

EFFECT OF NUCLEATION TEMPERATURE AND TIME ON CRYSTALLIZATION BEHAVIOR OF ZIRCONIA/ ZIRCON ADDED BOROSILICATE GLASS

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Keywords: Borosilicate glass; Alkali resistant glass; Glass transition temperature; Thermal properties

Abstract

Crystallization behavior of ZrO₂/ ZrSiO₄ added borosilicate glass has been investigated using various temperature and time. Addition of ZrO₂/ ZrSiO₄ in borosilicate glass composition is believed to improve the alkaline resistance characteristics and open window for many applications where chemical durability is a prime requirement. It is found that addition of ZrO₂/ ZrSiO₄ in the borosilicate composition increases the glass transition temperature (T_g) which in turn reduce the chances of crystal formation during cooling. A detailed thermal analysis with DTA and XRD was carried out initially to identify the glass transition temperature (T_g) and crystallization temperature (T_x). Finely powdered glass samples are more prone to devitrification compare with bulk samples. Dilatometer was utilized to explore shrinkage behavior of glasses with increasing temperature. FTIR is proved to be an effective instrument for identifying phase separation and crystallization behavior of glass.

1 Introduction

Borosilicate glass has kept its attraction for many decades to be used in the area of separation science, lab ware and immobilization of High Level Waste (HLW) [1–6]. Low dielectric constant coupled with negligible thermal expansion coefficient of borosilicate glass make it suitable for using in microelectronic packaging [7,8]. A major challenge arises when the applications require chemical durability. It is evident by many studies that Zirconia (ZrO₂) in the borosilicate system increases the alkaline resistance [9–12]. But using Zircon (ZrSiO₄) in the borosilicate system and its thermal behavior study has long been absent. Improving zirconium solubility without compromising the base borosilicate glass (SiO₂-B₂O₃-Na₂O) properties is desirable.

Nucleation and crystallization behavior is a major area of investigation due to its importance in identifying proper phase separation temperature for production of controlled pore glasses and optimizing sintering temperature for glass-ceramics. The present study has put more emphasis on thermal characterization and behavior study of ZrO₂/ ZrSiO₄ added borosilicate glass. More particularly the effect of nucleation temperature and time on crystallization is thoroughly investigated.

2 Materials and testing methods

2.1 Preparation of experimental glasses

The basic borosilicate glass contained three components: SiO₂, B₂O₃, Na₂O; whereas ZrO₂/ZrSiO₄ was added in different proportion to introduce ZrO₂/ZrSiO₄ into the glass. The compositions of glasses prepared in this study are shown in Table 1. Special grade (powder) of SiO₂, B₂O₃, Na₂CO₃, ZrO₂ and ZrSiO₄ were procured from Sigma-Aldrich for the preparation of the glasses. The glass components were mixed and rolled on ball-mill for 12 hours. The mixed batches were transferred to Alumina crucible and melted at 1450°C for 2 h in an electric furnace. The melts were then shock quenched directly into water to produce frits. The glass frits were crushed and grounded in a ball mill for 12 h to produce powder and screened through 212 µm and retained on 45 µm of sieve size

Glass	Composition (wt %)				
	SiO ₂	B ₂ O ₃	Na ₂ O	ZrO ₂	ZrSiO ₄
A	65	25	10		
B	62	25	10	3	
C	58	25	10	7	
D	54	25	10	11	
E	50	25	10	15	
AA	69	25	6		
EE	54	25	6		15

Table 1: Composition of Glasses

2.2 Thermal analysis

Differential Thermal Analysis (DTA) (Stanton Redcroft, UK) was used to investigate the glass transition temperature (T_g), crystallization behavior and the nucleation curve of the glasses. Non isothermal heating in air were recorded at a rate of 10, 15 and 20 °C/min, using 30 mg of sample and alumina as a reference material. The relation between crystallization peak temperature (T_p) and nucleation temperature (T_n) was also studied by holding temperature for 10 min and 2 h at different nucleation temperature in the range of 410–650 °C. The dilatometer was used to measure shrinkage on bulk glass specimen using heating and cooling rates of 10 °C/min in air from room temperature to 1000 °C. Dilatometer of Model 402 E, Netzsch Ltd., Germany was used for this purpose.

2.3 Heat Treatment

The thermal treatment was carried out with glass powder (particle size is in 45–212 µm range) using horizontal tube furnace (Carbolite Ltd., Sheffield, UK) at heating rate of 10 °C/min. The sintering temperature was in 630–700 °C range and held for 24 h. The heat treated glasses were then smashed to powder of certain size for further characterization.

2.4 X-ray diffraction analysis (XRD) and Fourier transform infrared (FTIR) spectroscopy

The original and heat treated glass powders were checked by X-ray diffraction analysis to determine the material phases. A Bruker advanced D8 X-ray diffractometer with Ni-filtered Cu K α radiation of wavelength 1.5406 Å at 40 kV and 40 mA setting was used to measure the XRD patterns with a step size of 0.1° in a range of 2 θ values from 10 to 80° at scanning speed of 10 sec /step. The FTIR spectra were obtained using an instrument (Perkin-Elmer GX instrument) with a resolution of 16 cm⁻¹ in range from 400 cm⁻¹ to 4000 cm⁻¹.

3 Results and discussion

3.1 Differential thermal analysis

Figure 1 presents the DTA curve of the glass powder EE and the data recorded for the heating rate of 20 °C/min. The glass EE powder was sieved through 212 µm and retained on 45 µm sieve. The particle size was determined by using Malvern Mastersizer S (Malvern Ltd., UK). The volume mean diameter, $D[4, 3]$, was found to be 80.1 µm. A change in slope is observed (see Fig.1) at about 499 °C and continued until it reached a plateau at about 600 °C. The first inflection point in the endothermic curve is denoted as T_g by most literature. Whereas the midpoint of the transformation temperature, T_{mid} , also termed as T_g by many studies. Therefore, either T_f and T_{mid} can be designated as glass transition temperature (T_g) for most applications [13,14]. In this study T_{mid} is considered as T_g . The exothermic gradient observed after the T_g in the DTA curve indicates crystallization with precipitation of cristobalite. The sharp exothermic peak observed at 672 °C is likely to be associated with glass crystallization. This sharp peak suggests bulk nucleation and denoted as maximum crystallization temperature (T_p) [15–17]. This first maximum in the thermal spectrum also defined by some as T_x , while others define T_x as the onset temperature for the first crystallization exotherm [2]. Whereas, the broad peak in the temperature zone 850–900 °C indicates surface nucleation [15–18].

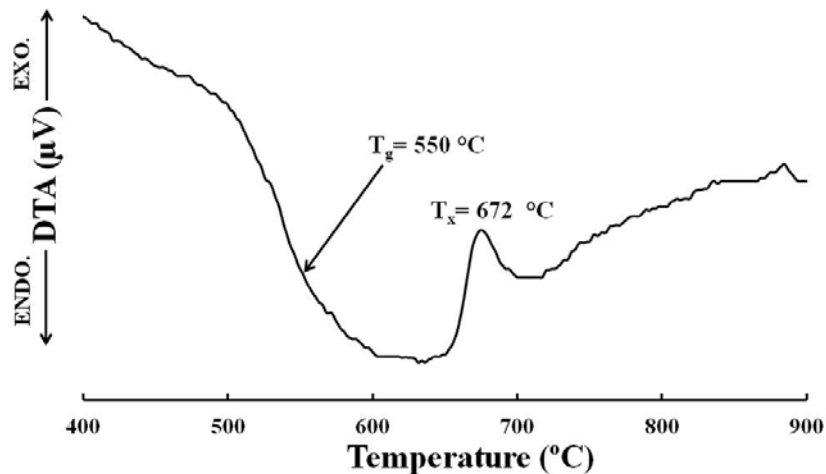


Figure 1. DTA curve of glass EE at a heating rate of 20 °C/min

It is widely accepted that T_g temperature depends largely on heating rate, particle size and sample size used in the measurement [2,19]. Figure 2 shows the effect of particle size on T_g for the glass AA on small frits and particle size in a range of 45-212 µm. It is observed that endothermic inflection starts earlier with glass frits compared with smaller particle size (45-212 µm) of same glass composition.

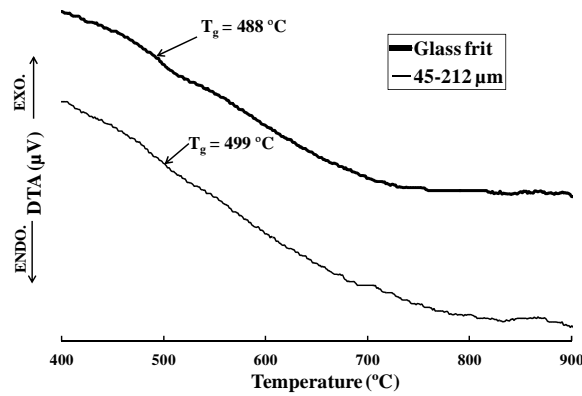


Figure 2. DTA curves of glass AA with glass frits and 45-212 μm particle size at a heating rate of 10 $^{\circ}\text{C}/\text{min}$

Apart from the glass sample with zircon (EE), no sharp peaks were observed for other glasses which suggest that surface crystallization is the prevailing mechanism for devitrification of other glasses. The broad exotherm in other glasses indicate the formation of cristobalite is continuous over a very wide temperature range. The appreciable separation between T_g and T_x in glass EE provides a sufficient kinetic window to perform heat-treatment. The results of the DTA analysis for all the glasses in three different heating rates are listed in Table 2. It is evident that glass transition temperature increases with increase of ZrO_2 content. Addition of ZrO_2 will increase the bridging oxygen atoms per silicon atom and the presence Zr^{4+} will make glasses more packed with higher T_g . This behavior is coherent with the theory where ZrO_2 is believed to act both as an intermediate and a network glass former [20].

Glass	10 $^{\circ}\text{C}/\text{min}$	15 $^{\circ}\text{C}/\text{min}$	20 $^{\circ}\text{C}/\text{min}$
	T_g	T_g	T_g
A	541	538	539
B	538	551	549
C	547	556	563
D	549	553	555
E	549	557	561
AA	499	497	495
EE	530	545	550

Table 2. DTA results in three different heating rate (10 $^{\circ}\text{C}/\text{min}$, 15 $^{\circ}\text{C}/\text{min}$, 20 $^{\circ}\text{C}/\text{min}$)

DTA has found to be effective to identify the optimum nucleation temperature by measuring the exothermic peak shift with nucleation temperature [16,17]. Table 3 presents the peak temperature of maximum crystallization (T_p) for glass EE with various nucleation temperature and time.

Nucleation temperature, T_n $^{\circ}\text{C}$	Peak temperature, T_p $^{\circ}\text{C}$	Peak temperature, T_p $^{\circ}\text{C}$
	nucleation time 2 h	nucleation time 10 m
550	656	660
570	651	659
590	637	658
610	No peak observed	656
630	No peak observed	No peak observed
650	No peak observed	No peak observed

Table 3. Peak temperature of maximum crystallization for glass EE

Crystallization peak temperature (T_p) vs. nucleation temperature (T_n) are shown in Figure 3. The nucleation temperatures were selected between T_g and T_p and holding for 2 h (Fig. 3a) and 10 min (Fig. 3b). Figure 3a shows a greater shift in peak temperature at around 590 °C and no other exothermic crystallization peak appeared afterwards. Whereas in Figure 3b, when the nucleation time is 10 m, the peak shifts toward maximum at about 610 °C. There was no crystallization peak observed beyond this temperature. Therefore the optimum nucleation temperature for glass EE can be considered between 590 – 610 °C.

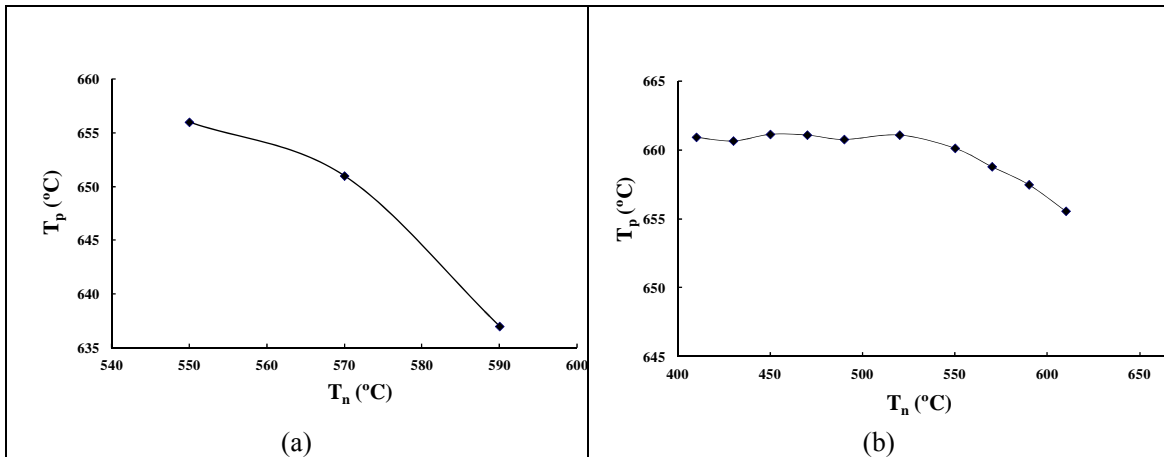


Figure 3. Crystallization peak temperature (T_p) vs. nucleation temperature (T_n): (a) nucleation time at T_n for 2 h; (b) nucleation time at T_n for 10 m

3.2 Dilatometry analysis

Figure 4 illustrates the linear shrinkage curve of bulk sample of glass AA which has been heated at a rate of 10 °C/min and without any isothermal hold. A total linear shrinkage of 4.8% is observed. The bulk sample begins to shrink at about 610 °C and continue with a sharp fall until reaching 670 °C. Beyond this point, there is no significant shrinkage observed in the curve.

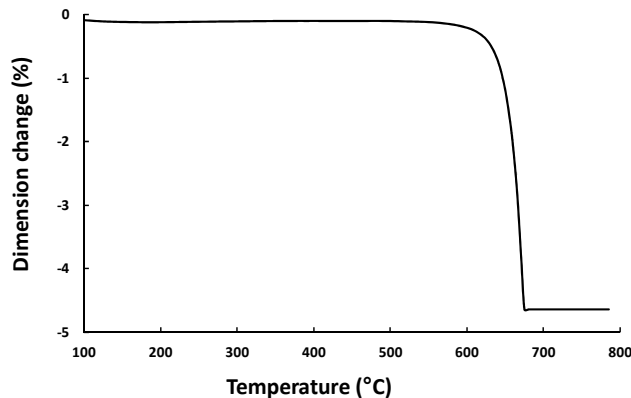


Figure 4. Linear shrinkage curve of bulk glass AA obtained at 10 °C min⁻¹

3.3 Using FTIR and XRD to detect crystallization and phase separation

FTIR has been widely accepted to interpret the structural modifications occurred during heat treatment [21–23]. The FTIR spectrum amorphous silica was reported in other studies and the major peak corresponding to the asymmetric Si-O-Si stretching vibration was recorded at about 1100 cm^{-1} [22,24]. The position of Si–O–Si band at about 1100 cm^{-1} changes depending on the type and amount of modifier cations introduced to the system. Addition of modifiers causes a shift toward lower wave numbers for the SiO_2 stretching band resulting from depolymerization of the silicate network [23, 25]. Figure 5 shows the FTIR spectra of as quenched and heat treated samples of glass C. XRD analysis is also reported to correlate the findings. It can be noticed from the FTIR spectrum that the as quenched non heat treated glass has peak shift of 49 cm^{-1} compared with amorphous silica and Si-O-Si stretching peak is reported at 1051 cm^{-1} . The peak starts shifting towards high wave number as heat treatment temperature increases until $680\text{ }^\circ\text{C}$. The peak then reverse the shift towards the lower wave number for heat treatment temperature at $700\text{ }^\circ\text{C}$ while keeping the isotherm same as 24h. The decrease of the IR peak wave number at $700\text{ }^\circ\text{C}$ could probably due to decreasing the extent of phase separation. The theory of immiscibility boundary could be a good agreement with this decreasing phase separation characteristics at $700\text{ }^\circ\text{C}$. At lower temperature, e.g. at $630\text{ }^\circ\text{C}$, the immiscibility boundary is wide but at higher temperature it is near to edges and thus the extent of phase separation could decrease. The increasing wave number with increment of heat treatment temperature in the range $630\text{--}680\text{ }^\circ\text{C}$ indicating higher degree of phase separation and can be attributed to the increasing number of Si-O-Si bridging bonds [22,23]. The broad band at about 680 cm^{-1} can be assigned to $\text{B}(\text{O},\text{OH})_4$ and BO_4 tetrahedrons [26]. A peak at $610\text{--}627\text{ cm}^{-1}$ is noticed to appear in samples heat treated at comparatively high temperature (680°C and 700°C). The XRD study also proves the crystallization and precipitation of cristobalite for these two samples. The presence of peak in this region ($610\text{--}627\text{ cm}^{-1}$), therefore, indicate the crystallization process [24]. Similar study with other glass compositions has also been conducted.

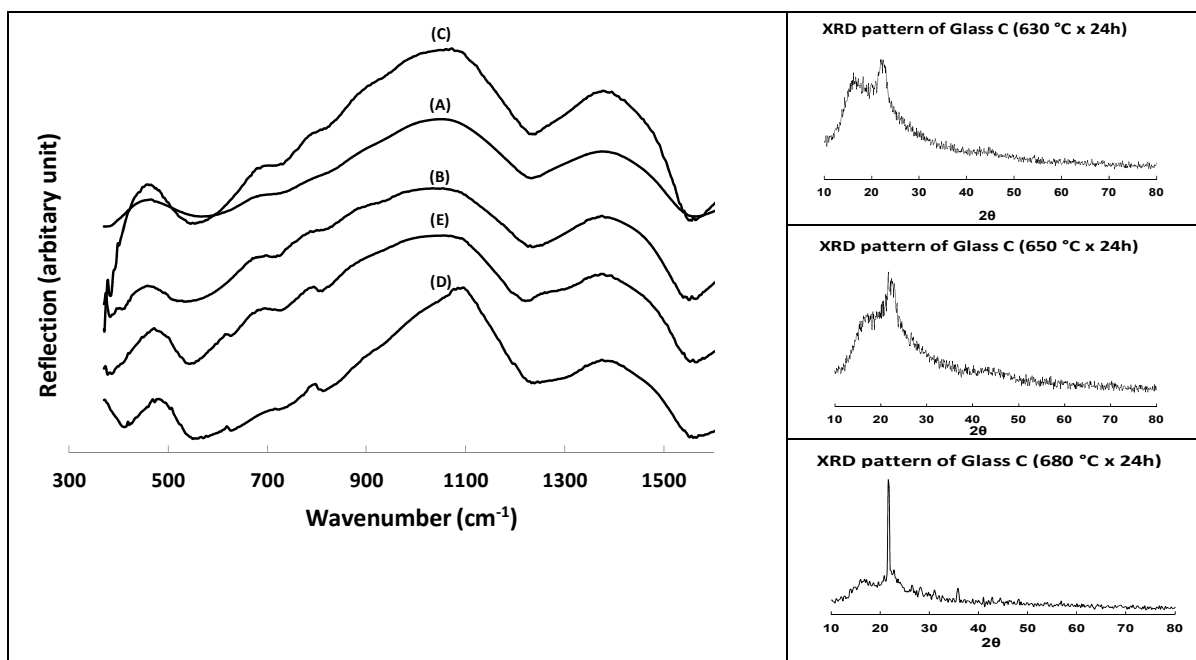


Figure 5. FTIR reflection spectra of Glass C as a function of heat treatment: (A) before heat treatment; (B) $630\text{ }^\circ\text{C}$ x 24h; (C) $650\text{ }^\circ\text{C}$ x 24h; (D) $680\text{ }^\circ\text{C}$ x 24h; (E) $700\text{ }^\circ\text{C}$ x 24h.

4 Conclusions

DTA has been used to identify the glass transition temperature and other thermal characteristics, e.g. formation of surface or bulk nucleation. Shrinkage characteristics of the glass compositions were measured by Dilatometer. DTA also proved to be effective in identifying optimum nucleation temperature. Increasing zirconia/ zircon in the composition also increases the glass transition temperature. Sharp exothermal peak is only apparent for zircon containing composition and can be attributed to surface nucleation. Whereas bulk nucleation phenomena is predominant for rest of the compositions and precipitation of cristobalite occurred over a wide temperature range. Fine powdered glasses are more effective compared with bulk samples in identifying glass transition temperature. Combined use to FT-IR and XRD found to be effective in identifying crystallization and phase separation.

References

- [1] Haller, W. *Application of Controlled Pore Glass in Solid Phase Biochemistry IN: "Solid Phase Biochemistry"*, edited by Scouten, W.H. John Wiley& Sons, New York , pp.535-597 (1983).
- [2] Shelby, J.E. and Lopes, M. (eds.). *Introduction to Glass Science and Technology*. The Royal Society of Chemistry (2005).
- [3] Du, W.-., Kuraoka, K., Akai, T. and Yazawa, T. Study of kinetics of the phase separation in sodium borate glasses. *Journal of Materials Science*, **35(15)**, pp.3913-3921 (2000).
- [4] Plodinec, M.J. Borosilicate glasses for nuclear waste immobilisation. *Glass Technology*, **41(6)**, pp.186-192 (2000).
- [5] Vienna, J.D. Nuclear Waste Vitrification in the United States: Recent Developments and Future Options. *International Journal of Applied Glass Science*, **1(3)**, pp.309-321 (2010).
- [6] Arab, M., Cailleteau, C., Angeli, F., Devreux, F., Girard, L. and Spalla, O. Aqueous alteration of five-oxide silicate glasses: Experimental approach and Monte Carlo modeling. *Journal of Non-Crystalline Solids*, **354(2-9)**, pp.155-161 (2008).
- [7] Park, J. and Lee, S. Mechanism of Preventing Crystallization in Low-Firing Glass/Ceramic Composite Substrates. *Journal of the American Ceramic Society*, **78(4)**, pp.1128-1130 (1995).
- [8] Tummala, R.R. Ceramic and Glass-Ceramic Packaging in the 1990s. *Journal of the American Ceramic Society*, **74(5)**, pp.895-908 (1991).
- [9] Nakashima, K., Noda, K. and Mori, K. Time-temperature-transformation diagrams for borosilicate glasses and preparation of chemically durable porous glasses. *Journal of the American Ceramic Society*, **80(5)**, pp.1101-1110 (1997).
- [10] Yazawa, T., Tanaka, H., Eguchi, K. and Yokoyama, S. Novel alkali-resistant porous glass prepared from a mother glass based on the SiO₂-B₂O₃-RO-ZrO₂ (R = Mg, Ca, Sr, Ba and Zn) system. *Journal of Materials Science*, **29(13)**, pp.3433-3440 (1994).
- [11] Simhan, R.G. Chemical Durability of ZrO₂ Containing Glasses. *Journal of Non-Crystalline Solids*, **54(3)**, pp.335-343 (1983).
- [12] Tsurita, Y. and Wada, K. 1998. Preparation of Porous Supports in the SiO₂-ZrO₂-Na₂O System. *Bulletin of the Chemical Society of Japan*, **71(2)**, pp.503-511 (1998).
- [13] Kerc, J. and Srcic, S. Thermal analysis of glassy pharmaceuticals. *Thermochimica Acta*, **248**, pp.81-95 (1995).
- [14] Reben, M. and Li, H. Thermal Stability and Crystallization Kinetics of MgO-Al₂O₃-B₂O₃-SiO₂ Glasses. *International Journal of Applied Glass Science*, **2(2)**, pp.96-107 (2011).
- [15] Lima, M.M. and Monteiro, R. Characterisation and thermal behaviour of a borosilicate glass. *Thermochimica Acta*, **373(1)**, pp.69-74 (2001).

- [16] Wakasugi, T., Burgner, L.L. and Weinberg, M.C. A DTA study of crystal nucleation in Na₂O–SiO₂ glasses. *Journal of Non-Crystalline Solids*, **244(1)**, pp.63-73 (1999).
- [17] Hu, A., Liang, K., Li, M. and Mao, D. Effect of nucleation temperatures and time on crystallization behavior and properties of Li₂O–Al₂O₃–SiO₂ glasses. *Materials Chemistry and Physics*, **98(2-3)**, pp.430-433 (2006).
- [18] Cattell, M.J., Chadwick, T.C., Knowles, J.C., Clarke, R.L. and Samarawickrama, D.Y.D. The nucleation and crystallization of fine grained leucite glass-ceramics for dental applications. *Dental Materials*, **22(10)**, pp.925-933 (2006).
- [19] Hernández-Crespo, M.S., Romero, M. and Rincón, J.M. Nucleation and crystal growth of glasses produced by a generic plasma arc-process. *Journal of the European Ceramic Society*, **26(9)**, pp.1679-1685 (2006).
- [20] Novaes de Oliveira, A.P., Bonamartini Corradi, A., Barbieri, L., Leonelli, C. and Manfredini, T. The effect of the addition of ZrSiO₄ on the crystallization of 30Li₂O/70SiO₂ powdered glass. *Thermochimica Acta*, **286(2)**, pp.375-386 (1996).
- [21] Agarwal, A., Davis, K.M. and Tomozawa, M. A simple IR spectroscopic method for determining fictive temperature of silica glasses. *Journal of Non-Crystalline Solids*, **185(1-2)**, pp.191-198 (1995).
- [22] Kato, Y., Yamazaki, H. and Tomozawa, M. Detection of phase separation by FTIR in a liquid-crystal-display substrate aluminoborosilicate glass. *Journal of the American Ceramic Society*, **84(9)**, pp.2111-2116 (2001).
- [23] Fujita, S., Kato, Y. and Tomozawa, M. IR peak shift due to phase separation of Na₂O–SiO₂ system glasses. *Journal of Non-Crystalline Solids*, **328(1-3)**, pp.64-70 (2003).
- [24] Piscicella, P. and Pelino, M. FTIR spectroscopy investigation of the crystallisation process in an iron rich glass. *Journal of the European Ceramic Society*, **25(11)**, pp.1855-1861 (2005).
- [25] Lubas, M., Sitarz, M., Fojud, Z. and Jurga, S. Structure of multicomponent SiO₂–Al₂O₃–Fe₂O₃–CaO–MgO glasses for the preparation of fibrous insulating materials. *Journal of Molecular Structure*, **744–747(0)**, pp.615-619 (2005).
- [26] Medvedev, E.F. Determination of sodium borosilicate bands in the IR spectrum of a multicomponent batch. *Glass and Ceramics*, **64(9-10)**, pp.300-304 (2007).