

Synthesis, Characterization and Electrical Properties of Intercalated Mixed Metal Ions Cu^{2+} - Mn^{2+} and Cu^{2+} - Zn^{2+} A-vanadyl Hydrogen Phosphate Hemihydrate Products

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ABSTRACT

$\text{Cu}_{0.25}\text{-Mn}_{0.25}\text{VOPO}_4 \cdot 4\text{H}_2\text{O}$ (Cu-MnVPO) and $\text{Cu}_{0.30}\text{-Zn}_{0.19}\text{H}_{0.01}\text{VOPO}_4 \cdot 1.8\text{H}_2\text{O}$ (Cu-ZnVPO) have been prepared from reactions of mixtures Cu^{2+} - Mn^{2+} and Cu^{2+} - Zn^{2+} metal ions with $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$. They were characterized by chemical, thermal analysis, X-ray powder diffraction and by FT-IR spectroscopy. Their conductivity determinations were made by ac-method at temperature ranges (25 -85°C) on compact discs using silver paste as electrodes. The variation of the ac conductivity as a function of frequency in the range 10Hz - 10KH was also studied. For the compound CuZnVPO, it is observed that ac conductivity increases with increasing temperature from room temperature up to 57°C, then another phase starts to form. In the range of 57-85°C, the ac conductivity reaches its maximum value, $9.4 \times 10^{-4} \text{ mho m}^{-1}$, and then remains constant. In case of CuMnVPO, the conductivity reaches its minimum value $5.5 \times 10^{-4} \text{ mho m}^{-1}$. The ac conductivity decreases with increasing temperature up to the transition point 72°C, where a new phase starts to forms and the conductivity remains constant. The activation energies for CuMnVPO and CuZnVPO, were calculated in the range 25°C to transition point and found to be 0.19, 0.12 (Ev)

KEYWORD: Electrical properties, intercalated Cu^{2+} - Zn^{2+} and Cu^{2+} - Mn^{2+} , α - vanadyl hydrogen phosphate hemihydrate.

INTRODUCTION

α -Vanadyl hydrogen phosphates-hydrate, $\alpha\text{-VOHPO}_4 \cdot n\text{H}_2\text{O}$, (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 (Norby, 1999; Alberti et al, 2001). These compounds are of interest due to their ability to exchange metal ions (Hogareth et al, 2005; Grotthuss, 1806), intercalate organic molecules (Bodes, 1972, 1988). These materials show potential applications as catalysts [Gobal & Calvo, 1972; Johnson et al, 1982] and as electrical conducting materials (Bruinik, 1972).

Vanadyl phosphates (VPO), employed industrially are usually promoted with metal compounds (Hogareth et al, 2005; Grotthuss, 1806). The promoters can be introduced in vanadyl phosphates as metals, metal oxides 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 (Bruinik, 1972; Casciola et al, 1999; Zima et al, 1996). $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$. The materials show a high protonic conduction. However, Research on electrical conductance on vanadyl hydrogen phosphates are still in its infancy. Earlier we have reported the electrical properties of intercalated Mn^{2+} , Cu^{2+} and Cd^{2+} of $\alpha\text{-VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ (shakshooki et al, 2011). The present paper describes the synthesis, characterization and electrical properties of the intercalated mixed metal ions Cu^{2+} - Zn^{2+} and Cu^{2+} - Mn^{2+} $\alpha\text{-VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ products.

MATERIALS AND METHODS

Chemicals

V_2O_5 , H_3PO_4 (85%), $\text{Mn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2$ are obtained from BDH, HNO_3 is obtained from Riedle De-Haen., and were used as such. Other reagents used were of analytical grade.

Instruments used for characterization

XRD Bruker axis D5005, AA Spectratodium model Alpha 4, Digital multimeter model and Voltmeter model HP.

Preparation of $\alpha\text{-VOHPO}_4 \cdot 0.5\text{HO}$.

This compound was prepared as previously described (Johnson et al, 1982; shakshooki et al, 2011).

Preparation of CuMnVPO and CuZnVPO

The intercalated compounds CuMnVPO and CuZnVPO were prepared by mixing aqueous solutions of 60ml of 0.05 M copper nitrate and 60ml of 0.05M manganese nitrate (or zinc chloride) with 1.0g of $\text{VOPO}_4 \cdot 0.5\text{HO}$. The mixture was continuously stirred under reflux for seven days. The product was filtered, washed with acetone and dried in air.

Conductivity measurements

The ac conductivity was measured for the materials, at a range of 25-85°C, using pellets of thickness 1.5 mm and a diameter of 10.0 mm. The opposite sides of pellets were coated with silver paste as a conduct material to form the electrodes for the two probe measurements.

RESULTS AND DISCUSSIONS

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 [8,12] its $d_{001} = 5.6\text{\AA}$.

XRD

The powder X-ray diffraction patterns for the obtained intercalates is shown in Figures (1,2) exhibit broad peaks with diminished intensity in comparison with, α -VOHPO₄.0.5H₂O. This result indicates that the intercalates are less crystalline than the parent compound[8,12]. The interlayer distance as measured by d_{001} reflection is 13.34\AA for CuZnVPO, while in the case of CuMnVPO compound there are two phases with d -values 13.43\AA and 18.17\AA , this implies that the metal ions substitute into the layered region of the parent compounds ($d=5.6\text{\AA}$) replacing the hydrogen of the OH groups.

TGA

The thermal analysis was carried out at range 25-800°C. The total weight loss found to be 24% for Cu ZnVPO and 36% for Cu MnVPO. The weight loss corresponding mainly to water of coordination. Their thermal behavior found to follow the same trend of intercalated Mn²⁺, Cu²⁺ and Cd²⁺ metal ions of α -VOHPO₄.0.5H₂O[12].

Conductivity

The ac conductivity for the compounds CuMnVPO and CuZnVPO were calculated in the range 25-85°C. The

variation of the ac conductivity as a function of frequency in the range 10Hz -10⁵KHz was also studied. For the compound CuZnVPO, it is observed that ac conductivity increases with increasing temperature from room temperature up to 57°C, then another phase starts to form. In the range of 57-85°C, the ac conductivity reaches its maximum value $9.4 \times 10^{-4} \text{ m}\Omega^{-1}$ and then remains constant. This conduction behavior has been observed in case of VOHPO₄.0.5H₂O[12]. On the other hand in case of CuMnVPO, the conductivity reaches its minimum value $5.5 \times 10^{-4} \text{ m}\Omega^{-1}$. The ac conductivity decreases with increasing temperature up to the transition point 72°C, where a new phase starts to form and the conductivity remains constant.

It was found that substitution of hydrogen of OH groups by manganese ions increases the conductivity with increasing temperature indicating PTCR behavior. On the other hand substitution of hydrogen by zinc ions decreases the conductivity, with increasing temperature which indicates NTCR behavior. Plots of conductivity versus frequency are presented in Figures (3,4). It is clear from these figures that the conductivity increases linearly with increasing frequency in the measured range. This means a higher frequency range study is needed.

Table 1. shows the values of the ac conductivity at 25°C and transition point (TP). The activation energies for both compounds were calculated in the range 25°C to transition point. The conductivity for both compounds is in the semiconductor range.

CONCLUSIONS

X-ray diffraction patterns for the obtained intercalates exhibit broad peaks with diminished intensity in

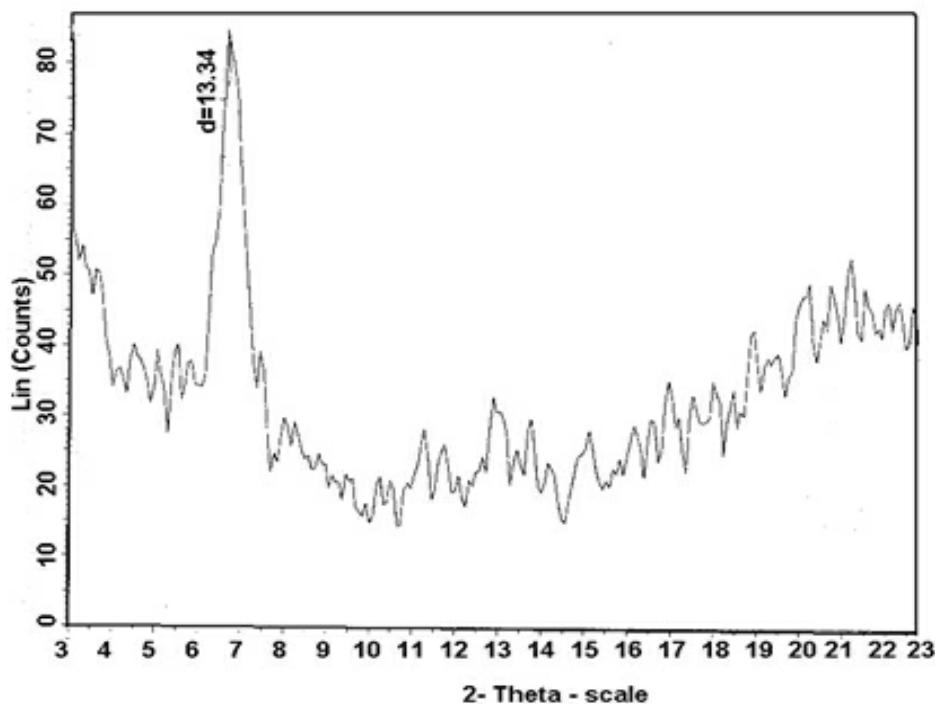


Figure 1: XRD pattern of CuZnVPO

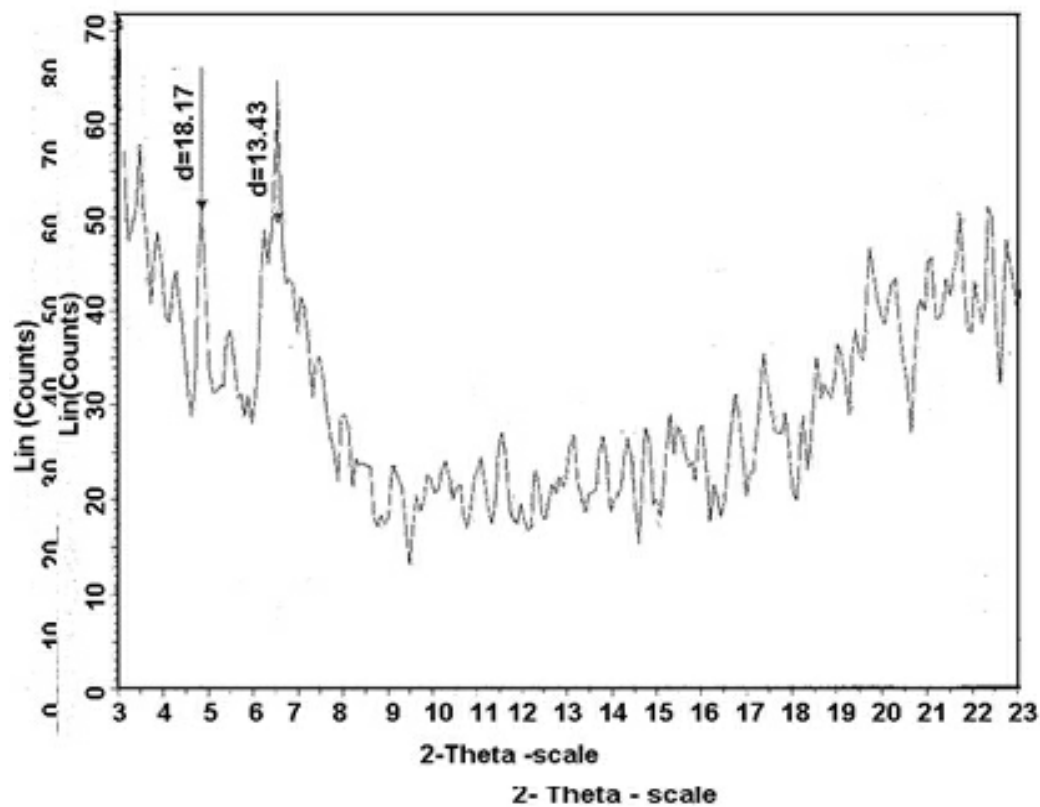


Figure 2: XRD pattern of CuMnVPO

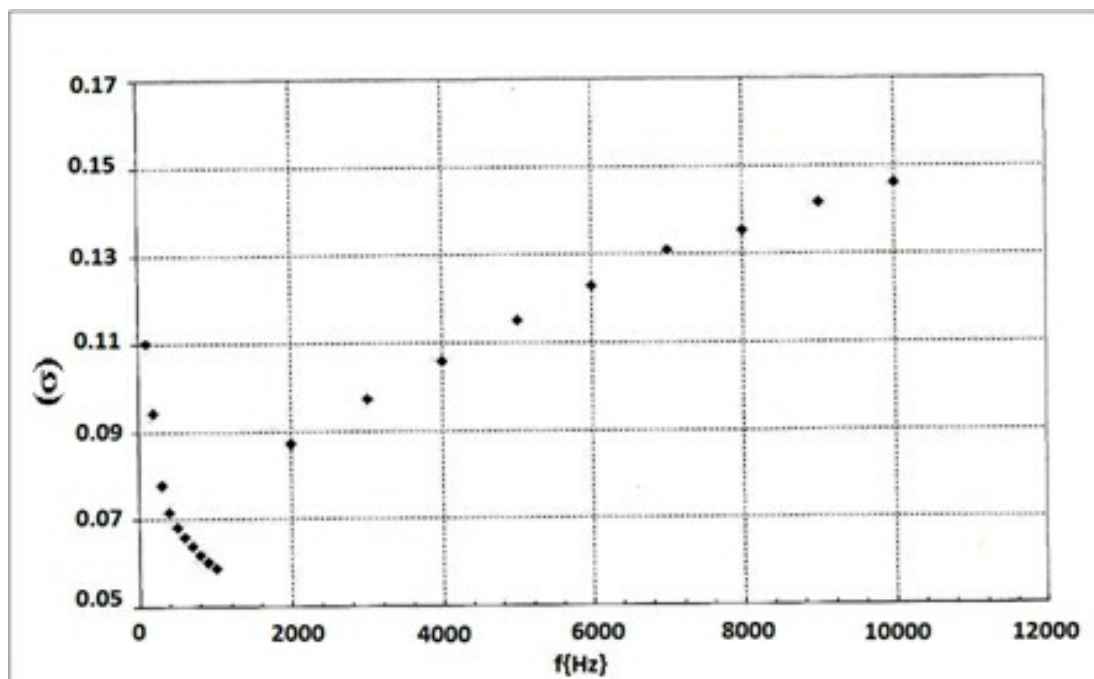


Figure 3. Effect of frequency on ac conductivity at r.t for CuMnVPO

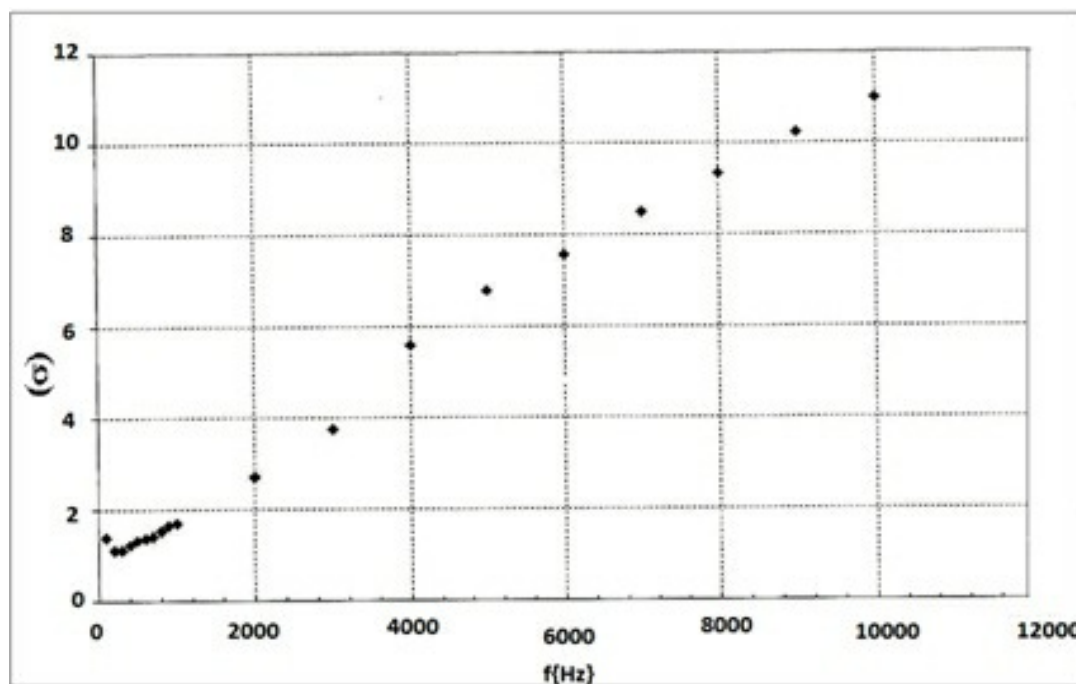


Figure 4. Effect of frequency on ac conductivity at r.t for Cu ZnVPO

Sample	$\sigma_{ac}(RT)$ mho.m ⁻¹ 10^{-4}	$\sigma_{ac}(57-85^{\circ}C)$ 10^{-4} mho.m ⁻¹	E ac (E v)
CuMnVPo	8.70	5.50	0.19
CuZnVPo	6.40	9.40	0.12

Table 1: Values of the ac conductivity and activation energies at 25°C and transition points (TP) for both compounds

comparison with, α -VOHPO₄·0.5H₂O. This result indicates that the intercalates are less crystalline than the parent compound. It was found that substitution of hydrogen of OH groups by manganese ions increases the conductivity with increasing temperature indicating PTCR behavior. On the other hand substitution of hydrogen by zinc ions decreases the conductivity, by increasing temperature which indicates NTCR behavior. However, the conductivity in general, increases linearly with increasing frequency. The intercalated metal ions material are a mixed protonic electronic conductors. The protons formed by the dissociation of the interlayer water molecules are responsible for the prevailing part of the conductivity at ambient temperature (Zima et al, 1996, 1999; shakshooki et al 2011; De et al, 2006). On the other hand, the increasing surface hydration is responsible for the appearance and the growth of the ionic conductivity which is significantly affected by metal ions diffusion (Zima et al, 1999; De et al 2006).

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