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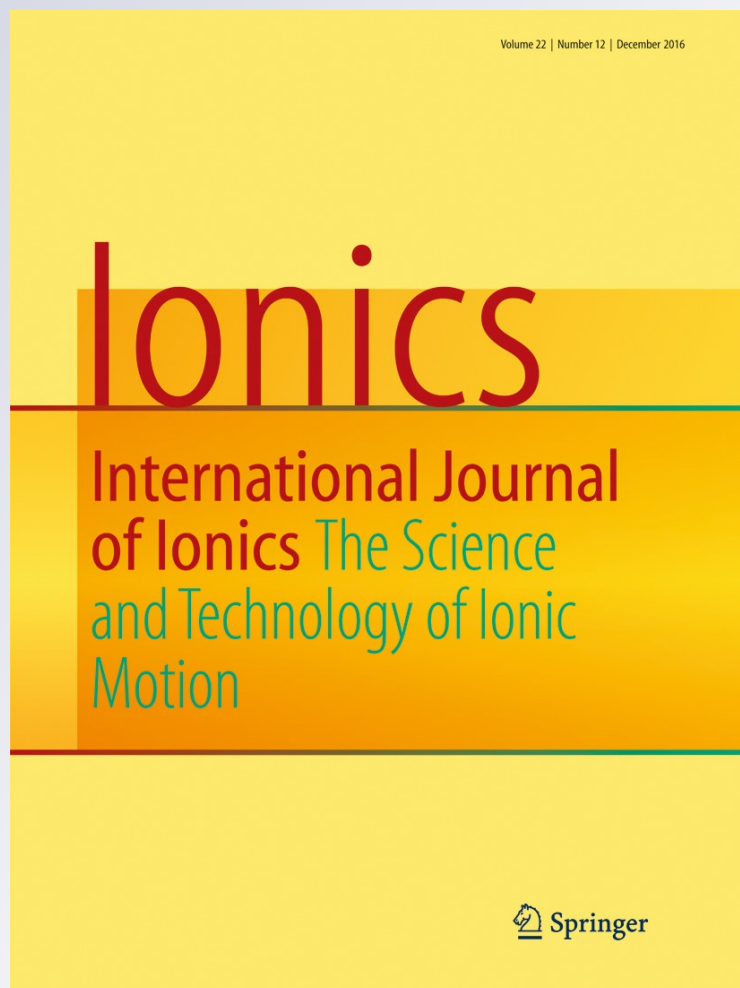
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Influence of Zn/Co ratio on dielectric behavior of $\text{Na}_2\text{Zn}_{1-x}\text{Co}_x\text{P}_2\text{O}_7$ glasses

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Abstract A series of zinc phosphate glass doped with cobalt $\text{Na}_2\text{Zn}_{(1-x)}\text{Co}_x\text{P}_2\text{O}_7$ ($x = 0, 1, 2$ and 5 mol%) was synthesized. These glasses were characterized by both infrared and large broadband dielectric spectroscopy. Infrared spectra indicate the increase of Zn/Co ratio creates defect in phosphate network due to the depolymeration of phosphate anions. The dc conductivity increases and activation energy decreases with the amount of cobalt ions in the glass network. The impedance measurements reveal that the total conductivity follows Jonscher's power law. The dielectric constant and dielectric loss increased with the temperature and decreased with the frequency whatever the cobalt proportion.

Keywords Phosphate glasses · Jonscher's law · Electrical conductivity · Ion transport · Dielectric behavior

Introduction

Phosphate glasses have been of large interest since they usually exhibit higher thermal expansion coefficients [1, 2], lower transition temperature [3], and higher electric conductivity than silicate [4] and borate glasses [5]. They are used for several applications such as optic [6], solid state batteries [7], photonics [8], and laser technologies [9, 10]. Since many

years, the ionic conductivity of phosphate glasses was extensively investigated. However, their structure, properties, conductivities, and dielectric behavior are not totally elucidated [11]. Among the techniques to investigate ionic transport properties of these materials, large broadband dielectric spectroscopy permits to cover wide ranges of temperatures T and angular frequency ω [12]. This technique is suitable in order to characterize the interaction between the extra-framework cations and the site where they are embedded. The studies of dielectric properties and breakdown help in assessment of insulating character and highlight the structural aspects of glasses. It has been reported that ionic conductivity as well as other dynamic properties (i.e., diffusion) depend on the kind of mobile ion trapped in the matrix of glass [13]. The doping of phosphate glasses by addition of alkali, alkaline earth, or transition metal ions increases their stability and durability [14, 15]. As example, the addition of Li, Na, Mg, Pb, or Cu ion into silver phosphate glass was considered to modify the electrical conductivity for application in solid state batteries [16, 17].

The ac conductivity (σ_{ac}) of glass material is commonly simulated using Jonscher's universal law [18] (Eq. 1):

$$\sigma_{ac}(\omega) = \sigma_{dc} + B\omega^s, \quad (0 < s < 1) \quad (1)$$

where σ_{dc} is the dc conductivity which is independent of frequency, B is the prefactor which is the function of temperature and composition, and s is the exponent of the power law. The frequency exponent s increases when the temperature T decreases. It tends to 1 when $T \rightarrow 0$ [19]. This parameter is directly connected to the glass doping, assuming an ion-ion interaction during ionic transport process [20].

In this paper, we have investigated the dielectric properties of phosphate glasses doped by cobalt. To do it, a series of zinc phosphate glass (NZPO) doped with Co^{2+} ($\text{Na}_2\text{Zn}_{1-x}$

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$x\text{Co}_x\text{P}_2\text{O}_7$ where $x = 0, 1, 2, 5$ mol%) was synthesized and characterized by infrared. Then, the dielectric properties of each glass were studied over large range of temperature from 283 to 473 K. From these data, the activation energy of ion conductivity and dielectric constant was obtained and discussed regarding their structures.

Experimental procedures

Glass samples with composition $\text{Na}_2\text{O} + (1-x)\text{ZnO} + x\text{CoO} + \text{P}_2\text{O}_5$ were synthesized following classical melting and quenching processes. A stoichiometric mixture of $\text{NH}_4\text{H}_2\text{PO}_4$ ($\geq 99.9\%$, POCH), Na_2CO_3 ($\geq 99.5\%$, Sigma-Aldrich), $\text{Co}(\text{NO}_3)_2$, $6\text{H}_2\text{O}$ ($\geq 99.9\%$, Sigma-Aldrich), and ZnO ($\geq 99.9\%$, Riedel) powders was carefully mixed together in an agate mortar. The mixture was progressively heated in a platinum crucible from 298 to 633 K in order to remove both ammonia and water. After grinding, the powders were heated at 993 K during 2 days in order to reach the complete departure of carbon dioxide. Then, the mixture was melted 6 h at 1093 K. Finally, the glass obtained was maintained 12 h at 573 K, in order to improve its mechanical stability. The sample identification and the respective molar composition are reported on Table 1.

The conductivity $\sigma_{ac}(T, \omega)$ and dielectric relaxation $\epsilon'(\omega)$ were measured [21] using a Novocontrol Broadband Dielectric Spectrometer (BDS 4000). The measurement have been performed at various temperatures T (from 283 to 473 K by step 10 K) and frequency ($f = 2\pi/\omega$) from 10^{-2} to 10^6 Hz. In order to reach thermal equilibrium, the sample was maintained 30 min before the experiments. The fine powder were compacted under 5.10^8 Pa to obtain disk-shaped pellets (diameter = 13 mm, thickness = 1 mm). A thick film (0.1 μm) of gold was sputtered on both sides of the pellet to ensure the electrical connection.

Fourier transform infrared absorption spectra (FTIR) were recorded at room temperature in the range $4000\text{--}400$ cm^{-1} by an infrared spectrophotometer (Nicolet Avatar 330 FT-IR). The samples were prepared by mixing zinc sodium phosphate glass doped with cobalt (1 mg) with KBr (100 mg) and subjecting the mixture to a suitable compaction to produce

transparent disks. The FTIR was carried out immediately after preparing the disks.

Results and discussion

Glass characterization

FTIR absorption spectra give information about molecular vibrations as well as rotation associated to covalent bond. For phosphate glasses, phosphate unit (PO_4^{3-}) bands are in the range of $1400\text{--}400$ cm^{-1} . FTIR spectra reported in Fig. 1 exhibit band at 1180 cm^{-1} which is attributed to the stretching of terminal (PO_3^{2-}) groups [22]. The three bands from 1100 to 700 cm^{-1} could be assigned to the symmetric and asymmetric motions of the bridging oxygen in linear P–O–P bonds. This indicates the presence of linear metaphosphate chains in the glasses [23]. The band in range $1093\text{--}1098$ cm^{-1} is related to the symmetric stretching of O–P–O [24]. The band at 920 cm^{-1} is attributed to the P–O–P asymmetric stretch. It shifts towards higher wave number values with the increase of cobalt concentration. [25] The band at 720 cm^{-1} is assigned to the symmetric stretching modes of the P–O–P linkage [25]. From the spectra, we can observe a band at 632 cm^{-1} for the sample which contains 2 and 5 mol% of cobalt. This band is assigned to vibration of $\text{Co}^{\text{III}}\text{--O}$ [26, 27]. The bands around $535\text{--}540$ cm^{-1} may be assigned either to the harmonics of P–O–P bending vibration or to the characteristic frequency of the $\text{P}_2\text{O}_7^{4-}$ group [28]. It was noticed that the intensity of the IR peak increased with the concentration of cobalt oxide. This should be interpreted as follow. In the undoped sodium phosphate glass, P–O $^-$ \cdots Na $^+$ bond exists. When the cobalt is added, Na $^+$ is replaced by Mg $^{2+}$ [29]. In this case, Co $^{2+}$ take place bond between two chains of phosphate glass in other to form P–O–Co $^{2+}$ bond.

Electrical properties

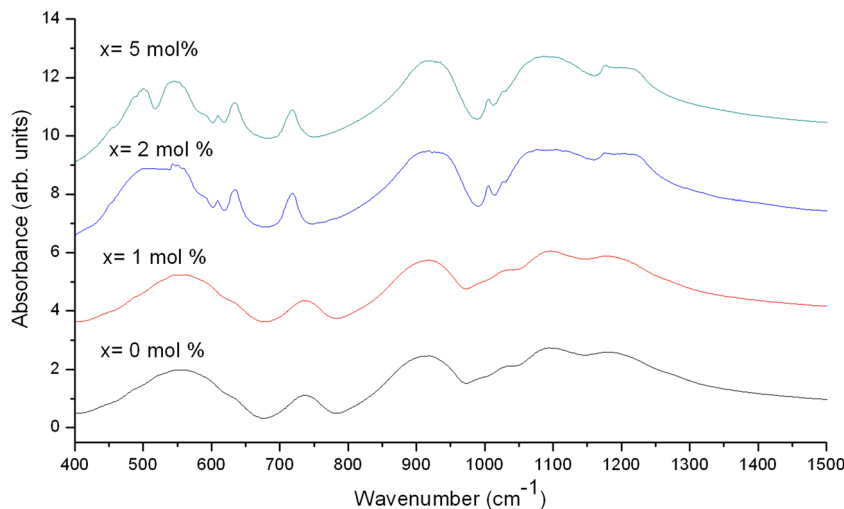
Ionic conductivity

The ac conductivity $\sigma_{ac}(\omega, T)$ as function of frequency ($f = \omega/2\pi$) measured at different temperatures for zinc sodium phosphate glasses doped with cobalt is reported in Fig. 2. Whatever the temperature, the conductivity $\sigma_{ac}(\omega, T)$ curves follow two distinct regimes. At high frequency, it increases due to dispersion effect. At low frequency, it reaches a constant value $\sigma_{dc}(T)$. This conductivity dc which is independent to frequency is commonly assigned to the long range transport of mobile alkali ion induced by applied electric field. The value of $\sigma_{dc}(T)$ is extracted from the plateau of $\sigma_{ac}(T)$ observed at low

Table 1 Composition and identification of the glasses

Molar composition (%)				
Glass	P ₂ O ₅	ZnO	Na ₂ O	CoO
NZPO 0	50.00	25.00	25.00	00.00
NZPO 1	50.00	24.75	25.00	00.25
NZPO 2	50.00	24.50	25.00	00.50
NZPO 5	50.00	23.75	25.00	01.25

Fig. 1 FTIR spectra of $\text{Na}_2\text{Zn}_{1-x}\text{Co}_x\text{P}_2\text{O}_7$ ($x=0, 1, 2, 5$ mol %) glass samples



frequency [29] and reported in Fig. 3. The temperature dependence of $\sigma_{dc}(T)$ follows the Arrhenius law (Eq. 2)

$$\sigma_{dc}(T) = \frac{\sigma_0}{T} \exp\left(\frac{-\Delta E_{dc}}{kT}\right) \quad (2)$$

where k is Boltzmann's constant, T is the temperature, σ_0 is a pre-exponential factor involving the mobility of the ion, and ΔE_{dc} is the activation energy of ionic transport process (Table 2). ΔE_{dc} is obtained by fitting the logarithm of $\sigma_{dc} * T$ as a function of $1/T$ (Fig. 3). It represents the energy barrier that sodium ions must overcome to diffuse throughout the solid structure [30].

The variation of σ_{dc} and ΔE_{dc} as functions of molar fraction of CoO is depicted in Fig. 4. The activation energy ΔE_{dc} of base glass is 0.95 eV and it reaches 0.78 eV with increasing the cobalt ratio. These results indicate that with the increase of cobalt amount, the transport of mobile charge is facilitated. A

similar observation was previously reported by Langar et al. in the case of vanadium ions in zinc phosphate glass [31].

We can observe an increase of conductivity with the cobalt amount in the glass excepted for $x = 0.02$. The increase may be due to a manifestation of the increasing concentration of mobile charges involved in the process of transfer. In zinc phosphate glasses, different processes contribute to the electrical conduction. In general, the ionic conduction is due to the motion of mobile ion (alkali or alkaline earth) and thus, the electrical conductivity is expected to be proportional to the concentration of the mobile ions. However, Owen [32] reported that the electrical properties of glass in a periodic field do not depend only on the mobile charge (ions or electrons). The dc conductivity depends on other relatively immobile ions or on dipole which involved the glass network. Hill and Jonscher [33] observed this for the ac conductivity in a wide range of materials, including several ones where conduction by hopping is expected. In the present case, cobalt is a transition

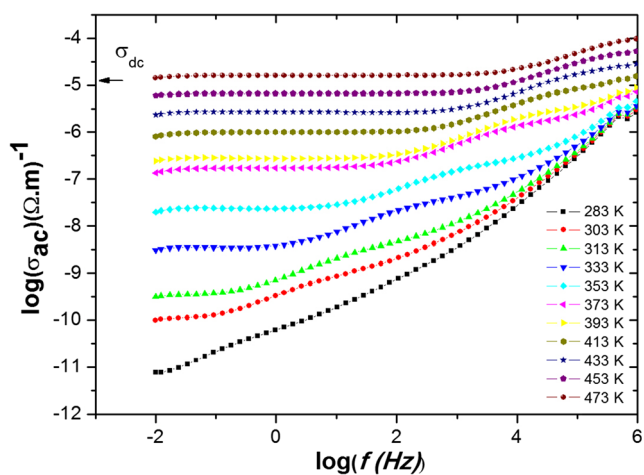


Fig. 2 Frequency dependence of the conductivity $\sigma_{ac}(\omega, T)$ at different temperatures for $\text{Na}_2\text{Zn}_{1-x}\text{Co}_x\text{P}_2\text{O}_7$ glass samples, where $x = 2$ mol%

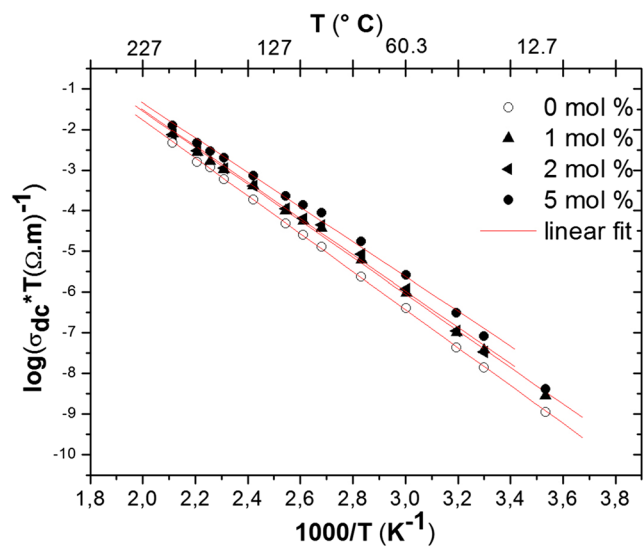


Fig. 3 dc conductivity versus reciprocal temperatures for $\text{Na}_2\text{Zn}_{1-x}\text{Co}_x\text{P}_2\text{O}_7$ ($x = 0, 1, 2, 5$ mol%) glass samples

Table 2 Summary of the data related to dc conductivity of $\text{Na}_2\text{Zn}_{1-x}\text{Co}_x\text{P}_2\text{O}_7$ glasses

x (mol %)	ΔE_{dc} (eV) ± 0.02	$\log(\sigma_0)$ ± 0.02	σ_{dc} ($\Omega\cdot\text{m}$) ⁻¹ at 473 K ± 0.02
0	0.95	7.32	1.02×10^{-5}
1	0.92	6.74	1.90×10^{-5}
2	0.91	6.41	1.62×10^{-5}
5	0.87	6.23	2.75×10^{-5}

metal with incomplete “d” orbitals. The latter are responsible for the formation of polaron. The oxidation of cobalt ions from Co^{2+} to Co^{3+} should be possible during melting, annealing, and crystallization processes. Co^{2+} ions occupy both octahedral and tetrahedral positions whereas Co^{3+} ions occupy mainly octahedral positions in the glass network [34].

Further, the ionic radius of Co^{2+} (70 pm) is smaller than the one of Zn^{2+} (74 pm). Following the ionic size, one can understand that the replacement of ZnO successively by CoO causes an increase in the disorder degree of the glass network. This facilitates the mobility of charge carriers Na^+ ions and electrons, which in turn explains the increase of σ_{dc} conductivity and decrease of ΔE_{dc} , with increasing cobalt concentration.

The conductivity decrease at 2 % cobalt is likely due to the structural changes occurring in glass network [35]. Indeed, when the cobalt concentration is greater than 2 %, there is creation of non-bridging oxygen. This induces defects in the network due to depolymeration of phosphate anions which facilitates likely the mobility of Na^+ ions, and thus increase in conductivity. A similar behavior is reported in the case of alkali alumino-silicate glass system [36].

Dielectric properties

The influence of cobalt doping on dielectric properties was also investigated. In Fig. 5 are reported representative curves

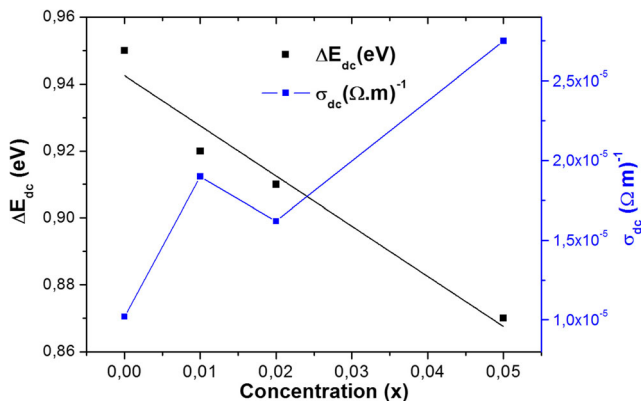


Fig. 4 Variation of activation energy and dc conductivity at 473 K as a function of cobalt concentration

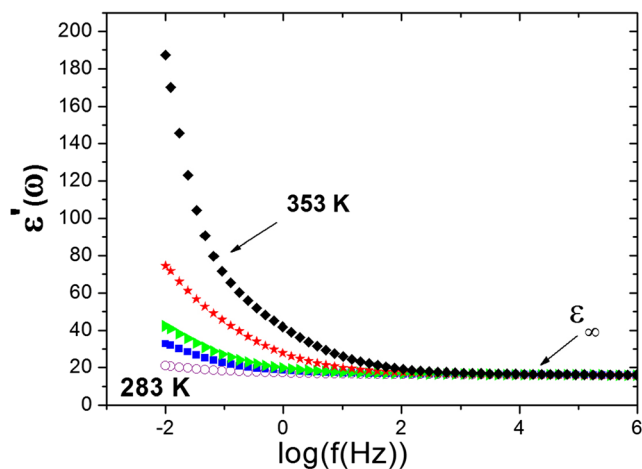


Fig. 5 The variation of real part of the dielectric permittivity, $\epsilon'(\omega)$, for the $\text{Na}_2\text{Zn}_{1-x}\text{Co}_x\text{P}_2\text{O}_7$ glass as a function of frequency, $x = 2$ mol% at different temperatures

of the dielectric constant $\epsilon'(\omega)$ dependence with frequency f at different temperatures. For all glasses, we can observe a decrease of ϵ' with frequency. This can be explained as follows. At low frequencies, the dielectric constant is due to the contribution of multi-component polarization: deformation (electronic and ionic polarization) and relaxation (orientation and interfacial polarization) [37]. With the increasing of the frequency, the dipoles become no longer to be able to rotate sufficiently rapidly. Thus, their oscillations begin to lag behind those of the field. At high frequency, the dipole becomes completely unable to follow the electric field. Thus, the contribution towards the polarization is negligible and the dielectric permittivity $\epsilon'(\omega)$ is enhanced. In this case, $\epsilon'(\omega)$ decreases until it reaches a constant value $\epsilon'_\infty(\omega)$. The latter is only due to the interfacial charge [38].

The real part of the complex dielectric permittivity as function of frequency can be described by the power law (Eq. 3):

$$\epsilon'(\omega) = B \cdot \omega^{(s-1)} + \epsilon_\infty \tag{3}$$

where ϵ_∞ is the background contribution to $\epsilon'(\omega)$ arising from an unrelated process at high frequency. In order to extract parameters B and s , Eq. 3 was linearized to Eq. 4. In Fig. 6 are reported examples (samples doped with cobalt for concentration, $x = 2$ mol%) of the linear dependence between $\log(\epsilon'(\omega) - \epsilon_\infty)$ and $\log(f)$ at different the temperatures:

$$\log(\epsilon'(\omega) - \epsilon_\infty) = \log(B) + (s-1)\log(\omega) \tag{4}$$

Usually, the parameter s may depend on the glass composition and the temperature [39]. Figure 7a shows the temperature dependence of the parameter s for all the four samples. The observed variation of s with temperature may be due to different contributions from conductivity and dielectric losses at different temperatures [40].

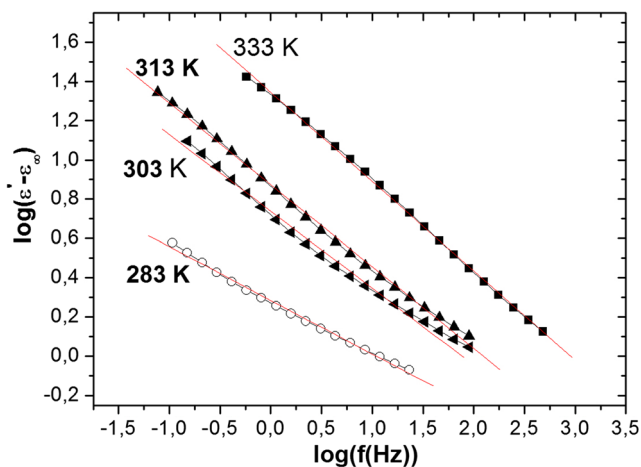


Fig. 6 $\log(\epsilon' - \epsilon_\infty)$ as function of $\log(\text{frequency})$ for the $\text{Na}_2\text{Zn}_{1-x}\text{Co}_x\text{P}_2\text{O}_7$ glass sample doped with cobalt for concentration, $x = 2$ mol% at different temperatures. The line was linear fitted to the experimental data points (Eq. 4)

Several models were used in order to explain the conduction mechanism. An agreement was found between the experimental data and those predicted by the correlated barrier-

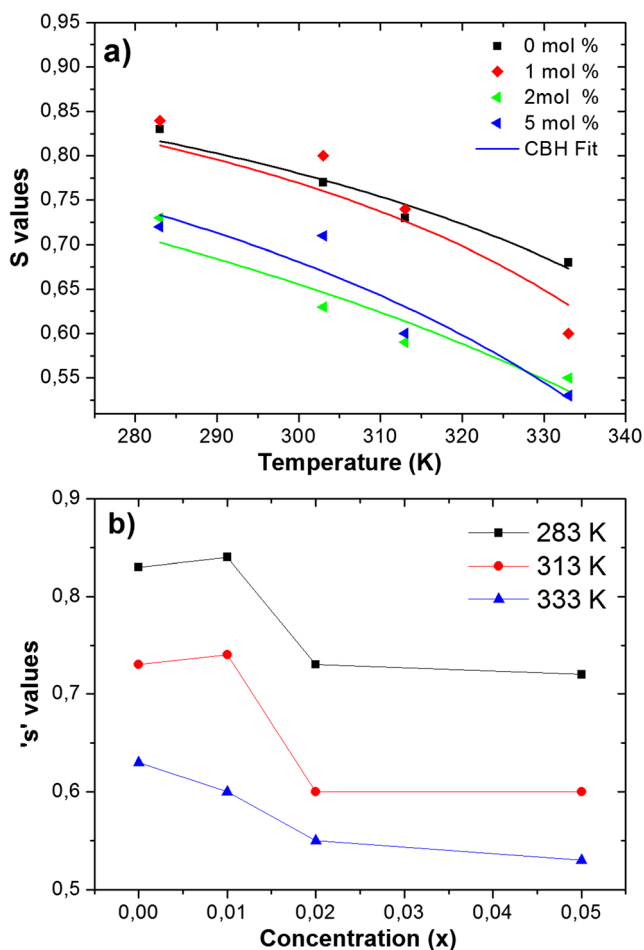


Fig. 7 The variation of the value of s for all glass samples as the function of **a** temperature (the lines are the CBH fit) and **b** cobalt concentration

hopping (CBH) model [41]. In this case, the frequency exponent s is given by Eq. 5 [41]

$$s = 1 - \frac{6k_B T}{W_M + k_B T \ln(\omega \tau_0)} \quad (5)$$

where τ_0 , W_M , T , ω , and k_B are the static relaxation time, the activation energy, the absolute temperature, the angular frequency, and the Boltzmann constant, respectively.

According to Fig. 7a, it is worth to mention that the values of s decrease roughly following Eq. 5 with rising temperature. This result suggests that correlated barrier-hopping model is the most suitable model to characterize the electrical conduction mechanism of the obtained doped disodium phosphate glasses. Such values are closely associated with proven carrier transport hopping electrons. It has been established that a value of s close to unity is considered to be associated with the lattice responses [42]. The distinction between lattice and carrier responses is that they correspond to intrinsic and extrinsic processes, respectively, due to some impurities or injected carriers as a result of transition metal ions.

Beside the temperature dependence, the values of s change with composition (Fig. 7b). Typically, s decreases with the increase of Co ratio whatever the temperature. It is the measure of the degree of interaction with the environment. Sidebottom concluded that the exponent s depends upon the dimensionality of the local conduction space, and it decreases with decreasing dimensionality [43].

According to that, the observed decrease of s value with increasing cobalt could be explained by the formation of non-bridging oxygen atoms which disrupt in the phosphate units [44].

The behavior of dielectric relaxation of sample was studied by plotting normalized $\tan(\delta)$ versus $\log(f)$, at various temperatures. The curves (Fig. 8) exhibit distinct maxima (ω_{\max}) which shifts towards higher frequency with increasing

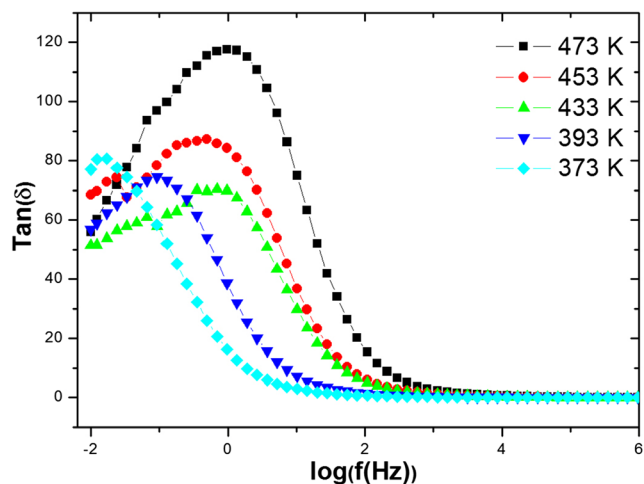


Fig. 8 The variation of dielectric loss with frequency at different temperatures for the $\text{Na}_2\text{Zn}_{1-x}\text{Co}_x\text{P}_2\text{O}_7$ ($x = 5$ mol%) glass sample

temperature. This indicates that dielectric relaxation follows a thermally activated process [45]. Usually, the dielectric losses at high frequency are much lower than those occurring at low frequencies at a specific temperature. This kind of dependence is basically associated with losses by conduction. Higher values of $\tan \delta$ at low frequency may be due to the migration of ions and conduction loss combine with the electron polarization [46]. At higher frequency, dielectric loss may occur only with ion vibration; therefore, $\tan \delta$ decreases with frequency [47].

Conclusion

$\text{Na}_2\text{Zn}_{1-x}\text{Co}_x\text{P}_2\text{O}_7$ glasses are synthesized with different concentrations of cobalt. The electrical properties of the glasses were studied over a wide range of temperature and frequency. The IR spectral studies suggest the formation of defect in the glass network with the cobalt content. These defects are likely due to the depolymeration of phosphate anions. Our results show a decrease of activation energy of dc conductivity process and an increase of dc conductivity with the amount of cobalt. This is interpreted by an increase of disorder degree of the glass network which facilitates the mobility of charge carriers Na^+ ions and electrons.

The complex dielectric permittivity has been fitted using Jonscher's universal power law. The values of frequency exponent s decrease with the temperature and the cobalt content. They follow roughly a correlated barrier hopping.

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