

01 Mar 2009

## Electrical Properties of Phosphate Glasses

Andrea Mogus-Milankovic

Ana Santic

Signo Tadeu Dos Reis

*Missouri University of Science and Technology*

D. E. Day

*Missouri University of Science and Technology, day@mst.edu*

Follow this and additional works at: [https://scholarsmine.mst.edu/matsci\\_eng\\_facwork](https://scholarsmine.mst.edu/matsci_eng_facwork)

 Part of the [Ceramic Materials Commons](#)

---

### Recommended Citation

A. Mogus-Milankovic et al., "Electrical Properties of Phosphate Glasses," *IOP Conference Series: Materials Science and Engineering*, vol. 2, IOP Publishing Ltd., Mar 2009.

The definitive version is available at <https://doi.org/10.1088/1757-899X/2/1/012004>

This Article - Conference proceedings is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Materials Science and Engineering Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact [scholarsmine@mst.edu](mailto:scholarsmine@mst.edu).

## Electrical properties of phosphate glasses

A Mogus-Milankovic<sup>1</sup>, A Santic<sup>1</sup>, S T Reis<sup>2</sup> and D E Day<sup>2</sup>

<sup>1</sup>Ruder Boskovic Institute, Department of Chemistry, 10000 Zagreb, Croatia

<sup>2</sup>Graduate Center for Materials Research, Missouri University of Science and Technology, Rolla, MO 65409-1170, USA

E-mail: mogus@irb.hr

**Abstract.** Investigation of the electrical properties of phosphate glasses where transition metal oxide such as iron oxide is the network former and network modifier is presented. Phosphate glasses containing iron are electronically conducting glasses where the polaronic conduction is due to the electron hopping from low to high iron valence state. The identification of structural defects caused by ion/polaron migration, the analysis of dipolar states and electrical conductivity in iron phosphate glasses containing various alkali and mixed alkali ions was performed on the basis of the impedance spectroscopy (IS). The changes in electrical conductivity from as-quenched phosphate glass to fully crystallized glass (glass-ceramics) by IS are analyzed. A change in the characteristic features of IS follows the changes in glass and crystallized glass network. Using IS, the contribution of glass matrix, crystallized grains and grain boundary to the total electrical conductivity for iron phosphate glasses was analyzed. It was shown that decrease in conductivity is caused by discontinuities in the conduction pathways as a result of the disruption of crystalline network where two or more crystalline phases are formed. Also, phosphate-based glasses offer a unique range of biomaterials, as they form direct chemical bonding with hard/soft tissue. The surface charges of bioactive glasses are recognized to be the most important factors in determining biological responses. The improved bioactivity of the bioactive glasses as a result of the effects of the surface charges generated by electrical polarization is discussed.

### 1. Introduction

Recent development of phosphate glasses for variety of technological applications, from rare-earth hosts for solid state lasers to low-temperature sealing glasses, have lead to renewal interest in understanding the structure and properties of these glasses.

However, many phosphate glasses have a relatively poor chemical durability, but iron phosphate glasses are an exception. The basic knowledge of the structure-electrical properties relationship of iron phosphate glasses is of fundamental importance to understand the processing conditions, which could expand their applications.

Changes in electrical conductivity for iron phosphate glass heat treated at various temperatures were also of interest. It is well established that glass tends come back to equilibrium by crystallization. However, this apparent disadvantage can be transformed into a positive point as long as the nucleation and growth of the crystalline species is controlled, leading to the new class of composite materials, the

glass ceramics. In this paper an overview of the influence of microstructure on electrical conductivity for iron phosphate glasses is presented.

Our recent study of the effect of electrical polarization on bioactive glasses is reported in this review. The discussion is focused on the electrical processes induced by electrical polarization.

## 2. Experimental

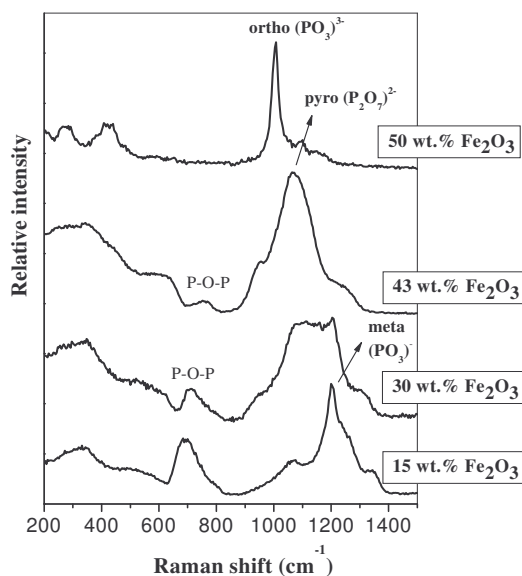
Iron phosphate glasses investigated in this study were prepared by melting at approximately 1000°C for 2 h in air in high purity alumina crucibles. The melt was quenched in air by pouring it into a steel mould and then annealed for 2 h at 450°C K. Electrical properties were obtained by measuring complex impedance using an impedance analyzer over a wide frequency range from 0.01 Hz to 4 MHz and in temperature range from 30 to 200°C. Bioactive glass, 13-93, was prepared from mixtures of reagent grade SiO<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, CaCO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> and melted in Pt crucible at 1250°C for 2 h. Glass was annealed for 10 h at 550°C. Thermally stimulated current (TSC) measurements were carried out using a Keithley 6514 Electrometer, in the temperature range from -150 to 450°C, while heating the sample at 5.2 Cmin<sup>-1</sup>.

## 3. Results and discussion

Our basic idea was to investigate iron phosphate glasses as a host for nuclear wastes. The research was focused on structure-electrical property relationship where parent glass was binary iron phosphate glass of the composition 40Fe<sub>2</sub>O<sub>3</sub>-60P<sub>2</sub>O<sub>5</sub> (F40) to which various metal oxides were added.

It is well known that phosphate glasses containing transition metal ions such as Fe are electronically conducting materials. The semiconducting behavior is due to the Fe ions being in two valence state as Fe(II) and Fe(III) with conduction taking place by electron hopping from low to high valence state and depends upon the average distance between iron ions and the relative fraction of Fe(II) and Fe(III) ions [1]. The charge transfer is usually termed a “small polaron hopping”. In iron phosphate glasses, the charge carrier concentration is associated with the total concentration of iron ions and to the ratio of Fe(II) ions to the total quantity of iron (Fe(II)/Fe<sub>tot</sub>).

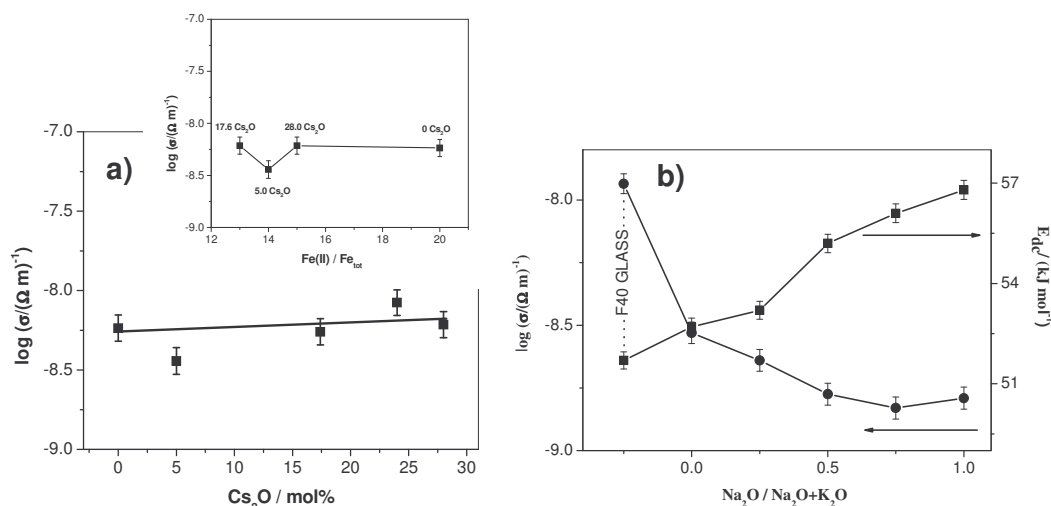
It should be noted that the iron oxide content increase in phosphate glasses results in a progressive alternation of the glass network, Figure 1. There is an evidence of systematic changes in the glass structure from chain like metaphosphate through pyrophosphate to orthophosphate structure [2]. On the other words, the average of the polyphosphate chains become shorter as the iron ions were effective in bonding ends of the chains to the surrounding glass structure. The variation in the properties of iron phosphate glasses has been attributed to the strengthening of the glass network through the formation of Fe-O-P bonds



**Figure 1.** Raman spectra of iron phosphate, xFe<sub>2</sub>O<sub>3</sub>(100-x)P<sub>2</sub>O<sub>5</sub> glasses (15 ≤ x ≤ 50).

The maximum conductivity of iron phosphate glasses occurs at a concentration ratio  $C=0.5$  for glass containing 45 mol%  $\text{Fe}_2\text{O}_3$  as reported in [3]. However, glasses containing more  $\text{Fe}_2\text{O}_3$  are not homogenous and it is possible that glasses could have segregated some Fe(II) ions to isolated microstructural island, which do not enter into the conduction process. Also, for glasses containing small amount of  $\text{Fe}_2\text{O}_3$ , it is possible that the relative spatial position of Fe ions are not random in glass but are situated in some kind of clusters containing various numbers of Fe ions. Charge transport then takes place along clusters.

Addition of the third component can change the electrical conductivity because of the difference in the average electric field strength of modifier cations. Our studies of electrical conductivity in alkali iron phosphate glasses provide that the conductivity varies slightly in the iron phosphate glass with different alkali content (up to 20 mol%), which is kind of anomaly.



**Figure 2.** The dependence of  $\sigma_{\text{dc}}$  and  $E_{\text{dc}}$  at 25°C upon (a)  $\text{Cs}_2\text{O}$  content. Inset: upon Fe(II) concentration and (b) mixed alkali ( $\text{Na}_2\text{O}+\text{K}_2\text{O}$ ) content for iron phosphate glasses

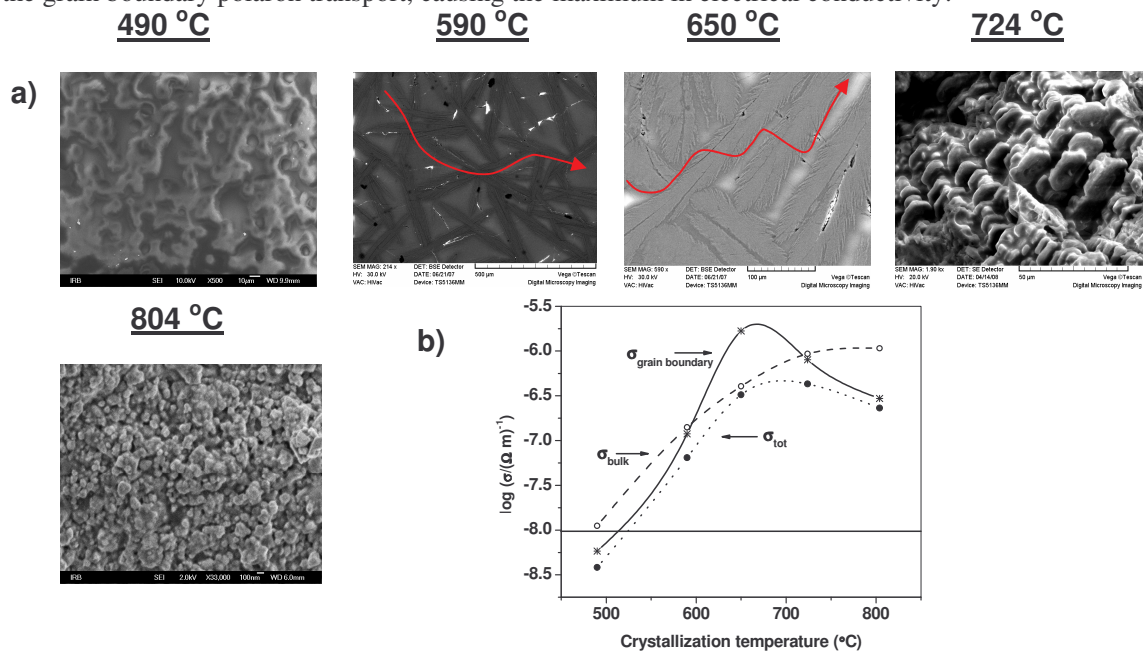
However, with increasing cesium concentration in cesium iron phosphate glasses the slowly moving cesium ions are more tightly bound to the non-bridging oxygen ions and make no measurable contribution to dc conductivity [4]. The dc conduction in these glasses is totally electronic, controlled by electron hopping between iron ions, Figure 2(a). The ionic conduction is immeasurably small because of the low mobility of the cesium ions. Moreover, the dc conductivity was essentially constant with increasing  $\text{Fe}_2\text{O}_3$  content or increasing Fe(II) ions.

It is well known that the substitution of a second alkali ion, at constant alkali content, caused a decrease in electrical conductivity up to five orders of magnitude and usually observed in ionic conductive glasses. The dc conductivity for the mixed alkali, sodium and potassium, iron metaphosphate glass is independent of the Na/K ratio and there is no evidence of any mixed alkali effect, Figure 2(b). The sodium and potassium ions have such a low mobility in both, single and mixed alkali iron phosphate glasses that they make no detectable contribution to the total conductivity that is electronic in origin. Since the charge carriers concentration are related to the iron ion content, the decrease in conductivity is attributed to the decrease in the number of carriers with decreasing  $\text{Fe}_2\text{O}_3$  content [5].

The effects of the heat-treating of iron phosphate glasses on their electrical conductivity have been studied by impedance spectroscopy (IS) over wide frequency region. Figure 3 shows the effect of crystallization on electrical conductivity. Concerning that the crystallized glasses exhibit two processes, the electrical conductivity using complex non-linear least square fitting procedure, can be distinguished on the conductivity for bulk (glass matrix) and grain boundary. The conductivity was measured for as-quenched glass and after thermal treatment up to 800°C.

The slight drop of total conductivity for glass heated at 490°C is attributed to the beginning of formation of iron pyrophosphate crystalline phase,  $\text{Fe}_3(\text{P}_2\text{O}_7)_2$ , which contains both Fe(II) and Fe(III) ions. With increasing heat treatment to 590°C, these glasses turned into nanomaterials consisting of crystallites of  $\text{FePO}_4$  (average size of 50 nm) embedded in glassy matrix and the conductivity of both grain-boundary and grains increases. Formation of nanocrystallites leads to an enhancement of glass matrix conductivity as compared with the as-quenched glass.

By inducing the crystallization at 650°C the total electrical conductivity increases because of the significant increase in conductivity of grain boundaries. It seems that the conductivity is governed by the grain boundary polaron transport, causing the maximum in electrical conductivity.

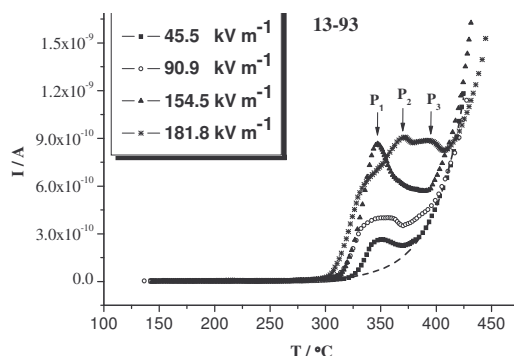


**Figure 3.** (a) SEM images of iron phosphate glass heat-treated at 490°C; 590°C; 650°C; 724°C; 804°C and (b) dependence of bulk and grain boundary conductivity upon crystallization temperature.

Further heat treatment, at 724°C, causes massive crystallization and formation of  $\text{Fe}_3(\text{P}_2\text{O}_7)_2$  crystals (grain size  $<1 \mu\text{m}$ ). Formation of microcrystallites causes a drop of total electrical conductivity due to the blocking of the conduction pathways for the electron hopping between Fe sites at the crystal/glass matrix interfaces. The conduction enhancement for larger crystalline grains (bulk) at 724°C indicates that the interfacial effects are not of importance for this microcrystalline sample. Further thermal treatment at higher temperature, 804°C, leads to predominant growth of  $\text{Fe}_3(\text{P}_2\text{O}_7)_2$  crystals. Slight increase of the bulk conductivity is explained by a strengthening of the interactions between Fe sites in crystalline phases, caused by well-defined conduction pathways. The decrease of total and grain boundary conductivity is a result of the presence of larger crystalline grains and disappearance of glassy matrix in fully crystallized sample [6,7].

The phosphate-based 13-93 bioactive glass was chosen for the investigations of electrical processes during application of electrical poling. Figure 4 shows the 13-93 glass poled under different electrical voltage at 120°C for 10 min. Subsequently, glass was quenched to  $-150^\circ\text{C}$  under the applied dc voltage. The induced depolarization current was measured exhibiting three peaks P1, P2 and P3. When high poling field was used, beside P1 associated to the  $\text{Na}^+$  and  $\text{K}^+$  ion transport, the P2 and P3 peaks occur. These two peaks are related to the formation of interfacial ion layer at the electrode-glass interfaces [8]. However, the maximum current density increases with increasing polarization voltage.

As expected the stored charges and current density are 2.5 times larger for 13-93 glass polarized with higher voltage.



**Figure 4.** Thermally simulated depolarization current of 13-93 glass under different poling conditions.

It was also shown that the enhancement of bioactivity was related to the formation of interfacial ion layer at the electrode-glass interfaces [9].

#### 4. Conclusion

The impedance spectra of binary iron phosphate glasses indicate a single conduction mechanism attributed to the electron hopping from Fe(II) to Fe(III) ions. The dc conductivity increases with increasing Fe<sub>2</sub>O<sub>3</sub> content. For the alkali-free iron phosphate glasses the dc conductivity was 5 to 10 times higher than that of the single or mixed alkali iron phosphate glasses containing a total of 20 mol% alkali. The mixed alkali, sodium and potassium, iron phosphate glasses does not show any mixed alkali effect, for glasses up to 20 mol% alkali.

It was shown that the crystallization of iron phosphate glasses is obtained below T<sub>g</sub>. At lower crystallization temperatures the nanocrystallites (average size of 50 nm) embedded in glassy matrix are formed. Further heat treatment causes massive crystallization (grain size < 10µm). The formation of nanocrystallites leads to an enhancement of glass matrix conductivity. However, microcrystallites formed at higher temperatures causes a drop in conductivity due to the reduction of grain boundary region suggesting that the conductivity depends on the electron hopping in crystalline phases. The conduction enhancement for nano-crystallized sample is most likely related to the interfaces between crystallites and glassy phase.

Increase in charge density induced by electrical polarization should have an influence on the surface activity of bioactive glass. However, more work is needed to find out whether the stored charges formed at the electrode-glass interface persist enough for a significant enhancement of the bioactivity.

#### References

- [1] Moguš-Milanković A and Day D E 1993 *J. Non-Cryst. Solids* **162** 275-86
- [2] Moguš-Milanković A, Day D E, Pivac B and Furić K 1997 *Phys. Chem. Glasses* **38** 74-8
- [3] Murawski L 1982 *J. Mater. Sci.*, **17** 2155-63
- [4] Moguš-Milanković A, Šantić B, Furić K and Day D E 1999 *Phys. Chem. Glasses* **40** 305-10
- [5] Moguš-Milanković A, Šantić B, Ray C S and Day D E 2001 *J. Non-Cryst. Solids* **283** 119-28  
Šantić A, Moguš-Milanković A, Furić K, Bermanec V, Kim C W and Day D E 2007 *J. Non-Cryst. Solids* **353** 1070-7  
Moguš-Milanković A, Šantić A, Reis S T, Furić K and Day D E 2005 *J. Non-Cryst. Solids* **351** 3246-58
- [6] Mariappan C P and Rolling B 2008 *Solid State Ionics* **179** 671-7
- [7] Obata A, Nakamura S and Yamashita K 2004 *Biomaterials* **25** 5163-9