Compositional dependence of properties in calcium substituted sodium borophosphate glasses containing VO^{2+} ions

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Abstract. Synthesis of calcium-substituted sodium borophosphate glasses with compositions $x\text{CaO} - (30 - x)\text{Na}_2\text{O} - 35\text{B}_2\text{O}_3 - 35\text{P}_2\text{O}_5$ ($x = 0, 2, 5, 7$ and 10 mol%, abbreviated as CNV x) containing additional 1.0 mol% of V_2O_5 following a melt-quench method has been carried out. Different analytical techniques *viz.* wide angle X-ray diffraction (to confirm non-crystalline nature), ultraviolet–visible spectroscopy (for optical band gap analysis), infrared absorption spectroscopy (for structural analysis) and differential thermal analysis (to evaluate characteristic temperatures) were employed to characterize the synthesized compositions. The optical band gap is calculated for both indirect allowed and indirect forbidden transitions. The values of the band gap decrease with increasing concentration of CaO (from 5 to 10 mol%) at the cost of Na_2O . The cut-off wavelength and Urbach's energy are determined from the optical absorption spectra and were related to the structural changes occurring in these glasses with an increase in CaO content. The results obtained from Fourier-transform infrared studies confirm that V_2O_5 and CaO play the role of network modifier oxides. Also, the significant shifting in IR bands with an increase in CaO content in the glass matrix suggests the formation of a new boron–oxygen ring. From differential scanning calorimetry measurements it is observed that substitution leads to the increase in natural bond orbitals, high degree cross-linking and thus strengthens the glass network. Glass transition temperature (T_g) is found to increase from 483 to 522°C . Electrical and dielectric properties are analysed using dc conductivity and impedance spectroscopy. Using impedance spectroscopy, different dielectric parameters *i.e.* dielectric loss (ϵ''), electrical modulus (M^*) and ac conductivity (σ_{ac}) etc. are evaluated as a function of frequency, temperature and composition. The frequency dependence of impedance exhibits the non-Debye relaxation behaviour and the total conductivity obeys Jonscher's power law.

Keywords. Band gap; differential thermal analysis; impedance spectroscopy; Jonscher's power law.

1. Introduction

Multi-component borophosphate glasses are often recognized due to their excellent performance towards a variety of applications [1]. Compared to their binary counterparts, these glasses have enhanced electrical conduction, glass formation range and optimized softening temperature which marks their suitability for solid state batteries [2], glass seals for solid oxide fuel cells, low melting glass solders [3,4] and non-linear optics [5,6]. The primary network forming units of borate glasses are 3-coordinated boron atoms, whereas that of phosphate glasses are 4-coordinated phosphorous atoms linked through covalent bonding with bridging oxygen atoms [7–10]. But, when the borate and phosphate matrices are mixed, a new linkage is formed between phosphate chains *via* P–O–B bonds [11,12]. Therefore, the properties of mixed borophosphate glass networks are different from individual borate and phosphate glass networks [13]. As a result of substitution of alkali/alkali earth modifiers in a borophosphate glass matrix, the degree of polymerization increases through the conversion of trigonal BO_3 units to tetrahedral BO_4 units [14] whereas in

the case of phosphate glasses polymerization decreases due to the replacement of P–O–P bridges with non-bridging oxygen [15]. Furthermore, the incorporation of a transition metal (vanadyl here) and rare earth ions in the borophosphate glass matrix leads to low melting temperature, high refractive index, high dielectric constant and good infrared (IR) transmission which make these materials suitable for application in optical fibres and non-linear optical devices [1].

The structural study of borophosphate glasses has been reported by many authors [5,16,17]. Their study reveals that the network of borophosphate glasses is mainly composed of BPO_4 and BO_4 units. Furthermore it has been found that the formation of BPO_4 units in the glass matrix makes the glass heterogeneous and produces a weak binding area around the structure of BPO_4 units that favour the easy migration of alkali ions [16]. The structural and ion transport study of the lithium borophosphate glass system was studied by Karan *et al* [17]. The study reveals that the inclusion of alkali oxide (Li_2O) forms continuous ion conducting channels in the glass matrix that are responsible for an increase in dc conductivity. Carta *et al* [4] studied the structural (Raman, IR, ^{31}P

and ^{11}B MAS NMR) and thermal properties of the sodium borophosphate glass system and concluded that these glasses can be used as bioresorbable materials due to their improved thermal stability and an increase in the bond length and the cross-linking network between phosphate and borate even at low content of B_2O_3 . Very recently, Tan *et al* studied high durability borophosphate glass and reported that addition of B_2O_3 increases the phosphate chain length, which leads to the ease of the fibre drawing process for biomedical applications [18]. As reported in the literature, a mixture of trivalent and pentavalent glass formers enhances the conductivity of the mixed glass [16,19]. Moreover, the replacement of alkali oxide with alkaline earth metal oxides like CaO and MgO to the glass matrix is believed to improve the mechanical strength, chemical stability, non-hygroscopic nature and thermal stability of the glasses [20,21]. Keeping in view the above points, an attempt is made to synthesize and investigate the physical, structural, optical, thermal, electrical and impedance spectroscopy characterization of vanadyl doped borophosphate glasses in the composition range $x\text{CaO} - (30 - x)\text{Na}_2\text{O} - 35\text{B}_2\text{O}_3 - 35\text{P}_2\text{O}_5 + (1.0 \text{ mol}\%) \text{V}_2\text{O}_5$.

2. Experimental

2.1 Synthesis

The glass samples with composition $x\text{CaO} - (30 - x)\text{Na}_2\text{O} - 35\text{B}_2\text{O}_3 - 35\text{P}_2\text{O}_5 + (1.0 \text{ mol}\%) \text{V}_2\text{O}_5$ in the range $x = 0$ (CNV1), 2 (CNV2), 5 (CNV3), 7 (CNV4) and 10 (CNV5) mol% were synthesized using Na_2CO_3 , CaCO_3 , H_3BO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$ and V_2O_5 (Himedia, India) as starting materials. The finely powdered raw chemicals were weighed in an appropriate amount using an electrical weighing balance (CAS CAUY 220). The weighed chemicals were mixed and ground in an agate mortar pestle. The obtained powdered mixture was collected in high alumina (99.9% pure) crucibles and melted in a muffle furnace at 1200°C for 1 h. In order to achieve better homogeneity, the melt was shaken manually at a regular interval of 15 min. Thereafter, the melt was quenched by sandwiching it between two stainless steel plates (preheated at 200°C) to obtain glass samples in a disc form. The obtained glasses were free from any bubble or stria. A part of each sample was ground into a powder form using a mortar and pestle for X-ray diffraction (XRD), Fourier-transform infrared (FTIR) and differential scanning calorimetry measurements. While for ultraviolet-visible (UV-Vis), dielectric and impedance spectroscopy, rectangular glass pieces were polished to optical quality using sand paper.

2.2 Characterization

XRD analysis of the powdered samples was performed in the range of 20 – 80° on an X-ray diffractometer (Rigaku Ultima IV) using Cu-K_α ($\lambda = 1.5406 \text{ \AA}$) radiation, at 40 kV and 40 mA. The density was measured at room temperature using the

Archimedes principle with Xylene as a standard immersion liquid.

FTIR spectra of all the synthesized glasses were recorded on a Perkin Elmer Frontier FTIR spectrometer at room temperature using a diffuse reflectance spectroscopy technique in the wavenumber range of 250 – 1600 cm^{-1} . The measurements were carried out at a resolution of 4 cm^{-1} . UV-Vis spectra of powdered samples were recorded on a Shimadzu (UV 2450 spectrophotometer) at room temperature in the wavenumber range of 200 – 850 nm .

Differential thermal analysis (DTA) of powdered samples was carried out from 200 – 900°C on a thermal analyser (STA 6000, Perkin Elmer, at the flow rate of 100 ml min^{-1}) at a heating rate of $20^\circ\text{C min}^{-1}$ using N_2 at the rate of 100 ml min^{-1} as a purging gas. The detailed information about thermal measurement is given by Khasa *et al* [22]. Characteristic temperatures viz. glass transition temperature (T_g), peak crystallization (T_p) and liquidus temperature (T_l) were evaluated from the obtained DTA curve. Rectangular shaped polished glass samples were taken for electrical conductivity measurement. Colloidal silver paint was applied on the opposite surface of each glass sample for electrode formation. dc conductivity measurements were carried out using a Keithley 2401 source-cum-electrometer in a four wire mode and a programmable pot muffle furnace in the temperature range of 353 – 633 K following a two probe method. A constant supply of 10 V was applied across the two terminals. Furthermore, in order to avoid the polarization effect, a toggle switch was used to change the polarity of the applied field and the value of current considered for conduction analysis was the average of dc current in both the directions.

Impedance spectroscopic measurements of polished rectangular samples (thickness ~ 5 – 8 mm) were carried out on an impedance analyser (HIOKI IM 3570) in the temperature range of 100 – 400°C and the frequency range of 1 kHz – 5 MHz .

3. Results and discussion

3.1 XRD, physical and optical basicity

Figure 1 shows the XRD profiles of all the synthesized glass compositions. The absence of any crystalline phase confirms the amorphous nature of the glasses under study. The study of density (ρ) gains fundamental importance in Glass Physics as it provides the information about change in the glass structure upon adding modifiers [23]. The density of glass is strongly influenced by any change in the coordination number, cross-link density, geometrical configuration and dimensions of interstitial spaces [23,24]. Furthermore, in order to obtain a better measure of compactness or expansion of the glass network structure, molar volume (V_m) is often calculated using the relation [25]:

$$V_m = M/\rho. \quad (1)$$

Figure 1. XRD profiles of $x\text{CaO} - (30 - x)\text{Na}_2\text{O} - 35\text{B}_2\text{O}_3 - 35\text{P}_2\text{O}_5 + (1.0 \text{ mol}\%) \text{V}_2\text{O}_5$ ($x = 0, 2, 5, 7$ and 10) composition.

Table 1 contains the measured values of ρ and the calculated values of V_m corresponding to each prepared glass composition. From this table, it can be clearly observed that density increases and molar volume decreases with enhanced substitution of CaO at the cost of Na₂O in the base borophosphate glass matrix. The value of density increases from 2.50 to 2.71 g cc⁻¹ while that of molar volume decreases from 37.7 to 34.6 cc mol⁻¹. The increase in the density can be governed by two factors: firstly, the molecular weight of Ca ions is more than Na ions. Secondly, the field strength of Ca²⁺ ions is higher than that of Na⁺ ions resulting in a compact glass structure [26]. Optical basicity for all samples was evaluated to understand the nature (covalent/ionic) of these glasses [27]. Duffy and Ingram [28] reported that ideal values of optical basicity can be predicted from the composition of the glass and basicity moderating parameters of various cations present in the glass matrix. The theoretical values of the optical basicity of glasses can be estimated using the formula:

$$\Lambda_{\text{th}} = \sum \frac{Z_i r_i}{Z_0 \gamma_i} \quad (2)$$

where Z_i is the oxidation number, r_i is the ratio of i^{th} cation to the number of oxides present and γ_i is the basicity moderating parameter of i^{th} cation which can be evaluated using the relation:

$$\gamma_i = 1.36(x_i - 0.26) \quad (3)$$

where x_i is Pauling's electronegativity of i^{th} cation. To understand the role of trends in basicity, oxide ion polarizability (α_0^{2-}) has been calculated using the equation proposed by Duffy [28]:

$$\Lambda_{\text{th}} = 1.67[1 - (1/\alpha_0^{2-})]. \quad (4)$$

This equation suggests that α_0^{2-} has the same trend as that of optical basicity. The calculated values of both Λ_{th} and α_0^{2-} are reported in table 1. The decreasing trends in basicity and polarizability (as seen from table 1) are an indication towards the enhanced covalent nature of the prepared glass compositions as the amount of CaO is increased. Thus, the addition of CaO decreases the polarizing power of the glass matrix that leads to a decrease in sigma bonding between V⁴⁺ ions and the ligands [29].

3.2 FTIR

There are numerous vibrational techniques available to investigate the structural changes in glasses [19]. Among them, IR spectroscopy has its own importance as it provides a quantitative analysis of the molecular vibrations associated with glass networks [28]. FTIR spectra of all the synthesized compositions are shown in figure 2. Several IR absorption bands along with some shoulders can be observed which may be assigned to their respective structural vibrations. As per the literature, the basic building units of borate glasses are BO₃ tetrahedra whereas those of phosphate glasses are PO₄ tetrahedra connected through covalent bonding with oxygen [25,30]. The structure of borate and phosphate glasses can be divided into three regions. The region between 600–800 cm⁻¹, 800–1150 cm⁻¹ and 1150–1600 cm⁻¹ in borate glasses corresponds to bending vibrations of three coordinated boron in various borate segments, stretching vibrations of BO₄ units and asymmetric stretching vibrations of BO₃

Table 1. Physical (ρ and V_m) parameters, optical basicity and ion polarizability of synthesized $x\text{CaO} - (30 - x)\text{Na}_2\text{O} - 35\text{B}_2\text{O}_3 - 35\text{P}_2\text{O}_5 + (1.0 \text{ mol}\%) \text{V}_2\text{O}_5$ ($x = 0, 2, 5, 7$ and 10) composition.

Sample code	Density (ρ) (g cc ⁻¹)	Molar volume (V_m) (cc mol ⁻¹)	Optical basicity (Λ^{th})	Ion polarizability (α_0^{2-})
CNV1	2.50	37.7	0.527	1.462
CNV2	2.52	37.3	0.526	1.460
CNV3	2.57	36.6	0.525	1.459
CNV4	2.61	35.9	0.525	1.457
CNV5	2.71	34.6	0.523	1.456

Figure 2. FTIR spectra of the prepared composition.

units respectively [31], whereas in the case of phosphate glasses, the regions between $700\text{--}900\text{ cm}^{-1}$, $900\text{--}1150\text{ cm}^{-1}$ and $1150\text{--}1400\text{ cm}^{-1}$ are attributed to vibrations of bridging P–O–P groups, vibrations of terminal P–O (and PO_3 group) and vibrations of non-bridging PO_2 groups respectively [32]. However, due to the same content of B_2O_3 and P_2O_5 , it is difficult to obtain direct information on the interconnection of borate and phosphate networks due to an overlapping between their characteristic bands. Furthermore, the addition of alkali oxide or alkaline earth oxide leads to a change in the structure of primary borate glass by converting some of the BO_3 units into BO_4 ones.

FTIR spectra of the synthesized compositions in the active IR borate region consist of five absorption peaks centred at ~ 612 , 870 , 1130 , 1360 and 1500 cm^{-1} . The absorption peak at $\sim 612\text{ cm}^{-1}$ can be attributed to the bending vibrations of BO_3 units [31,33]. The peak at $\sim 870\text{ cm}^{-1}$ may be assigned to the combined vibrations of both non-bridging PO_2 groups and sharing of BO_4 groups thus forming BPO_4 units [34–36]. A broad band which is characteristic of the asymmetric stretching vibrations of PO_2 groups is observed at $\sim 1130\text{ cm}^{-1}$. The IR peak observed at $\sim 1500\text{ cm}^{-1}$ along with a shoulder at 1360 cm^{-1} corresponds to the asymmetric stretching vibrations of BO_3 units [31]. This peak shifts towards a higher wavenumber indicates a blue shift. Furthermore, this peak is found to be highly intense and broad for the CNV4 sample.

IR analysis reveals that the incorporation of CaO up to 5 mol% does not have a remarkable impact on the glass structure. However, beyond 5 mol% of CaO, the change in the position and intensity of IR absorption peaks is noteworthy and strongly influences the glass structure. A close look at figure 2 suggests that for a higher concentration of CaO (CNV3, CNV4 and CNV5 samples), more resolved peaks are observed in the region of $1300\text{--}1500\text{ cm}^{-1}$ which

indicates the ordered arrangement in these compositions. The IR band at $\sim 1130\text{ cm}^{-1}$ is found to be red shifted from 1140 to 1125 cm^{-1} which is expected as the band formed by Ca with oxygen is more covalent than that of Na. Thus, the phosphorous oxygen bond P–O–Ca is more ionic than P–O–Na. The formation of P–O–Ca bonds replaces some of these P–O– Na^+ bonds on replacing Na_2O by CaO [37]. This leads to an increase in the cross-link density of the glass network. Another possible reason for shifting of this peak can be due to the formation of new BPO_4 units [38]. Furthermore, the peak at 1360 cm^{-1} is intensified and spreads with the addition of CaO indicating that most of the BO_4 units are converted to BO_3 ones leading to a generation of more non-bridging oxygen atoms (NBOs).

3.3 UV–Vis absorption spectra

The absorption spectra of glasses containing vanadium are usually complex due to the presence of three valence states of vanadium viz. V^{3+} , V^{4+} and V^{5+} [39]. The valence state attained by vanadium depends primarily on the type and composition of host glass [34]. In phosphate glasses, tetravalent (VO^{2+}) and trivalent vanadium units (VO^{3+}) are dominant species while in the case of alkali borate glasses, higher oxidation states are favoured [34,39]. Furthermore, from the literature [40,41], it can also be concluded that V^{5+} ions belong to the d^0 configuration and exhibit only UV absorption while V^{3+} and V^{4+} ions are known to exhibit the characteristic band in the visible region. The UV–Vis absorption spectra of $x\text{CaO} - (30 - x)\text{Na}_2\text{O} - 35\text{B}_2\text{O}_3 - 35\text{P}_2\text{O}_5$ glasses containing 1.0 mol% of V_2O_5 measured at room temperature in the wavelength range of $200\text{--}900\text{ nm}$ are shown in figure 3. A peak at $\sim 660\text{ nm}$ corresponding to the ${}^2\text{B}_{2g} \rightarrow {}^2\text{B}_{1g}$ transition of VO^{2+} ions is observed in all glass samples indicating that the V^{4+} state is present in a distorted octahedral coordination [42]. The broad absorption edge in each spectrum confirms the glassy nature of all prepared glass samples. The cut off wavelengths ($\lambda_{\text{cut-off}}$) are derived from optical absorption spectra and compositional trends in $\lambda_{\text{cut-off}}$ depict a red shift with enhanced CaO content. The optical bandgap (E_g) of the synthesized glass samples has been derived from Tauc plots i.e. $h\nu$ vs. $(\alpha h\nu)^{1/r}$ (with $r = 2$ and 3 for indirect allowed and indirect forbidden glass transition) by drawing an intercept on the x -axis corresponding to $(\alpha h\nu)^{1/r} = 0$ [43,44] (see figure 4). From table 2 it is noticed that the optical band gap exhibits an initial increase followed by stabilization but at 10.0 mol% there is a sharp decrease. The initial increase in optical band gap is in corroboration with the corresponding compositional dependence of thermal and density data. But, while looking at the dc electrical conductivity alongside its compositional dependence, a small contribution of the Moss–Burstein effect for initial composition, a synergic effect of both Moss–Burstein and NBO reduction for intermediate compositions and a prominent effect of Moss–Burstein phenomena for final composition (as the order of change in electrical conductivity is significant for composition

Figure 3. UV-Vis absorption spectra of prepared $x\text{CaO} - (30 - x)\text{Na}_2\text{O} - 35\text{B}_2\text{O}_3 - 35\text{P}_2\text{O}_5 + (1.0 \text{ mol}\%) \text{V}_2\text{O}_5$ ($x = 0, 2, 5, 7$ and 10) composition.

Figure 4. Tauc's plot for CNV2 composition for $r = 2$.

containing 10.0 mol% of CaO) is depicted through the compositional trends [45,46].

3.4 Thermal analysis

Thermal analysis is a qualitative and a quantitative technique to measure the heat flow and temperature associated with the transitions in materials as a function of temperature and time in a controlled atmosphere [47]. The interpretation of DTA curves provides the information related to physical and chemical changes which results from any change in heat capacity. DTA thermographs, as shown in figure 5, depict a typical glassy nature with a small endothermic peak signifying T_g ,

Table 2. Optical and thermal parameters of $x\text{CaO} - (30 - x)\text{Na}_2\text{O} - 35\text{B}_2\text{O}_3 - 35\text{P}_2\text{O}_5 + (1.0 \text{ mol}\%) \text{V}_2\text{O}_5$ ($x = 0, 2, 5, 7$ and 10) composition.

Parameters	CNV1	CNV2	CNV3	CNV4	CNV5
$\lambda_{\text{cut off}}$	450	451	444	450	480
E_g ($r = 2$) eV	2.44	2.46	2.50	2.47	2.30
E_g ($r = 3$) eV	2.22	2.26	2.30	2.26	2.02
T_g ($^\circ\text{C}$)	483	490	503	509	522
T_p ($^\circ\text{C}$)	569	569	591	601	614
T_i ($^\circ\text{C}$)	800	833	845	901	905

Figure 5. Thermal analysis of the synthesized $x\text{CaO} - (30 - x)\text{Na}_2\text{O} - 35\text{B}_2\text{O}_3 - 35\text{P}_2\text{O}_5 + (1.0 \text{ mol}\%) \text{V}_2\text{O}_5$ ($x = 0, 2, 5, 7$ and 10) composition.

a large exothermic peak signifying peak crystallization temperature (T_p) followed by a large endothermic peak signifying T_i [48]. T_g (x -axis correspondence at half of the endothermic shift), T_p (x -axis correspondence at the apex of the exothermic peak) and T_i (x -axis correspondence to the bottom of endothermic dip) have been evaluated from the DTA thermographs and the obtained values for each composition are listed in table 2.

It can be observed that the values of all characteristic temperatures (T_g , T_p and T_i) increase progressively with the replacement of Na_2O with CaO. The previous literature reveals that T_g depends on the cross-link density, strength and coordination of network forming units [49,50]. Therefore, an increase in characteristic temperature suggests a change in the nature of bonding between structural units. The replacement of P–O–Na bonds having a low field strength by new high field strength P–O–Ca bonds results in an increase in the cross-link density between the phosphate chains which ultimately enhance the glass transition temperature (as is also

evident from the corresponding trends in density and molar volume) [26,51]. Furthermore, the presence of B_2O_3 leads to an increase in the cross-linking between the metaphosphate chains through the formation of B–O–P bonds which cause an increase in T_g [4]. The order of T_g is in good agreement with other borophosphate glasses [35,52,53].

Moreover, the range of glass transition temperature, T_g , suggests that internal nucleation is taking place in the synthesized compositions [54].

3.5 Electrical conductivity

The dc electrical conductivity of all the prepared glass samples (cut and polished in rectangular shapes) was measured as a function of temperature in the range of 357–666 K. The temperature variation in conductivity is observed to follow the Arrhenius equation [55]

$$\sigma_{dc} = \sigma_0 \exp\left(\frac{-E_a}{KT}\right) \quad (5)$$

Figure 6. Arrhenius plot for the composition $x\text{CaO} - (30 - x)\text{Na}_2\text{O} - 35\text{B}_2\text{O}_3 - 35\text{P}_2\text{O}_5 + (1.0 \text{ mol}\%) \text{V}_2\text{O}_5$ ($x = 0, 2, 5, 7$ and 10).

where σ_0 is the temperature independent parameter, K is Boltzmann's constant and E_a is the dc activation energy. Figure 6 shows the Arrhenius plot of conductivity for all samples. The activation energy corresponding to each sample is estimated from the slope of the Arrhenius plot and the obtained values are reported in table 3. One can clearly observe from figure 6 that conductivity decreases and activation energy increases with an enhanced substitution of CaO at the expense of Na_2O . Electrical conductivity is believed to depend on the ionic size and oxidation state of the network modifier [56,57]. Alkaline earth ions possess lesser mobility than alkali ions and hence can be assumed to be virtually immobile inside the multi-component glass matrices [58]. Therefore, the observed decrease in electrical conductivity can be attributed to the reduced availability of mobile Na^+ ions [59,60]. The decrease in conductivity is further supported by a corresponding increased density and reduced molar volume leading to a hindrance in the movement of ions through glass matrix [61].

3.6 Dielectric properties

Figure 7 shows the variation of dielectric constant, ϵ' with frequency in the range of 1 kHz to 5 MHz for the CNV3 sample at different temperatures. An increase in the dielectric constant with an increase in temperature can be clearly observed which might be due to a decrease in bond energies [62]. It is presumed that temperature enhancement may reduce the intermolecular forces leading to an enhancement in orientation vibrations and thermal agitation of dipolar polarization. Moreover, it can be noticed from figure 7 that the dielectric constant is high at lower frequencies and becomes almost temperature independent at higher frequencies. Such behaviour can be explained by the increased net polarization which arises due to the hopping and accumulation of charge carriers from lower energy barrier sites to high energy barrier sites. At a lower frequency, large bulk polarization takes place due to the existence of the blocking electrode. Due to this, whole charge is piled up at a near electrode–sample interface which gives a large bulk polarization at low frequencies. However, in the high frequency region, charge carriers are unable to rotate rapidly causing a decrease in the number of oscillations and

Table 3. dc Conductivity (σ_{dc}), activation energy (E_{dc}) and ac conductivity (σ_{ac}) values for all the prepared compositions.

Sample code	Conductivity σ_{dc} at 360°C (S m^{-1}) $\times 10^{-3}$	Activation energy, E_{dc} (eV) $\times 10^{-1}$	Conductivity σ_{ac} at 1 MHz and 360°C (S m^{-1}) $\times 10^{-2}$
CNV1	21.3	7.45	0.63
CNV2	7.85	7.89	1.00
CNV3	4.43	8.09	1.45
CNV4	3.47	8.15	0.82
CNV5	0.93	8.30	1.26

Figure 7. Variation of ϵ' with frequency at different temperatures for CNV3 composition.

ultimately reducing the dielectric constant [63]. In the present compositions, Na^+ ions act as modifiers and induce dangling bonds alongside NBOs in the glass network. The structural defects so produced accumulate near the electrodes and are responsible for surface charge polarization. While at higher frequencies, the oscillations of charge carriers lay behind the applied field causing a decrease in the dielectric permittivity [64]. Remaining compositions were also found to exhibit similar trends in temperature and frequency variations of the dielectric constant.

3.7 Electric modulus

In order to eliminate the electrode polarization effect, an alternative approach called electric modulus analysis is used to investigate the complex electrical response of glassy materials [65]. The complex electric modulus (M^*) can be calculated using the formula [66]:

$$M^* = M' + iM'' \quad (6)$$

Figures 8 and 9 show the variation of the real (M') and imaginary (M'') parts of the electrical modulus at different temperatures for the CNV3 sample respectively. At higher frequencies, M' reaches a maximum while at lower frequencies it approaches zero indicating a negligible contribution due to electrode polarization [65]. However, in the case of the imaginary part of the electric modulus (M'') a characteristic peak originating due to relaxation behaviour at different temperatures is evident. The frequency corresponding to the maximum value of M'' is termed as f_M and shifts to higher frequencies with an increase in temperature [16]. The frequency region around f_M shows different relaxation regions i.e., the range of frequencies below f_M indicates the range in which the charge carrier ions (Na^+ here) drift over longer

Figure 8. Real part (M') of modulus isotherm vs. $\log f$ for CNV3 ($x = 5$) composition at different temperatures.

Figure 9. Frequency dependence of the imaginary (M'') part of modulus isotherm for CNV3 ($x = 5$) composition for different temperatures.

distance and are associated with hopping conduction, while the frequency region above f_M represents the region in which the charge carriers are spatially confined to their potential wells. These ions therefore, are free to move within the wells due to the relaxation polarization process [67]. Hence, the peak frequency f_M is an indication of transition from long to short range mobility.

3.8 ac Conductivity

Figure 10 depicts the composition dependence of the frequency variation in ac conductivity at 364 °C for all synthesized compositions. The trends in ac conductivity with frequency are almost similar to all other compositions and can be divided into two different regions: (i) plateau

Figure 10. Log σ_{ac} vs. Log f plots for all the prepared samples of $x\text{CaO} - (30 - x)\text{Na}_2\text{O} - 35\text{B}_2\text{O}_3 - 35\text{P}_2\text{O}_5 + (1.0 \text{ mol}\%) \text{V}_2\text{O}_5$ ($x = 0, 2, 5, 7$ and 10) composition.

and (ii) dispersion [68]. The plateau region corresponds to frequency independent conductivity which is observed for the lower frequency region suggesting the distribution of random ionic charge. This frequency independent conductivity region can also be due to the long range transport of mobile alkali (Na^+) ions in response to the applied field where diffusion contributes to the dc conductivity ($\sigma(0)$) [68]. However, dispersion is observed at higher frequencies due to high probability of the correlated forward-backward hopping along with the relaxation of dynamic cage potential. It further shifts towards higher frequencies with an increase in temperature [16]. Therefore, this transition of ac conductivity from the frequency independent region to the frequency dependent region signifies the onset of conductivity relaxation phenomena [62]. The dispersion in conductivity in the higher frequency region is analysed using Jonscher's power law [69], given by

$$\sigma(\omega) = \sigma(0) + A\omega \quad (7)$$

where $\sigma(0)$ is the frequency independent dc conductivity of the sample, A is the weakly temperature dependent quantity and n is the power law exponent lying in the range $0 < n < 1$. The values $\sigma(\omega)$ for all glass compositions at 633 K and 1 MHz are listed in table 3. No significant change in ac conductivity is observed with change in composition.

4. Conclusions

Glass samples were prepared in the compositional range $x\text{CaO} - (30 - x)\text{Na}_2\text{O} - 35\text{B}_2\text{O}_3 - 35\text{P}_2\text{O}_5 + (1.0 \text{ mol}\%) \text{V}_2\text{O}_5$ where $x = 0, 2, 5, 7$ and $10 \text{ mol}\%$ via the melt-quench technique. The amorphous nature of the prepared glasses was confirmed from peak free XRD profiles. Density and

molar volume were found to exhibit opposite behaviour. Increased value of density indicates an increase in cross-link density along with some structural changes inside the glass network. The dominant bonding present in the synthesized glasses was detected through FTIR spectroscopy. The values of the optical band gap were found to lie in the range of 2.23–2.45 eV and 1.96–2.15 eV corresponding to direct and indirect transitions respectively. The values of T_g were found to increase with enhanced CaO content suggesting an increase in rigidity of the glass system and a change in the nature of bonding between the structural units. The dc conductivity exhibited Arrhenius type temperature dependence while the ac conductivity was observed to obey Jonscher's power law.

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