Preparation and some properties of lithium vanadium bronzes

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Lithium vanadium bronzes with composition formula \( \text{Li}_x \text{V}_{2-x} \text{O}_5 \) (0.04 \( \leq x \leq 0.92 \)) have been prepared by solid-state reaction at 650°C in argon atmosphere. The products were characterized by X-ray powder diffraction and IR spectroscopy. The results reveal that four phases namely \( \alpha-, \beta-, \beta', \) and \( \gamma \)-phase are present in the studied range. The magnetic susceptibility for the investigated samples was measured using Gouys method. The values of the effective magnetic moments as calculated from experimental data indicate the presence of \( \text{V}^{4+} \) ions in all samples. The electrical conductivity as a function of temperature and lithium content was measured in the temperature range from room temperature to 483 K. The electrical conductivity of the samples is found to be affected by lithium content. The values of the electrical conductivity increase with temperature for the investigated samples. The electronic and ionic conductions are discussed.

Keywords: \( \text{Li}_x \text{V}_{2-x} \text{O}_5, \) XRD, IR, Magnetic susceptibility, Electrical conductivity

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The \( \text{V}_2\text{O}_5 \) network is viewed as exhibiting the characteristics of layer crystallographic shear structure. Its formula yields a wide vanadium oxide bronze (VOB) family and its structure has been described as \([\text{V}_2\text{O}_5]_n\) layers, built-up from \( \text{VO}_5 \) square pyramids sharing edges and corners, the assembly being held together via Vander Waals interaction. The term "vanadium bronzes" has been applied to the non-stoichiometric compounds of the type \( \text{M}_x \text{V}_{2-x} \text{O}_5 \), where \( \text{M} \) is an alkali metal, an alkaline earth metal, or a metal intercalated in variable amounts, \( x \), into the \([\text{V}_2\text{O}_5]_n\) network. These phases exhibit various crystal structures in which the vanadium atoms simultaneously coexist under both IV and V valance states. Lithium vanadium bronzes are a solid solution of lithium in \( \text{V}_2\text{O}_5 \) with the lithium atoms more or less ionized to give lithium ions and electrons. The electrons can be bound to lithium nuclei, bound to specific vanadium atoms to give localized \( \text{V}^{4+} \) centers or delocalized in conduction band arising from overlap of the 3d orbital of the vanadium atoms. The crystalline structure of lithium vanadium bronzes is characterized by two kinds of vanadium double chains along the b-axis, one is magnetic \( \text{V}^{4+} \) (\( S=1/2 \)) and the other one is non-magnetic \( \text{V}^{5+} \) (\( S=0 \)) chain. These chains are linked by corner sharing to form layers in (001) plain and the lithium atoms are situated between these layers. Various investigators have studied properties of \( \text{Li}_x \text{V}_2\text{O}_5 \) system due to their possible application as positive electrode for secondary batteries. This work aims to study the effect of lithium content on the formation and properties of \( \text{Li}_x \text{V}_2\text{O}_5 \). The products were characterized by X-ray diffraction (XRD), Fourier transformer infrared spectroscopy (FTIR), electrical conductivity and magnetic susceptibility studies.

Experimental Procedure

The Lithium vanadium bronzes, \( \text{Li}_x \text{V}_{2-x} \text{O}_5 \) where \( x = 0.04, 0.30, 0.48 \) and \( 0.92 \), were prepared according to the following equation:

\[
\text{V}_2\text{O}_5 + (x/2) \text{Li}_2\text{C}_2\text{O}_4 \rightarrow \text{Li}_x \text{V}_{2-x}\text{O}_5 + x \text{CO}_2
\]

The reaction is carried out by heating the finely ground and mixed reagents under argon atmosphere at 650°C for 12 h. High purity grade \( \text{V}_2\text{O}_5 \) (99%) was used, while \( \text{Li}_2\text{C}_2\text{O}_4 \) was prepared by neutralization of \( \text{H}_2\text{C}_2\text{O}_4.2\text{H}_2\text{O} \) and \( \text{LiOH.H}_2\text{O} \) solutions, where the end point was adjusted at \( \text{pH}=7 \). The prepared \( \text{Li}_2\text{C}_2\text{O}_4 \) was analyzed using X-ray powder diffraction pattern (Fig. 1) which indicates the high purity of the prepared \( \text{Li}_2\text{C}_2\text{O}_4 \) according to JCPDS card. X-ray powder diffraction patterns of the prepared samples of \( \text{Li}_x \text{V}_{2-x} \text{O}_5 \) were recorded using Philips X-ray diffractometer with Ni filter and monochromatized \( \text{CuK}_\alpha \) radiation (\( \lambda = 1.5418 \) Å). The IR spectra of \( \text{V}_2\text{O}_5 \) and the \( \text{Li}_x \text{V}_2\text{O}_5 \) samples were recorded in the frequency range of 400-1700 cm\(^{-1}\) by KBr-disc
method using FTIR-Nexus 670 (nicolite) spectrometer. The Gouy's method was used to measure the magnetic susceptibility as a function of temperature at different magnetic field intensities. The sample powder was packed in a cylindrical pyrex tube, where the sample length \( L \) was equal to 13 cm with its lower end in the uniform magnetic field. A non-inductive furnace was used to heat the sample. The temperature of the sample was measured using T-type thermocouple with its junction near the sample, keeping it freely suspended. The pull on the empty tube and the pull \( m \) on the sample were measured using an electronic balance (5-digits). The molar magnetic susceptibility was calculated using the relation

\[
\chi_m = \frac{2 m I g - M H^2}{\text{mol. wt.}}
\]

where \( M \), \( H \) and \( g \) are the mass of the sample, the uniform magnetic field intensity and the acceleration due to gravity, respectively. For conductivity measurements, the prepared samples were crushed to powders, pressed in a 1.25 cm diameter die at 5 ton and sintered at 650°C for 2 h under purified argon to yield pellets of approximately 1.25 cm diameter and 0.3 cm thickness. The surface of the sintered pellets was polished by use the use of emery paper to obtain parallel faces. Electrical conductivity measurements were made by means of ac two probe method using Standard Research System model SR 720 LCR meter in a temperature range from room temperature to 483 K at a frequency of 100 kHz and applied voltage of 1 ohm.

**Results and Discussion**

The X-ray diffraction patterns of the prepared samples are shown in Fig. 2. Identification of the different products was carried out by comparing experimental patterns with JCPDS data. Four distinct phases of lithium vanadium bronzes are identified in the range 0.04 \( \leq x \leq 0.92 \) namely \( \alpha\text{-Li}_{0.04}V_2O_5 \) with orthorhombic structure, \( \beta\text{-Li}_{0.30}V_2O_5 \) and \( \beta'\text{-Li}_{0.48}V_2O_5 \) with monoclinic structure and \( \gamma\text{-Li}_{0.92}V_2O_5 \) with orthorhombic structure. With respect to \( \alpha\text{-Li},V_2O_5 \), the structure established by Hardy et al. is directly obtained from \( V_2O_5 \) where a small amount of lithium (less than \( x = 0.1 \)) being introduced between the layers on sites that can be described as triagonal prisms. The space group of \( \alpha \)-phase with all vanadium crystallographic sites is identical to that of \( V_2O_5 \) and accommodating small amount of \( V^{4+} \) cations. The structure of \( \beta \) and \( \beta' \) phases is essentially identical to that of \( V_2O_5 \) in the resulting \( V_6O_{13} \) network and the lithium atoms are inserted in these tunnels. The structure of \( \beta \) and \( \beta' \) phases essentially differs by the positions of lithium atoms. In \( \beta' \) phase, homogeneity range is 0.22 \( \leq x \leq 0.37 \), lithium atoms occupy the \( Li_2 \) sites (maximum occupancy 50%) while in the \( \beta' \) phase, homogeneity range is 0.44 \( \leq x \leq 0.49 \), they lie in the \( Li_3 \) sites which may be fully occupied (Fig. 3 of ref. 2). \( \gamma\text{-Li}_3V_2O_5 \) has an homogeneity range of 0.88 \( \leq x \leq 1 \). The crystal structure exhibits puckered \( V_2O_5 \) layers held together by lithium atoms in octahedral coordination. Within the layers, an electronic localization has been established by crystallographic studies which also indicated that the square pyramids \( [V^{4+}O_5] \) and \( [V^{5+}O_5] \) attribute to the non-equivalent crystallographic \( V^{4+} \) and \( V^{5+} \) sites.
The IR spectra of $V_2O_5$ and the prepared $Li_xV_2O_5$ samples are shown in Fig. 4. In the spectrum of the pure $V_2O_5$, a sharp band assigned to $V=O$ stretching vibration and a broad band assigned to $V-O-V$ stretching vibration\textsuperscript{13,14} are observed at 1015 and 830 cm$^{-1}$, respectively. The spectrum changes with the increase in lithium content and with $x=0.30$ a new band appears at 998 cm$^{-1}$. In the samples with lithium content $\geq 0.30$, the original band at 1015 cm$^{-1}$ was replaced by the bands at 998 and 965 cm$^{-1}$ and they shift towards lower frequencies. On the other hand, the band at 815 cm$^{-1}$ shifted towards the lower energy with increasing Li concentration. These red shifts may be attributed to the formation of $Li...V=O$ bonds and the effect of Li ions on the polarity of $V-O-V$ bonds\textsuperscript{15}. The changes in the bond strength and subsequent changes in $V=O$ bond length were estimated by Kera\textsuperscript{16} from the band shifting around 1020 cm$^{-1}$ with alkali atoms addition. The bond strength of the $V=O$ groups is weakened by the insertion of Li ions; thus, the stretching frequency decreases from 1015 to 998 cm$^{-1}$ and 965 cm$^{-1}$. With the reduction in $V_2O_5$, the $VO_6$ polyhedral changes in symmetry and the $V=O$ bond expands linearly with the reduction\textsuperscript{17}. The expansion in the $V=O$ bond is accompanied by a decrease in the valence state of the vanadium ion and then by a change in the symmetry around the vanadium ion. In other words, the bond expansion is caused by the formation of $V^{4+}$ ion, that is $V^{4+}=O$. The transfer of electrons from alkali metals such as Li and Na to vanadium ions has been observed in alkali-vanadates by NMR and ESR spectrometry\textsuperscript{18}. Therefore, it can be concluded that the expansion in the $V=O$ bond by Li addition is caused not only by its steric effect, but also by the electron transfer from Li to the vanadium ion to form the $V^{4+}=O$ groups. With respect to the $V-O-V$ stretching
vibration in pure $\text{V}_2\text{O}_5$, the original band itself was broad; this band is found to shift towards the low frequency, on addition of Li. The X-ray results obtained in the present investigation are in agreement with the IR results that the intensities of the bands at 998 and 965 cm$^{-1}$ increase linearly with the Li content.

Figure 5 is a typical curve, which correlates the molar magnetic susceptibility and absolute temperature at a field of 1790 Oe as a function of Li content in the samples. From the figure it is clear, that, the $\chi_M$ increases with temperature at all Li content except at $x=0.04$ at which $\chi_M$ decreases. A hump is obtained at about 425 K, shifted to lower values with increasing the amount of Li in the sample. Ueda et al. found that the existence of Li in the sample and its transformation to Li$^+$ ions, leaving an electron which helps in reducing some V$^{5+}$ to V$^{4+}$, increase the magnetization in the system. This finding supports present data in Fig. 5. The free electrons (unpaired) play a role in the magnetic properties as well as the electrical properties of the samples because the two are of the same origin. It is obvious that at lower Li concentration, the amount that are transformed giving free electrons is not sufficient to play a part in magnetic process, though a peculiar behaviour was obtained at $x=0.04$ in the experimental data. The general feature of Fig. 5 is the antiferromagnetism evidenced by the appearance of humps. The shift in the hump position with Li contents means the increase in the paramagnetic region on the expense of the antiferromagnetic one.

Figure 6 indicates the behaviour of ($\chi_M$.T) as a function of T. The Curie-constant ($c$) corresponds to the straight part of the figure from which the effective magnetic moment $\mu_{\text{eff}}$, has been calculated by using the relation $\mu_{\text{eff}} = 2.84c$. The calculated values are reported in Table 1, from which it is obvious that $\mu_{\text{eff}}$ increases with Li$^+$ ion concentration. This expected result, enhances the above mentioned susceptibility.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$H=1790$ Oe</th>
<th>$H=2640$ Oe</th>
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<tr>
<td></td>
<td>$c$</td>
<td>$\mu_{\text{eff}}$, B.M.</td>
</tr>
<tr>
<td>0.04</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
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<td>0.99</td>
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</tr>
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<tr>
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Table 1 — Values of the Curie constant ($c$) and the effective magnetic moment ($\mu_{\text{eff}}$) at different Li content ($x$) for Li$\text{V}_2\text{O}_5$ samples

Fig. 5 — The temperature dependence of the molar magnetic susceptibility ($\chi_M$) of Li$\text{V}_2\text{O}_5$ bronzes at a magnetic field of 1790 Oe

Fig. 6 — $\chi_M$.T as a function of temperature for Li$\text{V}_2\text{O}_5$ bronzes at a magnetic field of 2640 Oe
data (Fig. 5). Same results were obtained from Fig. 7 as a typical curve, which correlates $\chi^1_M$ versus $T$.

Figure 8 shows the electrical conductivity of Li$_x$Y$_2$O$_5$ samples as a function of temperature and lithium content. The conductivity increased with lithium content up to $x = 0.48$, while the sample with higher lithium content ($x = 0.92$) exhibits the lower conductivity. The gradient of the linear curve decreased with increasing lithium content, from $x = 0.04$ to 0.048 but it increased with $x = 0.92$. The curves shown in Fig. 8 are regarded approximately as the electronic conductivities, since the ionic conductivity is smaller than the electronic conductivity. The deviation from electrical neutrality produced by the difference in the lithium content is compensated by the variation of the oxidation number of vanadium atom. The electrons participating in the conduction process come from the transition $V^{4+}\rightarrow V^{5+} + e$. Thus, the sample with the higher concentration of $V^{4+}$ ion has the higher concentration of conductive electrons. The ionic conductivity is proportional to the product of the concentration of the mobile ions and the mobility of the concerned ion. If the mobility does not vary with increase of alkali content, the conductivity should increase with increase of the conductive ions. The relation between lithium content and ionic conductivity was observed in the study of the mixed conduction in Li$_x$V$_2$O$_5$ by Kuwabara et al. They found that the mobility of the lithium ion decreases as the lithium content increases. Therefore, the decrease in the mobility of the lithium ion is the important reason for the observed decrease in the conductivity of the sample with higher lithium content ($x = 0.92$).

**Conclusion**

From XRD data, four phases of Li$_x$V$_2$O$_5$ bronzes namely $\alpha$, $\beta$, $\beta'$, and $\gamma$ are identified in the range of $x = 0.04$ to 0.92. The increase of lithium content, which is accompanied by increasing electron transfer from lithium to vanadium ion, affects the IR absorption bands position and they are shown to shift towards lower frequencies. The samples under investigation exhibit antiferromagnetic behaviour and the effective magnetic moment increases with lithium content. The prepared bronzes show electronic and ionic conductions. The decrease in the conductivity of $\gamma$-LiV$_2$O$_5$ may be due to the decrease in the mobility of lithium ion.
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References