

DSC and FTIR Studies in Potassium, Strontium Doped Boro-Phosphate Glasses

Anand Thipperudra¹ *N.Nagaraja² M. PrashanthKumar³ B. Arunkumar¹

1. Research Scholars, Physics Research Centre VTU, Rao bahadur Y. Mahballewarappa Engineering College, Ballari, Karnataka, India

2. Professor Physics Research Centre VTU, Rao bahadur Y. Mahballewarappa Engineering College, Ballari, Karnataka, India

3. Professor Dept. of physics Govt. first grade collage Kalaburagi, Karnataka, India

Abstract

A series of five samples of boro-phosphate glasses doped with K₂O and SrO within the composition of 20(B₂O₃) + 30(P₂O₅) + x (SrO) + (50-x) (K₂O) where x = 10, 20, 30, 40 and 50 were prepared by the melt quench technique. The samples were annealed to remove if any thermal strains present. The Non-crystalline nature of the glass samples was confirmed by XRD studies. The Samples were DSC studied in the temperature range from 423K to 673K and glass transition temperature was determined. T_g various nonlinearly with SrO mole fraction. FTIR study shows the existence of different structural groups such as BPO₄, BO₃ and BO₄ units in the network. Borophosphate glasses containing SrO and K₂O which exhibits different IR bands related to SrO structural units. In the FTIR studies the increase in number of NBO's were observed in the structure of the present glass composites with increase of SrO up to 30 mole fraction and further increase of SrO the number of NBO's decreased. Number of NBO's and glass transition temperature with mole fraction of alkaline earth ions termed as mixed cationic effect. This is for the first time the boro phosphate glasses doped with K₂O and SrO reported for dc electrical transport and structural studies.

Keywords: Borophosphate glasses, K₂O, SrO, NBO's, etc.

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1. Introduction

Glassy electrolytes characterized as amorphous structures are now widely used for solid state ionic devices such as lithium ion batteries, sensors, fuel cells, electro chromic displays and in high energy density batteries etc. Warburg et al in 1984 explored ion transport in glasses by applying dc voltage [1-5]. The ionic conductivity in oxide glass systems doped with alkali and alkaline earth ions is due to migration of ions from one ionic site to another ionic site by hopping [6-7]. However the amorphous structure and non-equilibrium nature of oxide glass systems often hinder the fundamental understanding of their ionic transport mechanism [8]. Generally the fast ion conducting glasses are formed by three components; glass network former, metal oxides acting as a glass network modifier and dopant cations. The glass network formers are oxide materials of covalent nature, the assembly of oxygen tetrahedral or trigonals for example B₂O₃ and P₂O₅ etc [9]. In ion conducting glasses the electronic contribution to the total conductivity is usually very weak, which is the consequence of periodic potential fluctuations imposed by the disordered structure [10]. Researchers reported mixed cation effect in ionic diffusivity as well as in the glass transition temperature in a glass system xNa₂O-(1-x) CaO-SiO₂ and xK₂O-(1-x) BaO-SiO₂ [11]. In these glasses the mixed cation effect is due to movement of two dissimilar ions of unequal size are escorted by the formation of intrinsic defects in glass forming network when mobile cation enters foreign sites. It is somewhat similar and opposite to mixed alkali effect in mixed alkali glasses but size is very less pronounced due to smaller mobility of the alkaline earth cations. In the alkali and alkaline earth glass systems the energy landscape is contain monocharged alkali ion sites and double charged alkaline earth ion sites and both types mobile cations apply either of vacant sites without readjustment [11-12]. The presence of single charged alkali ions in a number of alkali and alkaline earth glass systems, binary charged alkaline earth cations proved greater diffusivities than in two alkaline earth glasses [13, 14]. In many oxide glass systems mixed cation effect has not been observed [15, 16]. Only few of the researchers reported the classical mixed cation effect in few of the oxide glass systems due to migration of single cation species [17-18]. It is known that the structure and properties of oxide glasses are strongly dependent on the nature and concentration of the constituent oxides and dopants. Although there exist numerous studies on binary and ternary tellurite and phosphate glasses containing B₂O₃, MgO, NiO and WO₃, on thermal and structural behavior studied in detail [19-20]. Many researchers investigate the essential information concerning the structural and compositional differences of bulk glasses using FTIR [21]. Researchers reported that the vibrational modes of the borate and phosphate networks are mainly active in three infrared spectral regions. Assignments of various peaks in the spectra have been made on the basis of literature reports [22-23]. The designation of non-bridging oxygen atoms increase with BO₃ structural units and systems show bands at about 400-4000 cm⁻¹ [24-25]. Thermal characterization (DSC/DTA) provides valuable, indirect information about the

structural changes that take place in a glass system with the composition [26]. The change in glass transition temperature (T_g) values indicate definite changes in the glass network. The endothermic peaks corresponding to the glass transition (T_g) gives information on both the strength of inter atomic bonds and the glass network connectivity, in a similar way that the melting temperature does it for crystalline solids [27]. In many ion conducting glass systems the Nernst-Einstein relation have been used to relate the diffusion coefficient and electrical conductivity [28]. However there were not many reports in the literature on density, molar volume, dc electrical conductivity, FTIR and DSC studies on boro-phosphate glasses doped with K₂O and SrO.

In the present paper, the experimental results on XRD studies, room temperature density, molar volume, temperature dependent dc conductivity, high temperature activation energy, FTIR and DSC studies on boro-phosphate glass systems doped with K₂O and SrO in the composition range 20(B₂O₃) + 30(P₂O₅) + x (SrO) + (50-x) (K₂O) where x = 10, 20,30, 40 and 50 are presented.

2. Theory

2.1. Density and molar volume

The density of glass samples generally is given by Archimedes principle equation as,

$$\rho = \frac{W_{\text{air}}}{W_{\text{air}} - W_L} \rho_L \text{ g/cm}^3 \quad (1)$$

The molar volume of the glass samples is given by the following formula,

$$V_i = \frac{X_i M_i}{\rho_i} \quad (2)$$

Where ' V_i ' molar volume, ' x_i ' is the mole fraction, M_i is the molecular weight and ρ_i is the density of i^{th} glass sample where $i = 1, 2, 3, 4$ and 5^{th} glass sample. In oxide glasses mobile cationic concentration (N) has been evaluated using density values and the following equation,

$$N = 2[(\rho m_{\text{Alkali}} / M_{\text{Alkali}}) N_A] \quad (3)$$

2.2. Electrical conductivity

As per as many theoretical predictions and experimental results, various theoretical models were proposed to explain the conduction mechanism in ion conducting glass systems [29-30]. However no single theoretical model investigated till today which would explain completely the ion conduction mechanism over entire temperature range. In general the total conductivity of material σ_T is equal to the sum of the contributions of all charge carrying species σ_i and is given by

$$\sigma_i = \sum_i \sigma_i = \sum_i (t_i \sigma_i) \quad (4)$$

Where ' t_i ' represents the transference number or the fractional contribution of a particular species of σ_T . For glass systems in which the conduction mechanism is dominated by a single type of ion species, for example Ag⁺, Li⁺, K⁺ etc. the equation (1) simplified as,

$$\sigma_i = \sigma_{\text{ion}} \quad (5)$$

In general the conductivity of glass systems in which one type of mobile ion species taking part in conduction mechanism is given as,

$$\sigma = nZe\mu \quad (6)$$

Where ' n ' is the number of mobile ions per unit volume and ' μ ' is the mobility. Both are temperature dependent. Nernst-Einstein assumed the equivalence of the gradient in particle concentration which results from driving force for diffusion equal to external force. In case of ionic conduction the drift force is related to applied electric field, and Nernst-Einstein obtained the expression for diffusion coefficient and is given by the relation i.e.

$$D(\sigma) = \frac{\sigma kT}{n(Ze)^2} \quad (7)$$

Where ' D ' the diffusion coefficient, ' σ ' the electrical conductivity, ' k ' the Boltzmann constant, ' T ' the temperature of the glass system, ' n ' the mobile cation concentration, ' Ze ' the charge of the ion. From statistical random walk calculations on the basis of thermal activated process, the free energy for motion of cations for electrical conductivity in the oxide glass systems is given by [7],

$$\sigma = \frac{Ne^2 l^2 v_0}{6kT} \exp\left(-\frac{\Delta G_F}{2kT}\right) \exp\left(-\frac{\Delta G_m}{kT}\right) \quad (8)$$

$\Delta G_F = \Delta H_f - \Delta S_f$ the free enthalpy associated with the formation of an interstitial ionic pair, $\Delta G_m = \Delta H_m - \Delta S_m$ the free enthalpy (entropy) associated with the migration of cations, ΔH_m (enthalpy of motion) is the height of the potential barrier between two sites.

For glasses in which single type of ion transport dominating, for example alkali and alkaline earth doped oxide glass systems in which alkali ion is mobile and alkaline earth ion is immobile, the electrical conductivity from the above equation Eq. (7) can be simplified as [31-32].

$$\sigma T = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \quad (9)$$

Where ' σ ' is the temperature dependent dc electrical conductivity, ' T ' is the temperature of the sample and ' σ_0 ' is

the pre exponential factor and is given by,

$$\sigma_0 = \frac{Ne^2l^2v_0}{6kT} \exp\left(\frac{\Delta S_f + \Delta S_m}{2}\right) \quad (10)$$

Where 'N' is the mobile cation number density, 'e' the charge of the proton, *l* is the jump distance between two adjacent ionic sites, *v*₀ the vibrational frequency of ion in a potential well, 'k' is the Boltzmann constant, 'T' is the absolute temperature, and the dc activation energy is given by the expression,

$$E_a = \frac{\Delta H_f}{2} + \Delta H_m \quad (11)$$

In the present work, the conductivity of the glassy system has been found to obey the Nernst Einstein relation above the glass transition temperature as given by Eq. (7). Assuming a homogenous distribution of ions in the glass, the mean jump distance between adjacent alkali ion sites is related to alkali ion concentration as $l = (1/N)^{1/3}$.

3. Experimental techniques

The required amount of analytical grade chemicals such as Boric acid (H₃BO₃), Ammonium Sulphate (NH₄H₂PO₄), Potassium Sulphate (K₂SO₄) and Strontium oxide (SrO) were thoroughly mixed by manually grinding in an agate mortar then transferred to porcelain crucible. The grinded chemicals mixture was heated to melting temperature at 1253K in a high temperature electrical muffle furnace. When homogeneous transparent melt was formed, then the melt was rapidly quenched using two stainless steel plates and the random glass pieces formed were collected. The samples were subjected to annealing by heating them for an hour up to 573K and left them for slow cooling for 4 hour.

The samples were subjected to X-ray diffraction studies using Bruker D8 Advanced Diffractometer at IISER, Pune.

Room temperature density, ρ was determined by following Archimedes principle equation (1) using sensitive single pan balance (Citizen Cy204) with an accuracy of 0.1 mg and toluene C₇H₈ as an immersion liquid.

Glasses were well shaped to the required sizes for the measurement of dc conductivity. The thickness of the samples was lying between 1.3mm to 2.5mm and the cross sectional area ranging between 1.5 mm² to 1.8 mm². Silver paste was painted on two major surfaces of the samples. The DC conductivity measurements were carried out by following two-probe technique for the temperature range from 308K to 503K. The temperature of the sample was determined to the accuracy of ± 1 K using a chromel– alumel thermocouple and digital micro voltmeter. A constant dc voltage of about 5V was applied across the sample. The current passing through the sample and voltage was measured with the help of a digital Pico ammeter and digital multimeter respectively to an accuracy of ± 0.1 pA and ± 10 volts. The conductivity, σ of the samples were calculated using $\sigma = (l/\rho)$ where the electrical resistivity, $\rho = (RA/t)$, where *R* is resistance, 'A' the cross sectional area and 't' thickness of the sample.

Infrared absorption spectra were recorded on a FT-IR spectrometer in the wave number range 400-4000 cm⁻¹ using pellets made with KBr and finely ground glass powder in a 20:1 ratio by weight model RX-1 FTIR spectrometer in organic chemistry lab at IISER Pune.

The glass systems were subjected to DSC studies using Differential Scanning Calorimetry model-DSC Q20 V24.11 Build 124 from room temperature to 500 °C with a heating rate of 10 °C per minute at common chemistry lab IIT Mumbai.

4. Results and discussions

4.1. XRD Diffraction

All the samples showed no sharp peaks in their XRD pattern [33]. The XRD pattern of one sample BPSK4 and BPSK5 is depicted in Fig 1. Similar patterns were obtained for the remaining samples which confirm the non-crystalline nature of all the samples. To save the space only the graph of two sample is depicted.

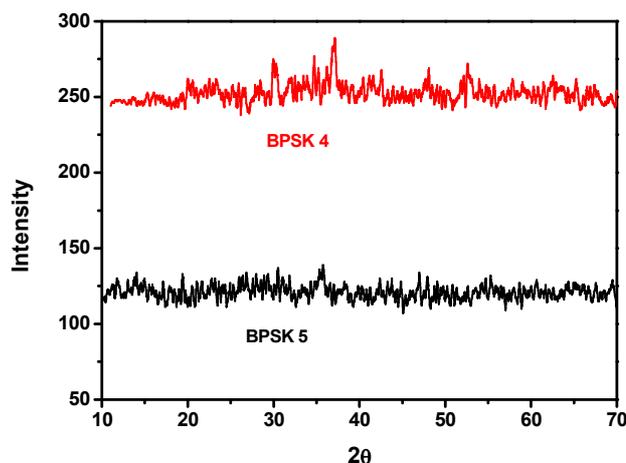


Fig.1. XRD Patterns of sample.

5. DSC

The temperature corresponding to the first dip has been considered to be the glass transition temperature. Similar natures of thermo grams were obtained for other four number labelled samples. Because of the availability of DSC for limited amount of time, variation of glass transition temperature versus mole fractions of SrO content is shown in figure 2.

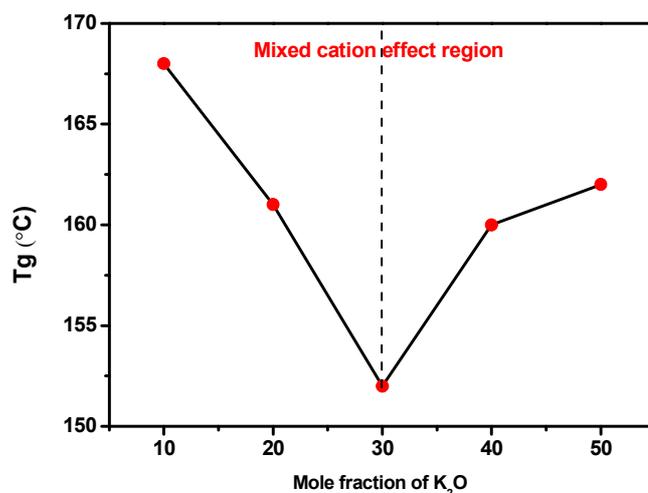


Fig.2. T_g (DSC) Vs Mole fraction (x) of SrO.

It can be seen that T_g varies non-linearly with mole fractions of SrO and become minimum around 0.3. In an oxide network, T_g is known to depend upon the packing in the network and hence the rapid decrease of glass transition temperature in the borophosphate glasses can be related to the cross-linking of the network thus providing better thermal stability for the mixed cation effect. Thus, the variation in T_g with composition can be attributed to the looseness of packing in the network. DSC curves of all compositions are shown in Fig 6. In many glass systems the density and glass transition temperatures varies non linearly but initially increases up to certain mole fractions of SrO hits the maximum peak and further increase of SrO both decreases [34].

In our present glasses 'N' ion concentration, 'l' jump distance, and observed the nonlinear variation in dc conductivity 'σ' activation energy 'W_{dc}', diffusion coefficient 'D' and Glass transition temperature 'T_g' can be attributed that the mixed cation effect taking place at x=30 mole fractions of SrO ion concentration.

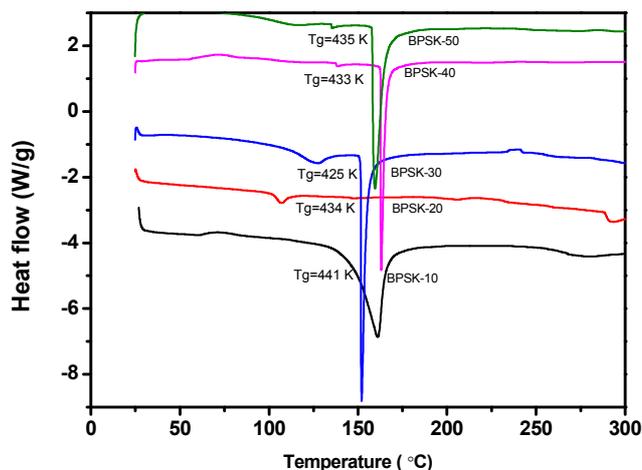


Fig.3. Tg (DSC) of all the 5 BPSK glass samples.

Table. 2 The variation of dc activation energy and conductivity, σ , at 500K

glass samples	N (m^{-3})	l (nm)	D (m^2/s)	σ ($ohm\ m^{-1}$)	W_{dc} (eV)	T_g (K)
BPSK 1	31.97×10^{28}	6.788×10^{-10}	8.78×10^{-19}	1.40×10^{-8}	0.52	441
BPSK 2	22.95×10^{28}	7.581×10^{-10}	2.16×10^{-18}	2.48×10^{-8}	0.48	434
BPSK 3	8.45×10^{28}	0.105×10^{-10}	7.07×10^{-17}	2.98×10^{-7}	0.22	425
BPSK 4	5.70×10^{28}	0.120×10^{-10}	4.22×10^{-18}	1.20×10^{-8}	0.48	433
BPSK 5	0.749×10^{28}	0.237×10^{-10}	7.66×10^{-16}	1.43×10^{-7}	0.18	435

6. FTIR STUDIES

The FTIR studies of oxide glasses gives the information not only about structure, but also about the coordination number of the compound with respect to oxygen, network formers and change in oxygen bonds of the framework which also is induced by the cations modifiers. The FTIR spectra of all the present series of samples of borophosphate glasses doped with SrO and K_2O ions, is depicted in figure (7). The positions and assignments of the absorption bands of glasses are summarized in the table (3). Based on the literature various types of peaks, its assignments were observed [38-40], such that in the present glass series as SrO ion concentration increases at the cost of K_2O .

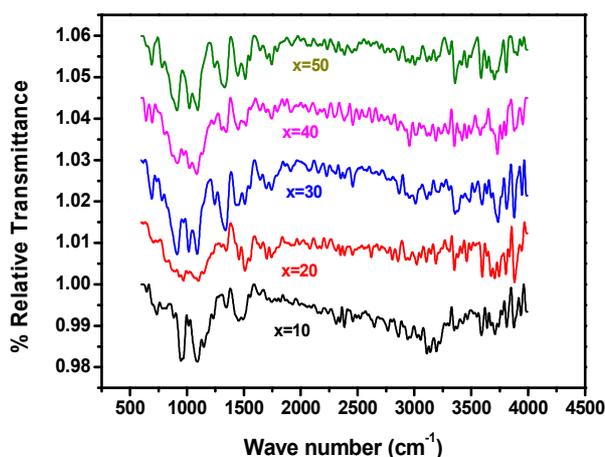


Fig.4. FTIR Spectra of all the 5 BPSK glass samples

From the figure 7. it observed that there are three distinct characteristic bands are present in the FTIR studies pattern for all the samples of borophosphate glass systems doped with SrO and K_2O , that is at

- i. Between wavenumber region 600 - 800 cm^{-1} – Various B-O-B and P-O-P bending modes in BO_3 , PO_3 , BO_4 and PO_4 , structural units are present.

- ii. Between 800 - 1250 cm^{-1} B-O stretching bond from BO_4 and P-O stretching bond from PO_4 tetrahedral units are present.
- iii. Between 1250 – 1600 cm^{-1} are present due to the asymmetric relaxation of B-O bonds from the BO_3 units and P-O bonds from the PO_3 structural units.
- iv. The band around 913-915 cm^{-1} reveals the presence of SrO [41] and at 720 cm^{-1} indicates the presence of K_2O in the structure of present series of glass samples.

In the spectrum the vibrational, asymmetric stretching and B-O-B network were seen at 704 cm^{-1} , 801-1098 cm^{-1} and 1010-1496 cm^{-1} , respectively. The B-O bands at 1345 and 945 cm^{-1} were seen for stretching vibrations both in the BO_3 and BO_4 units. The vibrational, asymmetric stretching and P-O-P network were seen at 616-741 cm^{-1} , 801-1098 and 1010-1496, respectively. The B-O bands at 993 and 1094 cm^{-1} were seen for stretching vibrations both in the PO_3 and PO_4 units. The P-O-P groups were shows asymmetric stretching in IR spectrum at 886 cm^{-1} which confirms the chain structure of borophosphate glasses.

The wave number for particular structural units and their assignments present in the glass systems were recorded from the FTIR spectrum and depicted in the table 3 and table 4.

Table:3 FTIR band assignments of BO_3 , BO_4 of SrO and K_2O doped Boro-Phosphate glasses

Glass samples label	Wave number / (cm^{-1})	Assignments
BPSK-10	647, 720,739,787, 779 935,967,1010,1231	600 - 800 cm^{-1} Various B-O-B and P-O-P bending modes in $[\text{BO}_3]$ $[\text{PO}_3]$ $[\text{BO}_4]$ and $[\text{PO}_4]$ units. 800 - 1200 cm^{-1} –B-O and –P-O bond stretching of the $[\text{BO}_4]$ $[\text{PO}_4]$ tetrahedral units. 1200-1600 cm^{-1} – Asymmetric stretching vibrations of B-O bonds and P-O from the $[\text{BO}_3]$ $[\text{PO}_3]$ trigonal units. 2000 ~3400 cm^{-1} are B_2O_3 and P_2O_5 functional groups.
BPSK-20	720,818,868,892,935, 945,967,969,1010, 1015,1065,1098,1147 1234	
BPSK-30	720,892,973,1022,1245, 1248,1337,1431,1455 1507,1554	
BPSK-40	720, 886, 971, 973, 1021, 1234,1236, ,1245, 1248,1266	
BPSK-50	780,967,913,1014,1236 3425,3420,3423, 3421,341	

Table: 4 Wave numbers of BO_3 , BO_4 , PO_3 , PO_4 and SrO K_2O .

Glass sample	BO_3	BO_4	PO_3	PO_4	SrO	K_2O
BPSK 1	1231	935	967	1010	945	720
BPSK 2	1234	945	969	1015	935	720
BPSK 3	1237	1022	973	1022	913	720
BPSK 4	1245	973	971	1021	913	720
BPSK 5	1236	913	967	1014	915	000

The broad band at 779 cm^{-1} may be attributed to the symmetric stretching vibration of P-O-P rings [35]. In the spectra boroxol group ring stretching takes place between 1450-1457 cm^{-1} and the B-O-B vibration at 1236-1248 cm^{-1} . For the BO_3 the bending and stretching vibrations is observed this is mainly due to the non-bridging oxygens (NBOs) at 689 and 1345 cm^{-1} respectively. Similarly in the Phosphate group ring stretching takes place between 1450-1457 cm^{-1} in the P-O-P vibration at 1245 cm^{-1} . For the PO_3 the bending and stretching vibrations is observed this is mainly due to the non-bridging oxygens (NBOs) [36]. Here, the oxygen atoms that are not shared between tetrahedral are known as non-bridging oxygen's [37]. When it links with trtrahedra together it is known as bridging oxygen. The Electrical conductivity of oxide glasses varies with variation of NBO's which results due to adding of Alkali/Alkaline earth ion [38]. In the FTIR of present series of glass samples the group of bands that occur at 1236-1496 cm^{-1} is due to the asymmetric stretching and the relaxation of B-O Bond of triangle BO_3 units [46]. Here when SrO ions added initially it converts BO_4 units into BO_3 and PO_4 units into PO_3 structural units and generates BO_3 and PO_3 units with NBO [39]. The concentration of NBO's increases with the addition SrO

ions into the glass matrix up to 30 mole fraction and further increase of SrO The NBO concentration decreases [40]. The bands near 647 and 1345 cm^{-1} and 993 and 1094 cm^{-1} can be attributed to bending vibrations of BO_3 and PO_3 triangles and stretching vibrations of BO_3 and PO_3 units with non-bridging oxygen's (NBOs), respectively [41].

Correlation between dc conductivity and structure of the glasses

In oxide glasses the conductivity is directly proportional to number of NBOS [42]. The variation of the dc conductivity with the reciprocal of temperature for all compositions is shown in Fig. 1. The values of the activation energy obtained from the least squares linear fits for different compositions are given in Table 1. It is observed that the conductivity is strongly composition dependent for lower SrO content and higher K_2O content i.e. $\text{SrO} < 30$ and $\text{K}_2\text{O} > 30$ mole fraction for present glass systems, while the conductivity shows a weak composition dependence for higher SrO and lower K_2O content. In the literature no such studies were reported on borophosphate glass systems doped with SrO at the cost of K_2O . In the present glass systems the study reveals that the conductivity reaches maximum and activation energy reaches minimum, the density hits minimum value and molar volume hits peak value at 30 mole fraction of the SrO content. This may be due to the fact that, in these glasses the BO_3 structural units with NBO's concentration increase due addition of SrO up to 30 and K_2O 20 mole fraction and further increase of SrO and decrease in K_2O there is decrease in NBO's concentration[43]. It seems that the structural transformations as well as the increasing number of non-bridging oxygen's are responsible for conductivity enhancement with the increase of SrO and decrease of K_2O content in the present glass systems for $\text{SrO} \geq 30$ and $\text{K}_2\text{O} \leq 20$ mole fractions. The conductivity enhancement in this region is solely due to the increasing number of non-bridging oxygens, which are the preferential sites for the K^+ and Sr^+ ions. While the conductivity becomes less composition dependent for $\text{SrO} > 30$ and $\text{K}_2\text{O} < 20$, as no major structural transformation occurs in this composition range.

5 Conclusion

A set of borophosphate glasses incorporated with SrO and K_2O have been prepared and has been characterized through XRD, FTIR and DSC studies. Their non-crystalline nature was confirmed by XRD, The samples were measured for room temperature density and molar volume was estimated. The density and molar volume behaves in opposite fashion and nonlinear with increasing mole fractions of SrO and hits minimum and maximum peaks respectively at 30 mole fraction of SrO. The high temperature dc activation energy was determined by fitting the measured experimental data for Nernst Einstein relation. The Conductivity and activation energy found to behave in opposite fashion and hits maximum and minimum peaks respectively, at 30 mole fractions of SrO. The FTIR study shows the existence of different structural units such as PO_4 , PO_3 , BO_3 and BO_4 units. The observed variation of glass transition temperature with composition has been correlated with the structural modifications of the network. The nonlinear variation of the observed physical parameters such as density, molar volume, dc conductivity, high temperature activation energy, glass transition temperature, diffusion coefficient and structure with respect to mole fractions of SrO ion at the cost of potassium ion revealed that the classical mixed cation effect taking place in the present series of glasses.

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