

Intercalated Compounds of Vanadyl Hydrogenphosphate Hemihydrate with Divalent Transition Metal Ions and Their Electrical Properties

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Summary. Alpha-vanadyl hydrogenphosphate hemihydrate, $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$, and its intercalated Mn^{2+} , Cu^{2+} and Cd^{2+} products were prepared and characterized by chemical, thermal analysis, x-ray powder diffraction and by FTIR spectroscopy. The carrier transport behaviour of these materials have been explained by measuring the dc-conductivity as a function of temperature in the range (25-200°C), in air, by using silver paint as electrode. The activation energy, calculated from the Arrhenius plot, with values increasing with decrease of the metal ions content.

Introduction

α -Vanadyl hydrogenphosphates-hydrate, $\text{VOHPO}_4 \cdot n\text{H}_2\text{O}$, (where $n = 0.5-4$), have layered structure formed by corner sharing VO_6 octahedral and phosphate tetrahedral. The water molecules lie in the interlayer cavities. The layers are hold together by hydrogen bonding and van der Waals bonds^(1,2). These compounds are of interest due to their ability to exchange metal ions^(3,4) and intercalate organic molecules^(5,6). These materials show potential applications as catalysts^(7,8) and as electrical conducting materials⁽⁹⁾. Vanadyl phosphates (VPO), employed industrially are usually promoted with metal compounds^(3,4). The promoters can be introduced in vanadyl phosphates as metals or salts. Investigation of electrical conductivity properties of solids offer the understanding of the fundamental mechanism of transport of electrons or ions, in crystalline or amorphous materials⁽⁹⁻¹¹⁾.

Here we are representing studies on the electrical conductance of α - $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ and its intercalated Mn^{2+} , Cu^{2+} and Cd^{2+} materials. Their carrier transport behaviour have been explained by measuring the dc-conductivity as a function of temperature in the range (25-200 °C).

Experimental

Chemicals

V_2O_5 , H_3PO_4 (85%), $Mn(NO_3)_2 \cdot 2H_2O$, $CuCl_2 \cdot 2H_2O$ and $Cd(NO_3)_2$ are obtained from BDH. HNO_3 is obtained from Riedle De-Haen.

Instruments used for characterization

SII-Exstar 6000 DTA/TG 6300 thermal analyzer (Sieko), X-ray diffractometer axis D5005 (Bruker), Atomic absorption spectroscopy ; spectratodium model alpha 4, FTIR Tensor 37 (Bruker), pH meter CG820, Digital multimeter model 3800d, Digital voltmeter model HP 42720 LCR meter (Huet-Paker) .

Preparation of α -VOHPO₄·0.5H₂O

To 7.5 g V_2O_5 , 22.6 ml of H_3PO_4 (85%) were added followed by the addition of 427.6 ml of ethanol. The solution was stirred under reflux for 24 h. The resultant light blue precipitate was filtered, washed with acetone and dried in air.

Preparation of $M_xVOH_{1-2x}PO_4 \cdot nH_2O$

(where $M = Mn^{2+}$, Cu^{2+} , Cd^{2+} , $x =$ the metal ions contents, $n = 1.24, 1.95$ and 1.49).

Procedure

To 1 g α -VOHPO₄·0.5H₂O, 60 ml of 0.05 molar metal salt, in nitric acid solution of pH4, were added and stirred at room temperature for 72 h. The resultant products were filtered washed with distilled water and dried in air.

From atomic absorption spectroscopy analysis , the metal ions contents found to be equal to 74.33 mg, 68.80 mg and 91.60 mg ,respectively. Accordingly the percentage of the metal ions in the molecule are (7.43, 6.88 and 9.16 %, respectively).

Thermal analysis

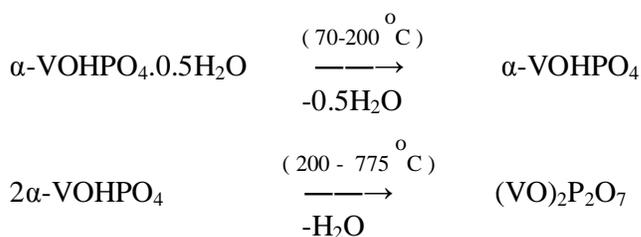
Thermal analysis were carried out at temperature range ~10-775 °C, with a heating rate 10 °C / min in air atmosphere.

Results and Discussion

α -Vanadyl hydrogenphosphate hemihydrate, α -VOHPO₄·0.5H₂O, was prepared and characterized by x-ray, thermal analysis and IR spectra and found to be similar to that already reported⁽⁸⁾ and was designated as compound **I**, its $d_{001} = 5.70 \text{ \AA}$.

TGA analysis and FT-IR Spectrum

Figure(1) shows the thermogram of α -VOHPO₄·0.5H₂O. The thermal decomposition occurs in two steps. The loss due to water of hydration occurs between 70-200 °C, followed by gradual formation of the final product (VO)₂P₂O₇ viz:



The IR spectra of α -VOHPO₄·0.5H₂O is shown in figure (2). The broad band in the region 3650-3000 cm⁻¹ (centered at 3373 cm⁻¹) is characteristic of stretching of the hydroxyl groups and water molecule. Small sharp band at 1648 cm⁻¹ correspond to stretching mode of OH and H-O-H bending, respectively. Broad multi sharp bands between 1138-925 cm⁻¹ are related to phosphate groups vibrations⁽¹²⁾.

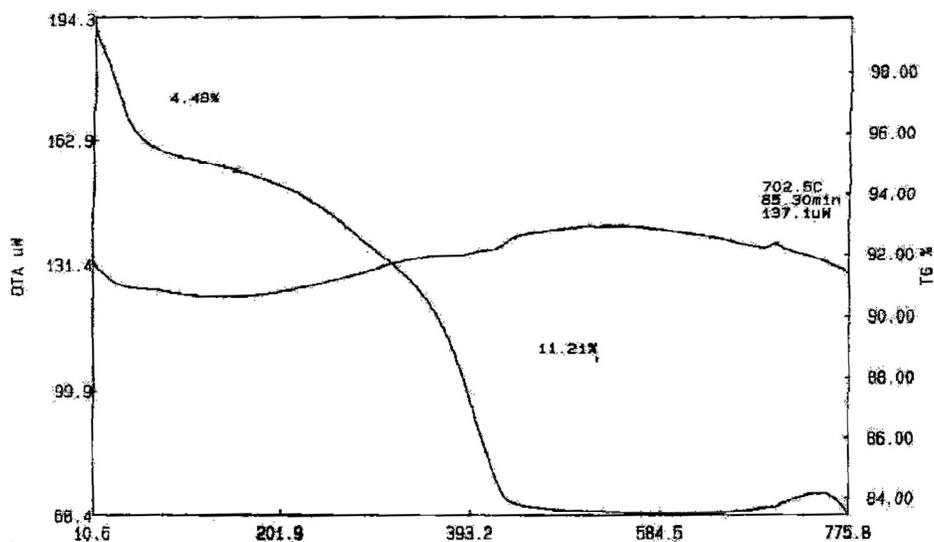


Figure (1) TG/DTA of α -VOHPO₄·0.5H₂O

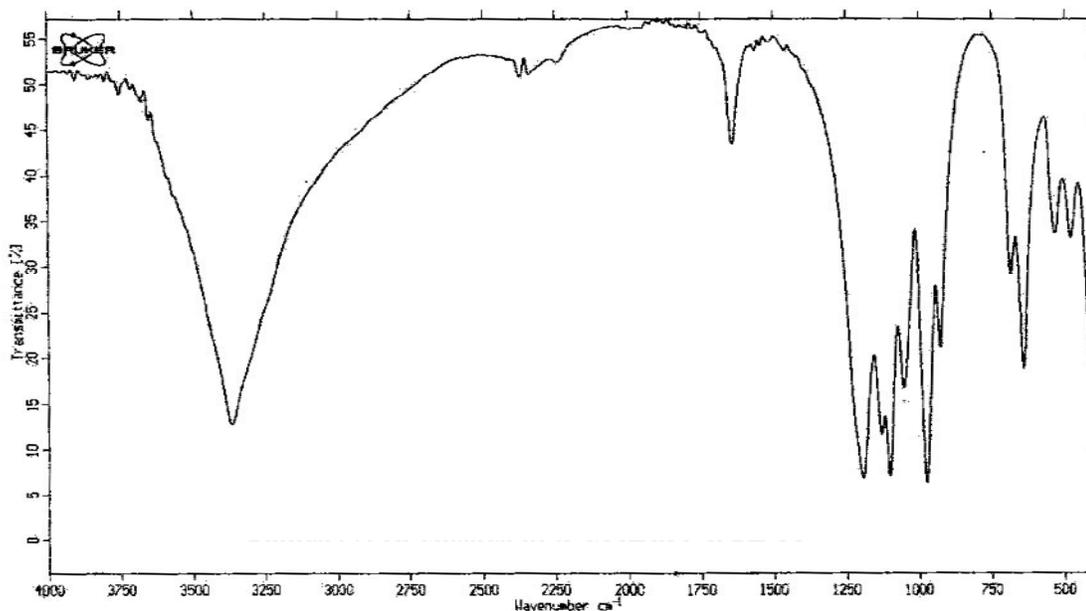


Figure (2) FT-IR spectrum of α -VOHPO₄ .0.5H₂O

Intercalated metal ions Mn²⁺, Cu²⁺ and Cd²⁺ vanadyl hydrogenphosphate compounds, Mn_{0.27}VOH_{0.46}PO₄·1.24H₂O, Cu_{0.23}VOH_{0.54}PO₄·1.95H₂O and Cd_{0.17}VOH_{0.66}PO₄·1.49H₂O, respectively, were prepared. Their metal ions contents were determined by atomic absorption spectroscopy and were designated as compounds **II**, **III** and **IV**, respectively.

X-ray powder diffraction

The x-ray patterns of the metal ions intercalated products are found to be different from that of parent compound, as shown in figures (3-5). There is a decrease in the total number of reflections for compounds **II** and **IV** and increase of reflection for compound **III**. In all cases a new phase was formed. The basal spacing as measured by d₀₀₁ reflection are between 6.314-8.097 Å, respectively. These values are higher as compared to the parent compound (5.70 Å). This result is associated with the metal ion replacing some protons in the HOPO₃²⁻ groups of the parent compound, which cause the expansion of the interlayer distance. Reflection with ~5.70 Å with very small intensity was observed which indicate the presence of hydrogen form phase. This implies that the hydrogen of P-OH groups are partially exchanged with the metal ions.

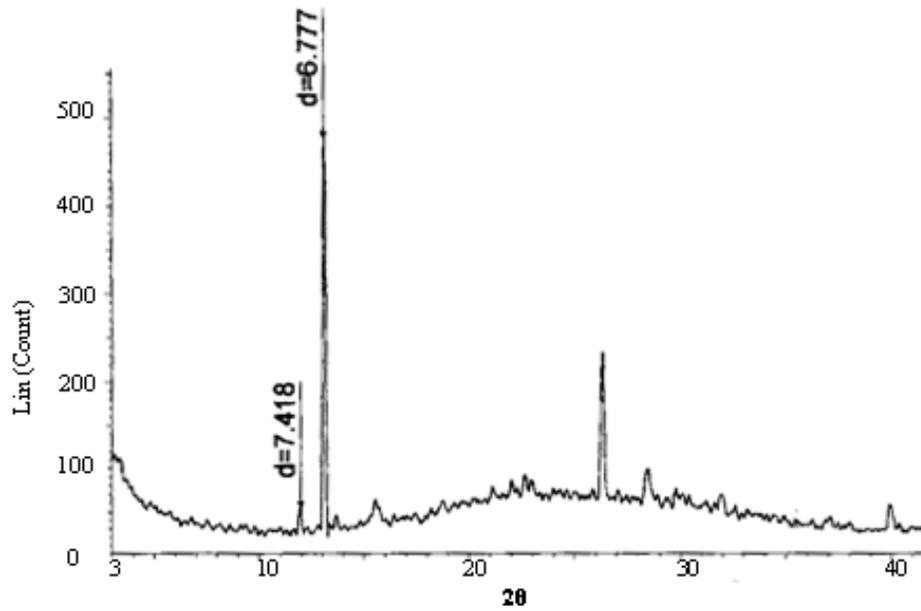


Figure (3) X-ray diffractogram of $\text{Mn}_{0.27}\text{VOH}_{0.46}\text{PO}_4 \cdot 1.24\text{H}_2\text{O}$

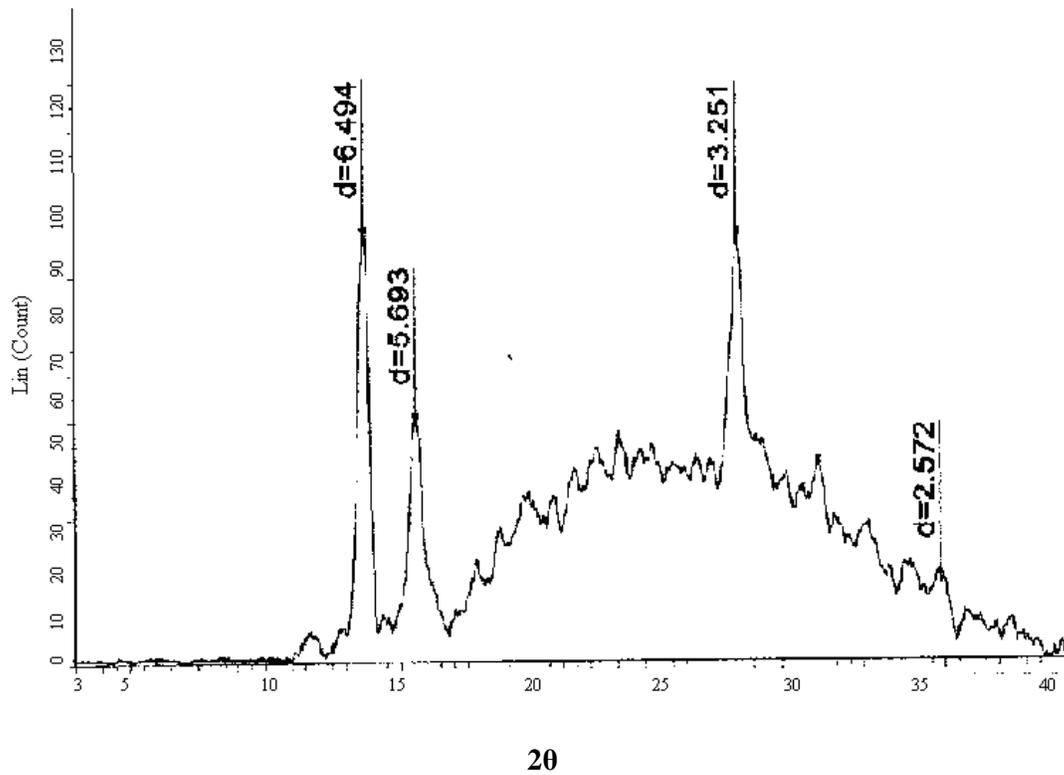


Figure (4) X-ray diffractogram of $\text{Cu}_{0.23}\text{VOH}_{0.54}\text{PO}_4 \cdot 1.95\text{H}_2$

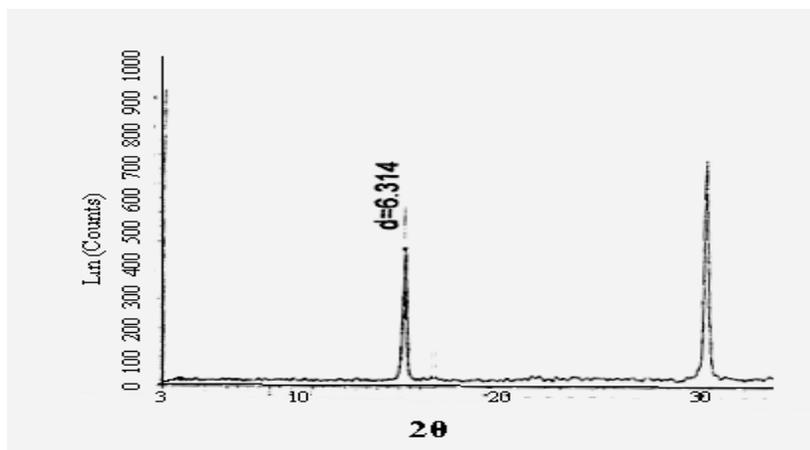


Figure (5) X-ray diffractogram of $\text{Cd}_{0.17}\text{VOH}_{0.66}\text{PO}_4 \cdot 1.49\text{H}_2\text{O}$

TGA analysis and FT-IR Spectrum

Typical thermogram, of the intercalated products, is shown in figure (6). The thermal decomposition occurs in three stages. Weight loss due to dehydration occurs between 70-350°C, followed by $\text{PO}(\text{H})_{1-2x}$ groups condensation and the formation of metal oxide. The total weight loss corresponding to compounds **II**, **III**, and **IV** found to be equal to 14.79, 20.63, and 17.06 %, respectively (the water of hydration found to be 1.24, 1.95, and 1.49 moles per formula weight, respectively). The final product $(\text{VO})_2\text{P}_2\text{O}_7$ is produced along with $2(\text{MO})_x$, where $\text{M} = \text{Mn}^{2+}$, Cu^{2+} , or Cd^{2+} , $x =$ metal ion loading. The water molecules are hold in the interlayer region and they are bonded to lattice vanadium and to intercalated metal ions. The layers are hold by van der Waals bond⁽⁸⁾.

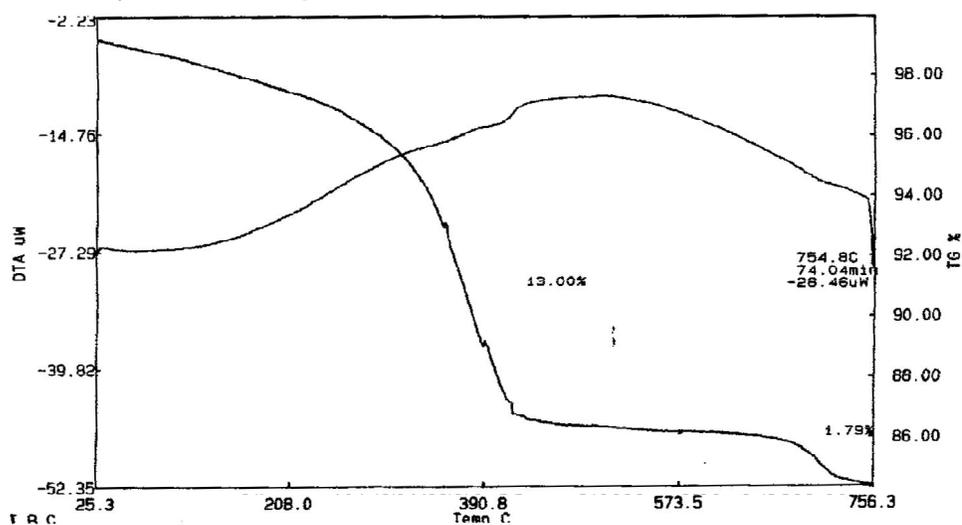


Figure (6) TG/DTA of $\text{Mn}_{0.27}\text{VOH}_{0.46}\text{PO}_4 \cdot 1.24\text{H}_2\text{O}$

IR spectra of the intercalated metal ions compounds are very similar, and show same trend of the IR spectra of vanadyl phosphates. Typical IR spectra , the $\text{Mn}_{0.27}\text{VOH}_{0.46}\text{PO}_4 \cdot 1.24\text{H}_2\text{O}$, is shown in figure (7) , the spectra exhibit broad absorption band around $3500\text{-}3400\text{ cm}^{-1}$. Medium sharp band at $\sim 1640\text{ cm}^{-1}$ correspond to stretching mode of OH and H-O-H bending, respectively. Bands around $1200\text{-}1053\text{ cm}^{-1}$ are assigned to phosphate groups vibration. The band at 980 cm^{-1} is due to V=O bond and a weak band at $\sim 680\text{ cm}^{-1}$ is due to VOP lattice. The new band centered at $\sim 891\text{ cm}^{-1}$ is assigned to M-O bond⁽¹²⁾.

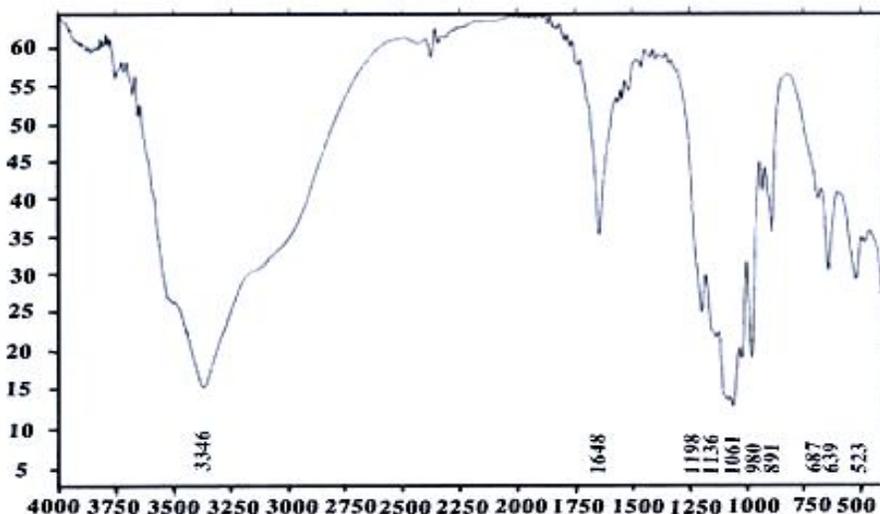
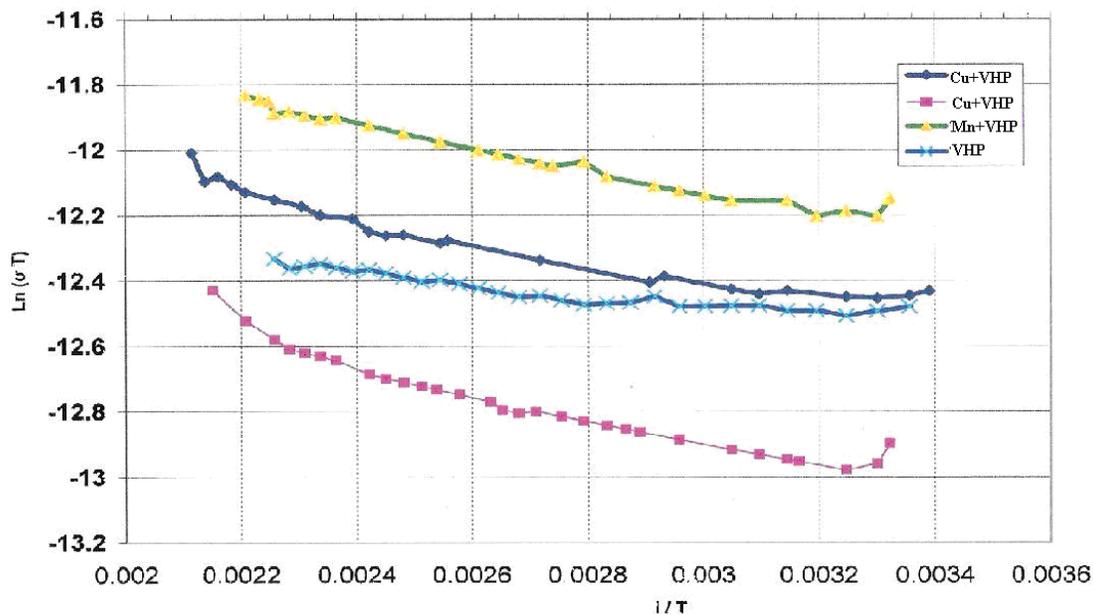


Figure (7) FT-IR spectrum of $\text{Mn}_{0.27}\text{VOH}_{0.46}\text{PO}_4 \cdot 1.24\text{H}_2\text{O}$

Conductivity

The dc conductivity of all the materials was measured between $25\text{-}200\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C}$ intervals, using pellets of 10 mm diameter and 1.5mm thickness. The opposite side of the pellets were coated with conductivity silver paste to ensure good electrical contacts. The Arrhenius plots from the observed resistance (**R**) at temperature (**T**) of samples **I**, **II**, **III** and **IV** are shown in figure (8). The conductivity (σ) was calculated as usually by $\sigma = [1/\mathbf{R}][\mathbf{d}/\mathbf{A}]$, where **d** is the Sample thickness and **A** is the area of silver painted electrodes. Graphs were plotted as **[Ln ($\sigma\mathbf{T}$) Vs $1/\mathbf{T}$]** have been presented in figure(8). For all materials a straight line is observed in temperature range $25\text{-}200\text{ }^\circ\text{C}$. This means that the conductivity fitted the relation $\sigma = (\sigma_0/\mathbf{T}) \exp(-\mathbf{E}_m/\mathbf{K}_t)$ at that temperature range.



Fig(8) $\ln(\text{seg} \cdot T)$ Vs $(1/T)$ for all the samples in the range of temp (RT-200 deg Celc)
 VHP = $\text{VOH}_{1.2x}\text{PO}_4 \cdot n\text{H}_2\text{O}$

The values of conductivity and activation energy for all samples are represented in tables (1 and 2).

Table 1. Activation energy of the Compounds

Sample	Temperature range	Activation energy $\epsilon_m = \epsilon_v$
$\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$	r.t---115°C	$(\epsilon_m)_1 = 0.02$
	115---200 °C	$(\epsilon_m)_2 = 0.06$
$\text{Mn}_{0.27}\text{VOH}_{0.46}\text{PO}_4 \cdot 1.24\text{H}_2\text{O}$	r.t--- 200°C	$(\epsilon_m) = 0.03$
$\text{Cu}_{0.23}\text{VOH}_{0.54}\text{PO}_4 \cdot 1.95\text{H}_2\text{O}$	r.t---140°C	$(\epsilon_m)_1 = 0.022$
	140---200°C	$(\epsilon_m)_2 = 0.054$
$\text{Cd}_{0.17}\text{VOH}_{0.66}\text{PO}_4 \cdot 1.49\text{H}_2\text{O}$	r.t---165°C	$(\epsilon_m)_1 = 0.033$
	165---200°C	$(\epsilon_m)_2 = 0.116$

Table 2. Conductivity at different temperatures

Sample	Temperature range	Conductivity σ (Sm ⁻¹)
VOHPO ₄ .0.5H ₂ O	r.t. ---115°C	σ (RT) = 2.59X10 ⁻⁹
	115---200°C	σ (115) = 2.37X10 ⁻⁹
		σ (200) = 2.81X10 ⁻⁹
Mn _{0.27} VOH _{0.46} PO ₄ .1.24H ₂ O	r.t---200°C	σ (RT) = 1.76X10 ⁻⁸
		σ (200) = 1.6X10 ⁻⁸
Cu _{0.23} VOH _{0.54} PO ₄ .1.95H ₂ O	r.t---140°C	σ (RT) = 1.27X10 ⁻⁸
	140---200°C	σ (140) = 1.16X10 ⁻⁸
		σ (200) = 1.29X10 ⁻⁸
Cd _{0.17} VOH _{0.66} PO ₄ .1.49H ₂ O	r.t---165°C	σ (RT) = 7.9X10 ⁻⁹
	165---200°C	σ (165) = 7.64X10 ⁻⁹
		σ (200) = 8.61X10 ⁻⁹

Conclusion

In this study it was found that all materials, within a certain temperature range, the plot indicated that a straight line could be obtained. The values of conductivity and activation energy for all samples are in good agreement with that obtained from other studies on different vanadyl phosphates, and show to follow the same behaviour of γ -titanium phosphate, γ -Ti.PO₄.H₂PO₄.2H₂O, incorporated with some divalent transition metal ions⁽¹³⁾.

The ionic onductance studies on tetravalent metal phosphate can be considered important, for use as catalysts and for fabricating fuel cells⁽¹⁰⁾.

Direct addition of solution of divalent transition metal salts into vanadyl hydrogenphosphate hemihydrate is a novel approach for the preparation of metal ions intercalates of vanadyl hydrogenphosphates⁽¹⁴⁾.

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Received: 20-5-2010

Accepted: 7-8-2010