Lithium-doped vanadates ($V_{2-x}Li_xO_5-\delta$ (0.15 $\leq x \leq$ 0.30)) are synthesized by melt-quench method. The physical, structural, optical, thermal and conducting properties of as-quenched samples are investigated using various experimental techniques to study their suitability for electrolyte in battery/solid oxide fuel cell application. X-ray diffraction (XRD) patterns confirm the formation of three different crystalline phases. FTIR and Raman spectra indicate that the doping of $Li_2O$ into $V_2O_5$ leads to a transition from $VO_5^-$ into $VO_4^-$ structural unit. The optical diffused reflectance spectra revealed that the optical band gap ($E_g$) decreases from 2.2 to 2.08 eV while Urbach energy ($E_U$) increases (0.31–0.41 eV) with the addition of $Li_2O$ content in place of vanadium. The thermal stability is studied by thermogravimetric analyser (TGA). The DC conductivity of the present samples is increased from 0.08 to 0.12 S cm$^{-1}$ at 450 °C with $Li_2O$ doping. These materials can be used as electrolyte for battery/solid oxide fuel cell due to their good conductivity (~0.12 S cm$^{-1}$) at 450 °C.

Solid oxide fuel cells (SOFCs) are most efficient electrochemical devices which convert chemical energy into electricity with heat and water as a by-product. SOFCs are considered as eco-friendly since there is no production of sulfur or nitrogen oxides (only CO$_2$) along with fuel flexibility (H$_2$, CO, hydrocarbons and biogases)\textsuperscript{1-3}. Since, the high operating temperature of SOFC leads to degradation, coefficient of thermal expansion mismatch, electrode sintering and catalyst poisoning among the components of SOFCs\textsuperscript{1-3}. Thus, a lot of research is carried out to develop new materials that can meet the requirements at lower operating temperature of SOFCs\textsuperscript{4-5}. Doped $V_2O_5$ materials can be a good choice for low temperature (600–800 °C) SOFCs applications due to their good conductivity at lower temperature\textsuperscript{6}. The electrical conduction in $V_2O_5$ based materials arises by exchanging of unpaired 3d$^1$ electrons (hopping) between $V^{4+}$ and $V^{5+}$ valence states, $V^{4+}$-$O$-$V^{5+}$-$O$-$V^{4+}$. These unpaired electrons are induced polarization around vanadium ions which leads to form polaron\textsuperscript{6,7}. Alkali metal oxide doped vanadates have been studied widely due to their numerous applications in optical and electronic devices\textsuperscript{1,2,8}. The chemical nature and concentration of dopants play a vital role to change the oxidation state of vanadium which leads to a creation of oxygen vacancies to maintain overall electrical neutrality of the vanadate systems\textsuperscript{5,10}. Punia \textit{et al}. have reported the increasing trend of density and molar volume due to change in structure from VO$_3$ tetrahedral to VO$_5$ trigonal bi-pyramid with the addition of $Bi_2O_3$ in zinc vanadates\textsuperscript{11}. In addition to this, alkali ions doped materials usually show mixed electronic and ionic conductivity behavior with temperature. Doped bismuth vanadates ($Bi_xV_{2-x}AlO_5-\delta$) show good conductivity ~0.2 S cm$^{-1}$ at 500 °C due to the higher oxygen vacancies and stabilization of high conducting $\gamma$-phase at room temperature\textsuperscript{12}. The highest conductivity i.e. $6.6 \times 10^{-4}$ S cm$^{-1}$ for $Bi_xV_{2-x}AlO_5-\delta$ ($x=0.2$) system at 500 °C has been reported by Ravikant \textit{et al}.\textsuperscript{4}. Chakrabarty \textit{et al}.\textsuperscript{13} studied the doping effect of $Na_2O$ on conducting properties of $Na_2O$-$V_2O_5$ system and found an increment in conductivity (0.05 $\times$ 10$^{-3}$–19.5 $\times$ 10$^{-3}$ Sm$^{-1}$) with $Na_2O$ concentration at room temperature. A study of $V_{2-x}MgO_x$ ($x=0.05$–0.30) systems has been revealed a decreasing trend in density (3.2–2.7 g cm$^{-3}$) and thermal stability with MgO concentration. The structural transition has occurred from VO$_3$ to VO$_5$ polyhedra with MgO dopant. DC conductivity decreases from 10$^{-1}$ Sm$^{-1}$ to 10$^{-4}$ Sm$^{-1}$ while activation energy increases from 0.27 to 0.44 eV with an increase in MgO content in place of vanadium\textsuperscript{6}. The optical bandgap increases whereas Urbach energy decreases with the increasing content of $Bi_2O_3$ due to decreasing oxygen vacancies\textsuperscript{14}.  

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Electrical properties of MnO₂ doped V₂O₅ system are also reported. Tsuzuki et al. have investigated V₂O₅-MO (M = Mg, Ca and Ba) systems and correlate the structural changes with electrical properties. In most of the cases, these doped systems are prepared by solid-state reaction/chemical method followed by slow cooling which leads to lower the conductivity due to ordering in oxygen vacancies. It has been reported by some research groups that quenched samples have higher disordering/defects which leads to increase in the overall electrical conductivity. The high quenching rate encourages the reduction of vanadium which leads to higher disordering and hence may increase the overall conductivity. Based on above discussion, it could be concluded that processing parameters and chemical nature of dopants affect the properties significantly particularly conductivity. Therefore, the motivation of the present work is to study the effect of systematic change of lower valance dopant (Li₂O) concentration on optical, thermal and conducting properties of V₂O₅ grown by melt-quench technique. The V₂−ₓLiₓO₅−δ (x = 0.15–0.30) systems have been synthesized by melt-quench followed by various characterization techniques to study their structural, optical, thermal and electrical properties to check their suitability as electrolytes for SOFCs applications.

**Results and Discussion**

**Physical properties.** Various physical parameters such as density, molar volume and ionic concentration and their inter-ionic distance and polaron radius are calculated for the as-quenched samples and depicted in Table 1.

| Sample ID | Molecular weight, \( M \) (gmol\(^{-1}\)) | Density, \( \rho \) (gcm\(^{-3}\)) | Molar volume, \( V_m \) (cm\(^3\)mol\(^{-1}\)) | Ionic concentration, \( N_i \) (×10\(^{23}\) cm\(^{-3}\)) | Inter-ionic distance, \( R_i \) (Å) | Polaron radius, \( r_p \) (Å) |
|-----------|-------------------------------------------|-----------------------------------|---------------------------------------------|----------------------------------|-------------------------------|------------------|
| VL-0.15   | 170.48                                    | 3.09                              | 55.17                                       | 1.63                             | 1.82                          | 0.73             |
| VL-0.20   | 166.68                                    | 3.00                              | 55.56                                       | 2.16                             | 1.66                          | 0.67             |
| VL-0.25   | 162.88                                    | 2.93                              | 55.59                                       | 2.70                             | 1.54                          | 0.62             |
| VL-0.30   | 159.08                                    | 2.86                              | 55.62                                       | 3.24                             | 1.45                          | 0.58             |

Table 1. Physical parameters with their labels of the as quenched samples.

Figure 1. Change in density and molar volume with Li₂O content in V₂O₅.
The polaron radius ($r_p$) values are also calculated using $R_i$ (Table 1). These polaron radius values decrease from 0.7 to 0.5 Å (Table 1) with Li$_2$O dopant due to increases $R_i$. The magnitude of polaron radius values suggested that they are highly localized and this localization effect increases with dopant (Li$_2$O) concentration.

Structural properties. X-ray diffraction (XRD). Figure 3 represents the XRD patterns of the Li$_2$O modified V$_2$O$_5$ as-quenched samples. The as-quenched samples exhibit three crystalline phases i.e. major orthorhombic Li$_{0.04}$V$_2$O$_5$ (ICDD: 01-085-0608), minor monoclinic Li$_{4}$V$_{10}$O$_{27}$ (ICDD: 00-046-0187) and minor monoclinic Li$_{0.30}$V$_2$O$_5$ (ICDD: 00-018-0755). The diffraction peak (001) at 20.3° corresponds to Li$_{0.04}$V$_2$O$_5$ major phase, which shows higher angle shift with Li$_2$O content as shown in the inset of Fig. 3. The shifting of peak towards higher diffraction angle side is the evidence of lattice contractions$^{19}$. This is due to the smaller cationic radius Li$^{1+}$ (0.167 nm) in comparison to V$^{5+}$ (0.171 nm). As a result of the substitution of the larger cationic radius of V by the smaller cationic radius of Li, the lattice compression (compressive strain) arises in the Li$_{0.04}$V$_2$O$_5$ crystalline phase$^{19}$. Further comparing the peak intensities of the phases, it is observed that the intensity of the major phase...
The intensity of the two other phases, i.e., Li0.30V2O5 and Li4V10O27, increases as dopant concentration increases, indicating a higher volume fraction of these phases as given in Table 2. The volume fraction of less symmetric phases (monoclinic) increases as dopant concentration increases.

**FTIR spectroscopy analysis.** Figure 4 shows infrared (IR) spectra at room temperature to investigate the structural changes with increasing concentration of Li2O dopant. The IR spectra exhibited prominent absorption bands at 1022, 1000, 957, 916, 819, 753, 602, 488 cm⁻¹. The absorption bands at 1022 and 1000 cm⁻¹ are ascribed to the vibrations of isolated V=O vanadyl groups in VO5 trigonal bipyramids. This characteristic stretching band with Li2O doping present samples, which is associated with the layer structure of the V2O5. The broadness of this band decreases with increasing Li2O content due to the decrease in the number of ionic groups and V=O bonds. Additionally, this band has a small shift to the lower wavenumber, which suggests the reduction of vanadium (V⁵⁺ to V⁴⁺/V³⁺) due to the addition of lithium content. The V=O bond length increases due to the larger size of V⁴⁺ (0.67 Å) than V⁵⁺ (0.60 Å), results in requiring lower energy for the lattice vibration. The high-temperature melt quenching of the present samples could be responsible for the reduction in the oxidation states of vanadium due to scarcity of oxygen in the furnace at high temperature. The band at 957 cm⁻¹ assigned to the symmetric and anti-symmetric stretching vibration of the isolated VO2 groups in the VO4 polyhedra. A small kink at 916 cm⁻¹ has appeared with the addition of Li2O content. It is also assigned to the asymmetric stretching vibrations of the isolated VO2 groups in VO4 polyhedra. Another band at about 819 cm⁻¹ is attributed to the vibrations of isolated [VO4] tetrahedral. The broadness of this band decreases with Li2O content and splits into two bands (819 and 753 cm⁻¹) at maximum Li2O content sample (VL-0.30). This new generated band is assigned to V–O–V stretching. The band at 602 cm⁻¹ is ascribed to the bending vibrations of V=O units. The band at 488 cm⁻¹ may be assigned to the bending modes of the V=O network consisting of [VO₄] polyhedral and a characteristic vibration of Li⁺ cations. This band shows a small shift to the higher wavenumber with the highest doping of Li2O (VL-0.30 sample), which shows that some portion of V⁴⁺ to V⁵⁺ oxidized to V⁵⁺. The bond length between vanadium and oxygen decreases due to the smaller size of V⁵⁺ as compared to V⁴⁺/V³⁺, which leads to strengthening of this vibration. According to Dimitriv et al., the

| Sample ID | E_r (eV) | E_v (eV) | σ_ac at 450°C and 10⁷ Hz (Scm⁻¹) | σ_dc at 50–250°C (Scm⁻¹) | E_a (eV) | Present phases | Volume fraction (%) |
|-----------|---------|---------|-------------------------------|--------------------------|---------|----------------|-------------------|
| VL-0.15   | 2.22    | 0.31    | 0.11                          | 0.08                     | 0.26    | Li₁₀.₋₁₂V₂O₅  | 95.35             |
|           |         |         |                               |                          |         | Li₁₋₂V₂O₅       | 3.05              |
|           |         |         |                               |                          |         | Li₄₋₂V₁₀O₂₇     | 1.58              |
| VL-0.20   | 2.16    | 0.37    | 0.17                          | 0.09                     | 0.21    |                 | 86.45             |
|           |         |         |                               |                          |         |                 | 8.30              |
|           |         |         |                               |                          |         |                 | 5.10              |
| VL-0.25   | 2.14    | 0.40    | 0.21                          | 0.11                     | 0.31    |                 | 80.74             |
|           |         |         |                               |                          |         |                 | 11.97             |
|           |         |         |                               |                          |         |                 | 7.27              |
| VL-0.30   | 2.08    | 0.41    | 0.29                          | 0.12                     | 0.43    |                 | 60.26             |
|           |         |         |                               |                          |         |                 | 20.70             |
|           |         |         |                               |                          |         |                 | 18.00             |

**Table 2.** Optical and conductivity parameters of the as quenched samples.
vanadates can exist in the form of layers and chains and smaller complexes, which depends on the ratio of V\textsubscript{2}O\textsubscript{5} and Li\textsubscript{2}O in the samples. The \textit{Li}\textsuperscript{1+} ions can be situated between the vanadate chains, whereas some Li ions can be form independent polyhedra (LiO\textsubscript{n}), which can be located in the chains themselves\textsuperscript{26}. This assumption suggests two different forms of Li ions distribution in the V–O polyhedra (interstitial sites or substitutional sites) as shown in Fig. 5(a,b). In interstitial condition, the Li ions can be located between vanadate chains and layers. Li ions can interact with the isolated V=O bonds, which leads to the longer bond length (Fig. 5(a)). In substitutional condition, Li ions can occupy positions in the vanadate chain, which leads to break the some of the weaker V-O-V bonds and form new V-O-Li bridges (Fig. 5(b))\textsuperscript{26}. Also, there is a possibility to take place a redox reaction (\(2\text{V}^{5+} + \text{O}^{2-} \rightarrow 2\text{V}^{4+} + \text{O}_2\)) during the melting of the batches at 900 °C. The V\textsuperscript{5+} ions take a part as a network forming positions with VO\textsubscript{5} structural units which can be formed V-O-Li linkages\textsuperscript{24}. Therefore, the influence of Li ions on the V=O band is restricted and have an indirect manifestation which leads to preserve this band at \(~\text{1022 cm}^{-1}\textsuperscript{26}. Thus, the V=O band is partially affected by Li\textsubscript{2}O doping in the present samples.

**Raman spectroscopy analysis.** Raman spectra of as-quenched samples (Fig. 6) show the expected vanadia signals around 139, 191, 279, 400, 484, 516, 689 and 988 cm\textsuperscript{-1}. The sharp Raman band at 988 cm\textsuperscript{-1} is attributed to the symmetric stretching of V=O groups in pure V\textsubscript{2}O\textsubscript{5}\textsuperscript{29,30}. The intensity of this sharp V=O band increases with lithium content, establishes the formation of multilayer structures of V\textsubscript{2}O\textsubscript{5}\textsuperscript{23}. The other Raman bands around 400 and 516 cm\textsuperscript{-1} are attributed to the existence of the characteristic layer structure of crystalline V\textsubscript{2}O\textsubscript{5}. Besides these, a small shoulder at 484 cm\textsuperscript{-1} is also observed, which can be due to the symmetric stretching of the V-O-V bonds in V\textsubscript{2}O\textsubscript{5}\textsuperscript{29,30}. The band at 400 cm\textsuperscript{-1} can also be due to the Li-O stretching. Another band at 279 cm\textsuperscript{-1} is assigned to the deformational mode of the surface vanadyl groups. The other band around 689 cm\textsuperscript{-1} is due to the stretching vibration of oxygen ion in bridging position between three vanadia centers\textsuperscript{29,30}. Finally, Raman band at 191 and 139 cm\textsuperscript{-1} are associated to the [VO\textsubscript{3}]-[VO\textsubscript{3}] vibrations and strongly accompanying with the layered structure. They are observed at low wavenumbers due to the heavy [VO\textsubscript{3}] units\textsuperscript{31}. Presence of all these vibrations (Figs. 4–6) substantiate the structural changes and formation of multiphase lithium vanadate in the as-quenched samples as discussed in X-ray diffraction and FTIR analysis sections.

![Figure 5. Schematic diagram of possible positions of the Li\textsuperscript{1+} ions into vanadium oxygen polyhedra: (a) interstitial sites; and (b) substitutional sites.](image)

![Figure 6. Raman spectra of Li\textsubscript{2}O doped vanadium oxide as quenched samples.](image)
UV-visible spectroscopy analysis. Figure 7(a) represents the UV-visible diffused reflectance spectra (DRS) as a function of wavelength for all the samples. The reflectance for VL-0.15, VL-0.20, VL-0.25 and VL-0.30 samples are 18.5%, 17%, 15.6% and 13.2%, respectively. The quenched reflectivity could be ascribed to the optical phonon confinement, which leads to the light trapping in the samples. This decrement in reflectivity with increasing Li$_2$O dopant into V$_2$O$_5$ lattice can be due to the reflectance onset/absorption edge towards longer wavelengths (red shift). It is good agreement with other reports. This reflectance data is used to calculate the optical band gap by Kubelka-Munk function.

$$F(R) = K/S = (1 - R)^2/2R$$

(1)

where, $F(R)$, $K$ and $S$ are the Kubelka-Munk function, absorption coefficient and scattering coefficient, respectively. The optical band gap is obtained from DRS using following equation.

$$F(R)h\nu = k(h\nu - E_g)^n$$

(2)

Where, $k$, $E_g$ and $\nu$ are the proportionality constant, optical band gap and incident photon energy, respectively. The exponent $'n'$ depends on the transition, where $n = 1/2$, 2, 3/2 and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transition, respectively. The direct optical band gap of all the samples is obtained using the Tauc plot (Fig. 7(b)) by extrapolating the straight-line portion of the plots of $(F(R)h\nu)^2$ versus $h\nu$ to energy axis (x-axis) at $\nu = 0$. The Urbach energy ($E_U$) of the samples can be calculated using the equation

$$\alpha(\nu) = \beta \exp(h\nu/E_U)$$

The inverse of the slope of the linear portion from $\ln F(R)$ versus $h\nu$ is used to measure the Urbach energy of the samples. The optical band gap decreases with increasing content of Li$_2$O into V$_2$O$_5$ for all the samples. The optical band gaps of the present samples are in the semiconductor range (2.22–2.08 eV) and comparable to earlier reported values by another research group. The sample with the lowest concentration of Li$_2$O (VL-0.15) shows the highest optical band gap (2.22 eV) while the sample with the highest concentration of Li$_2$O (VL-0.30) shows the lowest optical band gap (2.08 eV). It indicates that the Li$_2$O concentration increases the defects in the present systems. The existence of variable oxidation states of vanadium as confirmed by FTIR, Raman spectroscopy and TG analysis (as discussed in next section) can be responsible for the creation of defects and oxygen vacancies in the present samples. In addition, there is a possibility to create new energy level above the valence band due to doping of Li$_2$O. So, the filled valence band electrons easily excited to new generated energy level by dopant led to decrease the optical band gap of the samples. The Urbach energy ($E_U$) of the samples increases with increasing Li$_2$O content (Table 2). VL-0.30 sample shows the highest $E_U$ with the lowest optical band gap signifying the presence of higher disorder as compared to other samples. The optical band gap and Urbach energy both are following opposite trend to each other. It indicates that defects increase with an increase in the doping of Li$_2$O in place of V$_2$O$_5$.

Thermal properties. Figure 8(a) represents the DTA curves of lithium-doped V$_2$O$_5$ as-quenched samples in the temperature range of 30–800 °C. In DTA curves, all the samples exhibit three distinct endothermic peaks at a higher temperature (≥571 °C), which result from the melting points (Tm$_1$, Tm$_2$ and Tm$_3$) of three different phases as observed in XRD patterns. Figure 8(b) shows the TG curves of the Li$_2$O doped V$_2$O$_5$ as-quenched samples, which exhibit typical weight loss behavior. TGA thermograph shows a total weight loss of ~5% in the temperature range of 30–800 °C. The weight loss can be considered in three steps as marked I (30–120 °C), II (120–600 °C) and III (600–700 °C) in the TGA graph. The I step is assigned to the departure of adsorbed species and loss of water molecules. The II step is associated to the reduction of V$^{5+}$ to V$^{4+}$/V$^{3+}$ ions which can be shown by the following equation:

$$2V^{5+} + O^{2-} \rightarrow 2V^{4+} + O_2$$

(3)
In the III step, a little weight gain is observed in all the samples which can be related to the oxidation of $V^{3+}$ to $V^{5+}$ as written by the following equation

$$V_2O_4 + O_2 = V_2O_5$$

(4)

This weight gain during the oxidation at the higher temperature can be associated with the combination of $O_2$ and its vacancies in the present samples. The reduction of these systems is expected due to vanadium is believed to have a mixed valence state ($V^{2+}, V^{3+}$ and $V^{5+}$)$^{24,37,38}$. It is also observed that weight loss increases with the addition of $Li_2O$ on the cost of $V_2O_5$, which leads to a decrease in the thermal stability of the present samples (I and II steps). It is manifestation of waterphilic nature of the samples and it increases with an increase in $Li_2O$ concentration. The reduction of vanadium from $V^{5+}$ state to lower valance state is also increases with the addition of $Li_2O$ content. The chemical stability also decreases with $Li_2O$ concentration which is also manifested by Urbach energy and FTIR analysis of the samples. All the samples exhibit good thermal and chemical stability in the temperature range of ~300–550 °C without any phase transition (Fig. 8(a,b)) except VL-0.30 sample. However, sample with the lowest content of $Li_2O$ (7.5 mol%, VL0-0.15) shows the highest thermal and chemical stability in the temperature range of ~300–550 °C in comparison to other samples. Therefore, these samples can be used as electrolytes for solid oxide fuel cells or batteries applications.

**Conducting studies.** It is a well-known fact that hopping mechanism and band conduction are responsible for the electrical conduction in these types of materials$^{6,39}$. The frequency dependent conductivity, $\sigma_{ac}$, of the samples is determined using the following relation$^{6,39}$.

$$\sigma_{ac}(\omega) = \varepsilon_0 \varepsilon'' \omega \tan \delta$$

(5)

where, $\varepsilon_0$, $\varepsilon''$, $\omega$ and $\tan \delta$ are the permittivity of free space ($8.854 \times 10^{-12} \text{ Fm}^{-1}$), dielectric constant, dielectric loss, frequency (in Hz) of the applied electric field and tangent of loss, respectively. Figure 9(a–d) illustrates the AC conductivity ($\sigma_{ac}$) variation with frequency and temperatures (50–450 °C, step size of 50 °C). The conductivity is almost frequency independent at low frequency region (plateau region) and corresponds to the DC conductivity ($\sigma_{dc}$) of the samples$^{40}$. At the same time, the conductivity is dependent on frequency ($\sigma_{ac}$) at higher frequency region (dispersion region) and increases with increasing frequency$^{6,15,39,40}$. The plateau region signifies the randomness of ionic diffusion which is due to the long-range order transport and appreciable diffusion of mobile ions in response to the applied ac field while the dispersion region signifies the conductivity relaxation phenomena in present samples$^{6,15,40,41}$. It is also observed that $\sigma_{ac}$ increases with increasing temperature (50–450 °C) for all the samples which supports the semiconductor nature of the samples$^{6,42}$. Generally, the conductivity in such type of materials depends on the concentration and mobility of mobile ions/charge carriers i.e. electrons and holes$^{6,42}$. The mobility of mobile ions/charge carriers increases with increasing temperature which leads to increasing overall conductivity as observed in the present samples. It can be understood by the fact that thermal energy (temperature) excites more electrons from valence band to conduction band resulting in higher conductivity. Further, according to the Jonscher’s universal power law, $\sigma_{ac}$ can be written as

$$\sigma_{ac}(\omega, T) = \sigma_d(T) + A \omega^s$$

(6)

where, $A$ is the temperature dependent constant of the material, $\omega$ is the angular frequency and $s$ is the frequency and temperature dependent exponent that lies between 0–1. DC conductivity ($\sigma_d(T)$) is calculated to extrapolate AC conductivity at the lowest frequency (Fig. 9) and given in Table 2. The activation energy ($E_a$) of the conduction is calculated using the Arrhenius plot (Fig. 10) between $\ln(\sigma_d)$ and reciprocal of temperature (1000/T) by the following equation.

Figure 8. (a) DTA thermographs; and (b) thermal stability nature of $Li_2O$ modified $V_2O_5$ systems measured at 10 °C heating rate.
where, $\sigma_o$ and $k_B$ are the pre-exponential factor, and Boltzmann’s constant, respectively. The values of $\sigma_{ac}$ and $\sigma_{dc}$ show an increasing trend with an increase in lithium content (7.5–15 mol%) as shown in Fig. 11. AC conductivity lies in the range of 0.11–0.29 Scm$^{-1}$ at 450°C and 10$^7$ Hz whereas DC conductivity lies in the range of 0.08–0.12 Scm$^{-1}$ at 450°C. In vanadate materials, conductivity depends on the small polarons hopping (SPH) between V$^{4+}$ site to the neighboring V$^{5+}$ site. SPH directly affects by the mobility and number of mobile charge carriers.

On the replacement of V$^{5+}$ by Li$^+$, structure of the systems becomes more open due to transition from VO$_4$ tetrahedral to VO$_5$ trigonal bipyramid as discussed in physical parameters and structural properties. This structural change is responsible for a significant increase in oxygen vacancies with an increase in hopping of ions which leads to an increase in conductivity. In addition, decrement in density, inter-ionic distance, polaron radius and optical band gap of the samples also support this increasing trend of conductivity with the addition of Li$_2$O.
on the cost of V$_2$O$_5$ 

The calculated activation energy values of dc conduction are depicted in Table 2. The activation energy increases with increasing content of Li$_2$O except VL-0.20 sample and lies in the range of 0.26–0.43 eV (Table 2). These activation energy values clearly suggest that the ionic conduction increases with Li$_2$O concentration into V$_2$O$_5$ in the present samples.

**Conclusion**

The influence of Li$_2$O addition on physical parameters, structural, optical, thermal and conducting properties of V$_{2-x}$Li$_x$O$_5$-$\delta$ (0.15 $\leq$ x $\leq$ 0.30) systems have been investigated. XRD patterns confirmed the presence of three crystalline phases. The presence of mixed valence states of vanadium is confirmed by spectroscopic investigations. The optical band gap is decreased with Li$_2$O concentration. Thermal stability is found to decrease with the Li$_2$O addition in place of V$_2$O$_5$. AC and DC conductivity are found to enhance by the addition of Li$_2$O due to the creation of more hoping sites. Sample with the highest content of Li$_2$O (15 mol%, VL-0.30) exhibited the highest DC conductivity i.e. 0.12 Scm$^{-1}$ at 450 °C. It is observed that the transport mechanism in lithium vanadate systems is attributed to small polaron hopping (SPH) between V$^{4+}$ to V$^{5+}$ states, which is increased by the addition of lithium into vanadium. The present samples exhibit good DC and AC conductivity. Therefore, these materials can be considered as electrolytes for batteries/solid oxide fuel cells applications.

**Materials and Methods**

Powder of V$_2$O$_5$ (Loba, Chemie, 99% purity) and Li$_2$O (Sigma Aldrich, 97% purity) were used as raw materials to prepare compositions of V$_{2-x}$Li$_x$O$_5$-$\delta$, where x = 0.15(VL-15), x = 0.20(VL-20), x = 0.25(VL-25) and x = 0.30(VL-30) via melt and quench technique. The prescribed compositions are mixed using agate mortar and pestle in acetone medium for 2 h. The mixed batches were melted at 900 °C in recrystallized aluminum crucibles in an electric furnace followed by copper plates quenching in the air. The standard Archimedes principle is used to measure density ($D$) at room temperature of as-quenched samples with xylene as immersion liquid (0.863 gcm$^{-3}$). The molar volume ($V_m$) of as-quenched samples was calculated using the following equation,

$$V_m = \sum_i M_i/\rho$$

where, $\rho$ and $M_i$ are the density and molar mass of the samples, respectively. The concentration of Li ions (N) was calculated by $N_i = N_A \times$ mol% of cation $\times$ valency$/V_m$, where $N_A$ and $M$ is the Avogadro’s number and molecular weight, respectively. The average inter-ionic distance ($R_i$) was calculated using $R_i = (1/N)^{1/3}$. The polaron radius was calculated by $r_p = (R_i/2) \times (\pi/6)^{1/3}$. The X-ray diffraction (XRD) patterns of crushed samples were recorded by PANalytical X’Perts Pro MPD diffractometer with Cu-Kα radiations ($\lambda = 1.54$ Å). The scan rate and scan range were 2°min$^{-1}$ and 10–80°, respectively. Fourier transform infra-red (FTIR) spectra of as-quenched samples were recorded in the wavenumber range of 200–4000 cm$^{-1}$ at room temperature using Perkin Elmer-Spectrum-RF-1 FTIR spectrometer. The finely ground powder of as-quenched sample and KBr powder are mixed together to palletized for the FTIR measurement. The Raman spectra of the powder samples were recorded over the spectral range of 100–5000 cm$^{-1}$ using Features STR 500 Airix Raman system equipped with Ar laser (532 nm) as the excitation source.

A double beam UV-Vis spectrophotometer (Model: Hitachi 3900H) was used to record diffuse reflectance spectra (DRS) at room temperature between the wavelength 200–800 nm. Thermal analysis was carried out using TG/DTA (Exstar TG/DTA 6300) instrument of as-quenched powder samples in N$_2$ medium with a heating rate of 10 °C/min over the range of room temperature to 1000 °C. The dielectric and conductivity analysis carried out using SI-1260 Solartron analytical LCR impedance analyzer. Both sides of the as-quenched samples are coated with Pt using 3000-FC auto fine coater from JEOL to serve as an electrode. The variation in impedance with frequency and temperature were studied from 10Hz-1MHz and 50–400 °C, respectively.

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**Figure 11.** Change in AC and DC conductivity with Li$_2$O content in V$_2$O$_5$ for all samples.
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Author contributions
S. Khan carried out the majority of the presented work synthesis, characterizations and analysis of the lithium doped vanadium. The present study was conceptualized and supervised by K. Singh., Professor, Thapar Institute of Engineering and Technology, Patiala, India.

Competing interests
The authors declare no competing interests.

Additional information
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