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MICROHETEROGENEOUS STRUCTURE OF MELTED AND GEL GLASSES IN THE SYSTEM $PbO-B_2O_3$

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Glasses in the system $PbO-B_2O_3$ were synthesized by conventional melting technology and by a sol-gel method. The sample compositions were chosen in a large compositional range (from 7 to 35 mol. % PbO) according to the phase diagram of the system in which regions of macro- and micro-phase liquid-liquid phase separation are presented. The evolution of the micro-heterogeneous structure and phase formation after heat treatment of both types of glasses was studied using TEM in combination with XRD and IR spectroscopy. In the melted glasses, a large variety of micro-formations due to immiscibility and crystallization processes were observed, while the gel glasses possessed a more homogeneous structure containing only some droplet-like immiscibility heterogeneities. These glasses presenting an attractive medium for the creation of regularly distributed nano- and micro-sized immiscibility formations. They can be used for isolation of functional substances, and thus for obtaining different new nanocomposite materials.

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1. Introduction

Borate glasses are classical vitreous materials attractive for applications in different fields: refractory glass and glass-ceramics, medical and optical materials, optical fibres, glasses for thermal and sound insulation, waste immobilization, superionic devices, etc. [1, 2]. In many binary, ternary and multicomponent glasses, the presence of B_2O_3 stimulates the appearance of microheterogeneous formations due to liquid-liquid phase separation. Thus, the structural study of these glasses is an important task both from a fundamental and a practical point of view. Typical examples of borate systems containing regions of stable liquid phase separation and metastable immiscibility are the systems $MO-B_2O_3$ (M = Ca, Sr, Ba, Zn, Pb, Cd) [3]. The precursors used and the method of synthesis are also determining factors for evolution of the microaggregation and immiscibility processes [4].

There is available information for glass-formation in the lead-borate system when conventional melting technology has been applied, and also for the immiscibility process in the B_2O_3–rich compositional range [5, 6]. Using the sol-gel route it is possible to trace the structural evolution and phase formation in an amorphous matrix from low to high temperatures: sol-gel transformation, gel-glass transformation, crystallization, melting. This is in contrast to the conventional melting method, in which the glass-formation process goes from high to low temperature during the cooling of the melt.

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The purpose of this work was to study the evolution of the micro-heterogeneous structure of gel glasses produced by heat treatment in the system $PbO-B_2O_3$, and to compare their properties with those of glasses produced by the traditional melting method.

2. Experimental details

The precursors for the synthesis of the lead-borate gels were $Pb(OOCCH_3)_2.3H_2O$, $B(OCH_3)_3$ and CH_3COOH. The solutions were prepared following appropriate sol-gel technology. The composition of the prepared samples is given in Table 1.

Table 1. Composition of the obtained samples.

Sample №	Composition of gels, mol. %	
	PbO	B_2O_3
1	7,2	92,8
2	20,0	80,0
3	33,0	67,0
4	35,0	65,0

Taking into account the phase diagram of the system $PbO-B_2O_3$ [7], the prepared gel samples were thermally treated in the temperature range 100 to 650 ^oC. Glasses were obtained both by melting the gels and by classical melting of oxide batches at 780 ^oC, followed by slow cooling.

The phase composition and structural data for the synthesized gels and glasses were obtained using a XRD – TUR-M62 diffractometer (Cu-K_α radiation), by IR spectroscopy (using a Bruker, EQUINOX 55, FTIR Spectrometer (KBr pellet technique)), and by TEM using an EM 400 Philips electron microscope (C+Pt replica techniques).

3. Results and discussion

The XRD data show that the synthesized gels were amorphous and kept their structure after heat treatment up to 400°C. At higher temperatures, according the X-Ray diffractogramms, formation of the $PbO.2B_2O_3$ crystalline phase started (Fig. 1.).

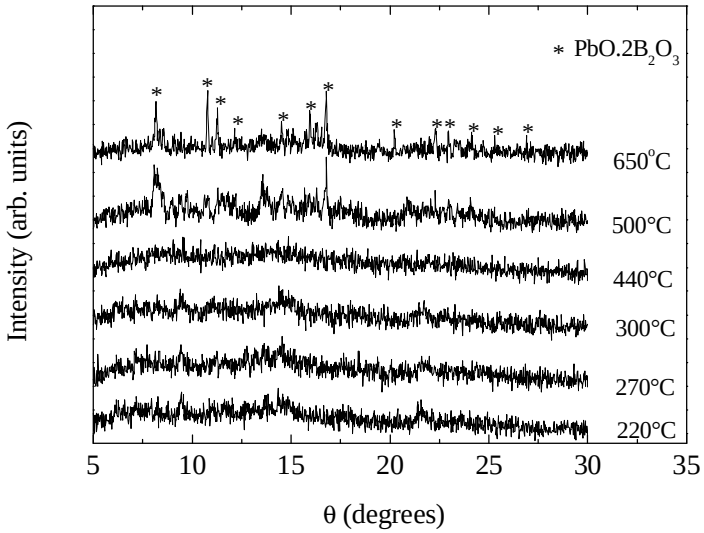


Fig. 1. X-Ray diffraction patterns of heat treated gels.

The IR spectra in the middle IR region from 400 to 4000 cm^{-1} of the gel products and melted glasses are shown in Figs. 2 and 3. Two spectral ranges are typical of the investigated samples: from 400 to 1500 cm^{-1} and from 2000 to 4000 cm^{-1}. The large absorption region centered at about 3400 cm^{-1} was assigned to the vibrations of OH-groups and water molecules. With increasing heat treatment temperature, their intensities decreased up to almost complete disappearance.

In the second spectral region, there were bands related to the vibrations of borate complexes (Fig. 2). These vibrations, related to the organic complexes, disappeared when the temperature was increased up to 400°C. The spectrum of the crystalline sample at 650 °C was more complicated, due to the formation of lead diborate ($PbO.2B_2O_3$).

The spectral behaviour in the temperature region around 400 °C is of special interest, because there are no more organic complexes and crystallization is not yet initiated in the samples.

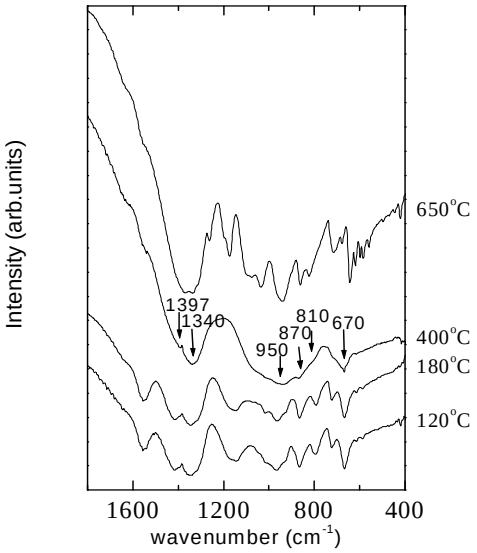


Fig. 2. IR spectra of gels thermally treated at different temperatures.

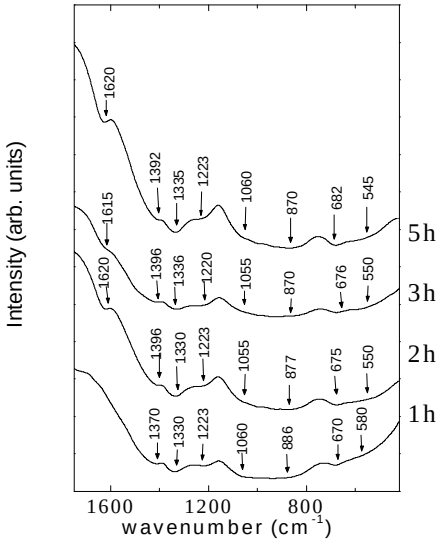
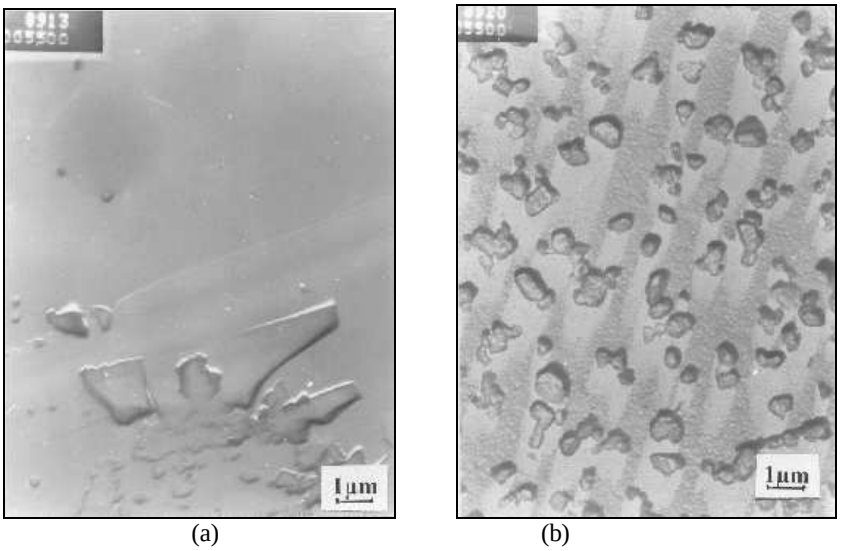


Fig. 3. IR spectra of melted glasses at 780 °C (1÷5 h) obtained from gels.



(a) (b)

Fig. 4. Microstructure of sample № 4, as obtained by: (a) gel; (b) classical melting technology.

One peculiarity of the IR spectra of glasses obtained by gel melting is that the bands were not well defined. Absorption maxima were observed in the regions 670-680 cm^{-1} and 850-1100 cm^{-1}, and complicated triplets at about 1340 cm^{-1} and 1390-1400 cm^{-1} (Fig. 3.). The assignment of the bands was made according to interpretation of the IR spectra of other borate glasses [8, 9]. The absorption at 1340 cm^{-1} could be related to the vibrations of BO_3 groups taking part in the formation of superstructural units. The one at 930-1050 cm^{-1} could be associated with the vibrations of BO_4 groups. Comparison of these spectra with the spectrum of the gel allows us to discuss the similarity and differences between a gel and melted glass. The gel glass possessed more defined maxima in the spectra, due to its well distinguished vibrations of the structural units. The spectra of the melted glasses were not well resolved, which may be interpreted in terms of the formation of a more disordered structure.

The data from the TEM observations (Fig. 4) show that the melted glasses obtained by gel precursors were more homogeneous than those for the melted batches. Micro-aggregates related to the crystallization were developed on the boundaries in some cases, together with small immiscibility droplets. This process was possible because the compositions studied were located near to the metastable immiscibility region. In the gel glasses, there was no formation of crystals, but only a small amount of amorphous droplets. These appear after a long heat treatment, performed at moderate temperatures in order to prevent the crystallization.

4. Conclusions

In the system $PbO-B_2O_3$, a gel glass which is thermally stable up to 500°C can be obtained by a low temperature sol-gel method. Gels heated to over 750°C and cooled to room temperature are transformed into homogeneous glasses. Glasses prepared by a conventional melting technique show a stronger tendency towards liquid-liquid microphase separation. The amorphous networks of the melted and gel glasses are characterized by the formation of superstructural units containing BO_3 and BO_4 groups.

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