

# Studies of lead–iron phosphate glasses by Raman, Mössbauer and impedance spectroscopy

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## Abstract

The effect of Fe<sub>2</sub>O<sub>3</sub> content on electrical conductivity and glass stability against crystallization in the system PbO–Fe<sub>2</sub>O<sub>3</sub>–P<sub>2</sub>O<sub>5</sub> has been investigated using Raman, XRD, Mössbauer and impedance spectroscopy. Glasses of the molar composition (43.3 – x)PbO–(13.7 + x)Fe<sub>2</sub>O<sub>3</sub>–43P<sub>2</sub>O<sub>5</sub> (0 ≤ x ≤ 30), were prepared by quenching melts in the air. With increasing Fe<sub>2</sub>O<sub>3</sub> content and molar O/P ratio there is corresponding reduction in the length of phosphate units and an increase in the Fe(II) ion concentration, which causes a higher tendency for crystallization. Raman spectra of the glasses show that the interaction between Fe sites, which is essential for electron hopping, strongly depends on the cross-linking of the glass network. The electronic conduction of these glasses depends not only on the Fe(II)/Fe<sub>tot</sub> ratio, but also on easy pathways for electron hopping in a non-disrupted pyrophosphate network. The Raman spectra of crystallized glasses indicate a much lower degree of cross-linking since more non-bridging oxygen atoms are present in the network. Despite the significant increase in the Fe<sub>2</sub>O<sub>3</sub> content and Fe(II) ion concentration, there is a considerable weakening in the interactions between Fe sites in crystalline glasses. The impedance spectra reveal a decrease in conductivity, caused by poorly defined conduction pathways, which are result of the disruption and inhomogeneity of the crystalline phases that are formed during melting.

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## 1. Introduction

Interest in phosphate glasses as a host for the immobilization and disposal of nuclear wastes started in the 1960s [1]. However, phosphate glasses have a relatively poor chemical durability, which limits their usability [2]. In 1984 Sales et al. [3] proposed the lead–iron phosphate glasses as a new, stable and easily prepared medium for vitrifying nuclear wastes. They found that the corrosion rate of these glasses was 1000 times lower than

that of borosilicate glasses, the only glass currently approved in the US. However, because of low waste loading and low corrosion resistance of its crystallized counterparts, they are not used in the current vitrification program [4].

On the other hand, binary iron phosphate glasses are candidates for immobilizing certain types of high-level nuclear wastes (HLW). Compared to borosilicate glasses, iron phosphate glasses can be melted at temperatures as low as ~1200 K and in excess of 40 wt% of nuclear wastes, poorly soluble in borosilicate glasses, without any adverse effect on their good chemical durability [5,6]. It is believed that the exceptionally high chemical durability of iron phosphate glasses is a result of more hydration resistant Fe–O–P bonds that replace more easily hydrated P–O–P bonds, present in common phosphate glasses [5,7,8].

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Lead-iron phosphate glasses waste forms, obtained by adding PbO to an iron phosphate glass, have recently been reinvestigated because of their improved chemical durability [9]. It was questioned whether lead should or should not be used in iron phosphate glasses. There were also doubts as to the role of Fe in the inhibition of corrosion. Reis et al. [9] found that the chemical durability of a 43.3PbO–13.7Fe<sub>2</sub>O<sub>3</sub>–43P<sub>2</sub>O<sub>5</sub> glass (mol%) is comparable to the best binary iron phosphate glass with an approximate composition of 40Fe<sub>2</sub>O<sub>3</sub>–60P<sub>2</sub>O<sub>5</sub> (mol%). They reported that the replacement of Fe–O–P for Pb–O–P bonds does not affect the chemical durability when the O/P ratio was 3.5.

The effect of iron on the structure and chemical durability of several iron phosphate glasses were previously investigated by Mössbauer, EPR, Raman and IR spectroscopy [10]. Knowledge of the structure of these glasses helps in identifying modifications in compositions and processing conditions, which could expand their applications.

In the present paper, the structural modifications in lead-iron phosphate glasses obtained by replacing of PbO with Fe<sub>2</sub>O<sub>3</sub> have been investigated by Raman and Mössbauer spectroscopy. To investigate the thermal stability of lead-iron phosphate glasses as a function of their composition and structure, differential thermal analysis (DTA) and X-ray diffraction (XRD) have been used. The objective was to study the correlation between the structure and electrical properties in (43.3 – x)PbO–(13.7 + x)Fe<sub>2</sub>O<sub>3</sub>–43P<sub>2</sub>O<sub>5</sub> (0 ≤ x ≤ 30) glasses. Lead-free iron phosphate glasses melted in the air are electronically conducting glasses where the polaronic conduction is a result of electron hopping from low to high iron valence state [11,12]. In these glasses, the charge carrier concentration is related to the total concentration of iron ions and to the ratio of Fe(II) ions in the total quantity of iron (Fe(II)/Fe<sub>tot</sub>) [5]. The contribution of

iron ions to the total electrical conductivity and the effect of glass structure on the origin of electrical conductivity have been examined.

The impedance spectroscopy method was used to investigate electrical properties of (43.3 – x)PbO–(13.7 + x)Fe<sub>2</sub>O<sub>3</sub>–43P<sub>2</sub>O<sub>5</sub> (0 ≤ x ≤ 30) glasses. It is interesting to note that the polaronic conductors display a behavior similar to ionic conductors because of their similar dependence on frequency and temperature. At low frequency, thermally activated polaron hopping processes give rise to the frequency independent conductivity. At higher frequency, the ac conductivity exhibits dispersion, increasing in a power-law fashion.

The dependence of the electrical conductivity upon temperature and frequency for lead iron phosphate glasses is discussed.

## 2. Experimental

### 2.1. Preparation and melting of glass samples

The glasses were prepared from the appropriate mixtures of reagent grade NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub> and PbO and melted between 1373 and 1473 K for 2 h in air in high purity alumina crucibles. The melt was quenched in air by pouring it into a 1 × 1 × 5 cm<sup>3</sup> steel mold. The samples were transferred to a furnace and annealed at 723 K for 3 h.

Microchemical composition and microstructure of bulk and crystallized glasses were characterized by scanning electron microscopy, SEM, equipped with an EDS detector (Vega TS 5136 Tescan). EDS analysis was performed to find exact composition of the glasses. The disc of the each glass was analyzed at five different positions and the mean composition is given in Table 1.

Table 1  
Composition and selected properties of (43.3 – x)PbO–(13.7 + x)Fe<sub>2</sub>O<sub>3</sub>–43P<sub>2</sub>O<sub>5</sub> (0 ≤ x ≤ 30), glasses and crystallized glasses

Sample code	Glass composition (mol%)			Glass composition (mol%) determined by EDS			Molar ratio		<i>T<sub>g</sub></i> (±2 K)	<i>T<sub>c</sub></i> (±2 K)	<i>D</i> (kg m <sup>-3</sup> ) (±20 kg m <sup>-3</sup> )	<i>R<sub>Fe-Fe</sub></i> (Å) <sup>a</sup> (±0.5%)
	PbO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	PbO	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	O/P <sup>b</sup>	(Fe + Pb)/P <sup>b</sup>				
A0(G) <sup>c</sup>	43.3	13.7	43.0	36.2	17.6	46.2	3.46	0.77	771	869	4.1 × 10 <sup>3</sup>	3.53
A1(G)	38.3	18.7	43.0	35.3	20.7	44.0	3.61	0.87	785	933	4.7 × 10 <sup>3</sup>	3.19
A2(G)	33.3	23.7	43.0	30.4	24.6	45.0	3.66	0.88	810	951	4.5 × 10 <sup>3</sup>	3.06
A3(G)	28.3	28.7	43.0	28.0	26.1	45.9	3.66	0.87	804	946	4.4 × 10 <sup>3</sup>	3.02
A4(C) <sup>d</sup>	23.3	33.7	43.0	32.9	23.8	43.3	3.70	0.93	779	864/918	–	–
A5(C) <sup>e</sup>	18.3	38.7	43.0	–	–	–	4.06	1.11	–	864/919	–	–
A6(C) <sup>e</sup>	13.3	43.7	43.0	–	–	–	4.18	1.17	–	864/919	–	–

<sup>a</sup> *R<sub>Fe-Fe</sub>* (Å) was calculated for glasses, where Fe ions are randomly distributed.

<sup>b</sup> Molar ratios of O/P and (Fe + Pb)/P for the A0–A4 glasses were calculated from the glass compositions obtained by EDS. For the A5 and A6 samples molar ratios of O/P and (Fe + Pb)/P were calculated from glass composition.

<sup>c</sup> Reference [16].

<sup>d</sup> Composition of glass matrix determined by EDS.

<sup>e</sup> Crystalline phases identified by XRD, Fig. 2.

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