

Characterization of Iron Sodium Phosphate Glasses Doped Ba²⁺ Cations for Using as Radioactive Waste Encapsulation

A.G. Mostafa¹, M.Y. Hassaan¹, A.B. Ramadan², A.Z. Hussein² and A.Y. Abdel-Haseib^{2*}

¹ ME Lab., Phys. Dept., Faculty of Science, Al-Azhar Univ., Nasr City, Cairo, Egypt.

² Egyptian Nuclear and Radiological Regulatory Authority (ENRRA), Nasr City, Cairo, Egypt.

*yousef6400@yahoo.com

Abstract: Glasses with the composition $(65-x) \text{P}_2\text{O}_5 + 15\text{Fe}_2\text{O}_3 + 20\text{Na}_2\text{O} + x \text{BaO}$, where $0 \leq x \leq 25$ mol % have been prepared by the conventional melt quenching technique. The hyperfine structure of these glasses was investigated using Mössbauer spectroscopy, which indicated the presence of iron cations in two different oxidation states (Fe^{2+} & Fe^{3+}), and all Fe^{2+} occupied the tetrahedral coordination state, while some Fe^{3+} occupied the tetrahedral coordination state and the other occupied the octahedral coordination state. The electrical properties of the studied glasses were found to be temperature and frequency dependent and their conductivity indicated that all glasses are semiconductors. The exponent (s) was found to be temperature dependent and the CBH and SPH models are the most applicable conduction mechanisms of the studied glasses at low and high BaO content respectively. The density as well as the hardness increased monotonically with increasing barium oxide content, while, conversely, the molar volume decreased. However, the applied investigations showed that these glasses can be used for encapsulating radio-active waste before interment underground.

[Mostafa AG, Hassaan MY, Ramadan AB, Hussein AZ and Abdel-Haseib AY. **Characterization of Iron Sodium Phosphate Glasses Doped Ba²⁺ Cations for Using as Radioactive Waste Encapsulation.** *Nat Sci* 2013;11(5):148-155]. (ISSN: 1545-0740). <http://www.sciencepub.net/nature>. 22

Keywords: Mössbauer spectroscopy; Shielding glasses; Iron phosphate glasses; Radioactive waste encapsulation

1. Introduction

Pure phosphate glasses have relatively poor chemical durability [1, 2], and little commercial importance due to their hygroscopic behavior. The addition of some transition metal oxides to the network improves their stability and their physical properties. Accordingly, these glasses represent new and promising materials of many technological and scientific interests [3-7].

In oxide glasses, transition metal ions occupy more than one oxidation state and they form either 4- or 6- fold coordination's with oxygen ions. Iron phosphate glasses are electrically classified as semiconductor [9-11], and this behavior is due to the fact that iron ions occupy two different valance states (Fe^{2+} and Fe^{3+}). Hence conduction in these glasses takes place by electron hopping between Fe^{3+} and Fe^{2+} , and the charge transfer is usually termed as small polaron hopping (SPH) [6-8]. The electrical conductivity depends strongly upon the distance between iron ions [9], and the charge carrier concentration is related directly to the ratio of Fe^{2+} cations to the total iron ($\text{Fe}^{2+}/\sum \text{Fe}$) [12]. It was found also that phosphate glasses containing some heavy metal oxides have high γ - ray absorption coefficient [13], and accordingly these glasses can be used to capsule some radioactive wastes.

Therefore, in this article, some iron sodium phosphate glasses doped with barium oxide were investigated applying density, molar volume,

hardness and electrical transport properties as well as Mossbauer spectroscopy aiming to check the ability of these glasses for encapsulating radioactive wastes.

2. Experimental Procedure

Glasses having the percentage molecular composition $(65-x) \text{P}_2\text{O}_5 + 15\text{Fe}_2\text{O}_3 + 20\text{Na}_2\text{O} + x \text{BaO}$ where $0 \leq x \leq 25$ mol% were prepared by the melt quenching technique [14], using reagent grade chemicals of purity not less than 99%. Phosphorous pent-oxide and sodium oxide were introduced as ammonium dihydrogen phosphate and sodium carbonate respectively while ferric and barium oxides were introduced as such. The batches were melted in porcelain crucibles at 1100°C for 1.5 hrs in an electric muffle furnace, and the melts were stirred several times to ensure complete homogeneity. After melting they were rapidly quenched between two pre-cooled brass plates to obtain solid glasses. The obtained samples (just after sitting) were annealed for 2 hrs at 400°C, and then the annealing furnace was turned off and left to cool to room temperature overnight, in order to relieve the glass samples from internal stress and strain.

The density (ρ) was measured at room temperature using Archimedes principle, taking toluene as an immersion liquid of stable density [$\rho_t = 0.866 \text{ g/cm}^3$], applying the following equation.

$$\rho = \rho_t \left[\frac{W_a}{W_a - W_b} \right] \quad \text{gm / cm}^3 \quad (1)$$

where ρ_t is the density of toluene, W_a and W_b are the sample weights in air and toluene, respectively.

The molar volume (V_m) values were calculated using the following equation [15],

$$V_m = \sum(n_i M_i) / \rho \quad \text{cm}^3 / \text{g.mol} \quad (2)$$

where M_i is the molecular weight of the i th oxide, n_i is the mole fraction of such oxide and (ρ), is the measured density of the glass sample.

Mossbauer effect (ME) spectra were obtained using a conventional constant acceleration Mossbauer spectrometer outfitted with 50 mCi ^{57}Co radioactive source at room temperature. The analysis and fitting of the obtained spectra were carried out relative to a metallic iron calibration spectrum.

The micro-hardness measurements were carried out using a Vickers Micro Hardness indentation tester (HV – 1000 - China). The indentation was made using a square based pyramidal diamond with face angle 136° , measuring microscope and video monitor. The hardness was calculated applying the following equation:

$$H_v = A (P/d^2) \quad \text{kg / mm}^2 \quad (3)$$

where A is a constant equal to 1854.4, P is the indentation load applied and d the mean value of the indentation diagonal. Five indentations were done, using polished glass samples, with a constant load of 200 g during 20 s for each, and then the mean value was then calculated to be the correct hardness value of the glass under study [16].

The dielectric properties as well as the ac conductivity were measured using self-calibrated LRC bridge (model SR 270) in the temperature range from 300 to 470 K and at three different frequencies (1, 10 and 100, kHz) in steps of 5 K. The bridge as well as all the connection cables were good shielded and connected to the earth. The two surfaces of each sample were polished to obtain disks of 7 mm diameter and 1 mm thickness and were then coated with silver paste to achieve good electrical contact.

3. Results and Discussion

It was established that, iron phosphate glasses containing some heavy metals, have high gamma ray attenuation coefficient and exhibit semiconduction properties [17]. However it can be supposed that iron phosphate glasses doped with Ba cations (as heavy metal) can be used as shielding glass and for encapsulating some radioactive wastes before interment underground. In this sense, the

properties related to the ability of these glasses to be used for this aim must be considered (such as structure, hardness and semiconducting properties).

The obtained density (ρ) and molar volume (V_m) values are represented graphically in Figs. (1, 2). It can be seen that density increased monotonically with increasing barium oxide content, while conversely, molar volume decreased gradually. This behavior can be attributed to the gradual replacement of the heavy BaO molecule [molecular weight (153.34)] by the lighter P_2O_5 molecule [molecular weight (141.95)]. The empirical density and molar volume are also exhibited in the same figures for comparison, where it was found that both the empirical density and molar volume show approximately the same trend as the experimental ones. But it can be observed that the values of the empirical density are usually higher than the experimental ones while the values of the empirical molar volume is usually lower than those of the experimental ones. This can be taken as evidence for the homogeneity of the obtained glassy phase of the studied samples.

The gradual decrease in the molar volume values was supposed to be due to the following factors:

1. The depletion in the number of oxygen ion density (oxygen of the network) since five oxygens were replaced by only one oxygen (during the replacement of P_2O_5 by BaO mole per mole).
2. The decrease of phosphorus as the main glass former cations.

Since the above two factors act to decrease the glass forming ability, the question now is, what about the structure of iron? In this sense, it can be supposed that some iron ions will occupy the glass forming positions. Therefore, ME spectroscopy was applied to study the structure of iron in the studied glass samples. The room temperature ME spectrum of the glass sample that contains 10 mol% barium oxide is shown in Fig. (3), as a representative spectrum.

The exhibited ME spectrum appeared to be composed of two broad peaks with different intensities, in addition to a small peak at the right hand side of the spectrum. The computer analysis and fitting indicated that, three separated paramagnetic doublets are presented in each spectrum indicating that, iron ions occupy three different sites nominated (I), (II) and (III). The hyperfine parameters [isomer shift (IS), quadruple splitting (QS) and width at half height (LW)], for all the studied samples are listed in Table (1).

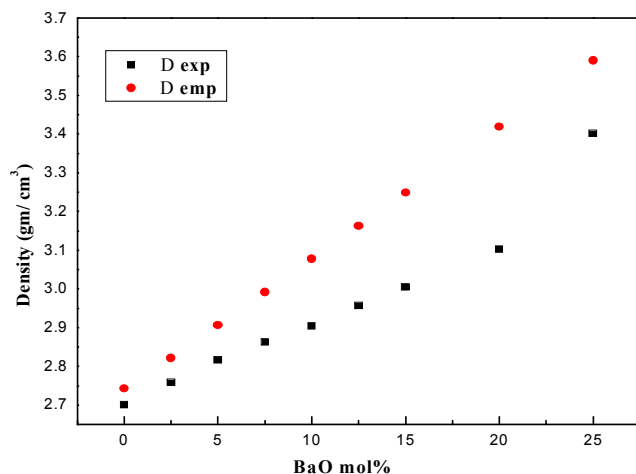


Figure 1. The experimental and empirical density values versus BaO content.

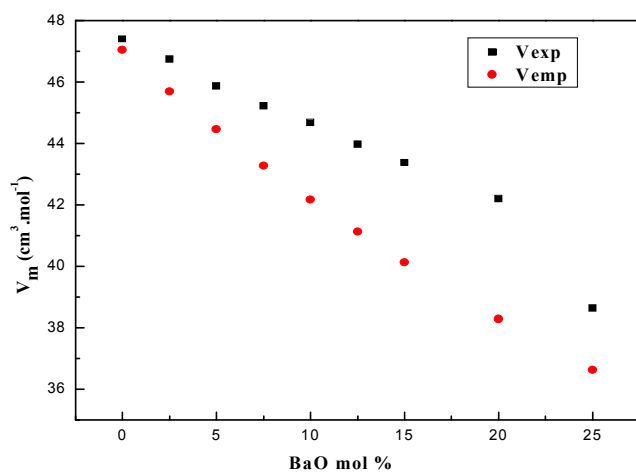


Figure 2. The experimental and empirical molar volume values versus BaO content.

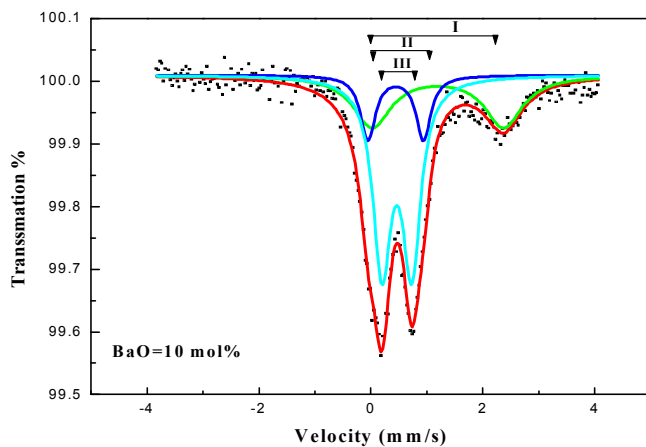


Figure 3. The obtained ME spectrum of the sample containing 10 mol % BaO, as a representative spectrum.

It is observed that, IS and QS values of the iron ions in site (I) fluctuate between (1.11 and 1.03) and (2.34 and 2.30) mm/s respectively. These values indicated that, iron ions occupy high spin tetrahedral ferrous states. The values of the IS and QS of the iron ions in site (II) are found to fluctuate between (0.45 and 0.43) and (1.03 and 0.88) mm/s respectively. These values showed that, iron ions in this site appeared as ferric ions occupying tetrahedral coordination state. The values of the IS and QS of iron ions in site (III) are found to fluctuate between (0.41 and 0.44) and (0.60-0.54) mm/s respectively. Also these values indicated that iron ions in site (III) appeared as ferric ions occupying the octahedral coordination state [18]. Accordingly it can be stated that, the iron ions in these glasses occupy two different oxidation states (Fe^{2+} and Fe^{3+}) where some Fe^{3+} ions occupy the tetrahedral coordination state and the rest occupy the octahedral coordination state, but all Fe^{2+} occupy the tetrahedral coordination state [18,19]. This means that some Fe^{3+} ions occupy the glass network former positions and some others occupy the glass modifier positions, but all Fe^{2+} ions occupy the glass network former positions.

However the ratio of the iron ions occupying the tetrahedral coordination ($\text{Fe}^{3+}_T + \text{Fe}^{2+}_T$) to the total iron ions in these glasses was calculated and exhibited in Fig. (4) as a function of BaO content. It is seen that the total tetrahedral iron increased approximately linearly. That is to say, as phosphorus (former cation) was gradually decreased, the iron ions occupying the glass network former positions increased also gradually. This indicated also that the introduced Ba cations occupy only the interstitial vacancies and / or act as bridges between some adjacent polyhedra forming O---Ba---O bonds [20].

From another point of view, the micro-hardness values of these glasses are of interest, especially when they will be buried under-ground and hence carrying-out measurable load. Therefore the hardness of the prepared samples was checked and the obtained values were exhibited in Table (2) and were presented graphically in Fig (5). From the obtained results it appeared that the hardness increased gradually with the gradual increase of barium oxide content at the expense of phosphorus pent oxide. That is the micro-hardness showed high sensitivity to the relative ratio of the introduced barium cations. This can be attributed to the introduced barium as heavy metal cation, and the decrease of oxygen anions in the glass network.

It was known that phosphorus pent oxide form chain and layer networks of low durability. Since barium cation may act as bridges between the layers and chains and have to cross-link the different layers in the network, the introduced barium cations

enhances the durability of phosphate networks which in turn increases extensively its micro-hardness. On the other hand, the depletion of the oxygen anions increases the relative ratio of barium to oxygen in the glass network which in turn increases the connectivity of the oxygen network by barium. This may act also to increase the hardness of these glasses.

On the other hand, the relative ratio of iron in the tetrahedral coordination state to total iron ($Fe_T / \sum Fe$) show also gradual linear increase (see Fig.4) which is approximately similar to the trend of hardness (see Fig.5). The gradual linear increase of density values, as BaO was gradually increased, confirm also the increase of the micro-hardness of the studied glasses.

Table 1. The obtained ME parameters for the studied glasses.

Composition (mol %)	State	IS(mm/s)	QS(mm/s)	LW(mm/s)	A%	Assignment
0	I	1.10	2.33	0.72	0.28	Fe ²⁺ (T)
	II	0.45	0.88	0.44	0.06	Fe ³⁺ (T)
	III	0.44	0.60	0.45	0.66	Fe ³⁺ (O)
2.5	I	1.03	2.34	0.71	0.30	Fe ²⁺ (T)
	II	0.45	0.94	0.45	0.06	Fe ³⁺ (T)
	III	0.43	0.54	0.45	0.64	Fe ³⁺ (O)
5	I	1.04	2.31	0.70	0.27	Fe ²⁺ (T)
	II	0.44	1.00	0.48	0.09	Fe ³⁺ (T)
	III	0.43	0.55	0.45	0.64	Fe ³⁺ (O)
7.5	I	1.07	2.30	0.73	0.27	Fe ²⁺ (T)
	II	0.45	1.01	0.43	0.12	Fe ³⁺ (T)
	III	0.41	0.58	0.45	0.61	Fe ³⁺ (O)
10	I	1.11	2.30	0.72	0.31	Fe ²⁺ (T)
	II	0.44	1.01	0.44	0.14	Fe ³⁺ (T)
	III	0.41	0.57	0.45	0.55	Fe ³⁺ (O)
12.5	I	1.10	2.31	0.70	0.27	Fe ²⁺ (T)
	II	0.43	0.99	0.44	0.20	Fe ³⁺ (T)
	III	0.43	0.54	0.45	0.51	Fe ³⁺ (O)
15	I	1.10	2.33	0.74	0.30	Fe ²⁺ (T)
	II	0.45	1.02	0.44	0.18	Fe ³⁺ (T)
	III	0.43	0.54	0.45	0.52	Fe ³⁺ (O)
20	I	1.10	2.32	0.70	0.37	Fe ²⁺ (T)
	II	0.45	1.02	0.43	0.18	Fe ³⁺ (T)
	III	0.44	0.56	0.45	0.45	Fe ³⁺ (O)
25	I	1.11	2.30	0.71	0.40	Fe ²⁺ (T)
	II	0.43	1.03	0.45	0.19	Fe ³⁺ (T)
	III	0.44	0.56	0.45	0.41	Fe ³⁺ (O)

Table 2. The measured values of the micro- hardness of the studied glasses.

Samples No	BaO mol%	H_v (Kg/mm ²)
1	0	98.4
2	2.5	98.2
3	5	99.3
4	7.5	100.01
5	10	101.2
6	12.5	101.4
7	15	101.8
8	20	102.4
9	25	102.8

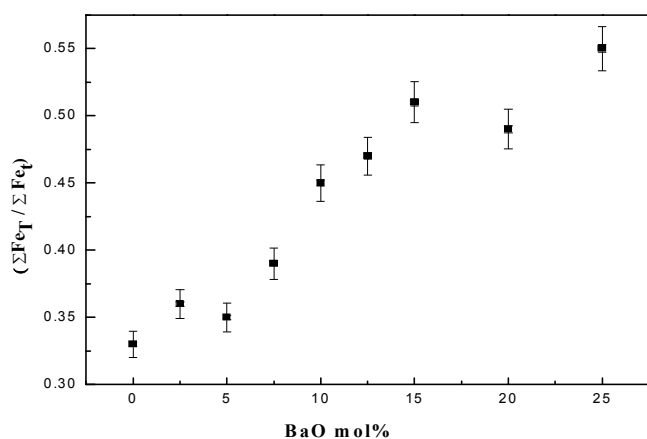


Figure 4. The relative ratio between iron in the tetrahedral coordination state to the total iron versus BaO content.

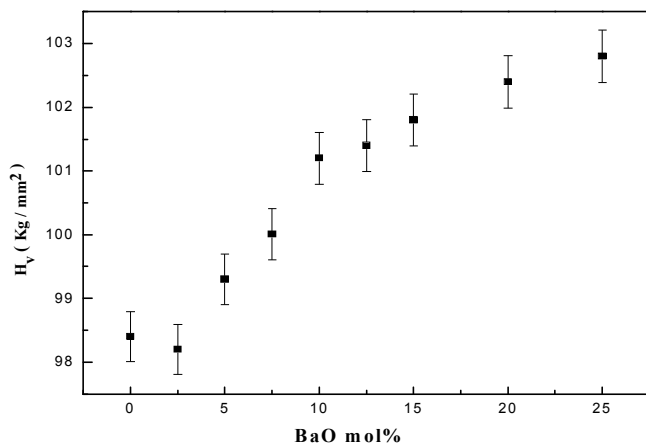


Figure 5. The obtained values of the hardness versus BaO content.

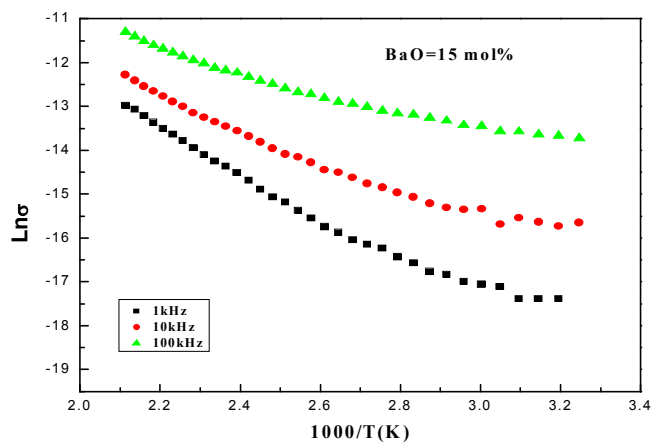
It is also of interest to measure the electrical transport properties of these glasses, since it is

suitable to select glasses with semiconducting properties in order to release directly any electrical charge formed as a result to the radiation comes from the interior radioactive wastes.

The ac conductivity of all amorphous solids and glasses obey the universal power law [21],

$$\sigma_{ac} = A \omega^s \quad (4)$$

where σ_{ac} is frequency dependent conductivity, A is a constant, weakly temperature dependent, ω is the angular frequency and s is the exponent factor and is usually less than unity. The temperature dependence ac conductivity at different frequencies (1, 10 and 100 kHz) for the sample containing 15 mol% BaO is shown in Figure (6), as representative figure.

Figure 6. The ac conductivity (σ_{ac}), as a function of both frequency and temperature for the sample containing 15 mol% as a representative curve.

It is appeared that σ_{ac} increases with increasing temperature, and it can be supposed that it is a thermally activated process. Also, the change in σ_{ac} at constant frequency (1kHz) and temperature (373K) as a function of BaO content, shows approximately gradual increase, Fig. (7).

It can be supposed that, the electrical transport depends mainly on the electron transfer between Fe^{2+} and Fe^{3+} cations, and to the mobility of Na^+ cations in the glass network. However, the increase in the ac conductivity can be attributed to:

1. The increase of the vacancies in the glass network as a result to the introduced large volume Ba cations, which act to increase the movement of the present Na^{2+} cations.
2. Since the total number of iron ions is constant and the molar volume show gradual decrease, that is the inter ionic distances between any two adjacent

Fe cations decreased, and the electron hopping between them will be easier.

The variation of the measured dielectric constant (ϵ'), and the dielectric loss factor (ϵ'') of the prepared glasses with the change of frequency and temperature was studied. Figure (8) shows the change in ϵ' as a function of temperature at three different frequencies (1, 10, 100 kHz) for the sample containing 15 mol% BaO, as a representative figure.

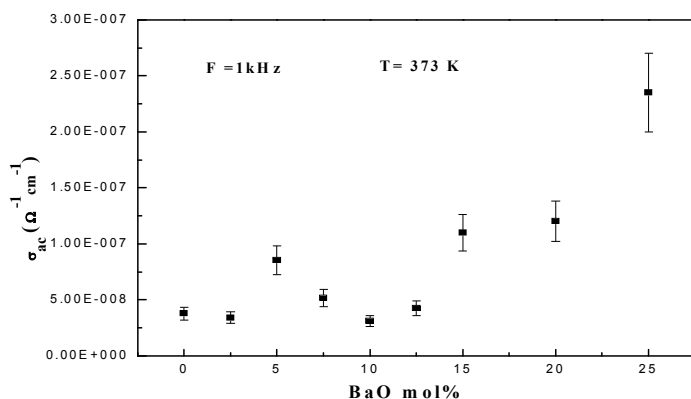


Figure 7. The ac conductivity (σ_{ac}), as a function of BaO content at fixed frequency and temperature.

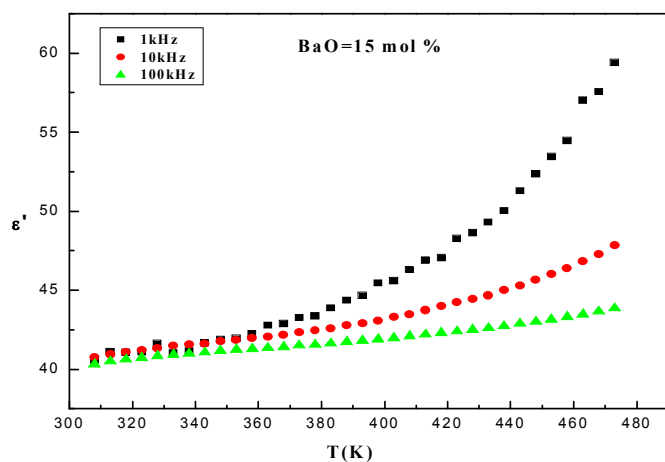


Figure 8. The variation of the dielectric constant as a function of temperature at different frequencies for the sample containing 15 mol%, as a representative curve.

It can be observed that, ϵ' increases gradually with increasing temperature in the range from 300 to 500 K and decreases with increasing frequency, and no maximum was observed in the temperature and frequency ranges for all samples. This behavior can be taken as evidences of non-ferroelectric behavior of all samples [22]. The increase of temperature affect directly the polarization of the permanent dipoles,

contributing to the dielectric constant [23] and it act to create a degree of freedom [24] associated with the allowed orientation of the permanent dipoles. It was found that the dielectric constant decreases with increasing frequency, which means that the response of the permanent dipoles decreases as the frequency was increased [25]. Such decrease in ϵ' with the increase of frequency may be due to the hopping frequency of electrons between Fe^{2+} and Fe^{3+} which is smaller than the applied frequency. In other words, at higher frequencies, the permanent dipoles cannot respond to the electric field variation and the contributions to the dielectric constant decrease to almost zero [26]. It can be observed also that ϵ' increases with increasing temperature at low frequency, which may be due to the electric field that accompanied by the applied frequencies. Such field will cause some ordering inside the sample and form an electric moment in the entire volume of the dielectric in each separate polarized molecule. The molecular dipoles in polar materials cannot orient themselves at low temperature. The thermal vibration of molecules contributes with an additional polarization due to the increased average magnitude of the permanent dipole moment [27-29].

The measured loss factor is a very important characteristic value which measures directly the phase difference due to the loss of energy within a sample at particular frequency. The variation of the dielectric loss factor (ϵ'') as a function temperature and frequency of the sample containing 15 mol % BaO as representative figure, can be shown in Fig. (9).

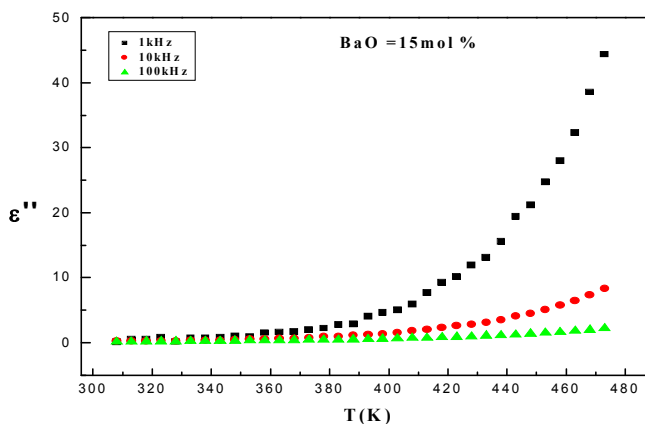


Figure 9. The variation of the dielectric loss factor as a function of temperature and frequency for the sample containing 15 mol% as a representative curve.

The normal behavior is the increase in ϵ'' with temperature after a stable region. The behavior

may be due to the thermal increase which in turn increases the disordered states of the dipoles and hence increases the energy loss inside the samples. That is, as the temperature was increased, the electrical conduction losses increase. For all frequencies the increase in ϵ'' with temperature is due to the relaxation of dipoles in cooperation with the resulting drop in the relaxation time.

The variation of the exponent factor (s) with temperature is shown in Fig. (10- a, b), where s appears to be temperature dependent in two different ways for different samples. That is, for the low BaO content glasses (up to 10 mol%), s shows gradual decrease as the temperature was gradually increased Fig(10-a), where the correlated barrier hopping (CBH) model is the applicable mechanism in these samples. On the other hand, for the samples containing high BaO content, (from 12.5 to 25 mol%) s increases with temperature from room temperature up to about 350 K, then it start to decrease gradually once again Fig.(10-b). This means that the small polaron hopping (SPH) model is the applicable conduction mechanism in these glasses [30].

Figure (11) shows the change in the activation energy (ΔE) as a function of BaO content where it can be seen that at low BaO content glasses [up to 5 mol%], ΔE show gradual increase until it reaches a maximum at the sample containing 5 mol% BaO, then, it starts to decrease gradually again. This figure represents approximately an inverse trend to Fig. (6) which shows the variation of the conductivity versus BaO content, and this appeared to be a logic result. It can be supposed that Ba^{2+} cations when added in low amounts (up to 5 mol%), it acted as obstacles prevents the easier movement of Na^+ cation and hence act to decrease the conductivity and increase ΔE . Then the gradual increase of barium cations at the expense of phosphorus cations, act to decrease the molar volume gradually, which in turns act to decrease the inter-cationic distances between any two adjacent iron cations. This increases gradually the process of electron hopping and hence the electrical conductivity, which in turn decreases gradually the value of ΔE .

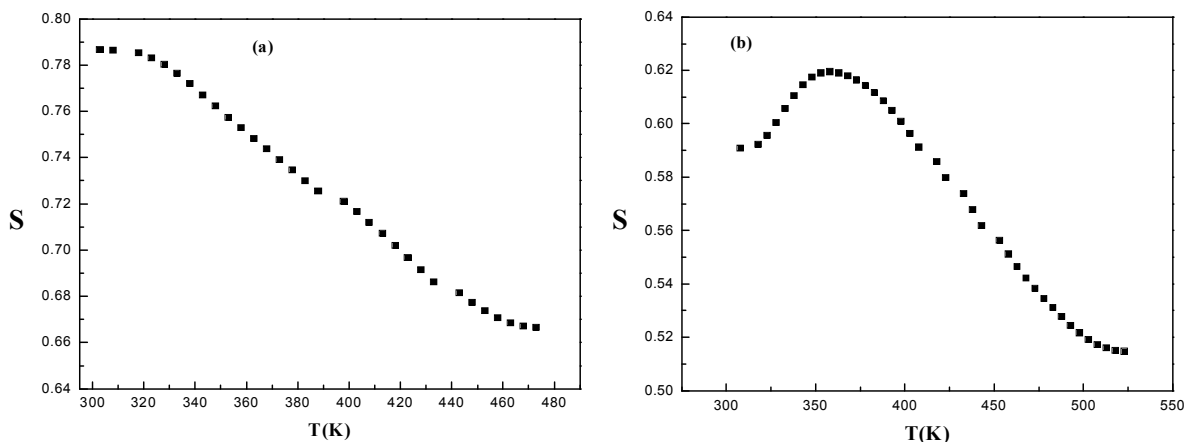


Figure 10. Representative curves showing the variation of the exponent factor (s), versus temperature of samples: a- containing low BaO content, b- containing high BaO content.

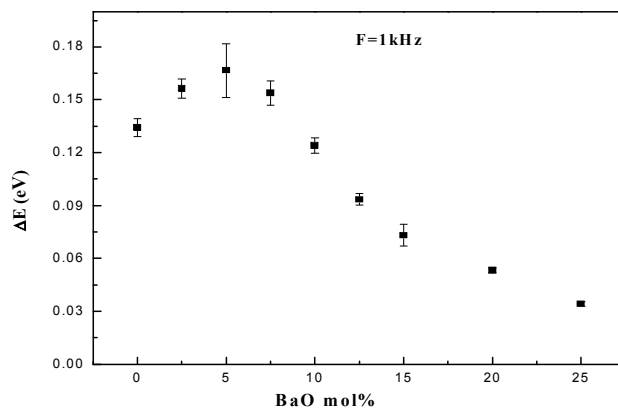


Figure 11. The electrical activation energy versus BaO content.

4. Conclusions

Some iron-sodium phosphate glasses containing BaO have been prepared and investigated aiming to be used as radioactive waste encapsulations. The introduced BaO act to increase the hardness and density of glasses monotonically. The iron cations in the tetrahedral coordination state increased gradually as well as the electrical conductivity, which may be due to the strengthening of the bond energies and the cross-linking of phosphate layers and chains by the introduced barium cations. It was concluded also that all the studied glass samples are in the semiconductor range and the correlated barriers hopping (CBH) model is the applicable conduction mechanism for glasses with low BaO content, while the small polaron hopping (SPH) model is the predominant conduction mechanism for glasses with high BaO content. Accordingly, it can be supposed that the studied glasses can be used to capsule some radioactive wastes before interment underground.

Corresponding Author:

A.Y. Abdel-Haseib

Egyptian Nuclear and Radiological Regulatory Authority (ENRRA), Nasr City, Cairo, Egypt.

E-mail: yousef6400@yahoo.com

References

- H. A. Sallam, N. H. Sheta, Sh. N. Radwan, S. El-Menyawy, T. Z. Amer and N. A. Eissa, Al-Azhar Bull. Sci., 9 (1998) 2.
- M. M. El-Desoky, K. Tahoon and M. Y. Hassaan, Mater. Chem. Phys., 69 (2001) 169.
- Y. M. Mostafa and k. El-Egili, J. Non-Cryst. Solids, 240 (1998) 144.
- Y. Lin, Y. Zhang, W. Huang, K. Lu and Y. Zhao, J-Non- Cryst. Solids, 112 (1993) 136.
- H. A. A. Sidek, IT. Collier, R. N. Hampton, G. A. Saunders and B. Bridge. Phylas. Mag. B, 2(1989)221.
- I. G. Austin and N. F. Mott, Adv. Phys., 18 (1969) 41.
- M. M. El-Desoky and Shereief M. Abo. Naf, J. Mater.Sci., Mater electronics, 15 (2004) 425.
- M. M. El – Desoky, A. Al-Hajry, M. Tokunaga, T. Nishida and M. Y. Hassaan, Hyperfine Interact., 156, 157 (2004) 547.
- A. Mogus-Milankovic and D. E. Day, J-Non-cryst- solids, 162 (1993) 275.
- A. Mogus- Milonkovic, B. Santic, S.T. Rris, K. func and D. E. Day, J. Non cryst. solids, 342 (2004) 97.
- N. F. Mott, J. Non-cryst. solids, (1968) 1.
- M. M. El-Desoky and I. Kashif, physica status soldi., 194 (2002) 89.
- F. H. El Batal, A. M. Abdelghany and R. L. Elwan, J. molecular structure, 1000 (2011) 103.
- A. K. Varshneya, “*Fundamentals of Inorganic Glasses,*” Society of Glass Technology, Sheffield, UK, 2006.
- Dorina Rusu and I. Ardelean, Materials Research Bulletin, 43 (2008) 1724.
- S. N. Salama, H. Darwish and H. A. Abo-Mosallam, Ceram. In, 32 (2006) 357.
- A. Santic, Z. Skoko, A. Gajovic, S.T. Reis, D. E. Day and A.Mogus- Milankovic, J. Non- cryst. Solids, 357 (2011) 3578.
- A. A. Hosseini and C. A. Hogarth, J. Mater. Sci. Lett, 7 (1988) 593.
- R. D. Husung, and Robert. Doremus, J. Sci, 5 (1990) 10.
- P. Bergo, S.T. Reis, W. M. Pontuschka, J. M. Prison and C. C. Motta, J. Non. Cryst. Solids, 336 (2004) 159.
- A. K. Jonsher, Nature, 267 (1977) 673.
- C. Kittel, “Introduction to Solid State Physics”, Wiley, New York, 1977.
- M. M. El- Kholoy, and L. M. Sharaf El Deen, Mater .Chem. Phys, 65 (2002) 192.
- R. J. Charles, J. Appl. Phys, 32 (1961) 1115.
- P. Bergo, W. M. Pontuschka and J. M. Prison, solid state comm.,142 (2007) 545.
- C. P. Smyth, “Dielectric behavior and Structure”, McGraw hill book company, New York, 1955.
- P. Subbalakshmi and N. Veeraiah, Mater. Lett., 56 (2002) 880 .
- V. N. Novikov, Physica B: Condens. Matter., 263& 264 (1999) 343.
- R. M. Fuoss, J.Am. Ceram. Soc., 63 (1941)378 .
- S. R. Elliott, Advances in Physics, 36 (1987) 135.

4/14/2013