

Structural studies of phosphate glasses

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Glasses are among the most suitable matrices for immobilization of intermediate and high-level radioactive wastes because of their high chemical, thermal and radiation stability. Glasses based on borosilicates are generally used for immobilization of radioactive wastes [1-9]. There is also a definite interest [10-12] in the synthesis of phosphate-based glasses for use in the immobilization of radioactive wastes. The advantages of phosphate glasses depend on their structural peculiarities [13-15]. It has been proved that phosphate glasses incorporate into their structure a significant amount of polyvalent elements from the wastes. This affects favourably the thermal and chemical stability of the materials obtained. Oxides of elements such as Cr, Mo and some fluorides, which are hard to incorporate in borosilicate glasses, are much more easily incorporated in phosphate glasses.

One of the advantages of phosphate glasses as an immobilization medium for radioactive wastes consists in their relatively low melting and softening points due to the presence of weaker bonds between the structural groups [13, 14, 16]. In the literature there are data [12] on phosphate glasses of the systems $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{Fe}_2\text{O}_3$ (Al_2O_3) [17] and $\text{PbO}-\text{Fe}_2\text{O}_3-\text{P}_2\text{O}_5$ used for immobilization of radioactive wastes. It is interesting to establish the possibility of immobilization of radioactive wastes by a glassy phosphate matrix incorporating Ba and Pb oxides simultaneously.

The purpose of the present work was to investigate the structural behaviour of phosphate glasses of the $\text{BaO}-\text{PbO}-\text{Fe}_2\text{O}_3-\text{P}_2\text{O}_5$ system for immobilization of radioactive wastes.

The chemical composition of the glasses under consideration is shown in Table I. Batches for glass melting were prepared by mixing Pb_2O_3 , BaO, Fe_2O_3 and P_2O_5 , together with the oxides of simulated radioactive wastes in an amount of 20 wt%. The glasses were melted in corundum crucibles at 800-950 °C, the temperature being kept constant for 100 min. The homogenized melt was poured into graphite formers pre-heated to 500 °C. The glasses obtained were kept at 500 °C for 200 min and allowed to cool to room temperature.

The structure of the glasses synthesized was investigated by transmission electron microscopy (TEM), and Mössbauer and infrared spectroscopies. The electron microscope investigations were performed by the carbon replica method with a Philips-400 electron microscope. The infrared spectra were recorded with a SPECORD M 80 (Jena, Germany) apparatus within the 1400-400 cm^{-1} region. The

TABLE I Chemical composition (in wt%) of samples

Component	Sample		
	P-1	P-2	P-3
PbO	18.34	18.34	25.67
BaO	6.37	4.00	3.37
P_2O_5	50.52	52.00	47.94
Fe_2O_3	10.78	7.29	6.49
La_2O_3	-	2.57	0.82
MnO_2	3.19	-	1.68
MoO_3	0.67	2.51	1.39
Na_2O	3.19	-	2.64
NiO	1.51	-	1.58
SiO_2	0.29	0.53	0.62
ZrO_2	-	3.07	1.29
SrO	0.38	0.70	0.91
Al_2O_3	2.06	3.90	3.02
CaO	2.56	1.20	1.06
CeO_2	-	1.44	0.32
Cr_2O_3	0.14	1.70	0.82
Cs_2O	-	0.75	0.41

samples were subjected to photometry in Nujol. The Mössbauer spectra were obtained by a standard transmittance scheme with a spectrometer using a constant acceleration Co^{57} source in a Pd matrix.

The results of electron microscope studies of the glasses are shown in Fig. 1. All the glasses exhibit microinhomogeneities with sizes of about 0.04 μm . These microinhomogeneities have no definite habit due to their small sizes and for that reason it is difficult to establish whether immiscibility or the onset of crystallization occur in the melt. It is worth noting that these structures are characterized by a uniform distribution in the whole volume as immiscibility or subnuclear formations. Fig. 2 shows the IR spectra of the glasses investigated. Absorption bands at 1260, 1150, 1090, 940-920, 740-720 and 520 cm^{-1} are observed.

The high-frequency bands at 1260, 1150 and 1090 cm^{-1} may be associated with antisymmetric and symmetric vibrations of the PO_2 groups in the PO_4 polyhedra forming the polyphosphate chain. The bands at 940-920 cm^{-1} and 740-720 cm^{-1} can be attributed to antisymmetric and symmetric stretching modes of the P-O-P bonds in the chains. The low-frequency band at 520 cm^{-1} can be assigned to bending modes of the PO_4 groups [18] (Fig. 2a).

In the spectrum of the P-1 composition there are two bands in the high-frequency region at 1150 and 1080 cm^{-1} . It should be pointed out that in the spectra of compositions P-2 and P-3 (Fig. 2b,c) the number of high-frequency bands increases. Since

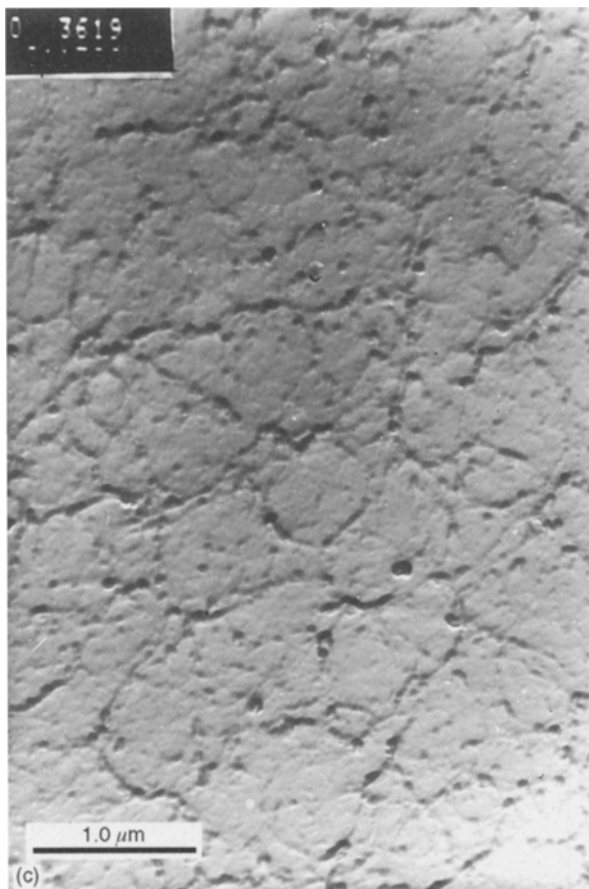
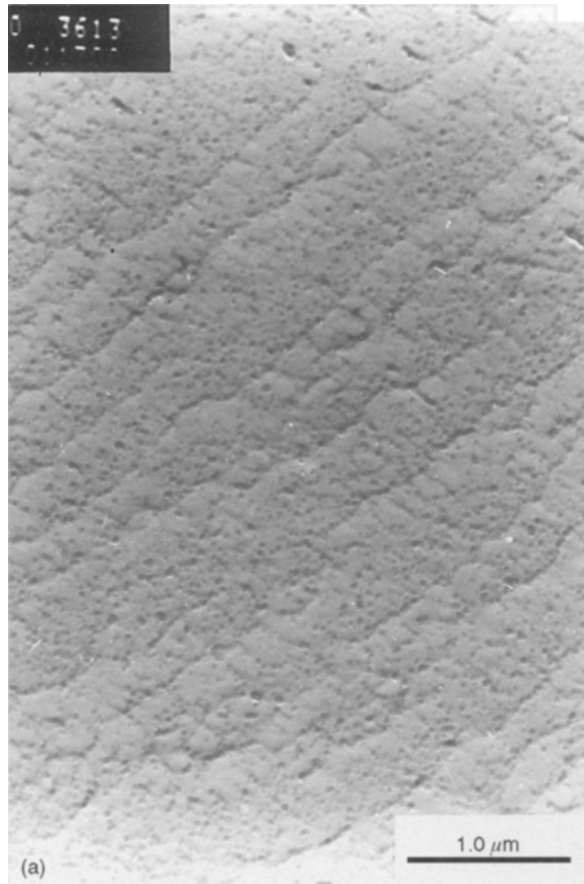


Figure 1 TEM photograph of phosphate glasses: (a) sample P-1; (b) sample P-2; (c) sample P-3.

high-frequency vibration in the spectra is threefold degenerated, the larger number of bands in the spectra of compositions P-2 and P-3 can be regarded as a result of the decreasing symmetry of the PO₄

groups. This means that the degree of deformation of the PO₄ tetrahedra is more pronounced than is the case for composition P-1.

The decreasing symmetry of the PO₄ tetrahedra is

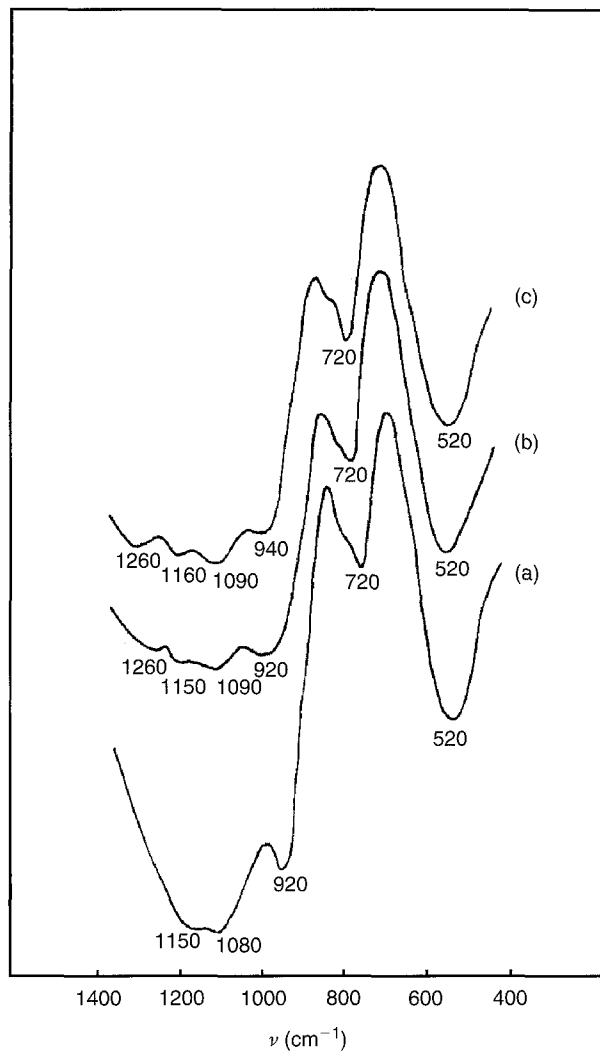


Figure 2 IR-spectra of phosphate glasses: (a) sample P-1; (b) sample P-2; (c) sample P-3.

probably due to the presence of various polyvalent cations participating in the composition of the oxides in the radioactive wastes. With compositions P-2 and P-3 the wastes contain some oxides such as La_2O_3 , ZrO_2 , CeO_2 and CsO which are absent from composition P-1. The cations in these oxides have large electric charges and exercise a polarizing effect on the neighbouring ions. When incorporated in the glassy network they may cause more pronounced distortion of the PO_4 polyhedra [19].

Fig. 3 presents the Mössbauer spectra of samples P-1, P-2 and P-3. The parameters of these spectra are shown in Table II. The Mössbauer data have been processed by a computer program using the least squares method. The presence of two symmetric doublets, indicating that Fe is mainly in the form of Fe^{3+} ions is established. The inner doublet corresponds to octahedral surroundings, and the outer to tetrahedral surroundings of the Fe cations.

The relative amounts of Fe ions in tetrahedral and octahedral positions have been determined by calculating the areas of the doublets obtained (Table II).

It has been established that the largest content of tetrahedrally coordinated Fe^{3+} ions corresponds to composition P-1, which demonstrated higher

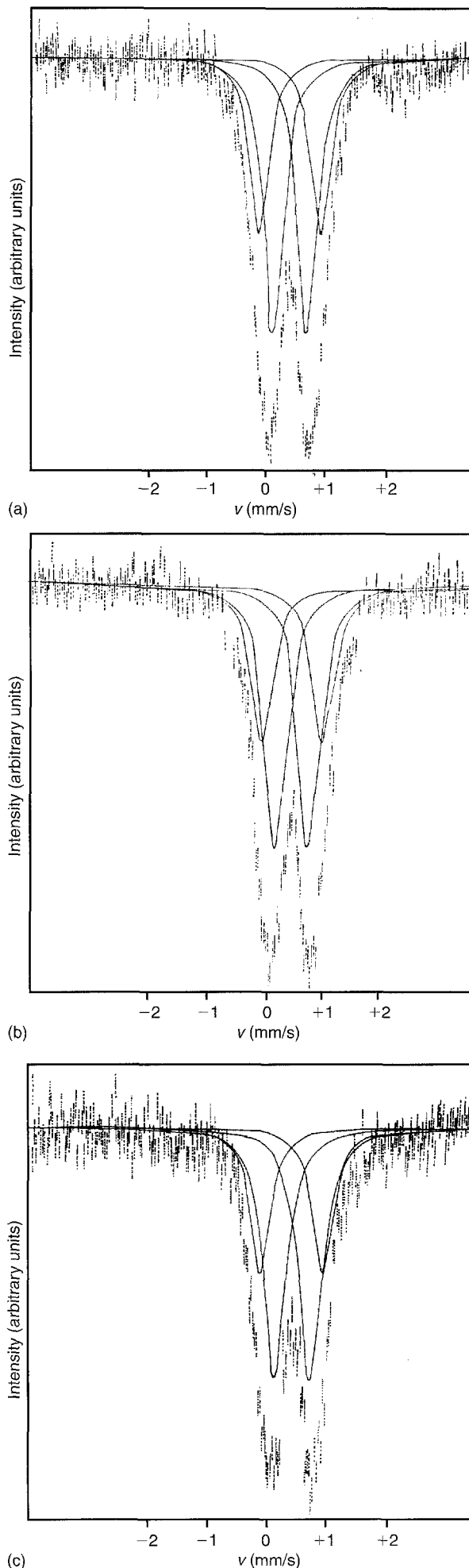


Figure 3 Mössbauer spectra of samples (a) P-1; (b) P-2; (c) P-3.

TABLE II Mössbauer parameters obtained from fitting the absorption spectra shown in Fig. 3

Sample	Isomer shift (mm/s)		Quadrupole splitting (mm/s)		Fractional occupation (%)	
	Is1	Is2	Qs1	Qs2	octahedral site	tetrahedral site
P-1	0.39	0.41	1.02	0.57	61.7	38.3
P-2	0.39	0.40	1.03	0.57	63.0	37.0
P-3	0.39	0.41	1.05	0.60	66.0	34.0

chemical resistance as determined by a MAAE method [20]. This might be attributed to the immediate participation of the FeO₄ groups in the structural network of the glass under investigation.

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