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A Study of High-Strength Borosilicate Glass by Crystallization and Ion Exchange for Bulletproof Materials

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Abstract:

For application in light-weight bulletproof glass, the borosilicate glass was strengthened by ion exchange and crystallization. Basically, the mechanical properties of borosilicate glass were better than soda-lime-silicate (SLS) glass. Properties of ion exchanged glass heated at different conditions were measured. The Vickers hardness, fracture toughness and bending strength of ion exchanged samples were 821.8 H_v, 1.3404 MPa·m^{1/2}, and 953 MPa, which is about 120%, 180%, and 450% higher than parent borosilicate glass, respectively. The borosilicate glass was heated by 2-step crystallization. As a result, the Vickers hardness, fracture toughness and bending strength of crystallized samples were 735.7 H_v, 1.0779 MPa·m^{1/2}, and 493 MPa, which is about 17%, 45%, and 149% higher than parent borosilicate glass, respectively. The results prove that light-weight bullet proof can be fabricated by ion exchange technique of borosilicate glass. The mechanical properties of borosilicate glass were increasing with additions of ZrO₂ (until 7.5 wt. %). Transmittance of ion exchanged and crystallized borosilicate glasses were decreased slightly at the visible range.

Keywords:

Borosilicate glass, crystallization, ion exchange, bulletproof

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Recently, many researchers are carrying out over the application of the transparent bulletproof glass to enhance of mechanical properties. Borosilicate glasses generally have excellent mechanical properties, but poor producing [1]. Thus, addition of ZrO₂ at various weight percent on borosilicate glass was confirmed thermal and mechanical properties. Pure zirconia exists in three crystal phases at different temperatures [2,3]. At very high temperatures (over 2370°C) the material has a cubic structure. At intermediate temperatures (1170 to 2370°C) it has a tetragonal structure. At low temperatures (below 1170°C) the material transforms to the monoclinic structure. The compositions of the borosilicate glass prepared are given in table 1. The hardness, fracture toughness, and bending strength of parent borosilicate glass were about 630 H_v, 0.7429 MPa·m^{1/2}, and 198 MPa, respectively. For application of transparent bulletproof materials, borosilicate glass was heated by 2-step crystallization [4,5] and ion exchange by employing screen printing technique in KNO₃ powder.

1. Experimental procedures:

Borosilicate glass was prepared in the composition of 81% SiO₂, 4% Na₂O, 2% Al₂O₃, 13.0% B₂O₃. For measurement of T_g, T_{c(max)}, measured by differential thermal analysis (TG/DTA-92, Setaram, France). DTA run was performed for borosilicate glass powder by 10 K/min as heating rate. The batches were melted in a Super Khantal Furnace (Lindberg Blue M, USA) at 1650 °C for 6 hr using a Pt-Rd crucible. Borosilicate glasses were heated at 10 K/min to the nucleation temperature between 520 ~ 560°C, (intervals of 10 K), then crystal growth was fixed at 650 °C (1 hr).

Table (1): Composition of the crystallized borosilicate glass (mol %)

Specimen	SiO ₂	Al ₂ O ₃	B ₂ O ₃	Na ₂ O	ZrO ₂ (wt. %)
N	81	2	13	4	0
NZ1	81	2	13	4	2.5
NZ2	81	2	13	4	5.0
NZ3	81	2	13	4	7.5
NZ4	81	2	13	4	10.0

The crystallized glasses were determined the morphology and composition of the crystallized phases using a scanning electron microscope (SEM, Hitachi S-3000M, Japan) and an energy dispersive X-ray spectrometer (EDX, Horiba EMAX, Japan).

Table (2): Composition of the ion exchanged borosilicate glass (mol %)

Specimen	SiO ₂	Al ₂ O ₃	B ₂ O ₃	Na ₂ O	ZrO ₂ (wt. %)
N4	81	2	13	4	0

N6	79	2	13	6	0
N8	77	2	13	8	0
N4Z4	81	2	13	4	4
N6Z4	79	2	13	6	4
N8Z4	77	2	13	8	4

Properties of ion exchanged glass heated at different conditions (temperature, time) were examined. The K⁺-Na⁺ ion exchange takes place at the glass surface and creates compressed stress which raise the mechanical strength of the glass. For all heat treated samples were excuted by X-ray diffraction (D/max III, Rigaku, Japan) using Ni-filtered CuK_α radiation. Hardness and fracture toughness were measured using Vickers Microhardness Tester (MXD-CX3E, Matsuzawa, Japan). More than 10 indentations were made for each specimen with a 10 second loading time at a maximum load of 500gf. The Vickers hardness was calculated from:

$$H_v = 0.4636 \cdot \left(\frac{P}{a^2}\right) \tag{2}$$

where P is the load of indentation, a is the radius of indentation. The fracture toughness was calculated from:

$$K_{IC} \cdot \Phi / H_v \cdot a^{\frac{1}{2}} = 0.15 \cdot K \cdot (c/a)^{\frac{3}{2}} \tag{3}$$

where H_v is Vickers hardness, Φ is the restraint constant(≈3), and a is the radius of indentation, K is a constant(≈3.2), and c is crack length.

$$\sigma = 3 \cdot P \cdot L / 2 \cdot w \cdot t^2 \tag{4}$$

where P is maxium load, L is outside the interval , w is width, t is thickness. For measurement of the mechanical strength, 3-point bending strength was employed to the bar type specimens using a Universal Testing Machine (H10K-C, Hounsfield, U.K.). To measure 3-point bending strength glass bars with diameter of 3 × 4 × 36 mm³ were cut out from borosilicate glasses and polished (# 1000 ~ 2000). The KNO₃ powder (Ducsan, Extra pure, Korea) was prepared for ion exchanged. The depth profile of Na⁺ and K⁺ was observed Electron Probe Micro Analyzer (EPMA, JXA-8900R, JEOL, Japan). Transmittance was measured using UV/VIS/NIR Spectrometer (Jasco, V-570, Japan). The scan speed and range of wavelength were 400nm/min, in the range of 200 ~ 800nm.

3. Results and discussion:

Fig. 1 shows that the glass transition temperature (T_g) and crystallization temperature (T_{c, max}) was 510 ~ 530 °C, 650 ~ 670 °C. Thus, the glass specimen was nucleated at 10 °C/min to the temperature range of 520 ~ 560 °C with intervals of 10 °C for 2 hr, and then crystallized at 650 °C for 1 hr. Fig. 1 shows the DTA traces for the borosilicate glass with ZrO₂ (NZ1 : 2.5 wt. %, NZ3 : 7.5 wt. %). Also give the evidence that ZrO₂ promotes the crystallization of albite (NaAlSi₃O₈). Albite is a plagioclase feldspar mineral and crystallizes with triclinic pinacoidal forms. As such it represents a plagioclase with less than 10% anorthite content.

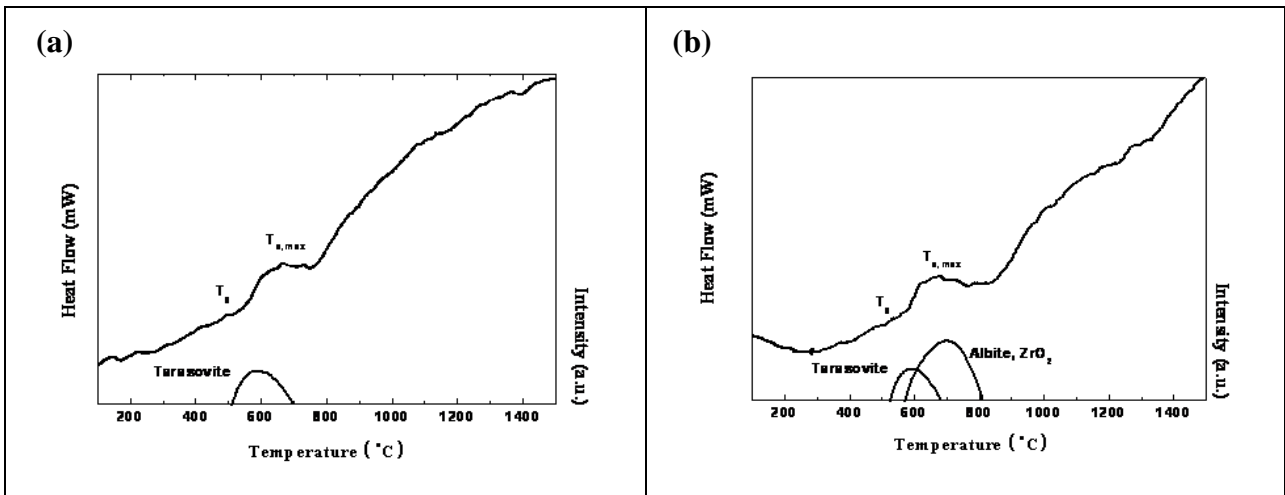


Figure (1): DTA curve of the parent borosilicate glass at 10K/min heating rate. The figure also shows the occurring phase. (a) N composition, (b) NZ3 composition

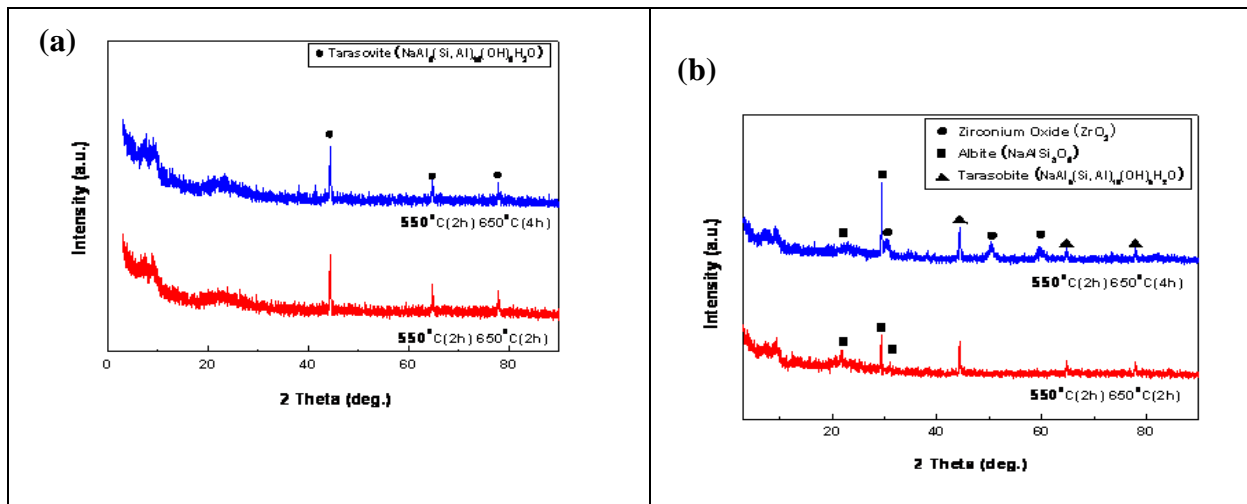


Figure (2): XRD patterns of parent and crystallized borosilicate glass. (a) N composition (b) N3 composition

It is found from the XRD data in Fig. 2(b) that precipitations of tarasovite, albite, ZrO_2 are observed. It means that the addition of ZrO_2 increased the albite phase. Fig. 3 shows that the crystallized phase additional ZrO_2 (c ~ f) and without ZrO_2 (a, b). Fig. 2, 3 give the evidence that ZrO_2 promotes the crystallization of albite and simultaneously suppresses the precipitation of ZrO_2 phase.

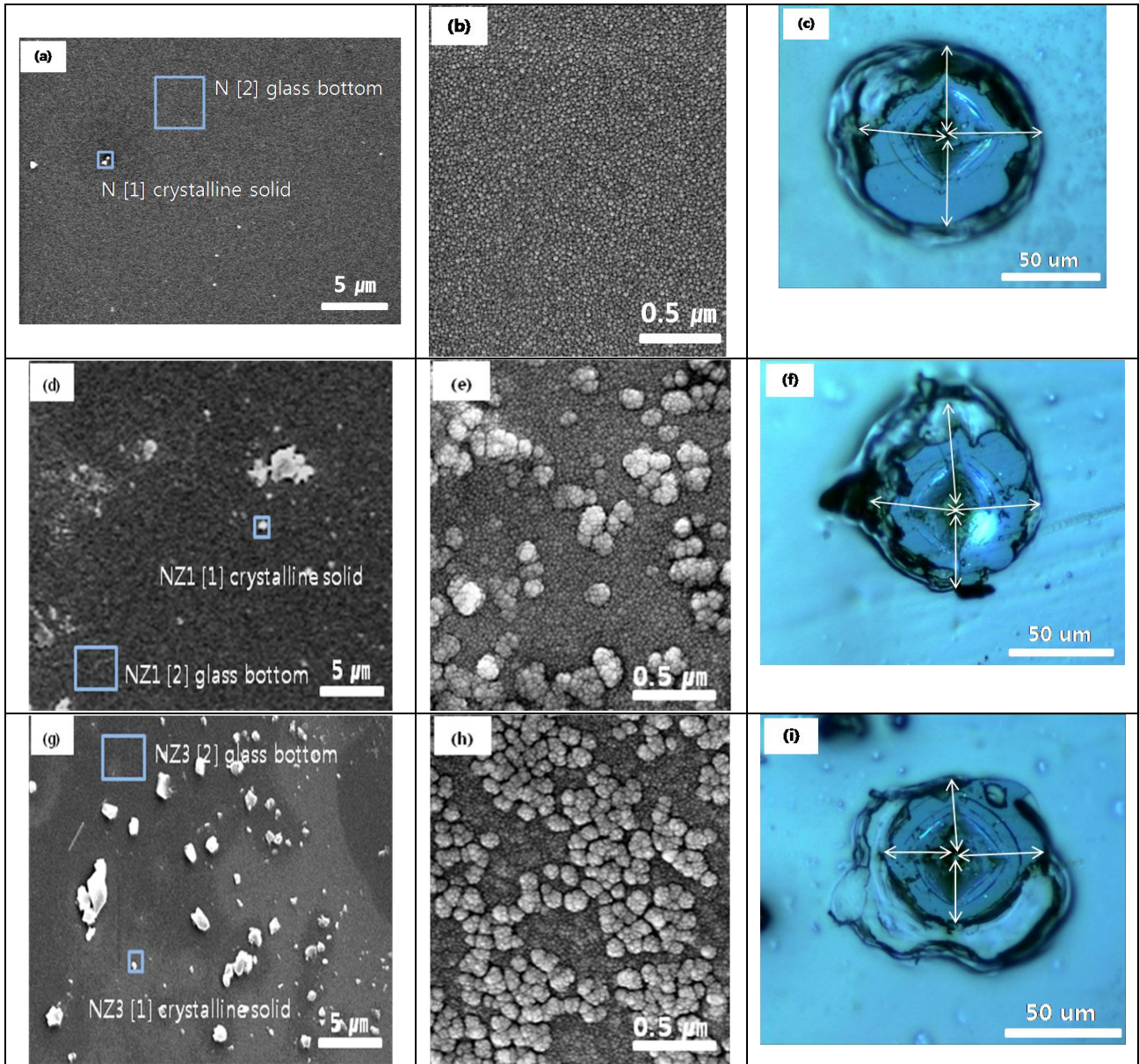


Figure (3): SEM image of nucleated borosilicate glass at 550 °C for 2 hr (crystal growth at 650 °C, 4 hr). (a), (b) N, (d),(e) NZ1, and (g), (h) NZ3 composition. Crack length of crystallized glass was (c), (f), and (i): 28.7, 27.0, 26.3 μm

Table (3): Compositions of each phase in crystallized borosilicate glass obtained by EDX (wt. %)

Compoition Element	N [1]	N [2]	NZ1 [1]	NZ1 [2]	NZ3 [1]	NZ3 [2]
O	42.25	42.63	55.93	53.59	26.10	24.33
Na	3.47	4.29	3.24	6.95	2.08	7.96
Al	1.94	2.00	1.44	4.17	1.74	7.53
Si	52.34	51.08	30.30	27.75	41.96	36.48
Zr	-	-	9.08	7.54	28.12	23.68
Totals	100	100	100	100	100	100

Such a increase in the additions of ZrO₂ (until 7.5g) leads to a increase in the strength to 493 MPa, which is about 149% higher than parent borosilicate glass. The crystal size of N, NZ1, NZ3 were about 28nm.

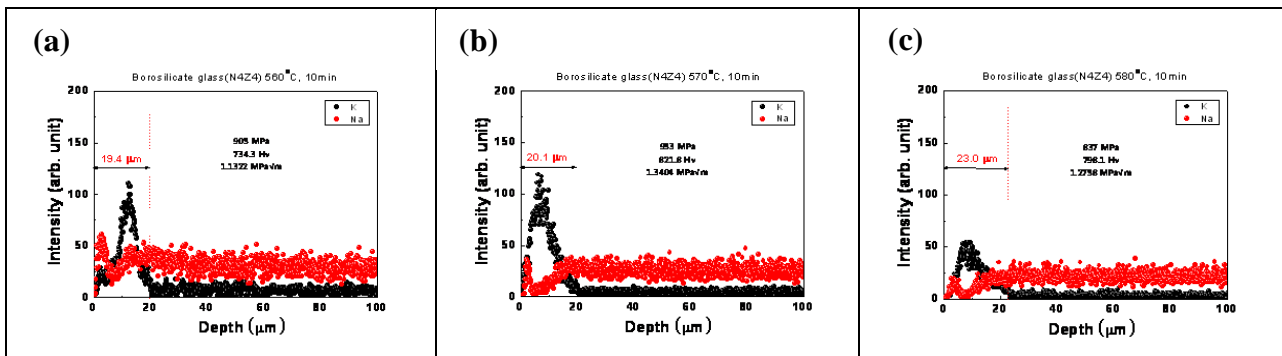


Figure (4): EPMA line profile of ion exchanged borosilicate glass by KNO₃ powder (a) 560 °C , (b) 570 °C, and (c) 580 °C for 10 min

Fig. 4 shows that EPMA line profile for the ion exchanged borosilicate glass was treated in KNO₃ powder containing different temperature for 10 min. In this process, K⁺, Na⁺ ion exchange takes place at the glass surface and create a compressed stress which raise to the mechanical strength of the glass. With the increasing heat-treatment temperature from 560 °C to 580 °C, the depth profile was increasing from 19.4 μm to 23.0 μm, but mechanical properties were reduced. Fig. 5 shows the EPMA of the ion exchanged at various time. With the increasing heat-treatment time from 0 min to 20min, the depth profile was increasing from 17.1 um to 29.4 um, but mechanical properties were decreased, too. It was also found out that excessive heat treatment brings about stress relaxation.

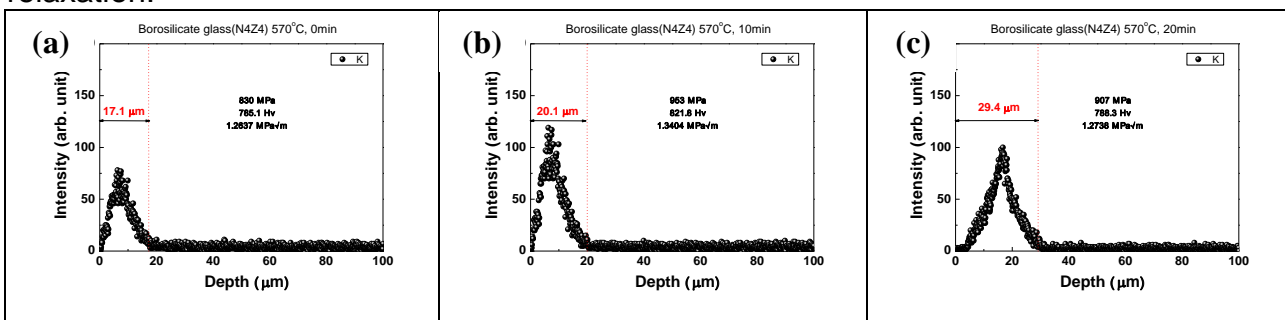


Figure (5): EPMA line profile of ion exchanged borosilicate glass by KNO₃ powder at 570 °C for (a) 10min, (b) 20min, and (c) 30min

Therefore, we have to find the best conditions of ion exchange according to the temperature and time. Fig. 6, 7 shows that mechanical properties of crystallized and ion exchanged borosilicate glass.

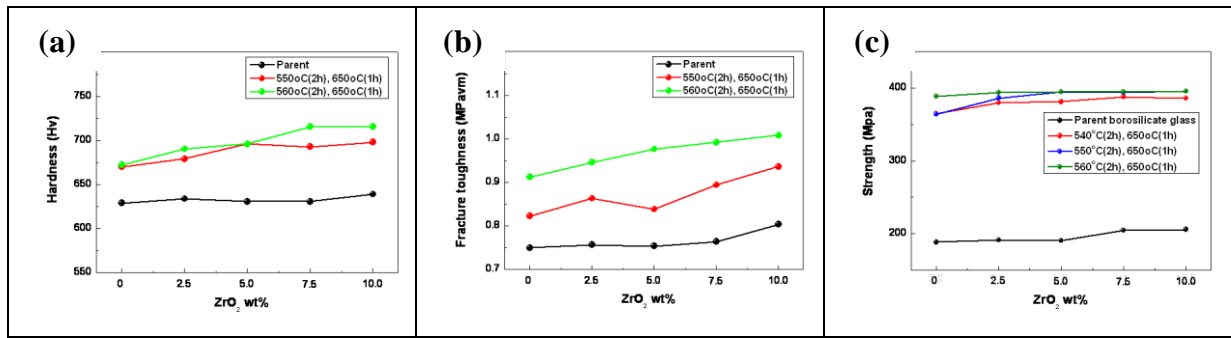


Figure (6): Hardness, Fracture toughness, and Strength of crystallized borosilicate glass at various wt% of ZrO₂ (crystal growth at 650 °C for 1 hr)

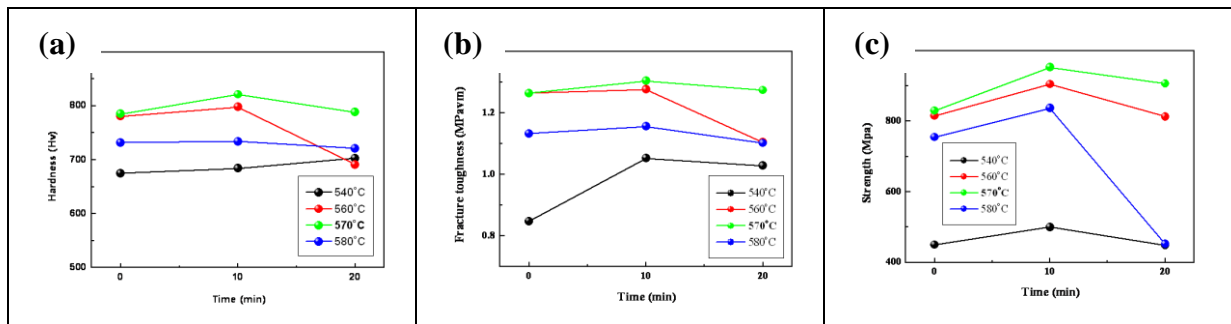


Figure (7): Hardness, Fracture toughness, and Strength of ion exchanged borosilicate glass at various time, temperature

Table (4): Mechanical properties of ion exchanged borosilicate glass at various time, temperature (composition : N4Z4)

	Time (min)	Hardness (H _v)	Fracture Toughness (MPa·m ^{1/2})	Strength (MPa)
Parent glass	-	685	0.7545	210
Ion exchanged borosilicate glass	0	785	1.2637	830
	10	821	1.3040	953
	20	788	1.2738	907

Table (5): Mechanical properties of crystallized borosilicate glass at various time, temperature (550 °C for 2 hr, 650 °C for 4 hr)

	ZrO ₂ (wt. %)	Hardness (H _v)	Fracture Toughness (MPa·m ^{1/2})	Strength (MPa)
Parent glass	-	630	0.7429	198.00
Crystallized borosilicate glass	0	702	0.9808	374.64
	2.5	708	1.0050	397.67
	5.0	714	1.0579	443.26
	7.5	736	1.0779	493.37
	10.0	724	1.0455	475.32

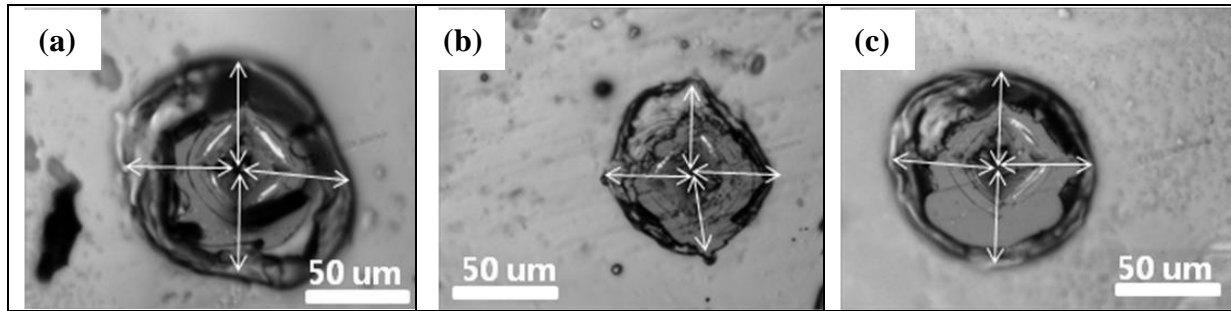


Figure (8): Optical microscope image of ion exchanged borosilicate glass at 570°C for (a) 0 min,(b) 10 min, and (c) 20 min

The Vickers hardness, fracture toughness and bending strength of crystallized samples were 735.7 H_v, 1.0779 MPa·m^{1/2}, and 493 MPa, which is about 17%, 45%, and 149% higher than parent borosilicate glass, respectively. The toughness of a material is the maximum amount of energy it can absorb before fracturing, which is different than the amount of force that can be applied. The Vickers hardness, fracture toughness and bending strength of ion exchanged samples were 821.8 H_v, 1.3404 MPa·m^{1/2}, and 953 MPa, which is about 120%, 180%, and 450% higher than parent borosilicate glass, respectively. Transmittance of ion exchanged and crystallized borosilicate glass was decreased slightly. The visible transmittance decreases with increasing crystal size. It is evident that the gradual decrease of visible transmittance is due to light scattering from the crystal phase particles. Scattering increases with increasing crystal size. As a result, the transmittance of crystallized glass was increasing with decreasing crystal growth time.

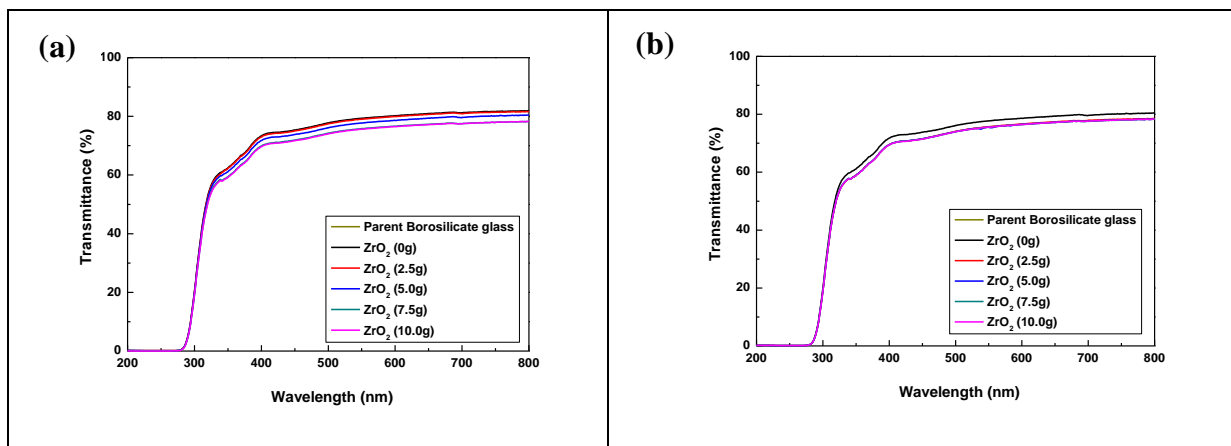


Figure (9): Transmittance of crystallized and ion exchanged borosilicate glass.

Crystallization at (a) 550 °C for 2 hr, 650°C for 2 hr, (b)550°C for 2 hs, 650°C for 4 hs

4. Conclusions:

For application in light-weight bulletproof glass, borosilicate glass was strengthened by crystallization and ion exchange. Also give the evidence that ZrO₂ promotes the crystallization of albite (NaAlSi₃O₈). Properties of crystallized and ion exchanged glass heated at different conditions were examined. As a result, the Vickers hardness, fracture toughness and bending strength of crystallized samples were 735.7 H_v, 1.0779 MPa·m^{1/2}, and 493 MPa, which is about 17%, 45%, and 149% higher than parent borosilicate glass,

respectively. The Vickers hardness, fracture toughness and bending strength of ion exchanged samples were 821.8 H_v, 1.3404 MPa·m^{1/2}, and 953 MPa, which is about 120%, 180%, and 450% higher than parent borosilicate glass, respectively. It is found out that ZrO₂ promotes the crystallization of albite phase. Transmittance of ion exchanged and crystallized glass were decreased slightly at visible range. A transparent bulletproof material of borosilicate glass has been ballistically tested after impacting by 5.45mm AK-74 steel core projectiles at distance of 50 meters. The thickness of bulletproof material was about 30mm (Korea Military Academy). It can be expected of transparent bulletproof materials in more light-weight and thinner (over 10~15%) by ion exchange and crystallization.

Acknowledgements:

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