Section 14. Nucleation and crystallization III

On the persistence of metastable crystal phases in lithium disilicate glass

Lori L. Burgner [a,*], Pierre Lucas [b], Michael C. Weinberg [a], Paulo C. Soares Jr. [c], Edgar D. Zanotto [c]

[a] *Materials Science and Engineering Department, University of Arizona, Tucson, AZ 85712, USA*
[b] *Department of Chemistry, Arizona State University, Tempe, AZ 85287, USA*
[c] *Department of Materials Engineering, DEMa, Federal University of São Carlos, UFSCar, 13565-905 São Carlos, SP, Brazil*

Abstract

The formation of metastable crystalline phases in lithium disilicate glass has been a subject of controversy for decades. Recent experimental results mainly obtained via the use of electron microscopy have provided strong evidence for the formation of metastable phases during the early stages of crystallization in this composition, and have initiated a re-examination of this topic. Here, we discuss one aspect of this problem relating to the stability of these non-equilibrium phases when glasses are heated for extended time periods (>100 h) at temperatures in the nucleation regime. Recently, we presented experimental evidence obtained via XRD which indicated that metastable phases do not persist at long times in lithium disilicate glass. This finding is in direct contradiction to a result reported earlier which suggests that metastable crystalline phases in lithium disilicate glasses are long-lived and can be detected with the aid of XRD. Presented herein are the results of a systematic experimental investigation addressing the potential sources of this discrepancy, namely, glass preparation procedure, glass composition, and water content. Consistent with the results of our previous investigation, in no instance do we find any XRD evidence for the persistence of metastable phases. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The nucleation of metastable crystalline phases in systems that appear to crystallize homogeneously is an important and controversial area of inquiry. The issue of metastable phase formation is of considerable scientific importance because it offers a possible explanation for the observed discrepancies between theoretically predicted and experimentally determined nucleation rates in glasses. Of the few glass-forming compositions which appear to nucleate homogeneously, lithium disilicate (LS_2) has been the most extensively studied, and most observations of metastable phases have been reported for glasses close to the LS_2 composition. Metastable phase formation is of paramount importance in the interpretation of crystal nucleation experiments in LS_2 and other glasses which are assumed to nucleate homogeneously. For example, if metastable phases form prior to the crystallization of the equilibrium LS_2 crystalline phase, then the possibility exists that the stable crystal phase forms heterogeneously on

---

* Corresponding author. Tel.: +1-520 621 6070; fax: +1-520 621 8059.
E-mail address: lorib@primenet.com (L.L. Burgner).

the metastable phase. If this process were indeed the case, then the present interpretations of homogeneous crystal nucleation experiments for this system would be invalid and the experimental results would have to be analyzed anew.

The subject of metastable crystal nucleation could be of technical importance, too. If the process of formation of metastable crystalline phases were thoroughly understood, then the appearance of such phases could potentially be promoted and regulated. This capability could lead to the production of new glass-ceramic materials.

Here we consider the issue of the long time stability of metastable phases that might form in LS_2 glass. The existing evidence in favor of the formation of metastable crystals in this system is not critically examined herein. We consider solely the questions of whether or not such phases persist in LS_2 glasses which have been heated for extended time periods (>100 h), and whether or not X-ray diffraction (XRD) can be used as a means for studying such phases.

Iqbal et al. [1] studied the crystallization of a lithium silicate glass containing 33.9 mol% Li_2O using (XRD) and other experimental techniques. Glasses were heated isothermally at 454°C (the temperature where the nucleation rate is maximum) for 50, 120, 312, 331, 480, and 551 h. XRD traces of the heated glasses indicated the existence of at least some metastable phase (or phases) in glasses which were heated for all the above times, save the glass which was heated for 50 h which appeared X-ray amorphous. In fact, after heating for 120 h, the only crystal phase detected was a metastable phase.

Burgner et al. [2] recently investigated the crystallization of an LS_2 glass which was heated isothermally for long times (>100 h) at several different temperatures in the nucleation region employing XRD analysis. They found that glasses heated at 454°C remained X-ray amorphous for heating times of at least 192 h. XRD of glasses heated for 360 h had only the dominant peaks of the stable LS_2 crystals against an amorphous background. Furthermore, XRD of glasses that were heated at higher (477°C and 500°C) and lower (440°C) temperatures had diffraction patterns of only stable LS_2 crystals.

In Ref. [2] several possible reasons for the apparent discrepancies between the results of Refs. [1] and [2] were offered. Here, we report the results of a systematic experimental investigation addressing the potential sources for this discrepancy, namely, glass composition, glass preparation procedure, and water content. The glass used in Ref. [2] was sub-stoichiometric (33.1 mol% Li_2O), while the glass utilized in the study of Iqbal et al. was hyper-stoichiometric. Thus, here we examine the crystallization of glasses containing slightly more Li_2O than the disilicate composition. Also, Refs. [1,2] utilized different glass preparation procedures. In Ref. [1], the precursor powders were sintered at 1000°C for 10 h prior to melting, while this intermediate heating step was not used in the glasses investigated by Burgner et al. Since it is possible that a solid state reaction took place during the sintering step which produced some sort of crystalline phase that is difficult to dissolve at the melting temperature, we investigate the effect of this sintering step on crystallization. It is also possible that the disparate results between Ref. [1] and Ref. [2] were due to different water contents of the glasses used in the respective investigations. Therefore, we also investigate crystallization of glasses containing different amounts of water.

2. Experimental

Four lithium silicate compositions were prepared; a hyper-stoichiometric composition containing 34.5 mol% Li_2O (glass 1), a disilicate composition (glass 2), a sub-stoichiometric composition containing 32.5 mol% Li_2O (glass 3), and a hyper-stoichiometric composition containing 33.8 mol% Li_2O (glass 4). Glasses 3 and 4 were prepared in Brazil at the Federal University of São Carlos (relative humidity 70–80%), and glasses 1 and 2 were prepared in the USA at the University of Arizona (relative humidity 10–20%). The preparation procedure for all the glasses was the same as described in Ref. [2], but glass 2 was given an isothermal sintering step in which the precursor powders were heated at 1000°C for 10 h. The

above information is summarized in the first two columns of Table 1.

Isothermal heat-treatments were performed in a horizontal tube furnace having a central hot zone constant to within $\pm 1°C$. Glass samples were heated at 454°C and 465°C for various times. The heat-treatment schedules employed for each of the four glass compositions are detailed in the last two columns of Table 1.

Surface layers of the heat-treated glass samples were removed, and both the interior (bulk) and surface materials were finely ground for XRD analysis. XRD data were collected on a diffractometer (Siemens D5000) using Cu K_α radiation. The spectrometer was equipped with a 7° wide position sensitive detector and a scan rate of 0.3°/min was employed. All scans were taken at scattering angles, 2θ, from 10° to 60°.

Additional XRD data were also collected on a diffractometer (Rigaku RU2000) equipped with a rotating anode X-ray source using Cu K_α radiation at 50 kV and 100 mA. Powder samples were scanned at scattering angle, 2θ, from 10° to 60°, using a step size of 0.02° and a collection time of 3 s.

The chemical compositions of the glasses were confirmed either by chemical analysis or the use of index of refraction measurements, and published data of the index of refraction as a function of Li_2O content [3–5].

The water concentrations in the glasses were measured with the aid of a Fourier Transform infrared spectrometer (Perkin–Elmer FTIR), using the procedure outlined by Davis et al. [6].

Optical microscopy was performed using a polarizing microscope. Portions of each heat-treated sample were cut away and subsequently thinned and optically polished on both faces. The resulting samples were examined between cross-polarizers to observe and photograph the birefringence resulting from crystalline phases.

3. Results

The chemical compositions of the prepared glasses were found to be: 34.5 ± 0.3 mol% Li_2O (glass 1), 33.3 ± 0.3 mol% Li_2O (glass 2), 32.5 ± 0.5 mol% Li_2O (glass 3), and 33.8 ± 0.5 mol% Li_2O (glass 4).

The water concentrations of the as-prepared glasses were determined from the peak heights of the 3500 cm^{-1} water band in the IR [6]. The water concentrations of glasses 1 and 2 were found to be similar in magnitude to those reported in Ref. [2], about 70 ppm $\pm 10\%$. It was also found that the water contents of glasses 3 and 4 were nearly double that of glasses 1 and 2 (approximately 138 ppm $\pm 10\%$). The different concentrations of water in the two families of glasses are consistent with

Table 1
Glass specification and heat-treatment schedule

Glass no.	Description	Heat-treatment temperature (°C)	Heat-treatment time (h)
1	34.5 Li_2O 65.6 SiO_2 (mol%) (prepared in Arizona according to Ref. [2])	454	150, 328, 476
		465	168, 240, 288, 360, 528
2	33.3 Li_2O 66.7 SiO_2 (mol%) (prepared in Arizona according to Ref. [2], but given additional intermediate sintering step)	454	150, 328
		465	168, 240, 288
3	32.5 Li_2O 67.5 SiO_2 (mol%) (prepared in Brazil according to Ref. [2])	454	120, 168, 240, 288
4	33.8 Li_2O 66.2 SiO_2 (mol%) (prepared in Brazil according to Ref. [2])	454	120, 168, 240, 360
		465	168, 240, 288, 360

the relative humidity in São Carlos and Tucson, where these glasses were made. Fig. 1 shows representative FTIR spectra showing the differences in water contents of the prepared glasses. Spectra (a) and (b) in Fig. 1 were obtained for samples of equal thickness from glass 1 and glass 3, respectively.

In reporting the XRD results it is noted that, unless stated otherwise, the diffraction patterns were obtained from heated samples that had their surfaces removed prior to pulverizing the material into a fine powder for XRD analysis (i.e., the interior of the sample). The term 'surface' is used to indicate a diffraction pattern obtained from the material that was removed from the heated sample (surface layer), and which was subsequently ground to a fine powder for XRD analysis.

Figs. 2(a)–(c) show the XRD traces of samples of glass 1 that had been heated at 454°C for 150, 328, and 476 h, respectively. Fig. 2(d) shows the diffraction pattern obtained from the surface of the sample heated at 454°C for 476 h. The vertical lines along the abscissa of Fig. 2 (and all subsequent figures) denote the positions and relative intensities of diffraction peaks corresponding to the stable LS_2 phase as per JCPDS card #40-0376. As observed in Fig. 2, glass 1 remained X-ray amorphous after heating for 150 h. After heating for 328 h, the more intense peaks of the stable LS_2 phase emerged against the amorphous back-
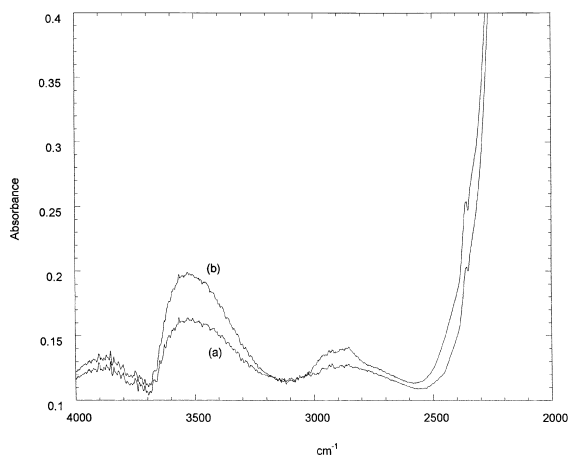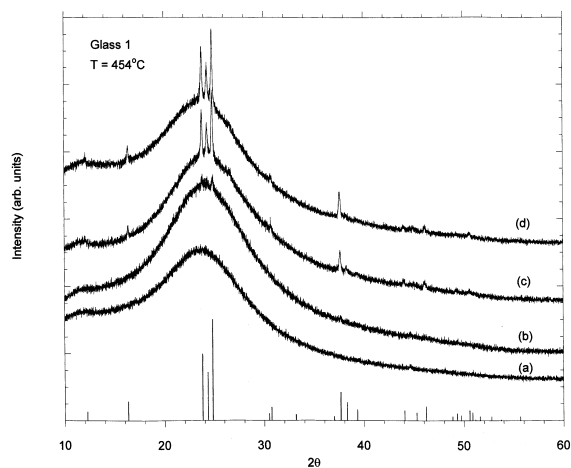

Fig. 2. XRD traces of glass 1 heated at 454°C for (a) 150, (b) 328, (c) 476, (d) 476 h-surface.

ground. Upon further heating, these LS_2 peaks intensified and other peaks corresponding to the stable phase appeared. Consistent with our observations for all heat-treated glass compositions, and as exemplified by Figs. 2(c) and (d), there were no apparent differences between the XRD traces obtained from surface and interior materials of heated samples, save the fact that diffraction peaks of surface materials had greater intensities.

The XRD traces of samples from glass 2 that had been heated at 454°C showed that the glass remained X-ray amorphous after heating for 150 h. After heating for 328 h, the more intense diffraction peaks of the stable LS_2 phase emerged against an amorphous background.

Crystallization of glass 3 that had been heated at 454°C for 120, 168, 240, and 288 h is similar to that observed for glasses 1 and 2. Glass 3 also remained X-ray amorphous after heating for 120 h. The more intense LS_2 peaks, although barely detectable, emerged after 168 h. After 240 h, these LS_2 peaks were clearly resolvable. Upon further heating, these peaks intensified and additional LS_2 peaks appeared.

Fig. 3 shows the series of diffraction patterns obtained from samples of glass 4 heated at 454°C for 120, 168, 240, and 360 h. Crystallization of glass 4 is consistent with that observed for all other glass compositions. However, for glass 4 the more
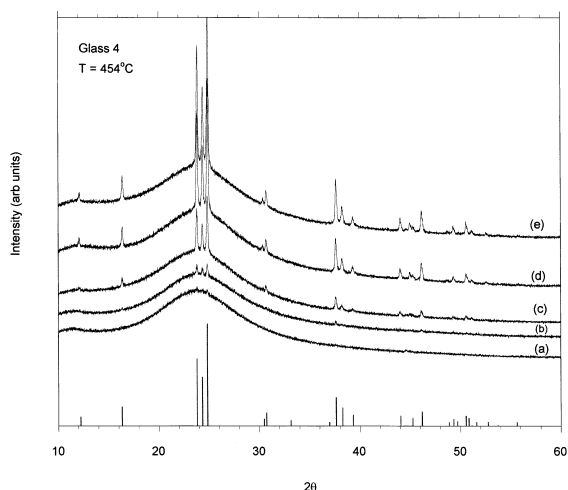

Fig. 1. FTIR spectra (a) glass 1; (b) glass 3.

Fig. 3. XRD traces of glass 4 heated at 454°C for (a) 120, (b) 168, (c) 240, (d) 288, (e) 360 h.

intense LS_2 diffraction peaks emerged after heating for 120 h. As shown in Fig. 4, upon further heating these peaks intensified and additional stable phase peaks appeared.

The XRD traces obtained from samples of glass 1 that was heated at 465°C are shown as a function of heating time in Fig. 4. As shown in Fig. 4, and as observed for all other compositions heated at 465°C, the only diffraction peaks detectable are the more intense peaks of stable LS_2. For each com-
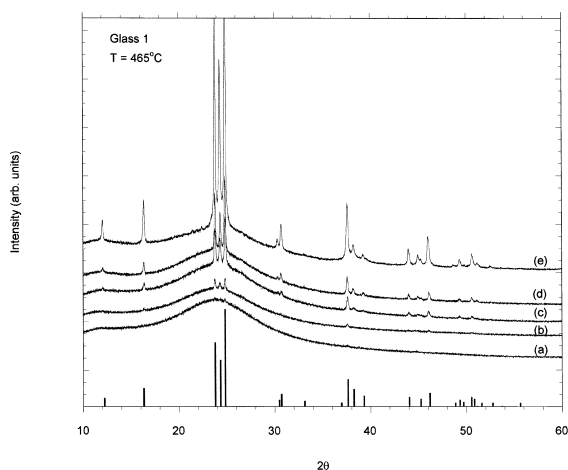
position, these LS_2 peaks intensified and additional peaks associated with the stable LS_2 phase appeared with increased heating time.

To ensure that our observations described above were not limited by instrument sensitivity; XRD measurements were also performed on an instrument equipped with a rotating anode X-ray lamp. This larger intensity X-ray beam allows for greater penetration depth in the material and provides a better signal-to-noise ratio, thus enabling greater resolution of small peaks, and hence detection of even small volume fractions of crystalline material which may not be resolvable via standard XRD equipment. Fig. 5 shows the diffraction pattern obtained via the rotating anode XRD instrument for glass 4 that had been heated at 454°C for 360 h. The diffraction pattern shown in Fig. 5 is very similar to that which was obtained using standard XRD equipment, i.e., only the stable LS_2 crystal phase was detected. Thus, we conclude that instrument sensitivity did not effect the observed crystallization.

For all samples in which crystalline material was detected by XRD, crystals were observable in the heat-treated glasses via optical microscopy using a 100× objective. Based on XRD results, we can conclude that what was observed by optical microscopy were equilibrium phase lithium disilicate crystals. The crystal morphology observed in all heat-treated samples of all compositions which

Fig. 4. XRD traces of glass 1 heated at 465°C for (a) 168, (b) 240, (c) 288, (d) 360, (e) 528 h.
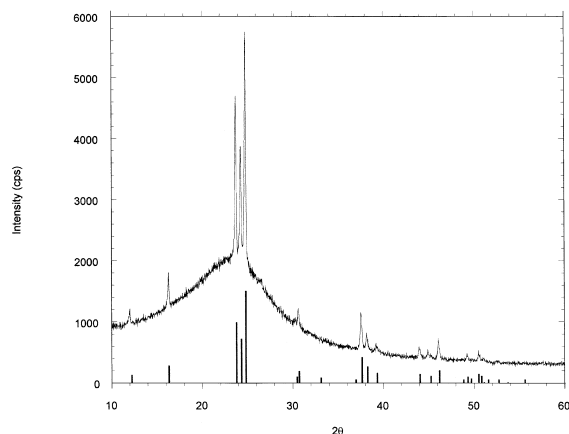

Fig. 5. Diffraction pattern obtained via rotating anode XRD of glass 4 heated at 454°C for 360 h.

contained detectable crystalline material in their XRD trace was similar. The observed crystals had the shape of prolate ellipsoids with an average minor-to-major axes ratio of 0.26. This ratio did not vary within errors regardless of composition or heat-treatment.

4. Discussion

Existing evidence for the formation of metastable phases during the initial stages of crystallization in lithium disilicate glasses has been obtained from both direct and indirect experimental techniques. Results of small angle X-ray scattering (SAXS) and electrical conductivity experiments conducted by Hench et al. [7,8] on sub- and stoichiometric LS_2 glasses that had been heated-treated at 500°C for times up to 24 h, suggested that a metastable phase formed prior to equilibrium crystallization of LS_2. Joseph and Pye [9] performed Raman spectroscopy on stoichiometric LS_2 glasses which had been heat-treated at 450°C and 500°C for times up to 15 h. Their Raman results support the conclusions of Hench [8] that a metastable phase forms during the initial stages of the nucleation process. More recently, Deubener and Brückner [10] performed transmission electron microscopy (TEM) on glasses with 33.5 mol% Li_2O that had been heat-treated at 454°C. Deubener provided provocative electron diffraction patterns of the metastable phases present in the heated glass. Zanotto [11] repeated the SAXS experiments of Hench and TEM experiments of Deubener and Brückner. Zanotto also observed the formation of metastable phase(s), thus confirming the previous reports. In Refs. [10,11], metastable phases were detected in the very early stages of crystallization, when the crystallized volume fractions were smaller than ∼2%, i.e., for short treatments at 454°C ($t < 20$ h).

Here our attention is directed to an investigation of one aspect of the problem of metastable crystal phase formation in lithium disilicate glass. In particular, we analyze whether glasses heated for sufficiently long times in the nucleation regime to enable detection of crystalline peaks in an XRD trace have any trace of metastable crystalline phases. We do not discuss the more general issue of the credibility of the existing evidence for metastable phase formation at all heating times, but consider the question of whether XRD is a viable experimental probe for investigating metastable phase formation.

As mentioned previously, Refs. [1,2] came to very different conclusions regarding the existence of metastable crystalline phases in lithium silicate glasses which were heated for extended time periods in the nucleation regime. The studies reported in Refs. [1,2] used similar glass preparation procedures, utilized similar XRD equipment operated under comparable conditions, but obtained quite different XRD results. In the present work, we considered and analyzed the following three possible causes for the discrepancy:
1. slight differences in composition,
2. intermediate temperature sintering, and
3. differences in water content.
By comparing the XRD results obtained for glass 2 in this investigation and those reported in Ref. [2], it is apparent that the intermediate sintering step had no effect on the observed crystallization. The glasses prepared in Brazil had approximately twice the water content of those prepared in Arizona. The water content of the glass used in Ref. [1] was not reported. However, since the glass preparation procedures used were nearly identical, it is reasonable to assume that the water content was not unusually large and was probably comparable to that of the glasses used in this study. A comparison of Fig. 2 with Fig. 3 indicates that the crystallization rates of the larger water containing glasses were larger than those of the drier glasses. This result is in accord with previous findings [12] which reported that both crystal nucleation and growth rates are accelerated by the presence of water in the glass. However, it is clear that regardless of the water concentration only a stable LS_2 phase formed. Furthermore, variations in composition did not have an effect on the observed crystallization. Thus, it appears that none of the above factors were responsible for the disparate results between Refs. [1] and [2]. In view of this finding, it will be useful to consider other experimental evidence that bears upon this issue.

James and Keown [13] examined the crystallization of a lithium silicate glass which contained 33.1 mol% Li_2O using TEM. Glasses were heated for 65 and 94 h at a temperature of 490°C. Selected area diffraction (SAD) was used to determine the crystal phase of observed crystals. Stable LS_2 was the only crystalline phase detected.

In a study by Barker et al. [14], the nucleation and growth as a function of annealing time of lithium silicate glasses containing 33.3 and 36 mol% Li_2O (composition by batch) was investigated. In their study, samples of these glasses were heated at the maximum nucleation temperature, 455°C, until crystallization was detected by XRD. For both glasses, after 10 days only lithium disilicate solid solution was detected.

Very recently, Mastelaro and Zanotto [15] have obtained additional XRD results. Mastelaro and Zanotto heated LS_2 glass for 86 and 100 h at a temperature of 460°C, and the only crystalline phase detected was stable LS_2. Fokin heat-treated LS_2 glass at 440°C for 350, 543, and 642 h. The XRD pattern of the glass heated for 350 h had only an amorphous peak, while the scans of the glasses heated for longer times showed only stable LS_2.

It is also important to note that TEM and NMR were also employed in the investigation of Iqbal et al. [1], and the following results were found. The TEM SAD investigation of a glass heated at 454°C for 93 h revealed stable LS_2 as the only crystalline phase present. Also, there were no signs of metastable phase for glasses heated up to 217 h (although a small amount of crystalline metastable phase was found when the glass was heated for 331 h). In addition, the authors stated that the NMR results obtained from glasses which were heated for less than 228 h were consistent with the formation of stable LS_2.

Hence, there seems to be substantial experimental evidence to indicate that metastable crystalline phases are not found in lithium disilicate glass which has been heated for extended time periods in the nucleation region, and thus XRD is not a suitable technique for examining potential metastable crystal phase formation in LS_2.

5. Conclusion

From the results presented herein and from previously published studies, we draw the following conclusions regarding the persistence of metastable crystalline phases in lithium disilicate glass. (1) It is most unlikely that metastable crystalline phases exist in LS_2 glasses that have been heated for long time periods in the temperature regime where internal nucleation occurs. (2) If some amount of metastable crystalline phases do persist to long times, they cannot be detected via the use of conventional XRD.

Acknowledgements

References

[1] Y. Iqbal, W.E. Lee, D. Hollan, P.F. James, J. Non-Cryst. Solids 224 (1998) 1.
[2] L.L. Burgner, M.C. Weinberg, P. Lucas, P.C. Soares Jr., E.D. Zanotto, J. Non-Cryst. Solids 255 (1999) 264.
[3] F.C. Kracek, J. Phys. Chem. 34 (1930) 2641.
[4] D. Hubbard, W. Cleek, J. Res. Natl. Bur. Stand. 49 (1952) 267.
[5] H. Verweij, J. Buster, G.F. Remmers, J. Mater. Sci. 14 (1979) 931.
[6] M.J. Davis, P.D. Ihinger, A.C. Lasaga, J. Non-Cryst. Solids 219 (1997) 62.
[7] D.L. Kinser, L.L. Hench, J. Am. Ceram. Soc. 8 (1968) 445.
[8] L.L. Hench, S.W. Freiman, D.L. Kinser, Phys. Chem. Glasses 12 (1971) 58.
[9] I. Joseph, L.D. Pye, Proc. 14th Int. Congr. on Glass, vol. 1, Central Glass and Ceramic Research Institute, New Delhi, Calcutta, 1986, p. 358, collected papers.
[10] J. Deubener, R. Brückner, M. Sternitzke, J. Non-Cryst. Solids 219 (1997) 62.
[11] E.D. Zanotto, J. Non-Cryst. Solids 219 (1997) 42.
[12] C.J.R. Gonzales-Oliver, P.S. Johnson, P.F. James, J. Mater. Sci. 14 (1979) 1159.
[13] P.F. James, S.F. Keown, Philos. Mag. 30 (1974) 789.
[14] M.F. Barker, T.H. Wang, P.F. James, Phys. Chem. Glasses 29 (1988) 240.
[15] V.R. Mastelaro, E.D. Zanotto, J. Non-Cryst. Solids 247 (1999) 79.