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Structure, magnetic, and electrical studies on vanadium phosphate glasses containing different oxides

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Abstract Glass system with molar composition (60% P_2O_5–30%V_2O_5–10%X) where X is Li_2O, Na_2O, K_2O, and BaO was prepared. The density and molar volume indicate that the density decreases while the molar volume increases with increasing ionic radius of doped oxides. IR studies reveal the coexistence of V^{4+} and V^{5+} ions (act as glass modifier and glass former, respectively). The observed paramagnetic behavior of samples indicates that $V^{4+} > V^{5+}$ (the ratio $V^{4+}/V^{4+} + V^{5+} > 0.52$ as obtained from chemical titration analysis). Mott's model of conduction was applied to discuss DC electrical conduction mechanism. The prepared glass exhibits semiconducting behavior. However, Ba ion is the only ion which did not contribute to the ionic conduction. The conductivity increases with decreasing ionic radius of doped oxides due to high mobility due to their small size. The effect of hopping distance on the electrical conduction and magnetic properties were discussed. An attempt was done to determine the expected temperature of Ba ionic conduction and its ionic activation energy.

Introduction

The P_2O_5 glass consists of PO_4 tetrahedral units with one double bonded oxygen and three bridging oxygen atoms [1, 2]. In the absence of cations, these units link via covalent bridging oxygens to form various phosphate anions. The addition of modifiers like Li, Na, K, and Ba change the PO_4 tetrahedral units to meta-phosphate composition in addition to non-bridging oxygen. Iron phosphate glass, with good chemical durability, is able to accept both more types of nuclear waste and up to six times more nuclear waste per unit volume than borosilicate glasses [3, 4]. Phosphate glasses containing fluoride, which have been doped with rare earth ions, have shown great promise for optical and laser applications due to their low absorption at particular frequencies [5, 6]. Phosphate glasses are also attractive as glass–metal seals due to their low melting temperature, low viscosity, and high thermal expansion coefficients [7]. Binary and ternary V_2O_5 glasses can exhibit a semiconducting behavior which arises from an unpaired $3d^1$ electron hopping between the transition metal (TM) ions when the TM ions exist in two or more valence states, i.e., an electron hopping from a V^{4+} site to a V^{5+} site [8]. The electrical and magnetic properties of vanadium phosphate glasses containing iron was studied [9]. The glass system showed semiconducting and paramagnetic behavior. Electrical conduction and dielectric properties of vanadium phosphate glasses doped with lithium were studied [10]. The two kinds of glasses, doped and undoped with lithium, confirm electron hopping between V^{4+} and V^{5+} ions. For doped glasses with high lithium content, the glass confirms the domination of ionic conductivity. The conductivity of vanadium phosphate glass containing different amounts of alkali content was studied [11–13]. The first two authors [11, 12] found that the conductivity decreases with increasing alkali content while the latter [13] found that the conductivity increases with increasing alkali content. The aim of this work is to study the effect of different oxides on the electrical, magnetic, and structure properties of vanadium phosphate glass.

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Experimental

Glass system with molar composition (60% P_2O_5–30%V_2O_5–10%X) where X is Li_2O, Na_2O, K_2O, and BaO was prepared from reagent grade chemicals (99% purity). Vanadium pentoxide (V_2O_5), ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$), lithium carbonate (Li_2CO_3), sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), and barium carbonate ($BaCO_3$) were thoroughly mixed in a porcelain crucible and melted at 1200 °C for 3 h in a muffle furnace until a hemogeneous melt was obtained. The melt was then quickly quenched to room temperature. Powder X-ray diffraction was performed on samples and the results showed that they were purely non-crystalline. The density (ρ) of the glass was determined at room temperature using Archimedes method with zylene as immersion fluid. Three samples of each glass were used to determine the density (as well as each measurement). Density values are precise to ±1%. The molar volume (M_V) was calculated from the obtained density data using the relation [14]

$$M_V = \sum M_i N_i / \rho \qquad (1)$$

where M_i and N_i are the molar weight and molar fraction of the oxide i, respectively. The infrared spectra in the range 400–4000 cm^{-1} were recorded at room temperature using a (FT/IR-4100 type A). The KBr disc technique was used to obtain the spectra. The DC conductivity measurements were carried out using Keithely 617 electrometer with range from 10 to 10^{-16} A. Discs about 2 mm thickness were used. The parallel surfaces were coated with silver paste to serve as electrodes. The experimental error in determining the activation energy for conduction is precise to ±0.015 eV. The magnetic susceptibility was measured using Gouy method, where a cylinder tube is filled with powder sample and weighted in presence and absence of magnetic field, is given by [15]

$$\chi_m = \left(2Lg\rho/\mu_o \Delta H^2\right)(\Delta m/m) \qquad (2)$$

where m is the sample weight in the absence of the magnetic field, $\Delta H^2 = H^2 - H_o^2$ is the difference in square magnetic field at the bottom and the top of the tube, $\Delta m = m_1 - m$, m_1 is the sample weight in the presence of the magnetic field H, g is the gravitational acceleration, μ_o is a constant, and L is the sample length. The positive, Δm indicates paramagnetic material and the negative, Δm indicates diamagnetic material.

Results and discussions

Figure 1 represents the dependence of density and molar volume on the doping oxides. The figure showed that the density decreases while the molar volume increases. This mean that oxides act as modifier in oxide glasses [16–18]. In other words, doping ions occupy interstitial positions in the glass network and forming non-bridging oxygen [14]. The presence of ions in these sites, producing non-bridging oxygen, expands the lattice, increases the molar volume and decreases the density [19]. The change of molar volume and density which depend on the ionic radius of doping ions confirms the presence of alkali ions as modifier. The infrared absorption spectra of glass system are shown in Fig. 2. All the prepared glasses show quite similar spectra, major obtained IR bands for all samples are about 414, 560, 600, 665, 940, 1020, 1100, 1375, 1625, and 3435 cm^{-1}. As for sample containing potassium, the band at 560 cm^{-1} became shoulder and the three bands at 925, 1020, and 1100 cm^{-1} became broad band about 1020 cm^{-1} while for the sample containing barium, the band at 560 cm^{-1} disappeared. The obtained IR bands have been assigned and are listed in Table 1.

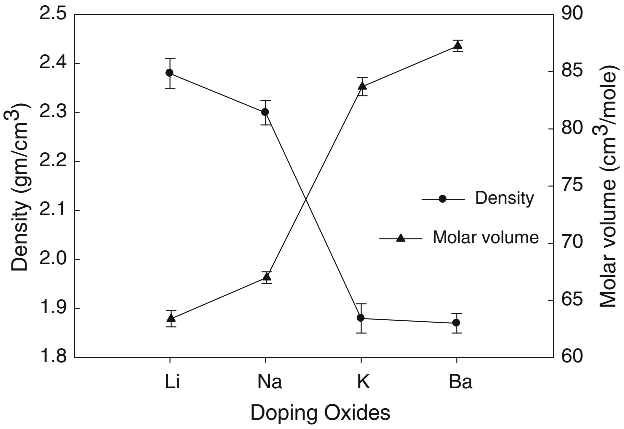

Fig. 1 Dependence of density and molar volume on doping oxide. *Lines* joining the points are guides to the eye

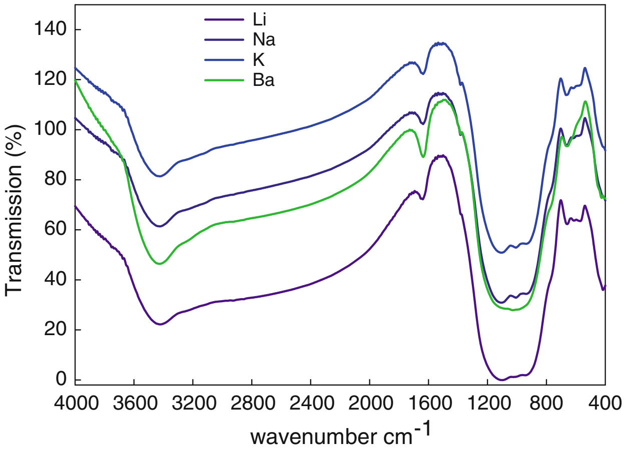

Fig. 2 IR absorption spectra for glass system

Table 1 Characteristic IR spectral band assignments

No.	Wavnenumber (C m^{-1})	Assignments	Ref
1	414	Coupled V–O and P–O bending modes for both VO_4 and PO_4 groups	[20]
2	560	Harmonics of bending P–O–P and O=P–O vibrations	[21]
3	600	Bending modes of the PO_4 group or due to the bending vibration of the P–O–P bonds	[20, 22]
4	665	Symmetric vibration of POP	[23]
5	940	Asymmetric stretching vibration of P–O–P bonds	[22]
6	1020	The vibrational band of VO_5 group	[24]
7	1100	Asymmetric vibration of PO_3 group indicate the presence of metaphosphate units	[25, 26]
8	1375	P=O stretching mode confirms the presence of metaphosphate units	[21]
9	1625 and 3435	H_2O	[21, 27]

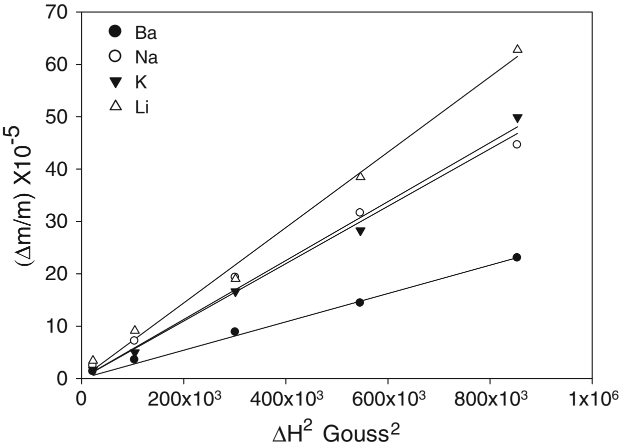

Fig. 3 Dependence of $\Delta m/m$ on the square magnetic field

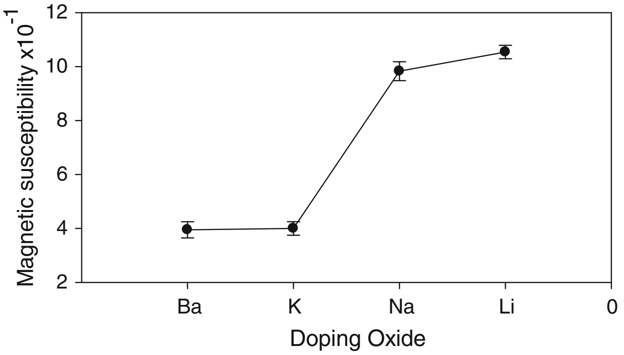

Fig. 4 Dependence of magnetic susceptibility on doped oxides. *Lines* joining the points are guides to the eye

The above assignment leads to the conclusion that the glass have the same structure and that the all doping ions play as modifiers and occupy the interstitial positions. This conclusion is in agreement with density and molar volume measurements. The glass samples are high hygroscopic and contains mainly metaphosphate chain groups and vanadium ions exist as V^{5+} (act as a glass former) and V^{4+} (act as a glass modifier). From Eq. 2, the plot of ($\Delta m/m$) versus ΔH^2 yields straight lines as shown in Fig. 3. The positive slope indicates the paramagnetic behavior. On the other hand (($\Delta m/m$) versus ΔH^2) shows negative slope in case of diamagnetic materials. IR spectra pointed out that vanadium ions in the studied samples exist as V^{4+} and V^{5+}, science the magnetic moment of V^{5+} is zero (i.e., diamagnetic ion) while for V^{4+} is $\approx 1.73\ \mu_B$ (i.e., paramagnetic ion) then, the observed paramagnetic reveals that $V^{4+}/V^{4+} + V^{5+} > 0.5$. Figure 4 shows the magnetic susceptibility as a function of doped oxide. The magnetic susceptibility decreases with increasing the ionic radius of the doped oxide ions in the same way like density. The paramagnetic behavior arises from the V^{4+} ions and as we will discuss later the separation distance between vanadium ions increase with increasing the ionic radius of doped oxide ions which in turn decrease the magnetization and the magnetic susceptibility. Sometimes the magnetic susceptibility treated as molar susceptibility and mass susceptibility but in all cases the aim is to define the behavior and trend of the magnetic properties. A general expression for χ_m (molar magnetic susceptibility) is

$$\chi_m = \chi_{\text{diamag}} + \left(N\mu^2/3KT\right) \tag{3}$$

where μ is the permanent magnetic moment per atom, N is Avogadro's number, T is the absolute temperature, K is the Boltzmann constant, and χ_{diamag} is the diamagnetic contribution to the molar susceptibility. Many authors used the measured magnetic moment to define the molar fraction of the different valance states, for transition element, exist in glass [28–30]. Figure 5 shows the fitted temperature dependence of electrical conductivity for glass doped with oxides [using Segmaplot graphic (11) Program]. It is clear that the dependence of ln σ on $1/T$ does not accord with the Arrhenius equation behavior for all samples except that one containing barium oxide. The absence of linearity for most glasses suggested that the nature of conduction is polaronic in nature and confirms the semiconducting behavior of glasses containing high amount of transition metal ions [13, 17]. Barczyński and Murawski [11] suggested that the

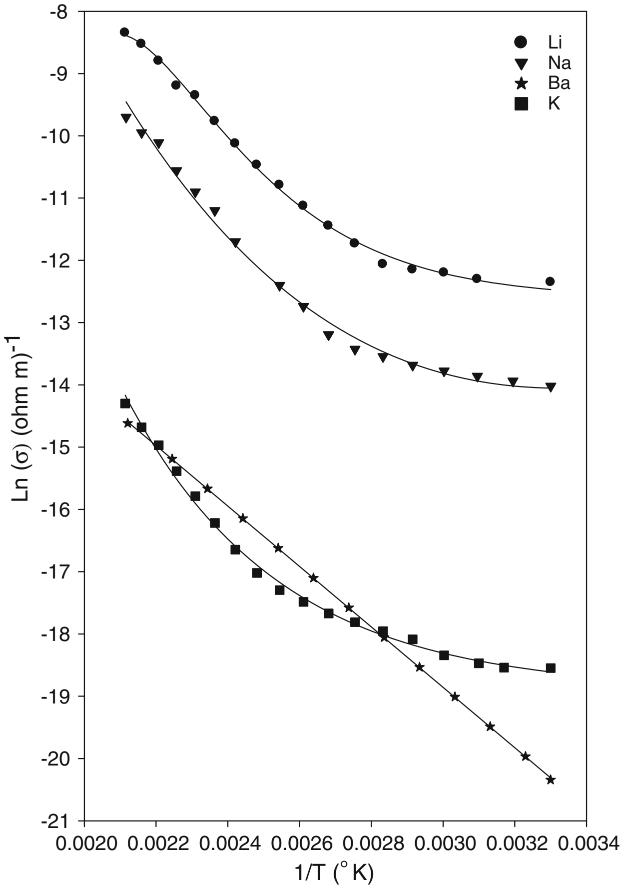

Fig. 5 Temperature dependence of electrical conductivity for different glasses

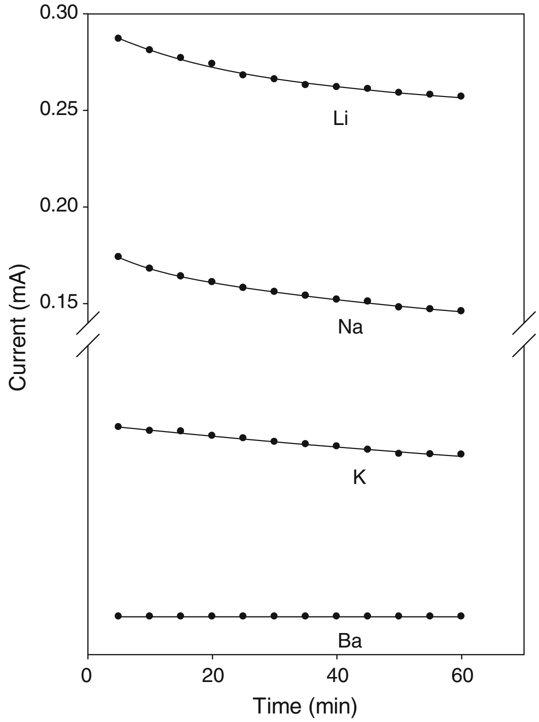

Fig. 6 Variation of current with time at constant temperature (300 K). *Lines* joining the points are guides to the eye

conduction of vanadium phosphate glasses containing different doping oxide is partly ionic and partially electronic and that ions are not mobile in these glasses, only Li ions can contribute in ionic conduction. Devidas et al. [13] suggested that all alkali can contribute in the ionic conduction of vanadium phosphate glasses. To ensure the electrical carrier charge type a constant direct electric field (100 V) was applied for a long time and current was found to decrease with time, up to nearly constant value, indicating the presence of two type carriers ions and electrons [14, 31, 32]. Figure 6 shows the variation of DC current with time at constant temperature. It is obvious that the current decreases with time until nearly constant value, only the sample containing barium is constant all through the range indicating that the conduction is only electronic. The dc conductivity of compound is given by $(\sigma_{\mathrm{dc}})_{\mathrm{total}} = \sigma_{\mathrm{ion}} + \sigma_{\mathrm{el}}$, where σ_{ion}, σ_{el} are the conductivity due to ions and electrons, respectively. The instantaneous value of current at a fixed temperature gives $((\sigma_{\mathrm{dc}})_{\mathrm{total}})$ total and the final stabilized value of it gives σ_{el}. The least square linear lines were fit to the data of temperature dependence of electrical conductivity for glass doped with different oxides [using Segmaplot graphic (11) Program] produce linear line with different slopes for all samples except the sample containing barium as shown in Fig. 7. The above findings suggest that a similar conduction mechanism for all glasses except the sample containing barium. The activation energies for conduction W_1 (low temperature region) and W_2 (high temperature region) are calculated from the slopes of lines in Fig. 7. The lower value of activation energy, in all temperature regions, for the studied glasses could be due to the electronic conduction mechanism [33]. Therefore, the conduction in the studied semiconducting glasses containing transition metal oxides as, V_2O_5 could be described according to the expression proposed by Mott as follows [13, 17, 33]:

$$\sigma = \nu C\,(1 - C)\,\left(e^2/RKT\right)\exp(-2\alpha R)\exp(-W/KT) \qquad (4)$$

where ν is the characteristic phonon frequency of the lattice, α the rate of wave function decay, R the average hopping distance, C the ratio of ion concentration in low valance state to the total concentration of transition metal ions, e the electronic charge, K the Boltzman constant, T the absolute temperature, and W the activation energy. Equation 4 represents non-adiabatic hopping mechanism of small polaron hopping conduction and is usually used to study the Dc conductivity of glass containing transition metal ions. The term exp $(-2\alpha R)$ represents the electron overlap integral between sites. Comparing Eq. 4 with the well known Arrhenius equation:

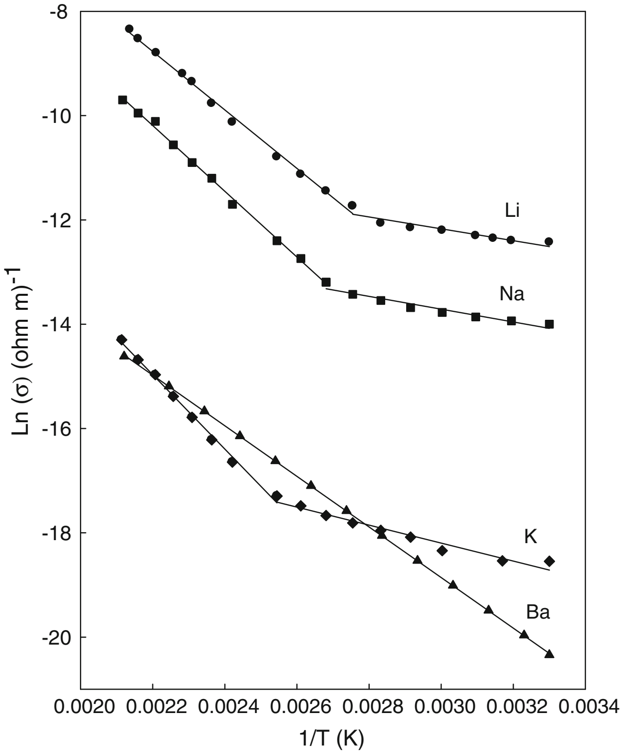

Fig. 7 The relation between Ln (σ) (ohm m)$^{-1}$ and 1/T (K) for different doping oxides

$$\sigma = \sigma_o \exp(-W/KT) \tag{5}$$

σ_o can be calculated from Fig. 7 and we can use

$$\sigma_o = \nu C(1 - C)\left(e^2/RKT\right)\exp(-2\alpha R) \tag{6}$$

Different values for ν were used [17, 33] to determine α for given values of R and C. The activation energy W is given by [13, 17]

$$W = W_H + W_D/2 \quad \text{for } T > \theta_D/2 \tag{7}$$

$$W = W_D \quad \text{for } T > \theta_D/4 \tag{8}$$

where W_H is the polaron hopping energy, W_D the disorder energy, and θ_D the Debye temperature. W_H can be calculated using the equation [17]:

$$W_H = \left(e^2/4\varepsilon_p\right)\left[\left(1/r_p\right) - (1/R)\right] \tag{9}$$

where r_p is the polaron radius and ε_p the effective dielectric constant. Assuming the uniformly distribution of transition metal ions inside the glass, the R values can be calculated using the equation [13, 34]:

$$R = (4\pi N/3)^{-1/3} \tag{10}$$

where N is the number of transition metal ions per unit volume. The r_p values can be calculated using the equation [17]:

$$r_p = \tfrac{1}{2}(\pi/6N)^{1/3} \tag{11}$$

The polaron binding energy W_p is given by [17]:

$$W_p = e^2/2r_p\varepsilon_p \tag{12}$$

Using the same assumption as Mansour et al. [17], the values of W_1, W_2, $W_2 - W_1$, R, r_p, ε_p, and W_H were calculated and tabulated in Table 2.

From the above discussion we can conclude that the electronic hopping conduction occurs between V^{4+} and V^{5+} [10, 13], and activation energy of electronic conduction (W_1) increase with increasing (R), the average hopping distance. This result is in agreement with the magnetic result which indicate that the magnetic susceptibility decrease with increasing (R) due to the decreasing of magnetization (magnetic moment per unit volume). In contradiction to [13, 17], one believes that (W_2) represents the total activation energy, for electronic and ionic conduction, while they suggested that it represent the electronic activation energy. The ionic conduction occurs for all samples except the sample containing barium. W_2 start at different temperature depends on the atomic weights of the doped ions in the matrix. One try to estimate the starting temperature of barium ionic conduction and the activation energy required for barium ions by subtracting W_1 from W_2, to get the activation energy for ionic conduction. The extension of (1/T) and ionic activation energy as a function of atomic weight for first three samples, yields the results as shown in Fig. 8. From it, one can conclude that the starting temperature of barium ionic conduction is 625 K and this temperature is out of reaching in our measurements. Also this temperature is out of glassy range, where the crystallization temperature as obtained from DTA spectra is about 863 K. The barium ionic activation energy is 0.691 eV, and this value is about twice for

Table 2 Some physical parameters of studied glasses

Glass	W_1 (eV)	W_2 (eV)	$W_2 - W_1$ (eV)	R (Å)	r_p (Å)	ε_p ($c^2\ N^{-1}\ m^{-2}$)	W_H (eV)
Li	0.098	0.48	0.382	3.16	1.274	32×10^{-10}	0.059
Na	0.12	0.54	0.42	3.22	1.296	26×10^{-10}	0.071
K	0.15	0.61	0.46	3.46	1.395	19×10^{-10}	0.09
Ba	0.42	–	–	3.51	1.414	6.7×10^{-10}	0.25

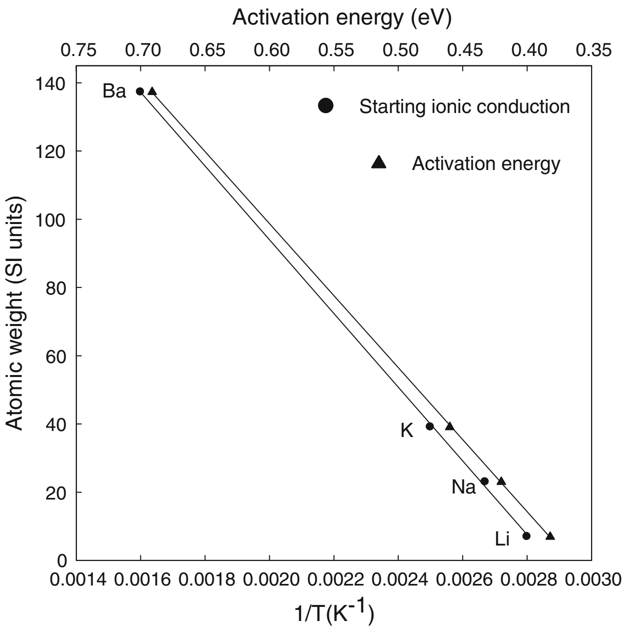

Fig. 8 Estimation of barium ion activation energy and starting ionic conduction. *Lines* joining the points are guides to the eye

lithium ion and about one and half for sodium and potassium ions. Finally, one found that the results are consistent with [12, 33], where the conductivity decreases with increasing doping atomic weights and the (ln σ) versus ($1/T$) yields straight lines with different slopes. Also, the results are partially in agreement with [11, 13], where the ionic conduction occurs for small ions (lithium, sodium, and potassium) while the ionic conduction of barium is not detectable. Finally, the obtained results are in contradiction with [34], where sodium and potassium show detectable contribution on the ionic conductivity.

Conclusions

Density, molar volume, and IR studies showed that doping ions occupy interstitial positions and act as glass modifiers. Vanadium ions exist in the two valance states V^{4+} (act as glass modifier) and V^{5+} (act as glass former). The valance states act as hopping centers in the electronic conduction. The DC conductivity decreases (the activation energy increase) with increasing both the hopping separation distances and atomic weight of doped ions. Magnetic susceptibility decreases with increasing both atomic weight and ionic radius which decrease the magnetization and increase the average separation distance. All doped ions shared the ionic conduction except barium ions which could be share this conduction at higher temperature and need more activation energy.

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