO_2) phase particles during fracture absorbing mechanical energy and thus increasing toughness of the material. (12)

In this work we aimed at preparation, characterization and studying the crystallization behavior of glass ceramics in the system Li_2O-B_2O_3-SiO_2 with different amounts of ZrO_2 till maximum saturation.

Experimental Procedure

Preparation of materials

Chemical composition of the base glass used in mass% is shown in Table 1. The base composition was mixed with different amounts of ZrO_2 (12.5, 15, 17.5, and 20 g over 100% batch compositions) which was added gradually till complete solubility avoiding any undesirable precipitation of ZrO_2 in the formed glass. This glass forming system was chosen keeping in mind crystallization of ZrO_2 alone and only after an additional thermal treatment in which time and temperature control the process. The samples were denoted L12.5, L15, L17.5 and L20 according to amount of ZrO_2 added.

TABLE 1. Chemical composition of base glass in mass%.

Name of sample	Li_2O	B_2O_3	SiO_2
L	5.64	26.29	68.07

After well mixing the batch compositions , materials were melted in a Pt crucible in an electrically heated Globar furnace at 1500°C for 3 hr with occasional swirling every 30 min to ensure homogenization. The melt was then cast into hot steel moulds which were then rapidly transferred to a muffle furnace for, annealing, adjusted at 550°C for 1 hr and then switched off to obtain strain-free glass samples.

Analytical methods

Differential thermal analysis (DTA) (Shimadzu, DTG-50/50H) was utilized to determine the glass transition temperature (T_g) and crystallization temperature (T_c) of the glass samples. The DTA measurements were performed using ~ 35 mg of powdered glass sample (of 90-250 μm grain size), in a ceramic crucible using powdered alpha Al_2O_3 as a reference material.

Identification of crystalline phases was carried out by X-ray diffraction (XRD, Rigaku Miniflex with graphite monochrometer, Cu Kα radiation) each measurement in the 2 theta range 27-33° was the sum of three runs, corresponding to 6 sec per step of 0.01°.

The crystallization of zirconia was measured through a weighted sum of the integrated intensities of (*hkl*111) tetragonal phase (T) and (*hkl* 111) + (*hkl* -111) monoclinic phase (M), while the relative percentages of the two phases were evaluated following the Toraya *et al.*(15,16) method. The integrated intensities were obtained using a computer program of Rigaku Miniflex. The program permits the performance peak separation, $K_{\alpha 2}$ elimination and background subtraction.

The surfaces of glass-ceramics samples were examined by the scanning electron microscope (SEM, JEOL JSM-5200), after etching by 1:1 of 5%HNO_3 and HF acid for 60 seconds, then coating with gold.

Mechanical properties were measured on the polished glass-ceramics samples using a microhardness testing machine (Mitutoyo, HM-100 series), and that by application of 0.2 kg (1.961 N) load.

Results and Discussion

Crystallization behavior

DTA results of ZrO_2-free glass and its' counterpart containing different additions of ZrO_2 (Fig.1) revealed increasing in transition temperature and decreasing the crystallization temperature by increasing ZrO_2 additions. It is noticed that, the glass transition temperature (T_g) increases from 502°C in the base glass (free ZrO_2) to 565°C when maximum percentage of zirconium was added (L20) while the crystallization peak temperature decreases largely from 912°C in the base glass to 703°C in the 20% ZrO_2.

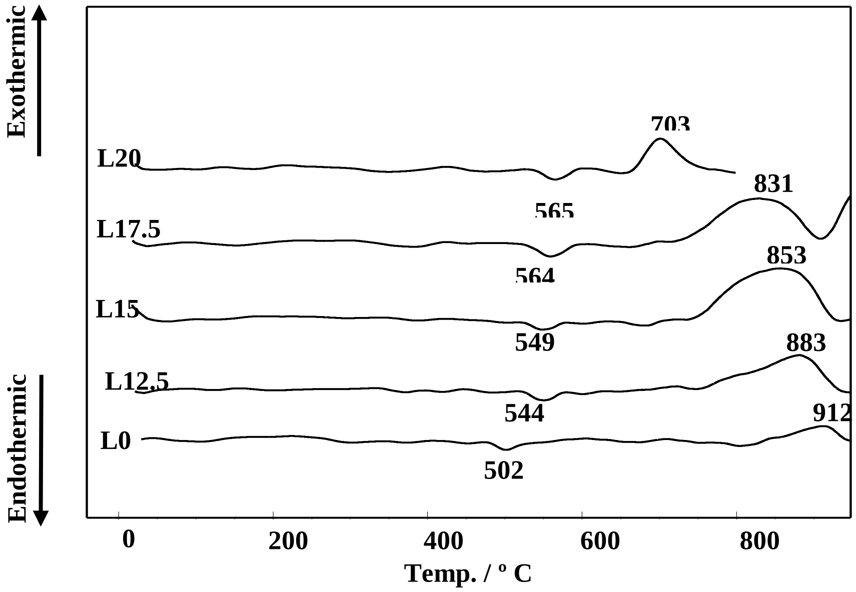

Fig. 1. DTA curves of Li_2O- B_2O_3- SiO_2 glass with 0 mass% (L0), 12.5 mass% (L12.5), 15 mass% (L15), 17.5 mass% (L17.5) and 20 mass% (L20) of ZrO_2.

The glass transition temperature (T_g) was increased by adding ZrO_2 due to increasing in the viscosity,[12)] while the decreasing in the crystallization temperature by adding ZrO_2 may be explained on the basis of increasing amount of ZrO_2 added which leads to enhancement of the precipitation of ZrO_2 phases. Another explanation may be a change in the structure of the residual glassy matrix, whereby the required diffusion of material is facilitated and the necessary reaction kinetics are initiated. (12)

Through training different heat-treatment schedules, the best temperatures for heat-treatment were found to be at 650 and 700ºC. The only formed phases were tetragonal and monoclinic forms of zirconia as shown in Fig. 2 and 3 (to reduce XRD figures we showed only here XRD figures for samples heat treated at 650ºC for 25hr and L20 sample heat treated at 700ºC for different times for its scientific importance and the other data were recorded within the text).

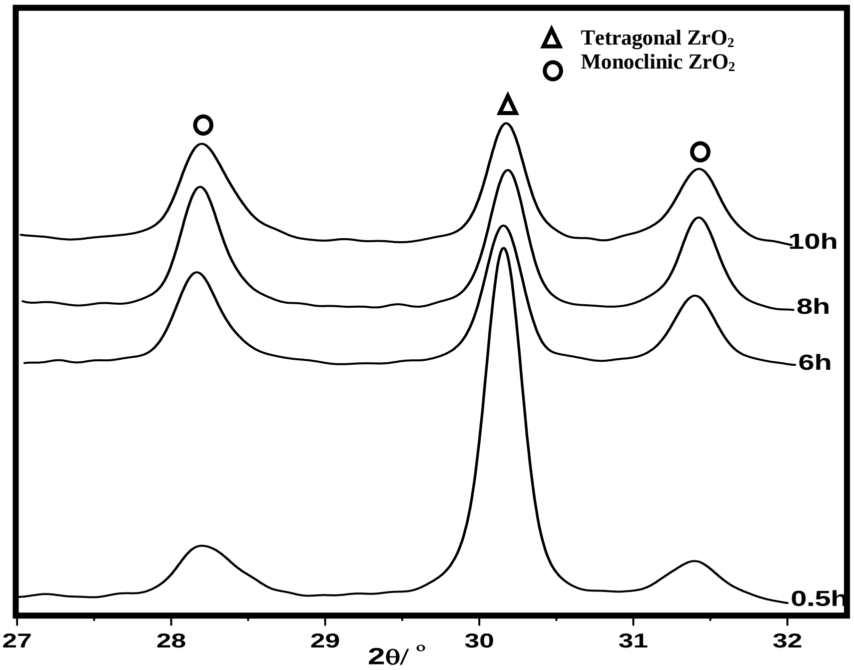

Fig.2. XRD patterns of Li_2O- B_2O_3- SiO_2 glass-ceramics with 20 mass% (L20) heat-treated at 700ºC for different time.

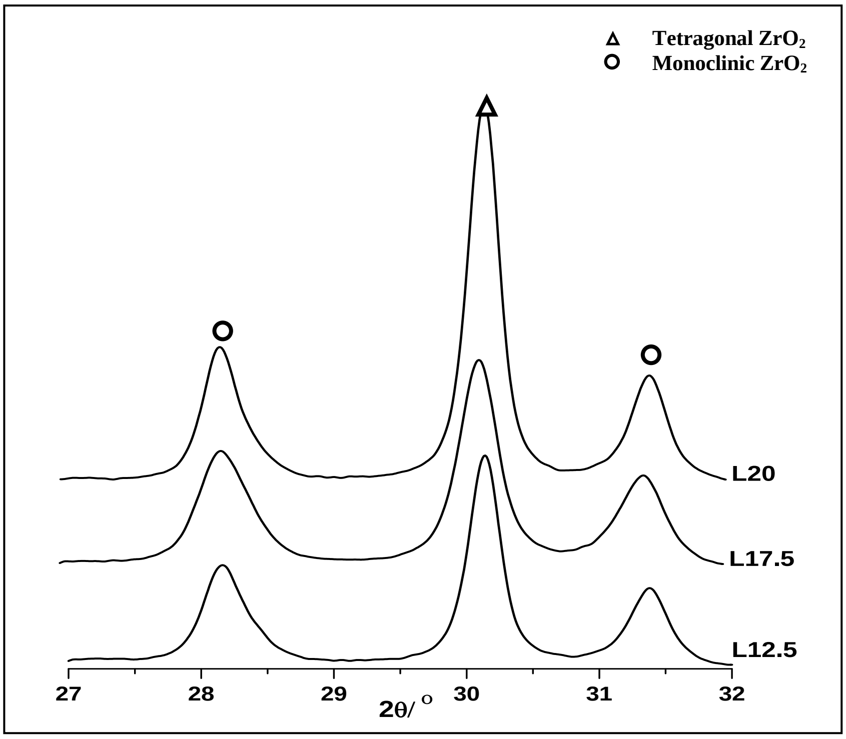

Fig. 3. XRD patterns of Li_2O- B_2O_3- SiO_2 glass-ceramics with 12.5 mass% (L12.5), 17.5 mass% (L17.5) and 20 mass% (L20) heat- treated at 650°C for 25 hr.

Data of different XRD analysis showed that, in L12.5 sample heat treated at 650°C, the tetragonal phase starts to appear after 4 hr and its intensity slightly increases to reach maximum after 10 hr. Monoclinic phase starts to crystallize after 8 hr.

By increasing the amount of ZrO_2 added, the intensity of tetragonal phase increases and the crystallization starts after lower time.

At the maximum percentage of ZrO_2 (20%), (Fig. 2) both major tetragonal phase and minor monoclinic phase were crystallized after the lowest time of heat-treatment (700°C/0.5hr). The maximum intensity of tetragonal phase is reached after 1 hr and by increasing time of heat-treatment at the same temperature, the intensity of tetragonal phase slightly decreases while the monoclinic phase was increased which is due to the martensitic transformation (transformation from tetragonal phase to monoclinic).

Figure 3 shows XRD of different samples heat treated at 650ºC for 25hr, revealing significant increase in the degree of crystallization of tetragonal form as major phase beside monoclinic form as minor phase. The tetragonal form was found to be enhanced by increasing time of heat treatment.

By increasing temperature of heat-treatment to 700ºC, the tetragonal and monoclinc phases start to form at lower time than in case of 650ºC.

Studying the effect of increasing time of heat treatment on the development and stability of the crystallized phases. It is noticed that the crystallization of t-ZrO_2 in L12.5, L17.5 and L20 samples was largely enhanced by about 2.97, 2.76, 3.28 order, respectively by heat-treatment at 650ºC for 25 hr and by about 2.71, 2.5, 2.5 order, by heat-treatment at 700ºC/15 hr, respectively than samples heat treated at 650ºC for 15hr.

Fraction of transformed ZrO_2

The fraction of transformed (*i.e.* monoclinic zirconia) was calculated from the X-ray integrated intensities of the m-ZrO_2 (*hkl*-111) and (*hkl* 111) peaks and from the t-ZrO_2 (*hkl* 111 peak) and plotted versus time of heat treatment as shown in Fig. 4a-c.

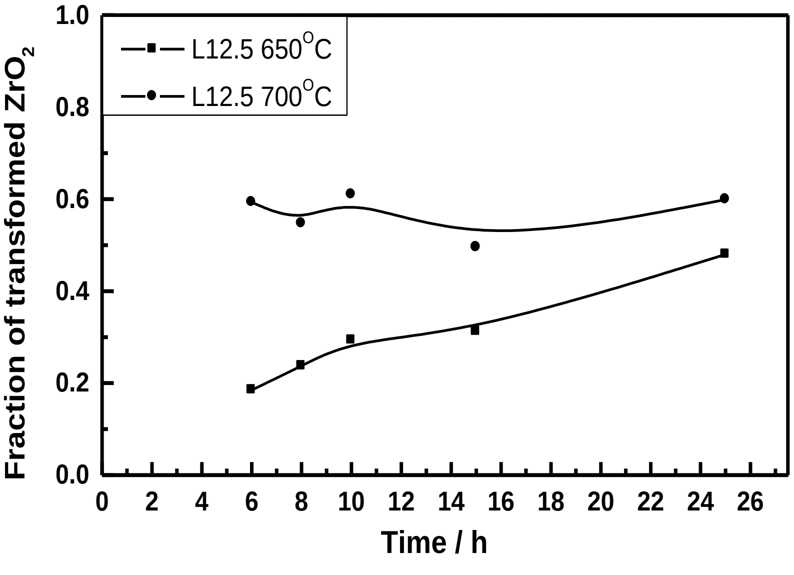

Fig.4a. Fraction of transformed, *i.e.* monoclinic, ZrO_2 versus heat-treatment times for Li_2O- B_2O_3- SiO_2 glass-ceramics with 12.5 mass% (L12.5) at different temperatures 650 and 700°C.

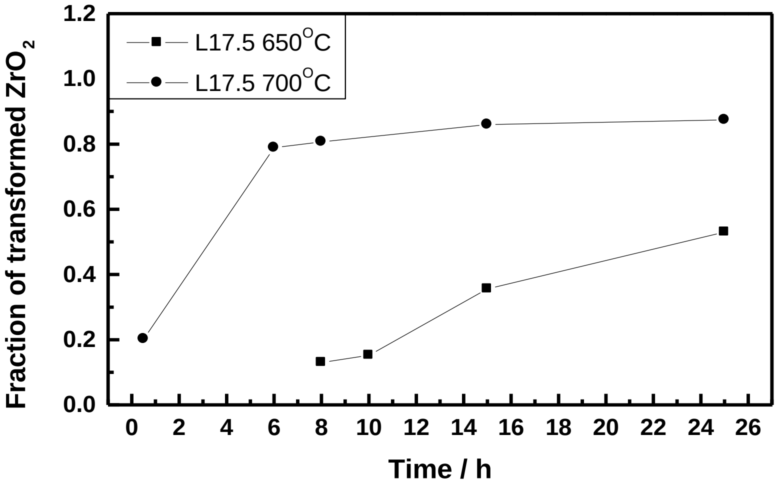

Fig.4b. Fraction of transformed, *i.e.* monoclinic, ZrO_2 versus heat-treatment times for Li_2O- B_2O_3- SiO_2 glass-ceramics with 17.5 mass% (L17.5) at different temperatures 650 and 700°C.

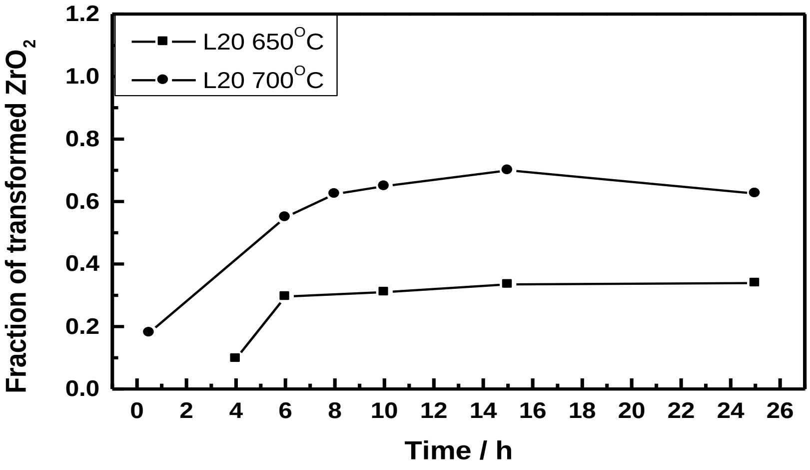

Fig.4c. Fraction of transformed, *i.e.* monoclinic, ZrO_2 versus heat-treatment times for Li_2O- B_2O_3- SiO_2 glass-ceramics with 20 mass% (L20) at different temperatures 650 and 700°C.

In general, the fraction of transformation for samples heat-treated at 700ºC is higher than that heat treated at 650°C. The fraction of transformed monoclinic is observed to increase continuously up to 6 hr, after that the fraction seems to exhibit constancy where the relative intensity between T and M forms are exactly constant as shown before from X-ray analysis.

By increasing time of heat-treatment (up to 6 hr) the particle size of tetragonal phase increases till it reaches the critical size after that the tetragonal phase is transformed to monoclinic phase and the transformed monoclinic phase increases. Also, with increasing the percentage of ZrO_2, the amount of transformed tetragonal is much more than the amount of transformation which occurs at the lower percentage of ZrO_2 leading to an increase in the fraction of transformed monoclinic.

Total intensity of ZrO_2 *for L group*

The crystallization kinetics have been studied by evaluating the sum of the integrated intensities of (*hkl* 111) tetragonal and (*hkl* 111) and (*hkl* -111) monoclinic diffraction lines using equation I (total) = I (T) + 0.80 I (M)

Figures 5a-c show the total intensity I (total) as a function of heat-treatment times at 650 and 700ºC. The total intensity is observed to increase with increasing the time of heat-treatment and also with the temperature as discussed before. In some samples as (L12.5) (Fig. 5a), although the time of heat-treatment increases to 25 hr the total intensity is observed to decrease due to the decreased intensity of tetragonal phase, so total intensity of ZrO_2 decreases more than that heat-treated at 15 hr.

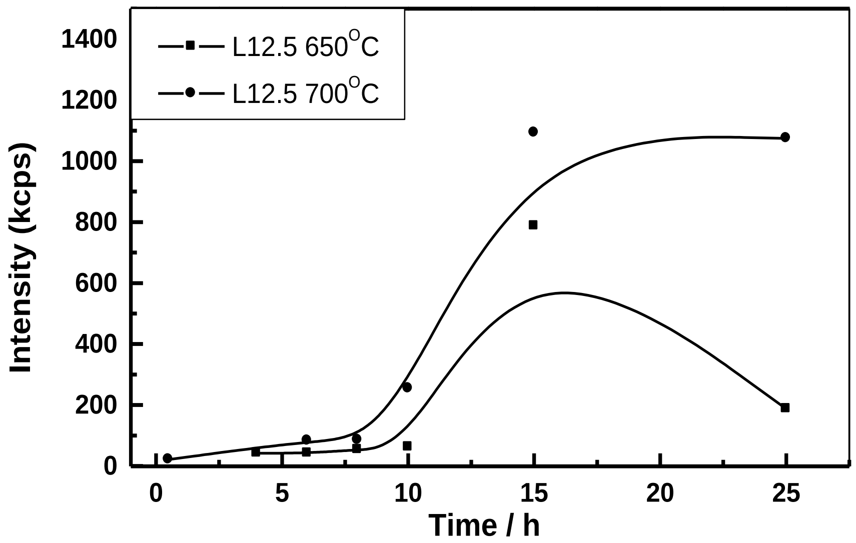

Fig. 5a. XRD total intensity I (total) versus heat-treatment times for Li_2O- B_2O_3-SiO_2 glass-ceramics with 12.5 mass% (L12.5) at different temperatures 650 and 700ºC

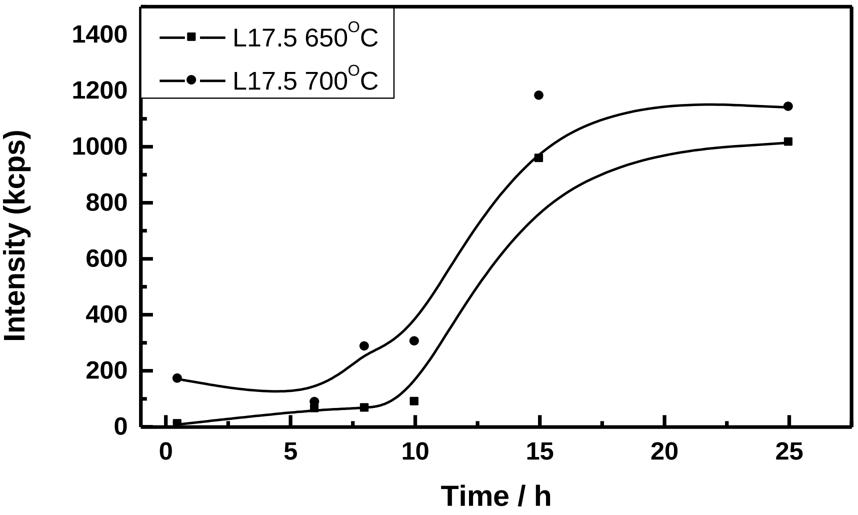

Fig.5b. XRD total intensity I(total) versus heat-treatment times for Li_2O- B_2O_3- SiO_2 glass-ceramics with 17.5 mass% (L17.5) at different temperatures 650 and 700°C.

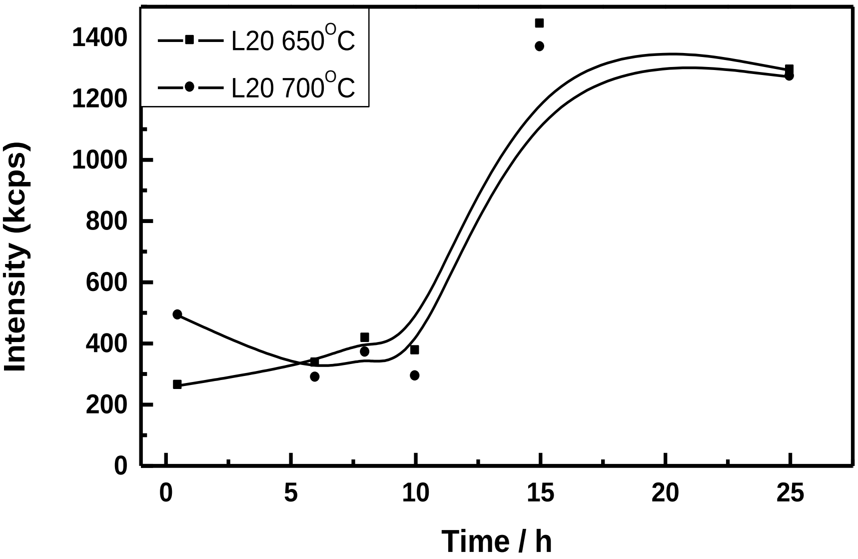

Fig.5c. XRD total intensity I (total) versus heat-treatment times for Li_2O- B_2O_3- SiO_2 glass-ceramics with 20 mass% (L20) at different temperatures 650 and 700°C.

Microstructure of glass-ceramics

SEM studying of different samples is shown in Fig. 6 -10. Studying the surface of sample L12.5 heat-treated at 650ºC/10 hr (Fig.6a) reveals crystallization of uniform microcrystalline structure of fine rounded crystals of monoclinic form between ultrafine smaller crystals of tetragonal form. It is observed that there are no cracks noticed which reveals to the smaller fraction of transformation at this heat-treatment. Figure 6b shows SEM of the surface of sample L12.5 heat-treated at 700ºC/0.5 hr which reveals dispersed crakes on the surface of sample in between well order rounded crystals.

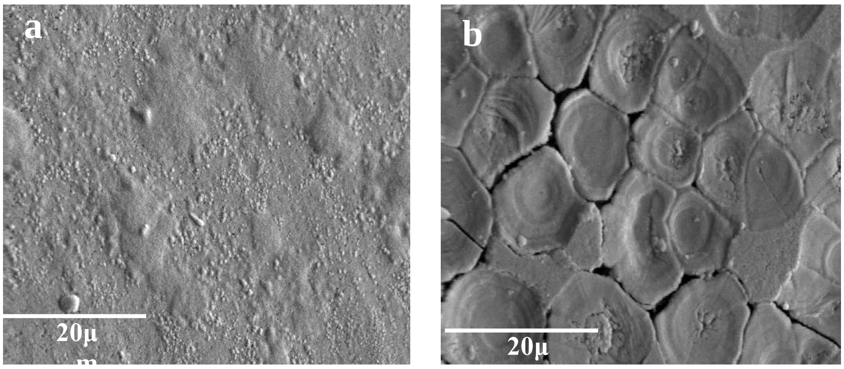

Fig. 6. SEM of L12.5 heat-treated at a) 650ºC for 10 hr and b) at 700ºC for 0.5 hr.

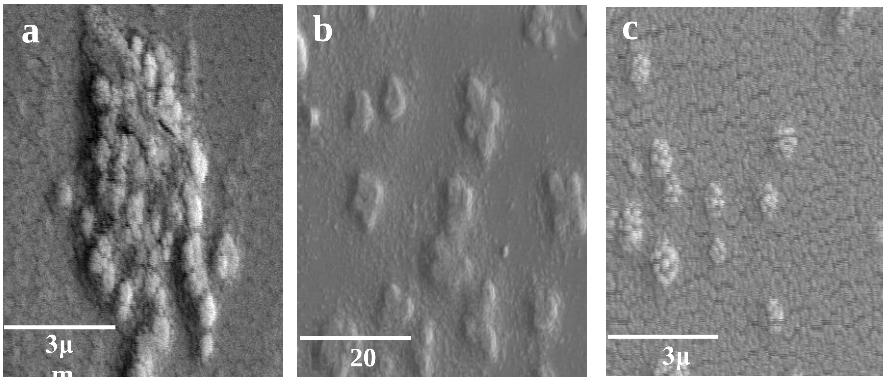

Fig. 7. SEM of L17.5 heat-treated at a) 650ºC for 4 hr and b&C) at 700ºC for 0.5 hr.

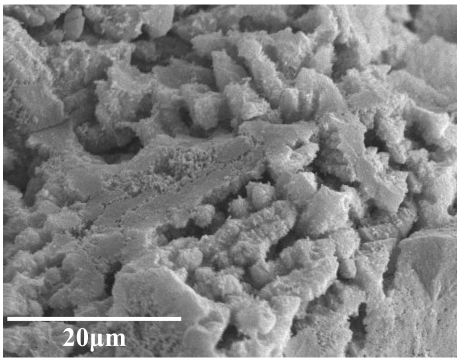

Fig. 8. SEM of L17.5 heat-treated at 700°C for 10 hr.

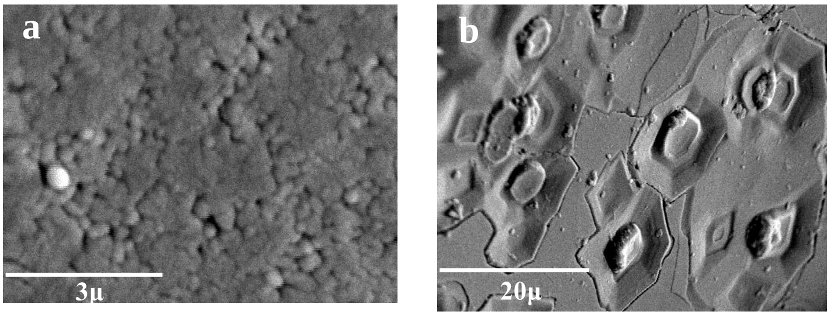

Fig. 9. SEM of L20 heat-treated at a) 650°C for 4 hr and b) at 650°C for 10 hr.

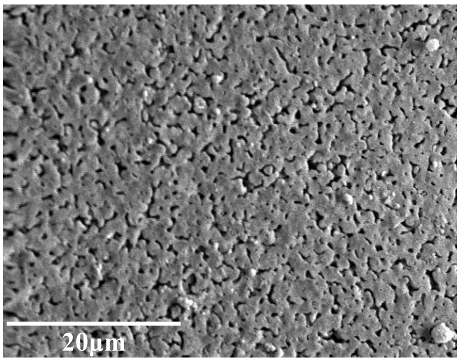

Fig. 10. SEM of L20 heat-treated at 700°C for 10 hr.

Sample L17.5 heat-treated at 650ºC/4 hr (Fig.7a) shows crystallization of unhedral ultrafine crystal of tetragonal form and coagulation of whitish well developed larger crystal of monoclinic are observed.

Figure 7b is the SEM of the surface of sample L17.5 heat-treated at 700ºC/0.5 hr which shows crystallization of uniform crystalline structure of ultrafine crystals of tetragonal form and between it collection of some larger crystals of monoclinic ZrO_2 are seen to be developed and collected with other forming cross-like crystal, embedded in glassy matrix. Figure 7c shows SEM of the fracture of the same sample, shows volume crystallization of uniform crystalline structure of fine crystals and larger whitish crystals of monoclinic phase appears on the surface of this texture, SEM of the fracture of the sample L17.5 heat-treated at 700ºC/10 hr (Fig. 8), shows higher degree of development of monoclinic crystal.

Figure 9a is the SEM of the fracture of sample L20 heat-treated at (650ºC/4 hr), reveals volume crystallization of uniform ultrafine rounded crystals. Minor whitish, larger crystals of monoclinic these are observed. SEM of the surface of sample L20 heat-treated at 650ºC/10 hr gives a picture for sequence of crystallization of monoclinic from the base of tetragonal and the cracks formed around it (Fig.9b).

Figure 10 is the SEM of the surface of sample L20 heat-treated at 700ºC/10 hr reveals ultrafine rounded growths with corrugated peripheries cemented by minor residual glassy matrix exhibiting a higher degree of crystallinity.

Microhardness of L Group

Figures 11a-11d show the microhardness values of L glass ceramics samples with different percentage of ZrO_2, by GPa, versus heat-treatment parameters. Generally, microhardness values are observed to increase with temperature, time and percent of ZrO_2 added. In the sample free from ZrO_2, the microhardness value reaches (7.85 GPa) at 650ºC/1 hr, and this value increases by increasing temperature and time of heat-treatment to 11.32 GPa at 700ºC/10 hr (Fig. 11a). By adding 12.5% ZrO_2, the microhardness value increases to 8.43 GPa at 650ºC/1 h and increase to 13.16 GPa at 700ºC/10 hr (Fig. 11b).

Figure 11c shows microhardness values of L17.5 sample. The microhardness values increases from 9.49 GPa to 14.7 GPa by increasing time from1 hr to 10 hr at 650ºC respectively. When temperature was raised to 700ºC, the hardness increases gradually till 6 hr, after that it starts to decrease to 12 GPa.

By adding the maximum percentage of ZrO_2 (20%), Fig. 11d, microhardness reveals high value ~ 9.79 GPa by heat-treatment at 650ºC/1 hr. Increasing time of heat treatment at the same temperature to 10hs shows maximum value ~ 14.99 GPa. When the temperature of heat-treatment increases to 700ºC, the microhardness increases gradually by increasing time to reach 13.94 GPa after 6 hr then starts to slightly decreases by increasing time to reach 10.18 GPa after10 hr.

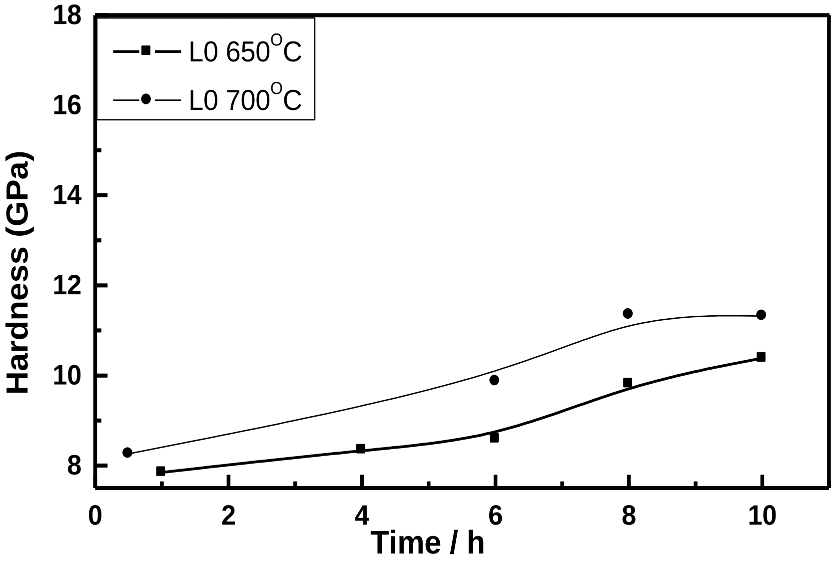

Fig. 11a. **Vickers hardness of Li_2O- B_2O_3- SiO_2 glass-ceramics with 0 mass% (L0) heat-treated at 650°C and 700°C versus heat-treatment time (hr).**

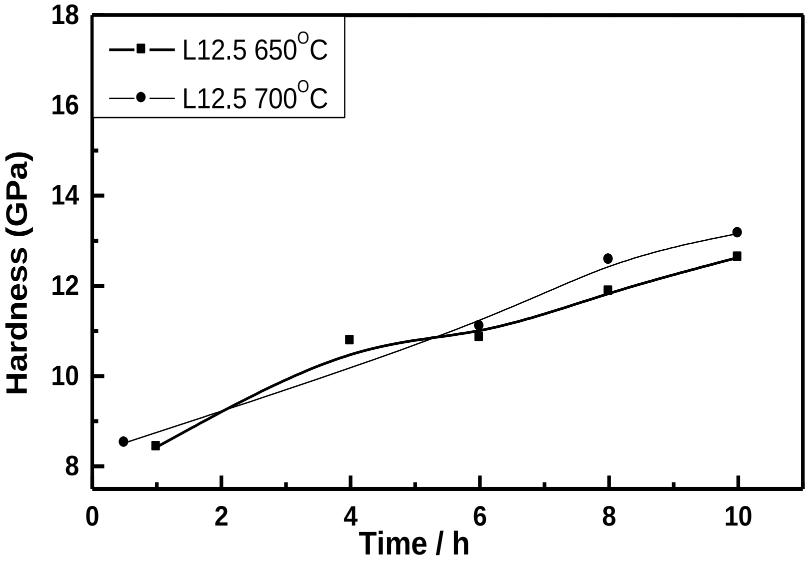

Fig. 11b. **Vickers hardness of Li_2O- B_2O_3- SiO_2 glass-ceramics with 12.5 mass% (L12.5) heat-treated at 650°C and 700°C versus heat-treatment time (hr).**

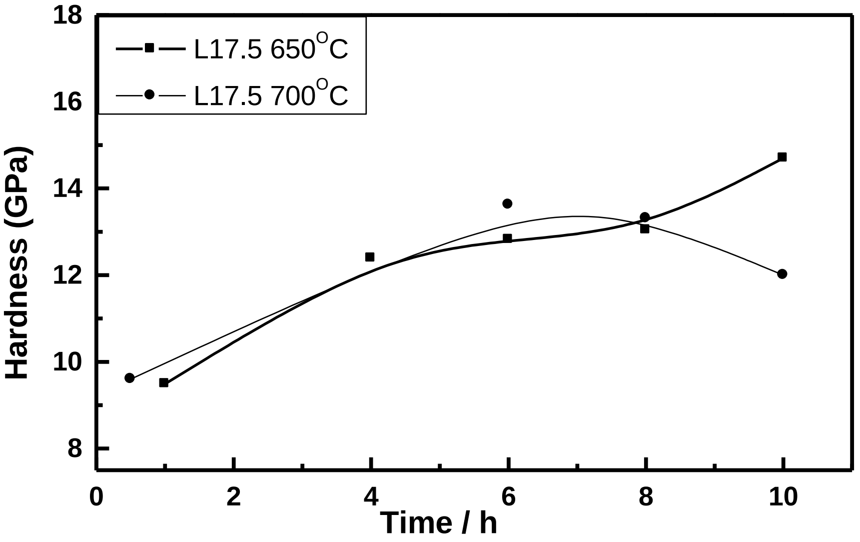

Fig. 11c.Vickers hardness of Li_2O- B_2O_3- SiO_2 glass-ceramics with 17.5 mass% (L17.5) heat-treated at 650°C and 700°C versus heat-treatment time (hr).

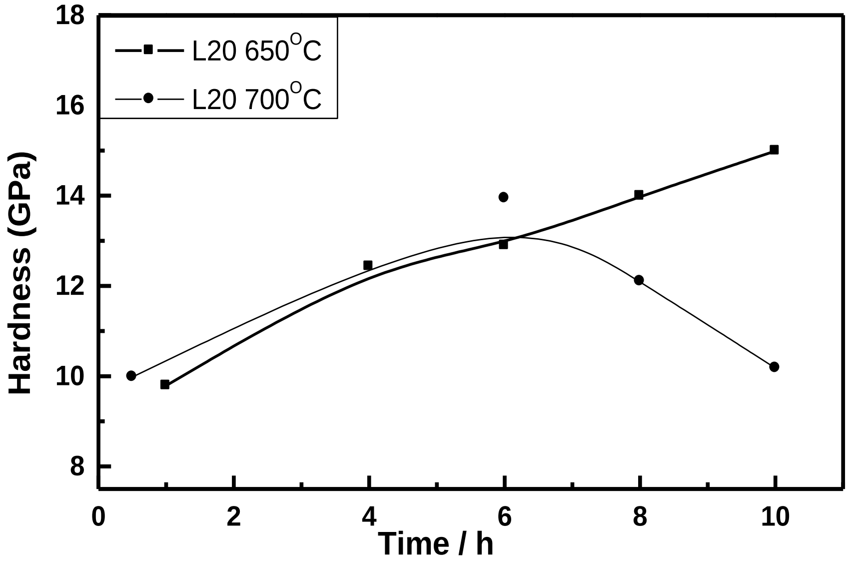

Fig. 11d. Vickers hardness of Li_2O- B_2O_3- SiO_2 glass-ceramics with 20 mass% (L20) heat-treated at 650°C and 700°C versus heat-treatment time (hr).

At low percentage of ZrO_2, the microhardness value increases by increasing temperature and time of heat-treatment. This result can be explained on the basis of critical size of T-ZrO_2. At first, the size of T-ZrO_2 increases till reaching the critical size, at which tetragonal phase is converted to monoclinic (Martensitic transformation). This causes microcrackes on surface of the samples. By applying any external stress (*i.e.*, microhardness testing), this stress diffuses in the formed microcrackes leading to higher hardness values.

At high percentage of ZrO_2, the transformation from T-M increases with increasing temperature and time of heat-treatment causing more and more microcrackes to be created resulting in a weaker surface (than when small ZrO_2 percentage was added) so lower hardness is observed at higher temperature and time. It can be concluded that the best percentage of ZrO_2, temperature and time of heat-treatment which give the highest hardness (14.99 GPa) is in the sample L20 heat-treated at 650ºC /10 hr.

Conclusion

Glass ceramic in the system LiO_2-B_2O_3-SiO_2 were prepared by adding ZrO_2 till maximum saturation. The maximum amount of ZrO_2 added were 20 g over 100% batch compositions. Addition of ZrO_2 was found to decrease the crystallization temperatures.

The crystallization of t-ZrO_2 was enhanced by increasing time of heat treatment. In generally, microhardness values are observed to increase with temperature, time and percent of ZrO_2 added.

The best percentage of ZrO_2, temperature and time of heat-treatment which give the highest hardness (14.99 GPa) is in the sample L20 heat-treated at 650ºC /10 hr.

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دراسة تحضير وتبلور زجاج سيراميكى غنى بأكسيد الزركونيوم مبنى على أكسيد اللينيوم وأكسيد البورون وأكسيد السيليكون

سلوى عبد الحميد محمد ، نجوى عبد الشافى غنيم و فاطمة حسن مرعى
قسم أبحاث الزجاج – المركز القومى للبحوث – الجيزة – مصر.

فى هذا البحث ندرس عمليه التبلور فى الزجاج المبنى على النظام اكسيد الليثيوم-اكسيد البورون-اكسيد السليكون مع اضافة كميات متزايده من اكسيد الزركونيوم حتى التشبع وذلك بهدف زيادة الصلادة للزجاج السيراميكى الناتج. و قد تم استخدام حيود الاشعه السينية و الميكروسكوب الالكترونى النافذ لدراسه الاطوار المعدنيه المتبلوره. بعد معالجات حراريه مختلفه مبنيه على التحليل الحرارى التفاضلى وجد تبلور صورتى التيتراجونال و المونوكلينيك لاكسيد الزركونيوم فقط. وقد تم حساب كميات الزركونيوم المتبلوره باستخدام حيود الاشعه السينيه ووجد انها تتوقف على كميه اكسيد الزركونيوم المضاف والمعالجة الحرارية المستخدمة. و بقياس الصلاده وجد انها تصل اعلى قيمه (14.99Gpa) فى العينات المحتويه على ٢٠٪ اكسيد زركونيوم ومعالجه عند درجة حرارة ٦٥٠ درجة لمدة ١٠ساعات.