Ostwald Ripening Phenomena in B₂O₃-PbO Glass System

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Lead borate glass was prepared by the quench method, followed by treatment at its isothermal temperature at different time periods. When the sample was rapidly cooled from the melt, it showed two distinguished opalescent layers. The SEM analysis and XRD pattern provide characteristics of glass without XRD peaks and their morphology show the aggregated spherical particles in the phase separated glass. This data show that phase separation occurred even when the melts were rapidly cooled. However, the sample shows a Ostwald ripen with increasing time of heat treatment, which implies that the size of particles increases and their number decreases. The infrared absorption spectra show shift edge for sample glass with heat treatment, which indicates a change of structural configuration, *i.e.* conversion of tetrahedral boron on triangular boron coordination.

Key Words: Lead borate glasses, Phase separation, Ostwald ripen, Structural configuration.

INTRODUCTION

The vitreous network of boron oxide (B_2O_3) can be described as made of boroxols cycles. These cycles join to form layers and thus confer a bidirectionality on the vitreous network. NMR study of B_{11} by Petrovskaya[1] showed a great diversity of structural units present in the alkaline borates systems or alkaline-earth borates systems which result from the complex association of elementary structural units of the plane triangles (BO_3^{3-}) and of tetrahedrons (BO_4^{5-}). A schematized representation of borates units is given in Fig. 1.

Glasses borates with a weak alkaline concentration have a structural network realized by the tetrahedral (BO_4) basic units which give a three-dimensional structure. For a composition of 30 % molar of alkaline oxide, fraction of boron atom in four co-ordination number reached its maximum value. For a higher alkaline oxide composition, the concentration in tetrahedral group (BO_4^{5-}) decreases with the profit of (BO_3^{3-}) group, presenting not bridging oxygen. Like consequence of the formation of not bridging oxygen, a progressive depolymerization of the network is deferred being able to lead to a complete rupture of the vitreous network then made up of small isolated borates groups.
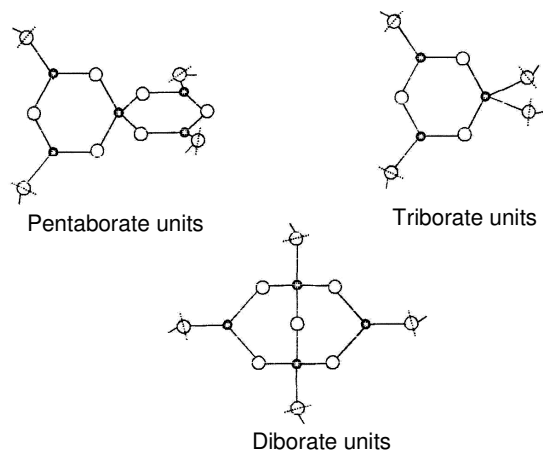
Fig. 1. Schematized representation of borates units

In the PbO-B_2O_3 glasses, PbO enter the glass structure in the form of both network modifier and network former[1].

At lower PbO content (< 15 mol %), lead acts as modifier forming BO_4^{5-} units in the borate network. Above 15-20 mol %, some lead enters the structure as network former in the form of PbO_4 pyramids[2]. The NMR results of Petrovskaya[1] indicate that the fraction N_4 of 4-coordinated boron ions has a maximum at about 50 mol % PbO.

This system of lead borate glasses has broad immiscibility range and can thus form two phases glasses. This glass can be used in manufacture of enamels in which the fusion is done easily with a separation of spontaneous phase.

Among glasses which have scientific interest, the Soda-borosilicate glasses of the system (SiO_2-B_2O_2-Na_2O). After their development, a treatment of separation of phase yields two phases; one rich in silica and the other rich in alkaline-borate. After that, the second phase is attacked with hydrochloric acid and a silica skeleton porous is obtained known by Vycor® glass, almost pure and which have remarkable properties.

The understanding of immiscibility is based on the thermodynamics of regular solutions[3,4] the separation process can yield glass with either droplet/matrix or interconnected microstructures[5]. In the case of an over-saturated solution, which undergoes a phase separation, there are two major development steps. The first one where the system separates, either by nucleation or spinodale mechanisms. This step is followed by a second one, where a rearrangement of the phase geometry occurs. It is at the coalescence or ripen step that the system tends to reduce its interfacial energy. The particles or the domains created will then achieve desirable dimensions and therefore, the degree of saturation of the matrix reaches its minimum level. It was noticed that the smaller particles tend to dissolve and go back in solution, whereas the larger ones grow at the smaller particles' depend. The overall effect is the swelling of the precipitate which reduces the overall interface[6].

The process known as the Ostwald ripens requires the solute's diffusion of the small neighbouring particles to the areas surrounding the larger particles.

In the present work, we have prepared a lead borate glass sample and then treated it for isothermal temperatures at different periods of time. Upon quenching, the glass shows phase separation in two distinguished layers. However, after heat treatment, some glass samples crystallized instantaneously, whereas others developed Ostwald ripen.

EXPERIMENTAL

Glass of composition $95B_2O_35PbO$ (weight %) labelled BP95 was prepared using a conventional melt quenching method. Lead oxide (PbO) and boric acid (H_3BO_3) were weighed and melted in porcelain crucible at 1000-1200 °C for 20 min in an electric furnace. The melt was then poured on a metallic mould to give glass with an opal colour, which was then treated at different times and temperatures.

The thermal expansion curve was determined using a conventional dilatometer type Dil 402C (MMCL: Material Mineral Composite Laboratory, Boumerdes, Algeria) with a heating rate of 5 K min^{-1}. The sample was a small bar, typically 8 mm wide and 20-25 mm long.

The glass transition temperature was determined from the expansion curve using the intercept method, while the dilatometric softening temperature (T_d) was defined as the temperature of maximum expansion.

The glassy state in quenched samples and the crystalline phases present in heat treated samples were identified by X-ray diffraction (XRD) analysis at room temperature using CuK_α radiation (MMCL).

The morphological observations were made using scanning electron microscopy (SEM; model Jeol JSM 6360 LV (CDTA: Advanced technological development centre, Algiers).

The infrared absorption spectra in the 4000-500 cm^{-1} wave number range were recorded using Thermonicolet Nexus infrared spectrophotometer and the standard KBr pellet technique.

RESULTS AND DISCUSSION

The conditions of heat treatment for different time and temperatures of sample glass BP95 are illustrate in Table-1.

Rapidly cooled sample from the melt show two opalescent distinguish layers. Fig. 2a and b provide SEM photographs and XRD pattern characteristic of glass without XRD peaks and their morphology show the aggregated spherical particles in the phase separated glass.

The thermal expansion curve of sample BP95 as quenched shows two transitions temperatures: $Tg_1 = 215.6$ °C and $Tg_2 = 150.8$ °C of the two phases as indicated in Fig. 3, T_d is *ca.* 228.4 °C.

TABLE-1
HEAT TREATMENT CONDITIONS OF GLASS BP95

Sample	Temperature (ºC)	Time (min)
BP95/ 0	0	0
BP95/15	414	15
BP95/20	414	20
BP95/30	414	30
BP95/60	414	60
BP95/150	414	150
BP95/360	414	360
BP95/960	414	960

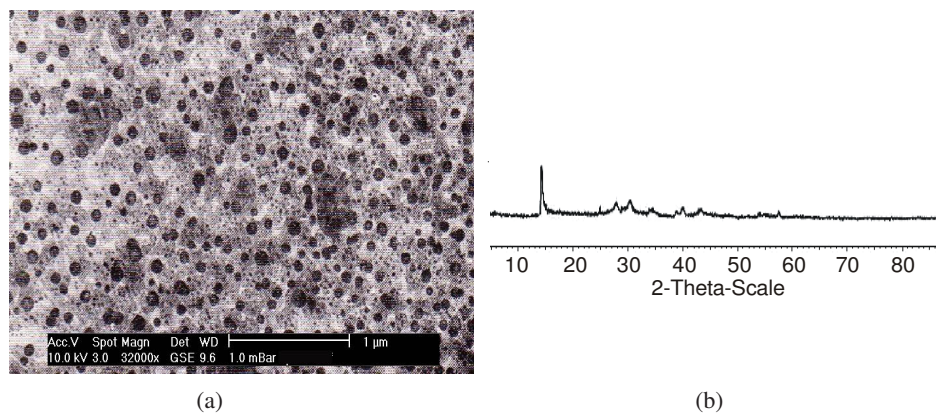(a)   (b)

Fig. 2.   (a) SEM micrograph of as quenched glass BP95; (b) XRD pattern of as quenched glass BP95
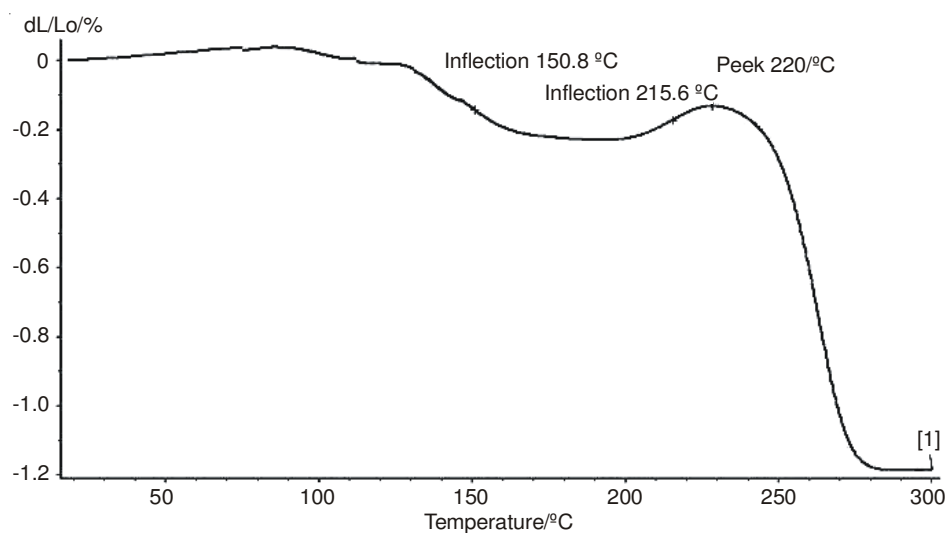

Fig. 3. Thermal expansion curve of glass sample BP95 as quenched

The phase separation already occurred, even when the melts were rapidly cooled. The samples are then heat treated at a fixed temperature for a given time period as shown in Table-1. Figs. 4 and 5 provides respectively, the SEM micrographs and the XRD pattern of the heat treated samples under time-temperature conditions indicate by the points labelled a b, c, d and e.
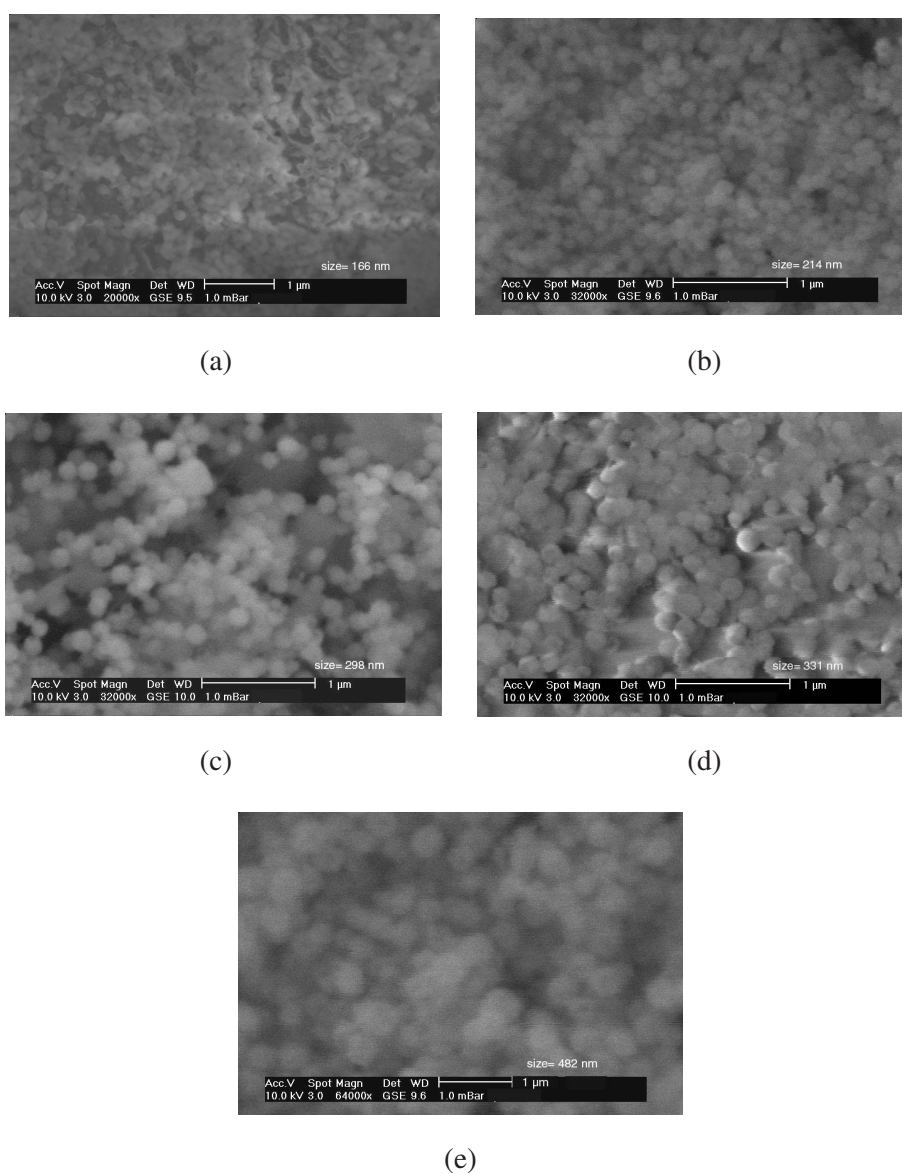

(a)   (b)

(c)   (d)

(e)

Fig. 4.   SEM micrographs of sample BP95 heat treated at 414 ºC; (a) 15 min, (b) 20 min, (c) 30 min , (d) 60 min, (e) 150 min
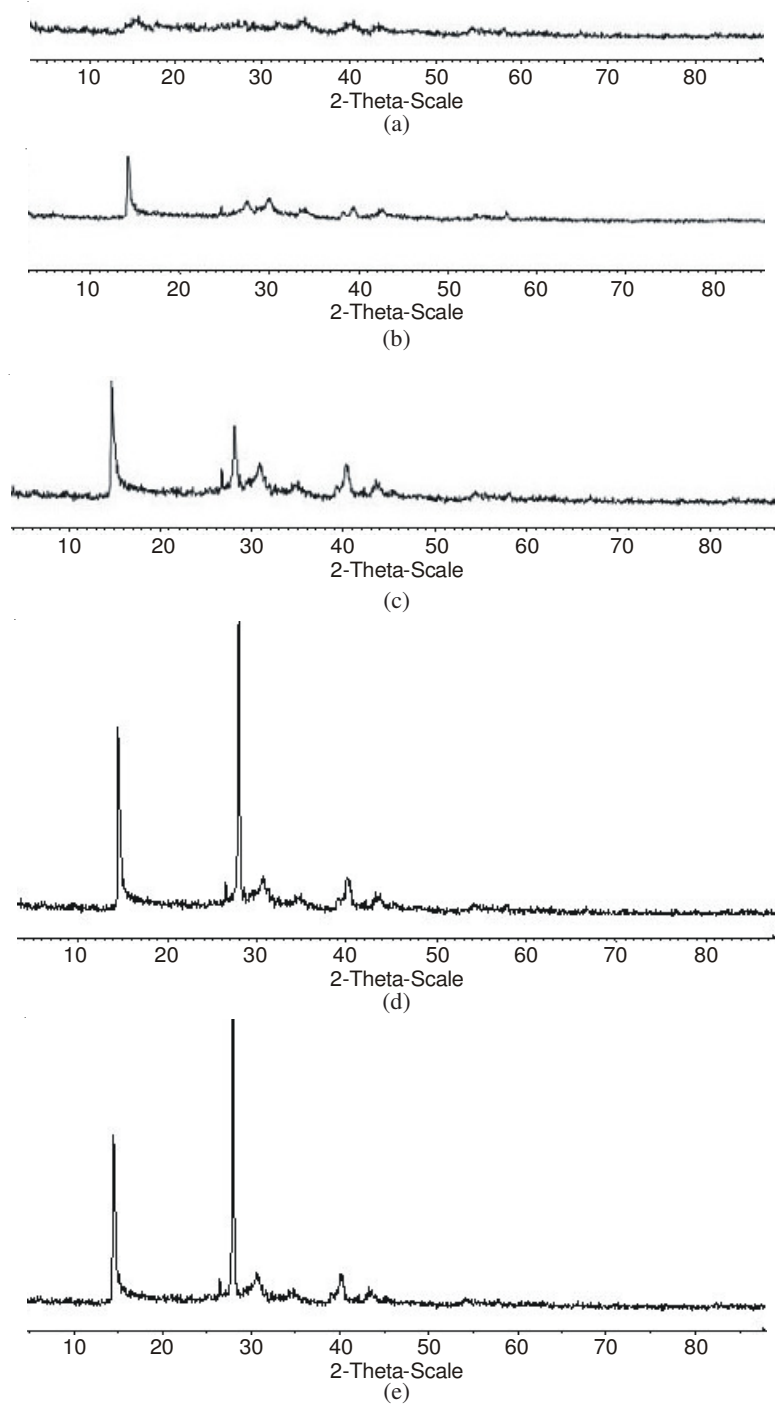
Fig. 5. XRD pattern of sample BP95 heat treated at 414 °C; (a) 15 min, (b) 20 min, (c) 30 min, (d) 60 min, (e) 150 min

The series of samples treated illustrates the effect of isothermal annealing at 414 °C for several times. The formation of sassolite (H_3BO_3) becomes noticeable with time of isothermal treatment in the XRD pattern and the accompanying SEM photographs shows crystallite spheres. A comparison of the SEM data of samples in Fig. 4a-e shows that, the periodicity or size scale of the structure represented by the diameter of a sphere increases with heat treatment time. There are agglomerations of spherical particles and their number decreases due to the Ostwald ripen.

We can distinguish two major development steps of the crystallization of glass BP95, the first one is where the system separates by a nucleation mechanism. This step is followed by a second one, where a rearrangement of the phase geometry occurs. It is at the coalescence step that the system tends to reduce its interfacial energy. The particles created then achieve desirable dimensions. The crystallization increases with the time of heat treatment.

FTIR Spectroscopy: The FTIR spectra of the quenched and heat treated glass samples is shown in Fig. 6 and exhibit broad absorption bands. In these samples, the distribution of structural units occurring is indicative of the general disorder in the anionic network.
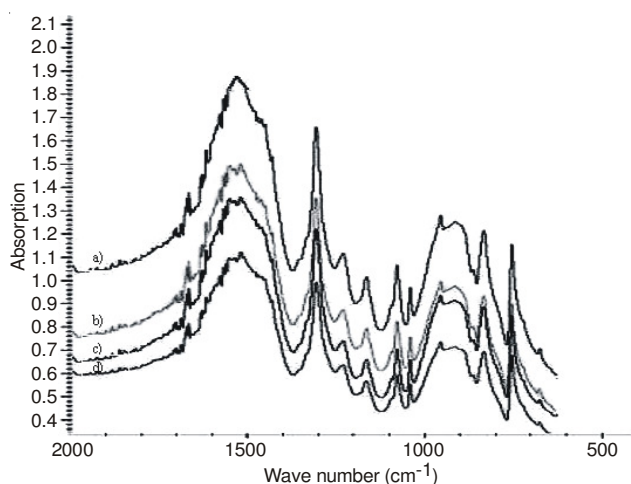

Fig. 6.   FTIR absorbance spectra of glass samples BP95 heated at 414 °C: (a) as quenched; (b) 15 min heated, (c) 360 min heated, (d) 960 min heated

In the 1100-500 cm^{-1} region, the presence of an absorption band is due to the stretching vibration of tetrahedral coordinated atoms B_4 in BO_4^- units. On the other hand, the absorption band in the 1500-1100 cm^{-1} region is due to the stretching vibration of the trigonal coordinated atoms B_3 in BO_3 units. There are two types of BO_3 triangles, the symmetric one with three bridging or nonbridging oxygen and the asymmetric one with one or two nonbridging oxygen[7]. It is known that the asymmetric triangle gives rise to two absorption bands in the range 1500-1100 cm^{-1} while the symmetric triangle gives only one[7,8].

As expected, the line width of the absorption bands of polycrystalline samples (Figs. 6b-d) are narrower and have high intensity than those of the glass sample (Fig. 6a) . As a result of heat treatment, the main absorption band that lies in the 1500-1300 cm^{-1} region splits into two bands. This phenomenon was noticed with all the samples at the same wavenumber values.

The appearance of two bands in the 1500-1300 cm^{-1} region and the broading of the absorption bands can be attributed to a wider distribution of structural units occurring in these samples with respect to the as quenched glass. This means that the heat treatment produces mainly a structural rearrangement of the anion network of the glasses[9]. The bands in the 3500-3000 cm^{-1} region are attributed at OH stretching.

In a study carried out by Khanna *et al.*[10], it was shown that the changes of the absorption bands with heat treatment are attributed to the expansion of glass melt due to the conversion of $B\varnothing_4^-$ units to $B\varnothing_2O^-$ units with increasing time (where $\varnothing$ represents bridging oxygen and O^- non-bridging oxygen). A microphase separation occurs in the glassy matrix forming two microregions, which exhibit a typical droplet structure of phase separated systems. These structural transformations are rapid and completed in the sample heat treated.

These results indicate that the microphase separation originating upon quenching glass, allows the nucleation of sassolite crystals with time and therefore, formation of isolated trigonal BO_3 linked with hydrogen atoms.

Conclusion

When heating lead borate glass at different isothermal time, rapid transformation of the glassy structure takes place. Microphase separation originating upon quenching glass allows, with time the nucleation of sassolite crystals and transforms the tetrahedral boron to trigonal boron linked with hydrogen atoms.

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