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ScienceDirect

Procedia Engineering 98 (2014) 56 – 61

Procedia Engineering

www.elsevier.com/locate/procedia

11th International Symposium on Systems with Fast Ionic Transport, ISSFIT 11

Impedance studies of phosphate-iron glasses containing niobium and titanium

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Abstract

The ac and dc conductivity in phosphate-iron-niobate glasses with addition of titanium oxide was investigated as a function of temperature and frequency with the use of impedance spectroscopy. The topography and microstructure of glasses were investigated by the means of X-ray diffraction (XRD), scanning electron microscopy (SEM), and confocal microscopy methods. The obtained results show that all samples are amorphous but they contain granular structures. The influence of titania on the properties of obtained glasses is discussed. The activation energy of dc conduction process is determined. The experimental results are discussed on the basis of Jonscher law and conductivity models collected by Elliot.

Peer-review under responsibility of the Gdansk University of Technology

Keywords: phosphate-niobate-titanate-iron glasses, small polaron hopping, overlapping polaron, impedance spectroscopy;

1. Introduction

Many oxide glasses containing more than 5-10 % mol of transition metal oxides exhibit electronic semiconductors behavior. Their electrical properties are determined by the transition metal ions present in two different valence states [1-3]. Their conductivity could be described by the Mott model of small polaron hopping between such ions [4].

Mott [1] has suggested that in glasses containing iron oxide, there is a great variety of environments for Fe ions and a wide spread of energy for the sites occupied by the electrons. Therefore the density of states would not necessarily be symmetrical [1, 2]. His suggestion is consistent with the results presented in Murawski review of

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Peer-review under responsibility of the Gdansk University of Technology
doi:10.1016/j.proeng.2014.12.488

properties of iron-phosphate glasses [2]. The Fe ions have the same coordination number, but can be incorporated in the glass structure in a different positions. These differences in iron sites may be caused by magnetic interactions between Fe ions. Electrical conductivity of iron-phosphate glasses show a good agreement with the Mott relation for non-adiabatic transport of small polarons [2].

P_2O_5 and Nb_2O_5 are glass-forming oxides. Studies on niobium-phosphate glasses showed that Nb^{5+} ions incorporate into bridging oxygen of P–O–P bonds and form O–P–O–Nb–O– type chains. Moreover P–O type bonds are mostly found in terminal sites of the chain, while Nb–O bonds are located in the middle of the chains [5].Therefore the combination of Nb_2O_5 and P_2O_5 is known to result in the formation of thermally stable glasses [5-8].

Titanium ions in oxide glasses may exist in two valance states, trivalent Ti^{3+} paramagnetic ions and diamagnetic tetravalent Ti^{4+}. The small amount of TiO_2 in the glass matrix enhances the glass forming ability and chemical durability of the glasses. Usually, only Ti^{4+} valence state exists in the glass networks and it participates in the glass network. It forms mostly TiO_4 and TiO_6 structural units [9]. But there are also reports which have suggested that titanium ions may exist in Ti^{3+} valence state in certain glass matrices. In these glasses they fulfill the role of modifiers and may significantly influence the electrical properties [9-11].

The aim of the present study was to investigate the ac and dc electrical properties and microstructure of phosphate-niobate-iron glasses containing titanium oxide.

2. Experimental

Glass samples of the composition of $35P_2O_5$-$30Fe_2O_3$-$(35-x)Nb_2O_5$-$xTiO_2$ where x= 0; 7.5 and 15 (in %mol) were prepared by the conventional melt quenching technique. Appropriate amounts of reagents ($(NH_4)_2HPO_4$ (≥99.9%, POCH), Fe_2O_3 (≥99.9%, POCH), Nb_2O_5 (≥99.9%, PLUKA AG) and TiO_2 (≥99.9%, anatase and rutile mixed, PROLABO)) were thoroughly mixed in an agate mortar and put on electric stove in temperature of 573K in order to carry out the decomposition process of $(NH_4)_2HPO_4$. Next powders were melted in porcelain crucibles at 1573 K for 1-2 h, depending on glass composition. The melts were poured on preheated (to 573 K) brass plate and pressed by another plate to obtain flat circular samples (dimensions: 1-2 mm thick, 20-30 mm in diameter). The obtained pellets were annealed at 673 K for 1 h and cooled with furnace.

The structure has been studied by the X-ray diffraction method with the use of a Philips X 'Pert Pro MPD system with the CuKα radiation. The XRD measurements were carried out on powder samples at room temperature. The topography of the surface of the samples was investigated with Confocal Microscope Olympus OLS 4000 Lext equipped with a CCD camera. Scanning Electron Microscope FEI Quanta FEG 250 using 30kV beam accelerating voltage with SE-ETD detector (secondary electron - Everhart-Thornley detector) working in high vacuum mode (pressure 10^{-4} Pa) was used to observe the structure of the uncoated glasses.

For the electrical measurements gold electrodes were evaporated at the polished samples. Impedance measurements were carried out in the frequency range from 1 mHz to 1 MHz with the ac voltage of 1 V_{rms} in the temperature range from 153 K to 423 K with the Novocontrol Concept 40 broadband dielectric spectrometer.

3. Results

The X-ray spectra of all invesitgated samples are presented in Fig. 1. XRD patterns consist of amorphous halo, typical for glasses. There are no reflexes characteristic for crystalline phase. Figures 2 and 3 show results obtained from microscopy observations. Confocal microscopy images (Fig. 2) show the topography of the glasses surfaces in microscale. It can be seen that all samples contain two types of structures. The first structures have size of an order of micrometers. These microstructures are randomly distributed on the surfaces. Figures 2 (a), (b) and (c) present that all glasses contain also much smaller nanostructures which are visible as black dots. These nanostructures are better visible in SEM pictures of samples fractures (Fig. 3). Their shape is substantially circular and size ranges from 80 nm to 350 nm. The dimension and amount of structures are difficult to be linked to composition of the glass. The nanostructures are uniformly distributed in the bulk of the samples.

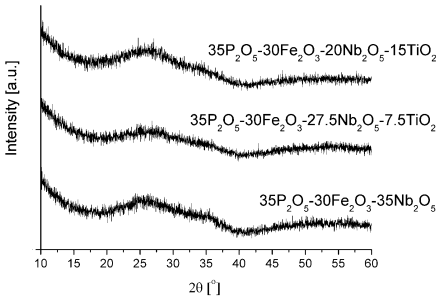

Fig. 1. XRD patterns for glass samples.

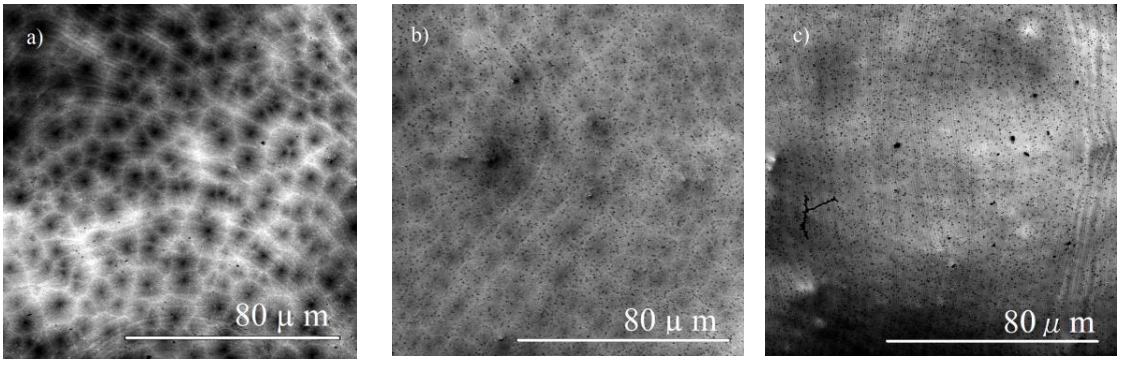

Fig. 2. The confocal microscopy images of $35P_2O_5$-$30Fe_2O_3$-(35-x)Nb_2O_5-xTiO_2 glass surfaces in which the contents of TiO_2 is respectively: (a) 0; (b) 7.5 and (c) 15 (in %mol).

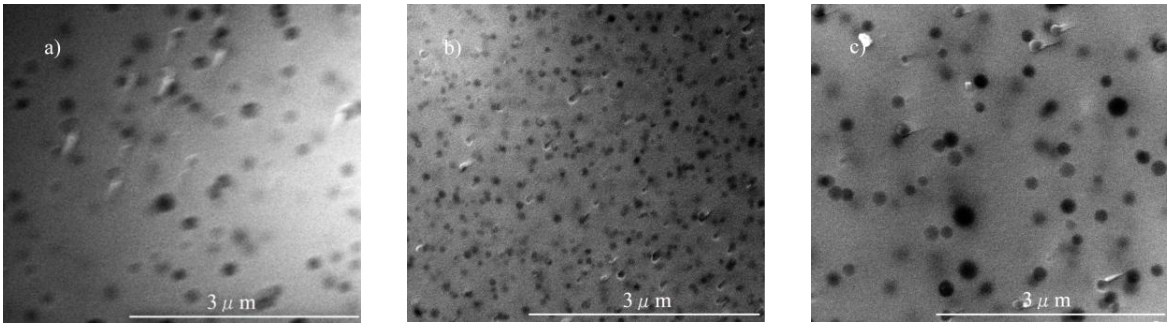

Fig. 3. Scanning electron microscopy images of $35P_2O_5$-$30Fe_2O_3$-(35-x)Nb_2O_5-xTiO_2 glass fractures where x = (a) 0; (b) 7.5 and (c) 15 (in %mol).

The real part of conductivity versus frequency measured at different temperatures for sample without titania and for samples with 7.5% and 15% TiO_2, are shown in Fig. 4. All samples show similar conductance behavior. The plots consist of two regions: dc plateau dominating in the low frequency region and ac component increasing with log of frequency in a linear fashion.

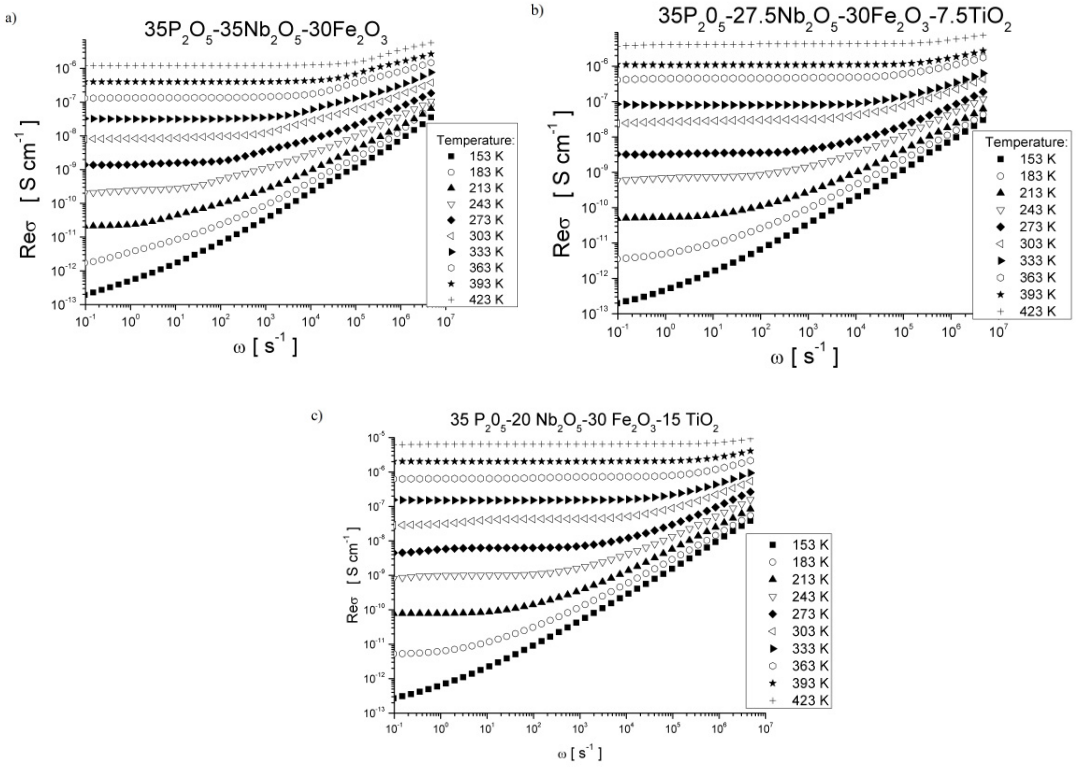

Fig. 4. Real part of conductivity versus frequency measured at different temperatures for $35P_2O_5$-$30Fe_2O_3$-(35-x)Nb_2O_5-xTiO_2 glass samples where x = (a) 0, (b) 7.5 and (c) 15 (in %mol). The error bars are smaller than the plot symbols.

4. Discussion

The measurements of glasses topography and structure (Fig. 1, 2 and 3) showed glass structure in all three compositions. There is also visible some phase separation in all glasses. The micro-agglomerates obtained only on the surfaces may be caused by the treatment associated with the preparation process. The topography of fractures consists only of nanogranules distributed within the glass matrix. No significant influence of the TiO_2 and Nb_2O_5 quantity on glasses structure has been observed in the case of the samples studied in this work.

The dependence of the ac conductivity on angular frequency in amorphous materials is usually found to obey the form (so called Jonscher law or universal dielectric response) [12]:

$$\sigma(\omega)=\sigma_{DC}+A\omega^{s(T)} \quad (1)$$

where σ_{DC} is the dc conductivity and $\sigma_{AC}=A\omega^{s(T)}$ is the ac component. The first term (dc conductivity) dominates in the low frequency region and the second one (power law behavior) in the high frequency region. Figure 4 shows that all samples fulfill the Jonscher law. The dc conductivity and the exponent *s* are determined using a numerical fitting of the above equation to the measured data. Figure 5 (a) presents the dc conductivity versus reciprocal of temperature. The Arrhenius equation $\sigma_{DC} = \sigma_0 exp(-E / kT)$ was used for determination of activation energy. Table 1

presents calculated values of σ_{DC} at 303 K and activation energy for all samples. It can be seen that glass dc conductivity increases with increase titania amount. However the values of activation energy almost do not change after TiO_2 addition. On the basis of the literature data we suppose that in iron-phosphate-niobate glass the Nb^{5+} ions incorporate into bridging oxygen of P–O–P bonds and build glass matrix [5]. Therefore adding Nb^{5+} ions to the glass composition, should not significantly influence the conduction mechanism which should remain the same as in iron-phosphate glass, i.e. non-adiabatic transport of small polarons [2]. However, the conductivity of $40FeO\text{-}60P_2O_5$ (in %mol) glass [2] is of three orders of magnitude lower and activation energy is higher than in our $35P_2O_5\text{-}35Nb_2O_5\text{-}30Fe_2O_3$ sample. These differences in conducting properties may suggest that the conduction mechanism is also different. Since titanium ions may exist in two valance states in glass matrix, we think that the TiO_2 addition to glass composition may give rise to additional polaron hopping centers. This may increase the conductivity what is observed in samples with TiO_2.

Figure 5 (b) shows the temperature dependence of the frequency exponent *s* for all samples. Obtained values of the exponent *s* and its dependence on temperature were compared to the models collected by Elliot [13]. The comparison shows that in all glasses the ac conduction process may be due to the overlapping polaron tunneling (OLP). It describes the polarons tunneling where an appreciable overlap of the polaron distortion clouds occurs. Elliot [13] has presented expected curve tendency of exponent *s* dependence on temperature for two exemplary values of reduced polaron radii, small and large. For large value of reduced polaron radius this exponent slowly decreases from unity with increasing temperature, what we also observed in our sample without TiO_2. For small value of reduced polaron radius the s exponent decreases with increasing temperature to a minimum value then it starts to increase. As shown in Fig. 5b, similar behavior was observed in our samples containing TiO_2. However it should be also taken into consideration that the values of s parameter significantly depend on the reduced polaron radius dimension and they are much higher for large radius than for small one. On the basis of the exponent s values and its temperature dependence we think that the value of reduced polaron radius is the smallest for the glass without TiO_2 and it increases after TiO_2 addition, and with increase of its amount. Summing up, on the basis of obtained results and relations we believe that the ac and dc conduction mechanism is overlapping polaron tunneling in all samples.

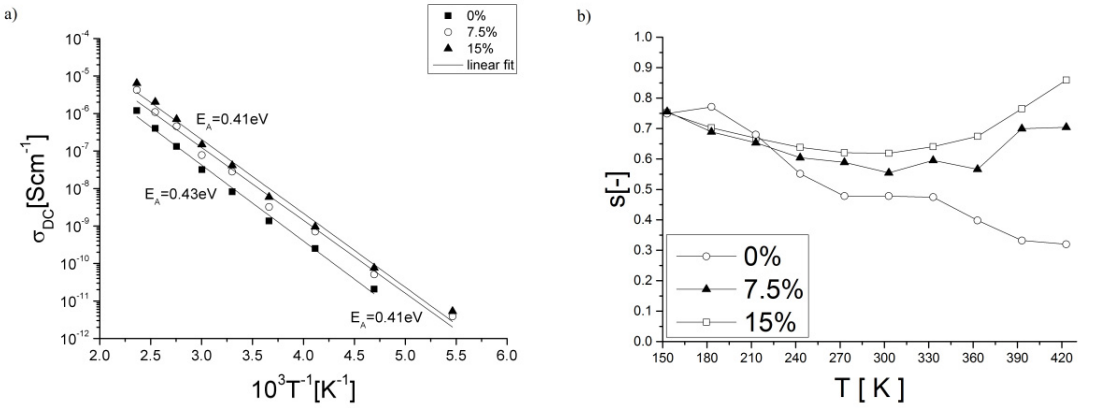

Fig. 5. (a) Dc conductivity versus 1000/T and activation energy; (b) temperature dependence of the frequency exponent s for all samples.

Table 1. Glass transition temperature and conductivity parameters.

Composition (in %mol)	E_A ($^+/_-$ 0.01) (eV)	$\sigma_{DC\ (T=303K)}$ (Scm^{-1})
$35P_2O_5$-$30Fe_2O_3$-$35Nb_2O_5$	0.43	$8.19*10^{-9}$
$35P_2O_5$-$30Fe_2O_3$-$27.5Nb_2O_5$-$7.5TiO_2$	0.41	$2.82*10^{-8}$
$35P_2O_5$-$30Fe_2O_3$-$20Nb_2O_5$-$15TiO_2$	0.41	$4.13*10^{-8}$

5. Conclusions

In conclusion, phosphate-niobate-iron glasses containing titanium oxides were prepared. The structure and topography measurements confirm their amorphous nature. Some structures were detected what suggest the phase-separation in obtained glasses.

The ac conductivity fulfill the Joncher law for amorphous materials. Dc conductivity increases with titania addition but activation energy almost does not change. On the basis of conductivity dependence on frequency, and temperature dependence of the frequency exponent *s*, we suppose that the conduction process may be due to the overlapping polaron tunneling in all samples. It is stated that the dimension of reduced polaron radius depends on TiO_2 addition and its amount.

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