Nickel ferrite doped lithium substituted zinc and niobo vanadate glasses: thermal, physical, and electrical characterization

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Abstract
This study reports a comparison of some thermal, physical, and electrical properties of lithium substituted zinc and niobo vanadate glasses doped with nickel ferrite prepared for the electrical application. These glasses were prepared using the melt quenching technique. Density and differential scanning calorimetry were used to derive various physical and thermal properties. Packing density, the concentration of atoms, separations between atoms were compared between doped and undoped glass families. Thermal stability was estimated and compared. It is found that glasses with 20 mol% of Lithium are more stable than the rest. The thermal stability increases significantly by doping Nickel Ferrite from 5 °C to 30 °C in zinc vanadate glasses. Packing density varies with mol% of lithium ions from 0.43 to 0.42 in zinc vanadate glasses and from 0.40 to 0.42 in niobo vanadate glasses. Doping of Nickel ferrite varies the packing density from 0.42 to 0.43 in zinc vanadate glasses whereas it stabilizes the packing density to 0.42 in niobo vanadate glasses. Out of the two families of glasses, zinc vanadate glass doped with nickel ferrite shows better stability and higher packing density compared with others. DC electrical conductivities of the two families of glasses are almost similar and nickel ferrite doping has a little effect on DC electrical conductivity. Thus it is concluded that the nickel ferrite enhances the stability of the glass while maintaining DC electrical conductivity. This observation is important from the point of view of the electrical application of these glasses.

1. Introduction

Source of renewable energies from solar, wind, biomass, hydropower, geothermal, battery, nuclear plants, etc are day to day demands of this energy-hungry world and the main focus of contemporary research is on the investigation to generate energies for a cleaner and sustainable world [1–6]. Storing energy and using it for different purposes is a crucial aspect. Batteries fall into this category. Recently vanadium-based glasses were used as the cathode material in Li-ion battery [7] and SiO₂ based glasses for ‘smart window’ [8].

As vanadium can exhibit different oxidation states, it is gaining attention in solid-state chemistry and material science [9, 10]. Transition metal oxide glasses like Vanadate glasses are known to show switching [11], polaronic conduction [12, 13], and ionic conductivity [14]. Polaronic conduction is due to the change of state from V⁴⁺ to V⁵⁺ [13], while the ionic conduction is ascribed to the movement of small alkali ions like lithium or sodium.

While investigating cathode material or solid electrolyte for the battery and energy harvesting, it is important to bear in mind that thermal stability is equally important other than good electrical conductivity. The commonly used solid electrolyte in Li-ion battery, LiCoO₂, has a disadvantage of losing the thermal stability at high temperatures [15]. Hence there is a need for the investigation of new solid electrolyte materials for energy storage/harvesting and in this communication, an attempt is made to look for the above properties in Zinc and Niobo vanadate glasses and its doped counterparts.
Substitution of the atoms with similar atomic size but different valence electronic structures in the glassy matrix brought an important role in improving glass-forming ability [16]. Doping with two or more different metallic ions in the glass is known to increase thermal stability [17]. The effect of the atomic size distribution on glass-forming ability of amorphous metallic alloys has been investigated. It is also found that doping enhances the resistance to crystallize and improves the ability to form a glass [18].

We chose to synthesize binary vanadate glasses with zinc and niobium oxide as co-formers as they widely differ in their valance state and atomic radius. Zinc has a comparable atomic radius with vanadium while Niobium is bigger than both zinc and vanadium. So it is interesting to see the effect of lithium substitution with both zinc and niobium for conductivity as well as stability. Recently Darioush Souri [19] has shown that the addition of Ag₂O to TeO₂-V₂O₅ glasses increases the glass transition temperature and improves the thermal stability of these glasses.

Ferrites have greater thermal stability. Increased ferrite loading in the matrix is known to enhance the thermal stability of the material [20]. Thus in this work, nickel ferrite was chosen as a dopant as it imparts magnetic property along with thermal stability.

In this communication, we present the analysis of the thermal and physical properties of the lithium substituted zinc and niobium vanadate glasses and correlate them to the DC conductivity. We also show that the doping of Nickel Ferrite increases the thermal stability but has a negligible effect on DC conductivity in our glass samples. The novelty of this work is in establishing the fact that the addition of Nickel Ferrite increases the thermal stability while more or less maintain the same electrical conductivity. This is an important observation which may be exploited in the electrical application of these type of glasses. A detailed analysis of electrical conductivity properties derived from Cole-Cole plots, electrical modulus analysis, etc for these glass families will be communicated shortly.

2. Experimental details

2.1. Glass preparation and XRD
Reagent grade chemicals V₂O₅, Nb₂O₅, Li₂CO₃, and ZnO (all from Sigma Aldrich) were used as starting materials to prepare glass samples. In addition to these, Nickel Ferrite (NiFe₂O₄) (NF), prepared via combustion technique (using a mixture of Nickel nitrate and Ferric nitrate in ethyl alcohol [21]) was used as dopant. The overall composition of each glass sample is given in table 1. These starting materials were mixed proportionally based on the following formulas: 70 V₂O₅-(30-x) Nb₂O₅-x Li₂O; 70 V₂O₅-(30-x) ZnO-x Li₂O; 68V₂O₅-(30-x) Nb₂O₅-x Li₂O—2 NiFe₂O₄ and 68 V₂O₅-(30-x) ZnO-x Li₂O—2 NiFe₂O₄, where x = 15, 20, 25; grounded finely using agate mortar to obtain homogeneous mixing. Batches of nearly 5 g in weight were weighed and taken into a ceramic crucible and heated up to 900 °C-1000 °C for about 80 min with occasional stirring. Then the melt was quenched between brass plates maintained at an elevated temperature of 100 °C to get glasses. These samples were then left to anneal on this plate for about 40 min until the temperature reached an average of 50 °C.

The thicknesses of the samples were ranging from 0.5 mm to 0.8 mm.

Powder x-ray diffractometry (XRD) performed on the samples using a Rigaku XRD machine with CuKα radiation (1.5416 Å) and revealed the amorphous nature. A broad hump was seen in the XRD pattern as shown in figure 1. The figure also confirms that the NF used as a dopant has gone into the glass matrix homogeneously and has not created any clusters of its own as no sharp crystalline peaks were observed in the pattern.

2.2. Physical property and thermal characterization:
Density of the prepared glasses were determined using the Archimedes principle, to an accuracy of ±0.004 g cc⁻¹. Xylene was used as an immersion liquid with a density of 0.864 g cc⁻¹ (declared by the manufacturer). A high resolution electronic weighing balance (with an accuracy of 0.0001 g) was used to measure the weights of the samples in air and liquid. The molar volume was calculated using the equation

\[ V_m = \frac{M}{\rho}, \]

where \( M \) is the molecular weight of the glass sample, which was calculated as \( M = \sum x_i w_i \), where \( x_i \) and \( w_i \) are the mole fraction and molecular weight of the component \( i \) and \( \rho \) is the density, respectively.

The thermal behaviors of the prepared glasses were recorded using Differential Scanning Calorimeter (DSC) (TA Instruments) at a heating rate of 10 K per minute. DSC curves of all glasses with and without doping are shown in figure 2. The glass transition \( T_g \) and onset of crystallization temperature \( T_c \) (to an accuracy of ±0.05 °C) were determined from these curves.

2.3. DC electrical conductivity measurements
A 5 mm diameter mask was used to paint high purity conducting silver (SPI supplies, USA) contact. The real and Imaginary part of the complex impedance was measured using Agilent Precision Impedance Analyzer 4194A over the frequency range of 100 Hz to 10 MHz with an oscillator level of 500 mV which was found to be well
| S.No | Sample Code | $V_2O_3$ (mol%) | $ZnO$ (mol%) | $Nb_2O_5$ (mol%) | $Li_2O$ (mol%) | $NiFe_2O_4$ (mol%) | $T_g$ ($^\circ$C) | $T_x$ ($^\circ$C) | $S = T_x - T_g$ ($^\circ$C) | Density (g cc$^{-1}$) | Molar Volume (cc) | Packing Density |
|------|-------------|----------------|--------------|-----------------|----------------|-------------------|----------------|----------------|------------------|-----------------|----------------|----------------|
| 1    | VZL 15      | 70             | 15           | 0               | 15             | 0                 | 236            | 242            | 6                | 2.999           | 4801.570       | 0.428          |
| 2    | VZL 20      | 70             | 10           | 0               | 20             | 0                 | 233            | 253            | 20               | 2.938           | 4814.563       | 0.426          |
| 3    | VZL 25      | 70             | 5            | 0               | 25             | 0                 | 238            | 248            | 10               | 2.867           | 4842.765       | 0.422          |
| 4    | VZLFe 15    | 68             | 15           | 0               | 15             | 2                 | 238            | 270            | 32               | 3.108           | 4832.394       | 0.424          |
| 5    | VZLFe 20    | 68             | 10           | 0               | 20             | 2                 | 235            | 270            | 35               | 3.024           | 4761.168       | 0.429          |
| 6    | VZLFe 25    | 68             | 5            | 0               | 25             | 2                 | 228            | 253            | 25               | 2.962           | 4732.333       | 0.430          |
| 7    | VNL 15      | 70             | 0            | 15              | 15             | 0                 | 236            | 254            | 18               | 2.863           | 5996.775       | 0.396          |
| 8    | VNL 20      | 70             | 0            | 10              | 20             | 0                 | 252            | 291            | 39               | 2.932           | 5453.635       | 0.414          |
| 9    | VNL 25      | 70             | 0            | 5               | 25             | 0                 | 238            | 262            | 24               | 2.888           | 5127.139       | 0.419          |
| 10   | VNLFe 15    | 68             | 0            | 15              | 15             | 2                 | 261            | 325            | 64               | 3.108           | 5557.444       | 0.425          |
| 11   | VNLFe 20    | 68             | 0            | 10              | 20             | 2                 | 265            | 311            | 46               | 3.04            | 5321.541       | 0.423          |
| 12   | VNLFe 25    | 68             | 0            | 5               | 25             | 2                 | 249            | 281            | 32               | 2.962           | 5034.673       | 0.425          |

**Table 1.** Glass content in mol%, glass transition temperature ($T_g$), onset crystallization ($T_x$), thermal stability ($S$), density, molar volume, and Packing density.
within the linear response limit. Temperature-dependent measurements were performed using a home built furnace with a temperature controller in the range 120 °C to 300 °C; the temperature was measured using a K type thermocouple to an accuracy of ±1 °C. Complex conductivity \( \tilde{\sigma} = \frac{k}{\tilde{Z}(f)} \) was calculated for each sample and for all the temperature range from 120 °C to 300 °C. We report here only the analysis of the frequency-independent DC part of the conductivity data.

Figure 1. XRD patterns of undoped and doped glasses with Nickel ferrite (a) VZL and VZLFe (b) VNL and VNLFe.

Figure 2. DSC Patterns of doped and undoped glass samples (a) VZL (b) NF doped VZL (c) VNL (d) NF doped VNL.
3. Results and discussion

3.1. Thermal properties

The thermal stability $S$ of the glasses against crystallization was calculated by the equation:

$$S = T_X - T_g$$

where, $T_X$ and $T_g$ are the onset of crystallization temperature and the glass transition temperature, respectively. The values of the glass transition temperature, $T_g$, the onset of crystallization temperature, $T_X$ and thermal stability $S$, are listed in table 1. The compositional dependence of the glass transition temperature $T_g$ and thermal stability $S$ of the glass samples are plotted in figure 3 in accordance with mol% Li$_2$O for undoped and NF doped glasses.

In figure 3(a) a comparison of $T_g$ and $S$ for VZL and VNL glass samples are made. $T_g$ and $S$ have an opposite trend with respect to each other in VZL samples whereas in VNL samples these properties scale one with the other. The VZL and VNL samples doped with NF have shown an almost linear variation of these properties.

3.2. Density, molar volume, and packing density

Density is used to determine various structural aspects of glasses [23]. The same family of glass samples may be differing in density because of the difference in packing and amount of constituents. It depends on the nature and how ions can enter the glass structure [24]. Packing density is an inherent property of glass. In the present glasses, there may be ionic and covalent packing.

Table 1 contains the calculated density values, molar volume, and packing factor for undoped and NF doped glasses. Hoppe suggested that the packing fraction may be more useful to express the experimental density of glasses even more than molar volume because the packing fraction is helpful in revealing the microscopic structure of the glass. He pointed out that packing is inherently limited by the choice of ionic radii, which have a larger impact on volume [25].

The glass sample having a component $x\%A_yB_z$, where $A$ is a cation, $B$ is an anion and $x$ is mol%, $y$ and $z$ are the valencies of the cation and anion, respectively. Then the packing factor $V_p$ is given by

$$V_p = \frac{4\pi N}{3}(y r_A^3 + z r_B^3)$$

where, $N$ is the Avogadro number, $r_A$ and $r_B$ are the ionic radii of the cation and anion, respectively.

Consequently, the packing density $V_d$ is calculated by

$$V_d = \frac{\rho}{M} \sum x_i V_p$$

where $\rho$ and $M$ are density and its molecular weight, respectively.

Figure 4 shows the variation of density and packing density with respect to variation in lithium content in undoped and doped glasses.

The packing density of the undoped glass samples is less than their doped counterparts. The packing density of undoped VZL is greater than the undoped VNL glass sample (see figure 4(a)). From figure 4(b), one can...
observe that in the case of NF doped VZL and VNL, packing density in VZLFe increases monotonically with the lithium content whereas it goes through a minimum in VNLFe as lithium content increases.10.1088/0034-4885/72/4/046501

3.3. Concentration and distance of separation between atoms

The concentration of ions A and B in the general formula $x\%A_xB_y$ is given by the following relation:

$$n(A) = \frac{bxN}{100V_m}$$  \hspace{1cm} (4)

where $x$, $N$ and $V_m$ are mole percentage, Avogadro number, and molar volume, respectively.

From values of concentration of atoms, the average shortest distance of separation between like atoms can be calculated using the relation:

$$r = \left(\frac{1}{n}\right)^{\frac{1}{3}}$$  \hspace{1cm} (6)

Using equations (4)–(6), the concentrations of Vanadium $n(V)$ and Oxygen $n(O)$, the separation between V atoms $r(V-V)$ and O atoms $r(O-O)$ are calculated. The values are listed in table 2. The average shortest separation between V and O, $r(V-O)$ for VO$_5^+$ configuration is calculated by considering vanadium to be at the center of a square made up of four oxygen atoms. There will be one oxygen connected to vanadium on top. For simplicity, all oxygen vanadium distances are considered to be the same. As can be seen from table 2, the values of $r(V-V)$ for VZL of undoped glasses lie between 1.78 nm and 1.79 nm, VNL undoped glasses lie between 1.923 nm and 1.825 nm. For VO$_5^+$, $r(V-O)$ for VZL lies from 4.65 Å to 4.66 Å and VNL from 4.99 Å to 4.74 Å. This shows that in VZL glasses the V—O distance is unaffected by the lithium substitution. But in VNL glasses the substitution of lithium has an effect of slightly decreasing the V—O distance.

The concentration of vanadium ions $n(V)$ for VZL and VNL is from (~1.76 to 1.74) × 10$^{20}$/cc and (~1.41 to 1.64) × 10$^{20}$/cc, respectively. Slight increase of $r(V-V)$ and $r(V-O)$ in the VZL family of glasses (doped and undoped) with the increase of lithium indicates that when lithium ions are added, the structure of the glass opens up as well as weakens. Therefore, the $T_g$ decreases. Similarly, the decrease of $r(V-V)$ and $r(V-O)$ for VNL glasses (doped and undoped) as the lithium mol% increases shows that the structure becomes compact and the glass strengthens. Thus the glass transition temperature $T_g$ increases. This may be because the atomic radii of Zn (138 pm) is smaller than that of Nb (146 pm) which has comparable atomic radius as that of Li (145 pm). As Zn is replaced by larger Li, the network opens up in the case of VZL glasses. In the case of VNL where the atomic radii of Nb and Li are comparable, the electropositivity of Li may prevail. As Li is more electropositive than Nb (electronegativity 0.98 as compared to Nb with electronegativity 1.6), the substitution of the former at the expense of the later breaks the oxygen bonds and creates more non-bridging oxygen. This collapses the glass network.

Figure 4. Variation of Density and Packing density in glass samples (a) undoped VZL and VNL (b) NF doped VZL and VNL with respect to % Li$_2$O.
From figure 5, we observe that as the packing density of the glasses varies, it affects the thermal stability. Here the concentration of lithium ions is also significant in addition to the nickel ferrite. The VNL families of glasses are less packed compared to the VZL family of glasses. The doped glasses have good thermal stability. A larger value of thermal stability may be needed for the crystallization of different phases inside the glass. Doping nickel ferrite has not only increased the thermal stability and packing density of the glass sample but it has also become the cause for more than one exothermic peaks to be formed up to the temperature we have run the DSC measurements. The presence of more than one peaks shows that different phases could be crystallized in the glass.

From all the corroborative studies performed on the VNL and VZL family of glasses, we have found that the addition of Nickel Ferrite greatly increases the thermal stability of these glasses. This may be of technological importance as higher thermally stabilized glasses are more useful in industry. Among VNL and VZL family, VZL is thermally more stable and have higher packing density.

### 3.4. DC electrical conductivity

The DC conduction in glasses can be due to polaron hopping or ionic motion or sometimes both/mixed. Moving ions carry a charge and thus produce an electrical response that can be detected by a variety of experimental techniques [26]. There are experimental facts that in materials with high ion concentration, at any given time only part of the ions are actively involved in a back-and-forth motion and become the cause for conduction [27, 28]. Information about these motions on different time and length scales can be obtained by using impedance or conductivity spectroscopy.

The total conductivity obeys Joncher’s power law. The real part of the frequency-dependent conductivity has a relation:

\[
\sigma(\omega) = \sigma_0 + \sigma_1 \omega^n
\]

where \(\sigma_0\) and \(\sigma_1\) are constant, \(\omega\) is the angular frequency, and \(n\) is the power law exponent. The exponent \(n\) can be determined experimentally by fitting the measured conductivity to the above equation.

### Table 2. Concentration of ions, atom-atom separation and stretching force constant between atoms of glass samples.

The values are derived from the molar volume which is calculated using density values accurate to 3rd decimal. Thus the 3rd decimal place is retained for all the derived values in the table.

| Sample Code | \(n(V) \times 10^{-20}/\text{cc}\) | \(n(O) \times 10^{-20}/\text{cc}\) | \(r(V-V)\) (nm) | \(r(O-O)\) (nm) | \(r(V-O)\) VO\(^5\) (Å) |
|-------------|-----------------|-----------------|----------------|----------------|-----------------|
| VZL15       | 1.756           | 1.786           | 1.786          | 1.316          | 4.654           |
| VZL20       | 1.751           | 1.787           | 1.787          | 1.317          | 4.658           |
| VZL25       | 1.741           | 1.791           | 1.791          | 1.320          | 4.666           |
| VZLFe 15    | 1.695           | 1.807           | 1.807          | 1.331          | 4.705           |
| VZLFe 20    | 1.720           | 1.798           | 1.798          | 1.325          | 4.683           |
| VZLFe 25    | 1.731           | 1.795           | 1.795          | 1.322          | 4.674           |
| VNL15       | 1.406           | 1.923           | 1.923          | 1.417          | 4.987           |
| VNL20       | 1.346           | 1.863           | 1.863          | 1.373          | 4.824           |
| VNL25       | 1.644           | 1.825           | 1.825          | 1.345          | 4.735           |
| VNLFe 15    | 1.474           | 1.893           | 1.893          | 1.395          | 4.934           |
| VNLFe 20    | 1.539           | 1.866           | 1.866          | 1.375          | 4.862           |
| VNLFe 25    | 1.627           | 1.832           | 1.832          | 1.350          | 4.774           |

From figure 5, we observe that as the packing density of the glasses varies, it affects the thermal stability. Here the concentration of lithium ions is also significant in addition to the nickel ferrite. The VNL families of glasses are less packed compared to the VZL family of glasses.

The doped glasses have good thermal stability. A larger value of thermal stability may be needed for the crystallization of different phases inside the glass. Doping nickel ferrite has not only increased the thermal stability and packing density of the glass sample but it has also become the cause for more than one exothermic peaks to be formed up to the temperature we have run the DSC measurements. The presence of more than one peaks shows that different phases could be crystallized in the glass.

From all the corroborative studies performed on the VNL and VZL family of glasses, we have found that the addition of Nickel Ferrite greatly increases the thermal stability of these glasses. This may be of technological importance as higher thermally stabilized glasses are more useful in industry. Among VNL and VZL family, VZL is thermally more stable and have higher packing density.

### Figure 5. Packing density and Stability of glass samples (a) VZL and VNL (b) NF doped VZL and VNL with respect to %Li_2O.
is the dimensionless frequency exponent dependent on temperature and decreases with increase in packing density. But at temperature 220°C, glass; otherwise, both doped and undoped glasses have a similar trend of decreasing conductivity with an extent. But the doping is found to increase the thermal stability of these glasses.

Figure 6 shows the conductivity spectra of representative glass samples. The DC conductivity was extracted by extrapolating the frequency-independent region of the spectra. Figure 7 presents the variation in DC conductivity as a function of packing density at various temperatures. In figures 7(a)–(c) it is observed that the packing density decreases slightly in case of undoped and increases in case of doped VZL glasses as lithium is added. The DC conductivity is seen to decrease first and then increase as the lithium content increases in VZL glasses while the doped VZL glasses (VZLF) show a monotonic decrease in conductivity with respect to increase in packing density. But at temperature 220°C, glass with 20 mol% lithium content shows highest conductivity.

It is observed that in VNL family of glasses DC conductivity decreases as packing density increases as a function of lithium concentration. An increasing temperature slightly changes the behavior of 25 mol% lithium glass; otherwise, both doped and undoped glasses have a similar trend of decreasing conductivity with an increase in packing density (see figures 7(d)–(f)).

Table 3. DC conductivity values of the present glass samples at different temperatures.

| Sample Code | 120 °C | 140 °C | 160 °C | 180 °C | 220 °C |
|-------------|--------|--------|--------|--------|--------|
| VZL 15      | 3.47 × 10⁻⁷ | 1.08 × 10⁻⁶ | 1.95 × 10⁻⁶ | 3.67 × 10⁻⁶ | 1.7 × 10⁻⁶ |
| VZL 20      | 3.2 × 10⁻⁷ | 8.61 × 10⁻⁷ | 1.33 × 10⁻⁶ | 2.47 × 10⁻⁶ | 4.14 × 10⁻⁶ |
| VZL 25      | 6.24 × 10⁻⁷ | 1.55 × 10⁻⁶ | 2.92 × 10⁻⁶ | 5.68 × 10⁻⁶ | 1.37 × 10⁻⁵ |
| VZLF 15     | 3.35 × 10⁻⁷ | 9.45 × 10⁻⁷ | 1.89 × 10⁻⁶ | 3.12 × 10⁻⁶ | 1.70 × 10⁻⁶ |
| VZLF 20     | 2.76 × 10⁻⁷ | 7.03 × 10⁻⁷ | 1.38 × 10⁻⁶ | 2.57 × 10⁻⁶ | 3.5 × 10⁻⁶ |
| VZLF 25     | 2.52 × 10⁻⁷ | 6.36 × 10⁻⁷ | 1.29 × 10⁻⁶ | 2.62 × 10⁻⁶ | 1.67 × 10⁻⁶ |
| VNL 15      | 2.2 × 10⁻⁶ | 6.66 × 10⁻⁷ | 1.21 × 10⁻⁵ | 2.1 × 10⁻⁵ | 4.54 × 10⁻⁶ |
| VNL 20      | 7.67 × 10⁻⁷ | 2.0 × 10⁻⁶ | 3.12 × 10⁻⁶ | 3.76 × 10⁻⁶ | 3.07 × 10⁻⁶ |
| VNL 25      | 6.28 × 10⁻⁷ | 1.78 × 10⁻⁶ | 3.17 × 10⁻⁶ | 3.65 × 10⁻⁶ | 1.62 × 10⁻⁶ |
| VNLFe 15    | 4.27 × 10⁻⁶ | 1.23 × 10⁻⁵ | 2.1 × 10⁻⁵ | 3.46 × 10⁻⁵ | (5.22 × 10⁻⁶)⁴ |
| VNLFe 20    | 4.79 × 10⁻⁷ | 1.19 × 10⁻⁶ | 2.29 × 10⁻⁶ | 4.73 × 10⁻⁶ | 2.06 × 10⁻⁶ |
| VNLFe 25    | 3.37 × 10⁻⁷ | 1.10 × 10⁻⁶ | 2.17 × 10⁻⁶ | 4.25 × 10⁻⁶ | (1.04 × 10⁻⁶)⁴ |

* Estimated Value.

\[ \sigma'(\omega) = \sigma \left( 1 + \left( \frac{\omega}{\omega_b}\right)^\eta \right) \]  \hspace{1cm} (8)

Where, \( \sigma'(\omega) \) and \( \sigma \) are AC and DC conductivities. \( \omega_b \) is the threshold or onset frequency above which the AC contribution takes over and \( \eta \) is the dimensionless frequency exponent dependent on temperature [29].

Figure 6 shows the conductivity spectra of representative glass samples. The DC conductivity was extracted by extrapolating the frequency-independent region of the spectra. In the figure, the spectra are shown from 100 Hz to 10 KHz. Data lower than 100 Hz was noisy and after 10 KHz the frequency dependency of conductivity sets in. Table 3 lists the DC conductivity values at different temperatures for all the glass samples.

A closer look at table 3 reveals that the doping of Nickel ferrite has not enhanced the conductivity to a large extent. But the doping is found to increase the thermal stability of these glasses.

Figure 7 presents the variation in DC conductivity as a function of packing density at various temperatures. In figures 7(a)–(c) it is observed that the packing density decreases slightly in case of undoped and increases in case of doped VZL glasses as lithium is added. The DC conductivity is seen to decrease first and then increase as the lithium content increases in VZL glasses while the doped VZL glasses (VZLF) show a monotonic decrease in conductivity with respect to increase in packing density. But at temperature 220°C, glass with 20 mol% lithium content shows highest conductivity.

It is observed that in VNL family of glasses DC conductivity decreases as packing density increases as a function of lithium concentration. An increasing temperature slightly changes the behavior of 25 mol% lithium glass; otherwise, both doped and undoped glasses have a similar trend of decreasing conductivity with an increase in packing density (see figures 7(d)–(f)).
A decrease in packing density represents more open space and lower hindrance to the movement of the mobile ions responsible for electrical conduction. Thus even though the variation in packing density is very small there is a change in conductivity in VZL and VZLFe glasses.

On the other hand, a gradual increase in packing density in VNL and VNLFe glasses hinders the movement of the mobile ions resulting in a monotonic decrease in conductivity.

4. Conclusion

In the present study, the thermal, physical, and DC electrical properties of lithium substituted zinc and niobo vanadate glass samples were investigated especially paying attention to the impact of doping nickel ferrite. XRD, Density, and DSC measurements were carried out. Physical and thermal properties like packing density, the distance between atoms, the concentration of species, thermal stability were derived from these measurements. The thermal stability increases significantly by doping Nickel Ferrite from 5°C to 30°C in zinc vanadate glasses. Packing density varies with mol% of lithium ions from 0.43 to 0.42 in zinc vanadate glasses and from 0.40 to 0.42 in nickel vanadate glasses. Doping of Nickel ferrite varies the packing density from 0.42 to 0.43 in zinc vanadate glasses whereas it stabilizes the packing density to 0.42 in nickel vanadate glasses. The variation of density of cross-linking, the tightness of the packing in the network, the coordination of the network formers are the causes for variation of densities, molar volume and packing density of the glass samples. The change of atomic sizes and electronegativity within the composition were also playing a great role in the thermal and structural changes of the glass samples. It is found that lithium substituted zinc vanadate glasses and its doped counterparts are more thermally stable than the niobo vanadate glasses. Due to coordination change in the glass systems as temperature varies, DC conductivity of glass shows anomalous behavior.

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**Authors contributions**

GVH and KPR formulated the research, KPR provided the facilities to carry out the research. BG performed the experiments and collected the data, BG and GVH analyzed the data. All the authors contributed to the manuscript.

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**References**

[1] You J, Dou L, Hong Z, Li G and Yang Y 2013 Prog. Polym. Sci. 38 1909
[2] Dresselhaus M S and Thomas J L 2001 Nature 414 332
[3] Rashid S M, Deb B and Gupta R 2018 J. Appl. Conf. Proc. 1998 020017
[4] Akia M, Yazdani F, Motaee E, Han D and Arandiyan H 2014 Biofuel Res. J 1 16
[5] Mohan D, Pittan C U Jr and Steele P H 2006 Energy Fuels 20 848
[6] Long J W, Dunn B, Rolison D R and White H S 2004 Chem. Rev. 104 4463
[7] Ayfon S, Krumeich F, Mensing C, Borgschulte A and Nesper R 2014 Sci. Rep. 4 7113
[8] Ke Y, Balin I, Wang N, Lu Q, Tok A I, White T J, Magdassi S, Abdulhalim I and Long Y 2016 ACS Appl. Mater. Interfaces 8 33112
[9] Qu Q, Zhu Y, Gao X and Wu Y 2012 Adv. Energy Mater. 2 950
[10] Li Y, Yao J, Uchaker E, Yang J, Huang Y, Zhang M and Cao G 2013 Adv. Energy Mater. 3 1171
[11] Mansour E, Moustafa Y M, El-Damrawi G M, Abd EI-Maksoud S and Doweidar H 2001 Physica B 305 242
[12] Austin I G and Sayer M 1974 J. Phys. C: Solid State Physics 7 905
[13] Owen A E 1977 J. Non-Cryst. Solids 25 370
[14] Ungureanu M C, Lévy M and Souquet J L 2000 Ceramics—Silikáty 44 81
[15] Nitta N, Wu F, Taelee J and Yushin G 2015 Mater. Today 18 252
[16] Inoue A, Zhang T and Masumoto T 1990 Mater. Trans., JIM 31 177
[17] Bingham P A, Hand R J and Forder S D 2006 Mater. Res. Bull. 41 1622
[18] Pisarski W A, Goryczk T, Wodecka-Dus B, Plonska M and Pisarska J 2005 Mat. Sci. Eng. B—Adv 122 94
[19] Souri D 2017 J. Non-Cryst. Solids 475 136
[20] Flaifel M H, Ahmad S H, Hassan A, Bahri S, Tarawneh M A and Yu L 2013 Composites: Part B 52 334
[21] Sivakumar P, Ramesh R, Ramandan A, Ponnusamy S and Muthamizhcheivan C 2011 Mater. Res. Bull. 46 2208
[22] Roling B 1999 J. Non-Cryst. Solids 244 34
[23] Charles R J 1958 J. Appl. Phys. 29 1549
[24] Doweidar H 1998 J. Non-Cryst. Solids 240 55
[25] Hoppe U 1999 J. Non-Cryst. Solids 248 11
[26] Dyre J C, Maass P, Roling B and Sidebottom D L 2009 Rep. Prog. Phys 72 046501
[27] Roling B, Martiny C and Bruckner S 2001 Phys. Rev. 63 214203
[28] Murugavel S and Roling B 2004 J. Phys. Chem. B 108 2564
[29] Almond D P and West A R 1983 Nature (London) 306 456