

Electrical Conductance of α -VOPO₄ 2.5H₂O

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Abstract Layered α -vanadyl phosphate, α -VOPO₄ 2.5H₂O, was prepared, found to be nanosized with average diameter equal to ~57.96 nm, which was calculated from the full width at half maximum of the peak, from XRD analysis, using Scherrer's equation. The layers are held together by van der Waals bonds. It was characterized by XRD, TGA, FT-IR and scanning electron microscopy (SEM). The conductivity determination (σ) was made by ac-method at temperatures range (25-95°C) on compact discs of the material using graphite electrodes. The conductivities (σ) were found to be $1.74 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$, $2.51 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ and $7.17 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ at 25, 60 and 95°C, respectively. The conductivity (σ) is increased by increasing of temperature. The relation between the conductivity (σ) and the inverse of absolute temperature was linear in the two regions, the low temperature region (25 - 60°C) and the high temperature region (65 - 95°C). The activation energy was calculated for the two regions using the Arrhenius equation, and found to be 0.113 and 0.339 eV, respectively.

Keywords Electrical conductance, α -VOPO₄ 2.5H₂O, Activation energy

1. Introduction

Vanadium forms a variety of oxides with interesting potential applications. Yielding various compounds among them vanadyl phosphates, being widely used as commercial catalyst [1, 2]. Vanadyl phosphate can exist in several crystalline phases [3, 4] in both anhydrous and hydrated form. In layered hydrated vanadyl phosphate of general formula VOPO₄.nH₂O (where n = 2 - 2.5), the water molecule play an important role in electrical properties. The layers consist of distorted VO₆ octahedra sharing all their equatorial oxygen's with four PO₄ tetrahedra, the weakly bonded axial oxygen being replaced by a water molecule (coordinated water). The rest of water molecules are inserted into the space between PO₄ tetrahedral of adjacent layers. All water molecules are linked together by hydrogen bonds making a double layer between VOPO₄ sheets [5, 6]. The strong acidic character of vanadyl phosphate layers lead to formation of H₃O⁺ ions in the interlayer region [6]. The layers are held together by van der Waals bonds [3, 7].

Proton conductors are often considered to be electrolytes in which hydrogen is transport forwards and evolved at the cathode during electrolysis. Proton transport include transport of proton (H⁺) and any assembly that carries protons (H⁺), H₂O, H₃O⁺, NH₄⁺....etc. [5, 6]. The transport protons (H⁺) between relatively stationary host anions is termed "Grotthuss" or "free proton" mechanism and classical mass diffusion (vehicle mechanism). In Grotthuss

mechanism, hydronium ions are oriented in proper position for proton conduction. In vehicle mechanism proton transports by water molecule charge carrier as H₃O⁺ [8 - 12]. Electrical current arises from migration of positive ions (H⁺) which are attached to negative [V-O]⁻ on the layer. Strong electrostatic act between H⁺ and [V-O]⁻ ions. At room temperature VOPO₄.nH₂O mixed protonic-electronic conduction with dominant protonic [5, 6].

In this paper we have investigated the electrical conductance of α -VOPO₄ 2.5H₂O at different temperature ranges.

2. Experimental Details

2.1. Chemicals

V₂O₅, H₃PO₄ (85%) (of BDH) were used as such. Other reagents used were of analytical grade.

2.2. Instruments

X-ray powder diffract meter Philips, using Ni-filtered CuK α (λ = 1.54056Å), TG/DTA SII Extra 6000 thermogram. and TG/DTA Perkin-Elmer SII, Scanning electron microscopy (SEM) Jeol SMJ Sm 5610 LV, Fourier Transform IR spectrometer, model IFS 25 FTIR, Bruker and pH Meter WGW 521.

2.3. Preparation of α -Vanadyl Phosphate

α -Vanadyl phosphates, VOPO₄.2.5H₂O (VOP), was prepared as described previously [13]. In detail, 35 ml H₃PO₄ (85%) in 250 ml distilled water were added to 10g V₂O₅ with stirring at room temperature. The resulting mixture was stirred under reflux for 24 h. The resultant product, green

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olive precipitate, was filtered washed with cold ethanol and dried in air.

2.4. Conductivity Determination

The conductivity determinations (σ) of layered α -vanadyl phosphate, α -VOPO₄·2.5H₂O, was measured by the usual ac-method and the sample holder was exactly the same as used in earlier conductivity and thermo-emf work [11, 15-18] in form of compact discs of 1.2 cm in diameter was prepared at about 8×10^5 kP/cm² pressure, area is 1.13cm² and thickness of about 0.115 cm, at a temperature range 25 to 95 °C using graphite as electrodes. The material was heated at 80°C for about one hour in dry atmosphere, left in air at room temperature (~20°C) for 48 h till constant weight prior ac measurements.

3. Results and Discussion

Layered α -vanadyl phosphate, was prepared and characterized by X-ray diffraction (XRD), Fourier Transform IR (FT-IR), thermo gravimetric analysis (TGA) and scanning electron microscopy (SEM).

3.1. XRD

The X-ray diffraction pattern of crystalline layered α -VOPO₄·2.5H₂O is shown in figure (1), which indicates good degree of crystalline with interlayer spacing (d_{001}) equal to 6.86Å. The average diameter of α -vanadyl phosphate found to be equal to 57.96 nm which were calculated from the full width at half maximum of the peak, from XRD analysis, Figures (1,2), using Scherer's equation:

$$D = 0.9\lambda / B_{2\theta} \cos \theta_{\max}, \quad (1)$$

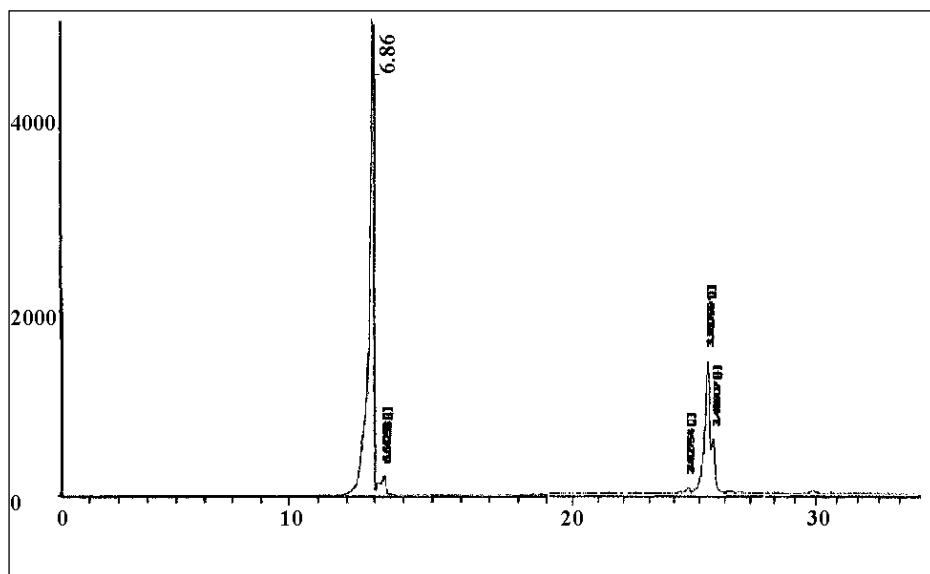


Figure 1. XRD pattern of α -VOPO₄·2.5H₂O

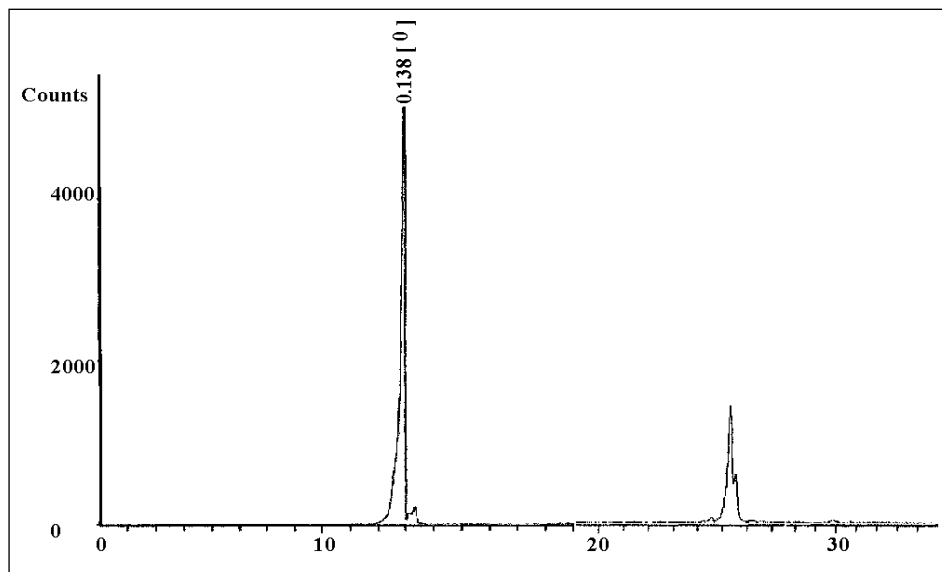


Figure 2. XRD pattern of α -Vanadyl phosphate full width at half maximum of the peak which is 0.138°

where D is the average crystal size in nm, λ is the characteristic wave length of X - ray used ($\lambda = 1.54056 \text{ \AA}$), Θ is the diffraction angle and the $B_{2\Theta}$ is the angular width in the radius at intensity equal to half of the maximum peak intensity [14]. From the image of SEM Figure (3) we calculate the thickness of a square plate by carefully random selecting of three stacking square plates, the average size from SEM image found to be $\sim 76.2 \text{ nm}$.

3.2. SEM

Figure (3) show the scanning electron micrographs(SEM) of α -vanadyl phosphate $\text{VOPO}_4 \cdot 2.5\text{H}_2\text{O}$. The image of the matrix demonstrates that the crystallites of α -vanadyl phosphate consists of irregular stacking of square plates. From the image of SEM we calculate the thickness of a square plate by carefully random selecting of three stacking square plates from the figure, as follows the figure, as follows ($10 \mu\text{m} \equiv 7 \text{ mm}$. So $0.07\text{mm thickness} \rightarrow 10\mu\text{m} \times 0.07 \text{ mm} / 7\text{mm} \times 1000 = 100\text{nm}$, $0.05\text{mm}=71.418\text{nm}$, and $0.04\text{mm} = 57.142\text{nm}$).

The thickness of the selected plates found to be in the range of nanosized scale, and were 100, 71.42 and 57.14 nm. Based on $10 \mu\text{m} \equiv 7\text{mm}$. The average size considered to be $\sim 76.2 \text{ nm}$.

3.3. FT-IR

Fourier transform spectra of α -vanadyl phosphate found to be similar to that already reported [13].

3.4. TG/DTA/DTG of PVA, α -Vanadyl Phosphate

Figure (4) shows the thermal decomposition of, α - $\text{VOPO}_4 \cdot 2.5\text{H}_2\text{O}$. Thermal analysis was carried at the range $35\text{-}900^\circ\text{C}$. The loss of water of hydration occurs in two steps with two endothermic peaks at 125°C and 175°C . Endothermic peak at 740°C accompanied by weight loss equal to 3.12%. The total weight-loss found to be equal to 24.85%, calculated value 25.1%.

3.5. Conductivity

The conductivity (σ) α -vanadyl phosphate α - $\text{VOPO}_4 \cdot 2.5\text{H}_2\text{O}$ was found to be $1.74 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$, $2.51 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$, $7.17 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$, at 25, 60 and 95°C , respectively. This material could be classified, according to literature [17, 18], as semiconductor or fast ionic conductor since the value of the conductivity is the order of liquid electrolytes with negligible electronic conductivity. Semiconductors have been attracted considerably due to their potential applications in various electrochemical devices, such as, solid state batteries, sensors, timers, fuel cells, memories, capacitors, etc. The conductivity (σ) was calculated using the equation.

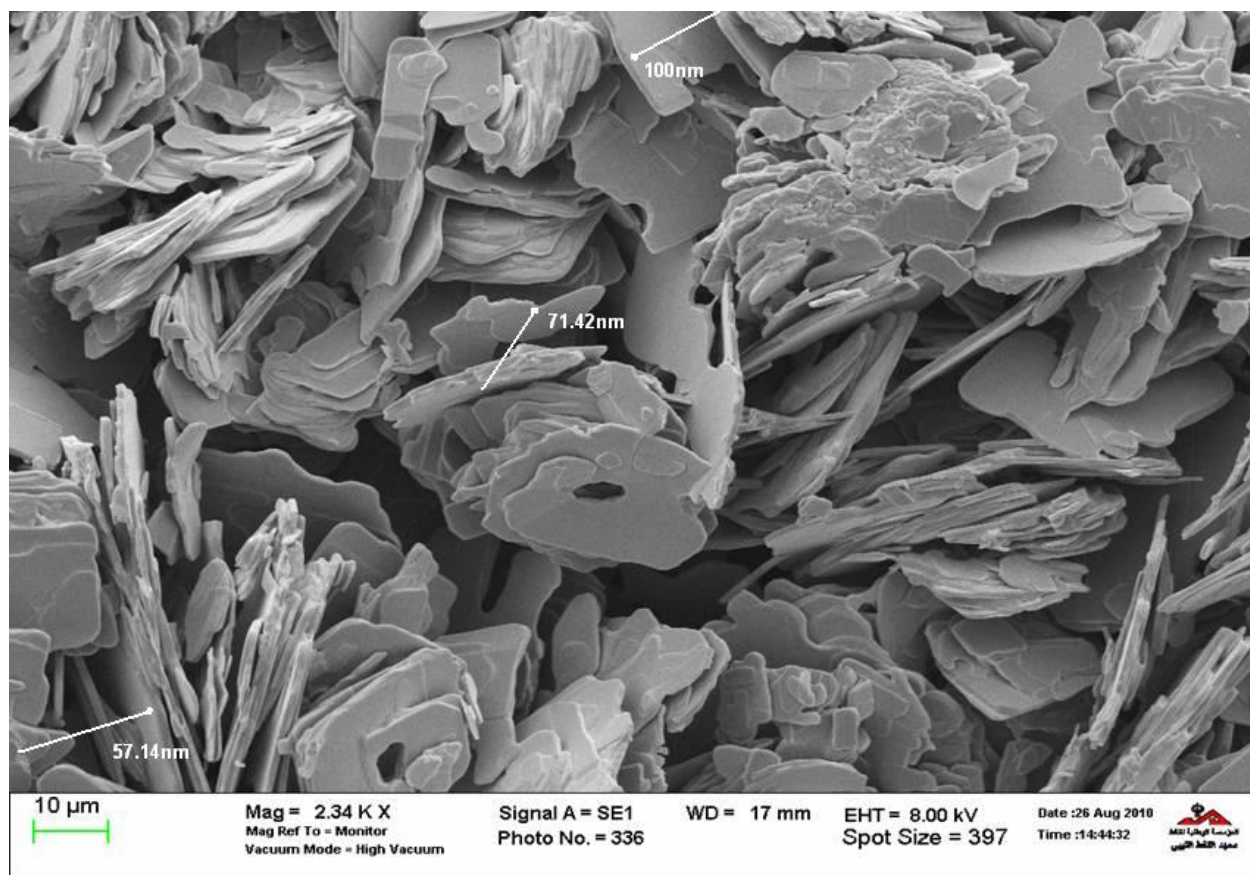
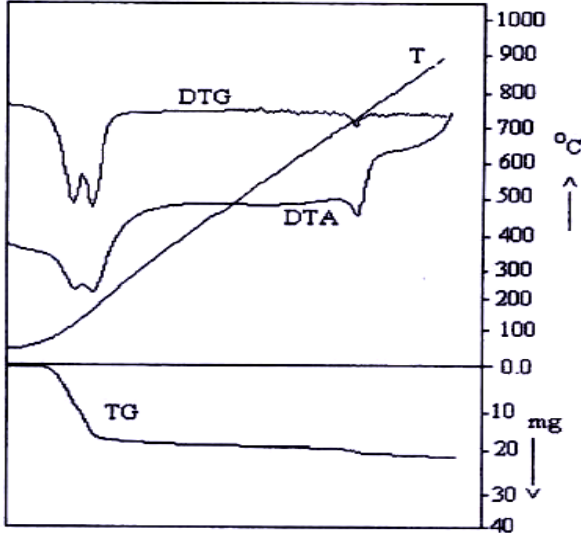


Figure 3. SEM miograph image of α -vanadyl phosphate

Figure 4. TGA of α -VOPO₄·2.5H₂O

$$\sigma = It / VA, \quad (2)$$

where I is the current, t is the thickness of the pellet, V is the voltage and A is the area of the pellet. The ionic conductivity σ_i , arises when an electric field, E , is applied to an ionic solid. As a result a current density, J , developed in the material which is given by

$$J = \sigma_i E, \quad (3)$$

The ionic conductivity σ_i is related to the mobile ion density N , the mobile ion charge (Ze) and the velocity of the mobile ion per unit electric field or ion mobility, μ ,

$$\sigma_i = N (Ze) \mu \quad (4)$$

It is known that the ion mobility changes with the temperature as

$$\mu = \mu_0 \exp(-E_a / k_B T) \quad (5)$$

Thus

$$\sigma = \sigma_0 \exp(-E_a / k_B T) \quad (6)$$

Where

$$\sigma_0 = N Ze \mu_0 \quad (7)$$

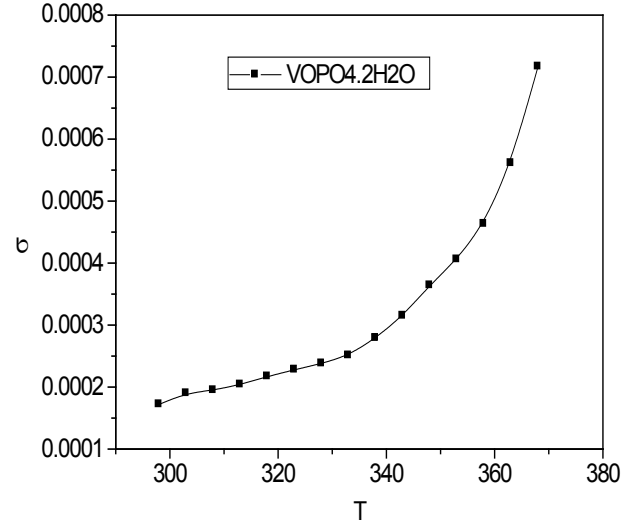
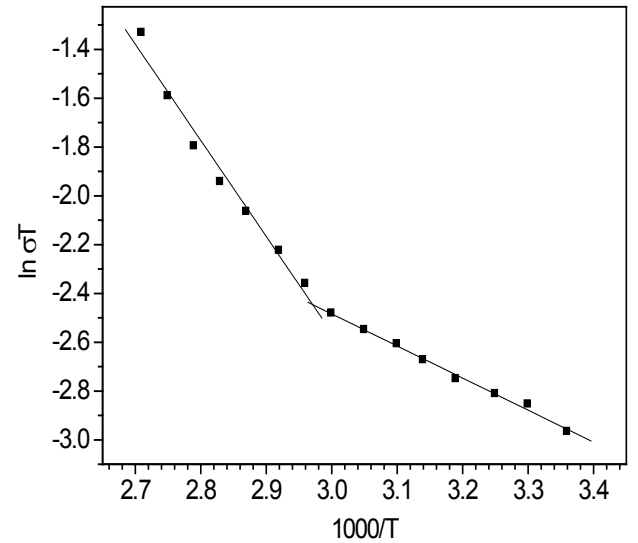
Fig.5 shows the variation of the conductivity (σ) of the material with the absolute temperature. The conductivity (σ) is increasing by increasing of temperature which means that the conductivity depends on temperature in the studied range of temperatures.

The temperature dependence of the ionic conductivity (σ) for VOP₄·2H₂O is shown in fig. 6. The relation between the conductivity (σ) and the inverse of absolute temperature was linear in two regions, the low temperature region (25-60°C) and the high temperature region (65-95°C). The activation energy was calculated for the tow regions using the Arrhenius equation:

$$\ln(\sigma T) = \ln(\sigma_0) - (E_a / k_B T) \quad (8)$$

The activation energy for the two regions was found to be

0.113eV and 0.339 eV respectively.

Figure 5. The variation of the conductivity (σ) of α -VOPO₄·2.5H₂O with the absolute temperatureFigure 6. $\ln(\sigma T)$ of α -VOPO₄·2.5H₂O as a function of inverse temperature

The conductivity (σ) of this material against temperature behavior can be expressed by the equation:

$$\sigma = (\sigma_0 / T) \exp(-E_a / k_B T) \quad (9)$$

It leads to an activation energy (ΔE) of 0.113eV and 0.339 eV which is the activation energy that the ion has to overcome in order hop from one site to another in the crystal material.

A turning point at about 65°C may be attributed to a change of higher temperature self defect conductivity with higher activation energy to extrinsic conductivity with lower activation energy. For instance, to an occurrence of minor quantity of V^{5+} or V^{3+} ions [19,20]. Therefore the conductivity of this material at temperature range study qualifies it be classified as semi ionic conducting material.

4. Conclusions

In the present work, Layered α -vanadyl phosphate, α -VOPO₄·2.5H₂O, was prepared and characterized. The conductivity (σ) was determined at the temperature range (25 - 95°C) and were found to be $1.74 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$, $2.51 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ and $7.17 \times 10^{-4} \Omega^{-1} \text{cm}^{-1}$ at 25, 60 and 95°C, respectively. The conductivity of α -VOPO₄·2.5H₂O at room temperature (25°C) can be considered mixed protonic-electronic conductor. However; in the temperature range (60 - 95°C) the electronic conductance is enhanced by the presence of water molecules on its sites. The activation energy was calculated for the two temperature regions (25 - 60°C) and (65 - 95°C), and found to be 0.113 and 0.339 eV, respectively.

REFERENCES

- [1] Hucknal, D.J, Selective oxidation of hydrocarbons, Academic Press, London(1974).
- [2] Genti, G., Gavani, F. and Trifiro, F., Selective oxidation of heterogeneous catalysis, Fundamental and Applied. Catalysts, Kluwer Academic Plenum Publ., New York(2001). J. of Chem. 1(2007) 45 -52
- [3] Yang, Y. C. , Lai, Y.C., Salaza, J. R., Zima, V., Li, K. H. and Wang, S. L., Untypical (VOPO₄)- layer in vanadyl phosphates, Inorg. Chem., 4a (2010) 6196-6202.
- [4] Benziger, J. B., Gylans, V. and Sundaresan, S., New precursors to vanadium phosphorous oxide catalysts, Cat. Today, 33 (1997) 49 – 56.
- [5] De, S., Dey, A. and De, S. K., Mixed protonic electronic conductivity and dielectric response in layered vanadyl phosphate nanocomposites, J. of Chem. Phys. ,125 (2006) 224704
- [6] Palombari, R., Electrical-Transport properties of hydrated and anhydrous vanadyl phosphate in temperature range 20 - 200°C, Chem. Mater,8 (1996) 2505-2509.
- [7] Yakuried, O. V., Steel, I. M., Yakovleva, E. V. and Dimitron, Q. V., Hydrogen bonds in the crystal structure of vanadyl phosphates, Crystallography report, 57 (2012) 722 – 732.
- [8] Agmon, T., The Grotthuss mechanism, Chem. Phys. Lett., 244(1995), 456 – 462.
- [9] Stenina, L. A., Aliey, A. D., Glokhoy, V., Spiridonov, F. M. and Yaroslavtser, A. B., Cation mobility and ion exchange in acid tin phosphates, Solid State Ionics, 162 (2003) 191- 195.
- [10] Shskshooki, S. K., Ellafi, M. M. K., and S. K.El-Mashri, Thermal behavior, FT-IR and ionic conduction of granular zirconium phosphates and mixed zirconium titanium phosphates, Sohag Bulletin for Pure and Appl. Sci., 1 (2011) 159 – 170.
- [11] Shakshooki, S. K., Ellafi, M.M. K., ElTorki, F. M. and S. K.El-Mashri: Proton conductance of glassy tin phosphate, Acad. J. of Sci.,1(2) (2012) 289- 296.
- [12] El-Azzabi, O. H.M., Shakshooki, S. K., Benomran, M. and Suliman, Y. A., Synthesis, characterization and electrical porperties of intercalated mixed metal ions Cu²⁺-Mn²⁺ and Cu²⁺-Zn²⁺ α vanadyl hydrogen phosphate, Sci. J. of Physics, ISSN 2276-6367, (2012) 1-4. 7, (2012) 1-4.
- [13] Shakshouki, S. K., El-Mehdawi, R. M., Mehabis, M. T., El-Rais, M. A., Etter, S. O. and Moktar, R.A., Uptake of some divalent metal ions on layered α - VOPO₄·2.5H₂O and its 1.10phenanthrodine,2,2-bipyridine and 4,4-bipyridine intercalated products, Jordan J. of Chem. 1(2007) 45 -52.
- [14] Allen, T. Particle Measurements, 3rd Edition, Chapman and Hall, London (1992).
- [15] El-Gemal, M.T., Saleem, M. and Avasthi M. N., Ionic conductivity of Ag₇L₄PO₄ solid electrolyte, Phys. Stat. sol. (a), 57 (1980) 499,
- [16] M. M. Khalifa Ellafi, S. M. El-Mashri and M.N. Avasthi, Study of a new solid superionic material Ag₇P₃S₁₁, Physica B, 321 (2002) 388-392.
- [17] Chowdari, B.V.R., Radhakrishna, S., (eds.) ' Solid State Ionic Devices', World Scientific Publishing, Singapore(1988).
- [18] Kartini, E., Collins, M. F., Indayaningsih, N., Svensson, E. C.,: Solid State Ionics, 138 (2000) 115-121.
- [19] Kartini, E., Kennedy, S. J., Itoh, K., Kamiyama, T., Collins, M. F.: Solid State Ionics, 167 (2004) 65, 1-2.
- [20] Yaroslavtsev, A. B., Kotov, V.Yu.: Russ. Chem. Bull. (2002) 515.