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Hydrothermal synthesis and characterization of $M^{+}_{2}O - Cr_2O_3 - P_2O_5$ crystalline materials

A M Sunitha[1*], G S Gopalakrishna[2] and K Byrappa[3]

[1]UPE project fellow, University of Mysore, Mysore-570006
[2]Department of Studies in Earth science, University of Mysore, Manasagangotri, Mysore 570 006, INDIA
[3]Department of Studies in Earth science, University of Mysore, Manasagangotri, Mysore 570 006, INDIA
*Corresponding Author: *suniam2012@gmail.com*

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Abstract

$M^{+}_{2}O - Cr_2O_3 - P_2O_5$ (M^{+}= Na, K) materials were synthesized by hydrothermal techniques. The resultant materials were characterized by SEM, powder XRD, FTIR and impedance spectroscopic studies. The powder X-ray results have revealed, $Na_2O - Cr_2O_3 - P_2O_5$ material crystallized in orthorhombic system and $K_2O - Cr_2O_3 - P_2O_5$ material crystallized in monoclinic. These are prospective solid electrolytes at moderate temperature.

1. Introduction

It is well known that the phosphates have been considered as prospective materials in technology, *viz* in electronic devices, sensors, laser materials, piezoelectric, luminescence, opto-electronics, ceramics and solid electrolytes [1-6]. Since the last three decades, the interest has focused on the preparation of micro/nano scale materials due to the large surface/volume ratio, which drastically enhances their physical and chemical properties. The properties of these materials are mainly dependent on the size, shape and surface morphologies of particles [7-10,]. The authors have reported a few numbers of fine phosphate materials, which seems to be potential solid electrolytes and magnetic materials. [11, 12] Here, the authors are reporting the impedance characterization of$M^{+}_{2}O - Cr_2O_3 - P_2O_5$phosphate materials.

2. Experimental Procedure

The synthesis experiments of $M^{+}_{2}O - Cr_2O_3 - P_2O_5$ materials were carried out by hydrothermal method at moderate temperature and pressure conditions, reported earlier [11, 12]. Synthesis of phosphate materials by hydrothermal technique is the better method compare to other methods, owing to its advantages like synthesis takes at relatively low temperature and it is a closed system, hence gaseous fugacity plays an important role in the synthesis process. The resultant products of the experiments are in purer form [13]. The reagents used are of analar grade of $M^{+}OH$ (M^{+} =Na and K) (99.99%), H_3PO_4 (98%), Cr_2O_3 (99%) and HNO_3 (69-72%), from Glaxo chemicals without further purification. Initially, a known quantity of $M^{+}OH$ and H_3PO_4 were taken in a Teflon lined stainless steel autoclave with a capacity of 50ml. Later a known quantity of Cr_2O_3 and mineralizer HNO_3 were added to it and thoroughly stirred till homogeneity attained. The crystallization was carried out by spontaneous nucleation and the rate of nucleation was minimized through programmed slow rate of heating (5-10^{o}C/h). The experiments were carried out for 48 hours continuously at a temperature range of 250-260^{o}C and pressure of 60-80 bars and followed by

sudden quenching to the ambient conditions. The resultant product was thoroughly washed with distilled water using ultrasonic cleaner. $M^{+}_{2}O$ - Cr_2O_3 - P_2O_5 fine crystalline materials were obtained under the following ratio (in grams):

$M^{+}_{2}OH$: Cr_2O_3: H_3PO_4 : 1.0 – 2.0: 2.0 - 2.8: 8 –12

3. Characterization

SEM study has made by using JOEL, JSM-840A Scanning Microscope as shown in Fig 2a-b. Powder XRD spectra were recorded for uniform phase materials by Rigaku Miniflex Diffractometer with graphite monochromatized CuKα radiation (λ=1.5405 Å) at room temperature (Fig 3a-b). FTIR-Spectra were recorded using a high resolution Perkin Elmer Infrared Spectrophotometer in the range of 4000-400cm^{-1}. Impedance spectroscopy analysis was measured at room temperature (RT) in the frequency range of 100 mHz – 100KHz using Zahner Impedance Analyzer (Model - IM6) [12] .

4. Results and Discussion

SEM photographs of the resultant products obtained by hydrothermal synthesis were relatively of fine materials exhibiting smooth surface with rhombohedral to prismatic morphology and having size of 0.3-10 μm (Fig 1-2).

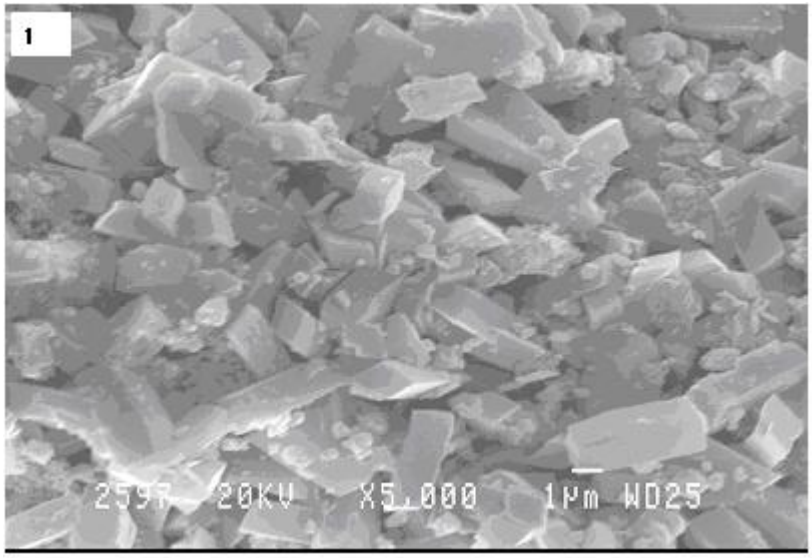

Fig. 1 SEM photographs of Na_2O - Cr_2O_3 - P_2O_5 material.

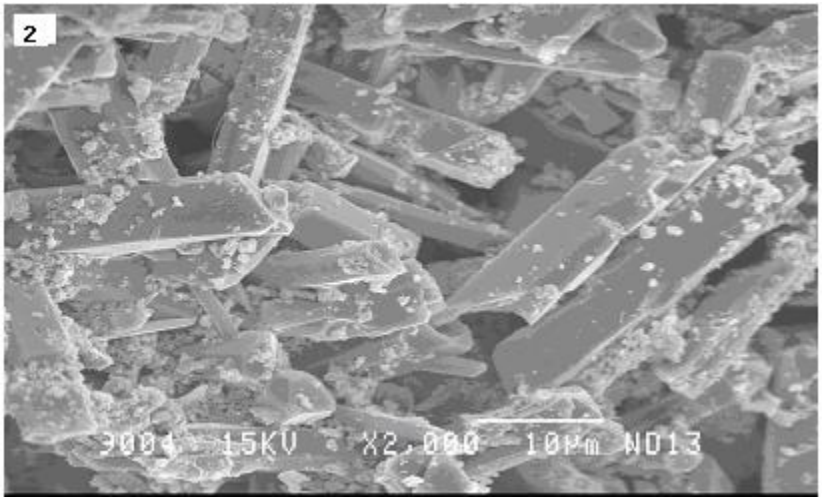

Fig. 2 SEM photographs of K_2O - Cr_2O_3 - P_2O_5 material.

The XRD spectra of the materials have exhibited sharp intensive peaks. The peaks have been indexed and cell parameters were calculated by reciprocal lattice method using spatial indexing computer program (Crysfire-2002) [14]. Na_2O - Cr_2O_3 - P_2O_5 and K_2O - Cr_2O_3 - P_2O_5 materials have crystallized in orthorhombic and monoclinic systems with the cell parameters; a =20.76764, b = 8.86712, c = 8.53437 Å, v = 1571 $Å^3$ and a = 11.8194, b = 6.1518, c = 11.0347 Å, β = 94.846°, v = 799.47 $Å^3$ respectively.

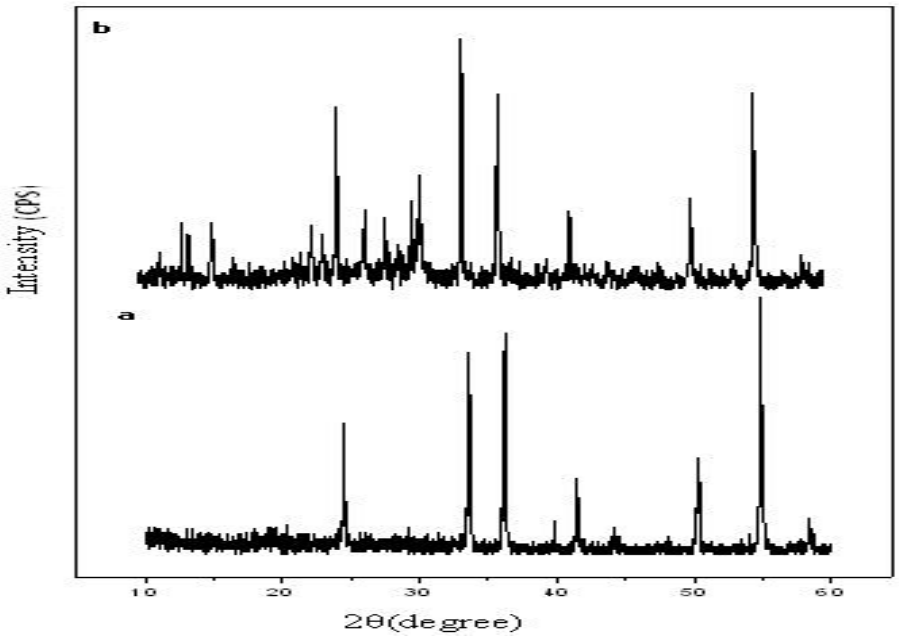

Fig. 3 Powder XRD patterns of a) Na_2O - Cr_2O_3 - P_2O_5 and b) K_2O - Cr_2O_3 - P_2O_5 materials

FTIR spectra have exhibited number of prominent broad and narrow multiple vibrational bands especially in four frequency regions at ν_1 = 3028.66-2795.62cm^{-1}, ν_2 =2362.07-2148.31 , ν_3 =1687.41-1400.07cm^{-1} and ν_4=1199.31- 452.22cm^{-11} as shown in Fig 4a-b ν_1 are due to the presence of H-O-H molecules. The vibration bands ν_2 and ν_3 are due to the presence of Cr-O and M^+- O molecules. The vibrations ν_4 are due to the presence of P - O - P bonding. The multiplication and fineness in the vibration bands of phosphates, especially in the lower frequency region are due to the complexity and a high degree polymerization of $[PO_4]^{3-}$ to $[P_2O_5]$ tetrahedron [13, 15].

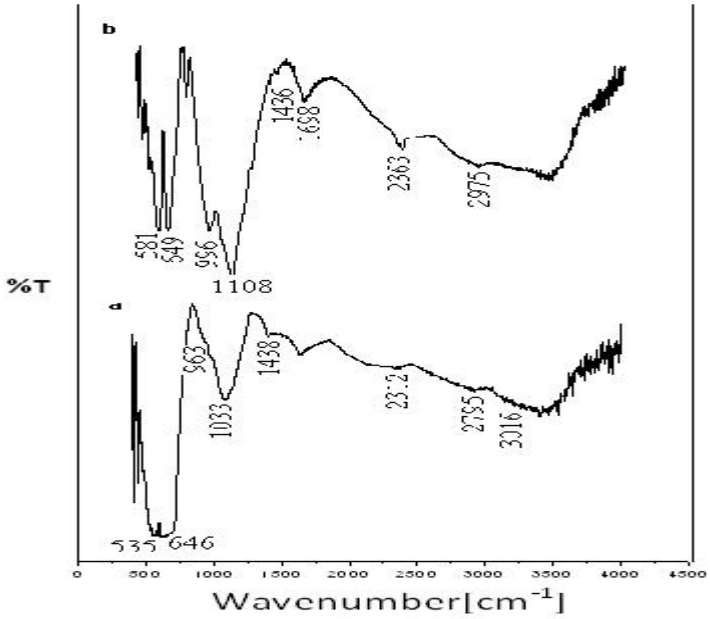

Fig.4 FTIR spectra of a) Na_2O - Cr_2O_3 - P_2O_5 and b) K_2O - Cr_2O_3 - P_2O_5 materials

Complex impedance diagram of Z' vs. Z'' i.e. Cole-Cole plots are given in fig.5-6. Na_2O - Cr_2O_3 - P_2O_5 material consist of an arc with spike. Where as K_2O - Cr_2O_3 - P_2O_5 material consist of a narrow arc followed with an open arc. These plots were analyzed further with Zeeman 2.0 software. The experimental Cole-Cole plots were well fitted to the theoretical curves and equivalent circuit modeling were obtained along with various parameters as illustrated in Fig (5-6). Equivalent circuit models attribute about grain, grain boundary and electrode effects [16]. The equivalent circuit for the Na_2O - Cr_2O_3 - P_2O_5 material consists of a resistor (R_s) and a sub circuit (consist of parallel R_1-CPE_1 combination) in series with a resistor R_2.$R_{s\ is}$ the result of contact between electrode and electrolyte, R_2 is of ohmic resistance of the electrolyte and R_1-CPE_1 is either due to the grain boundary effect or capacitance of the electrolyte. The second material K_2O - Cr_2O_3 - P_2O_5 is fit to resistor (R_s) and array of 3 sub circuit (parallel R_n-$C_n$combination). $R_s$is the result of contact between electrode and electrolyte. R_1-CPE_1 is attributed due to the resultant of grain boundary effects. R_2-CPE_2 and R_3-CPE_3 are corresponding to double layer capacitance.

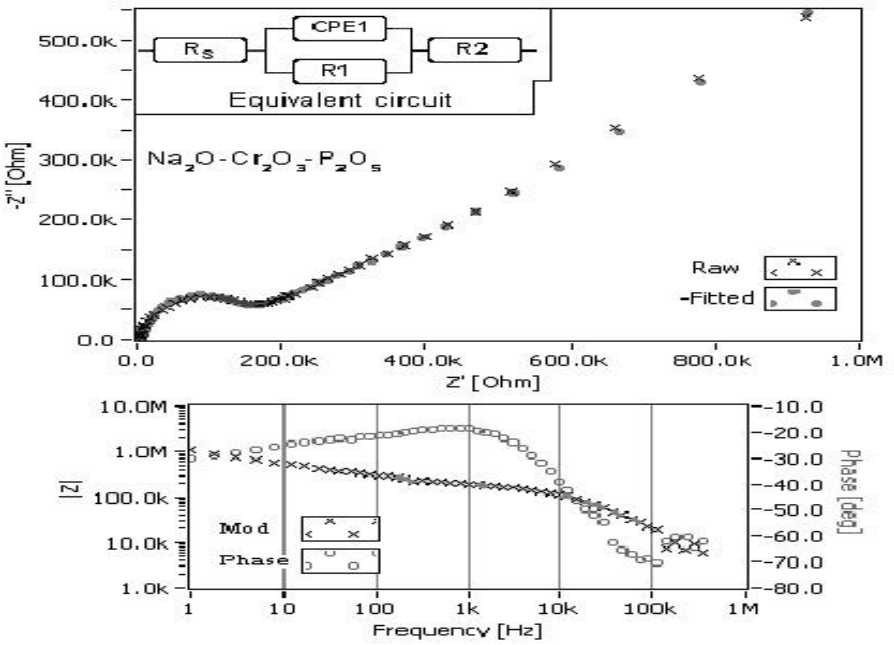

Fig.5. Z' vs. Z'' of Na_2O - Cr_2O_3 - P_2O_5 crystalline materials

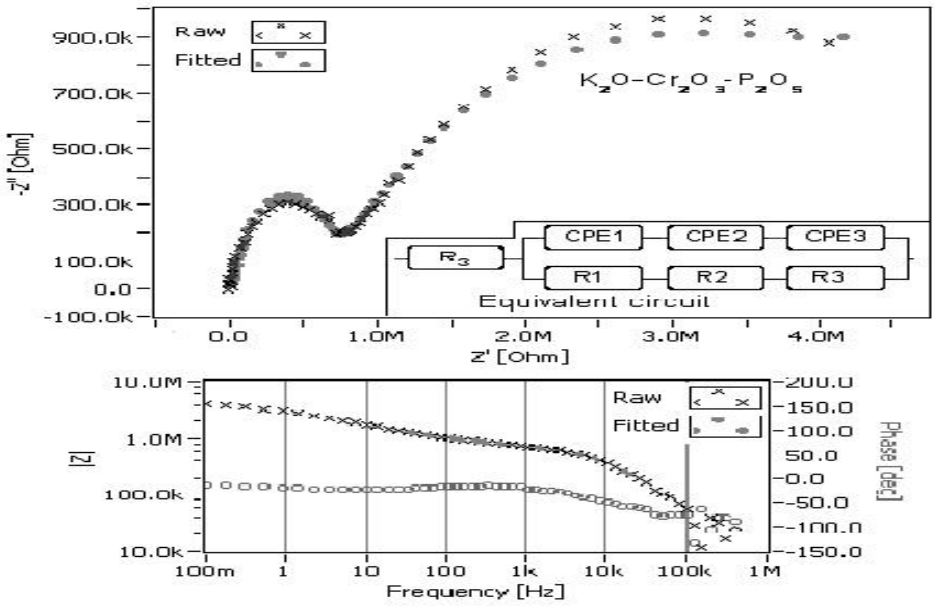

Fig.6. Z' vs. Z'' of K_2O - Cr_2O_3 - P_2O_5 crystalline materials

AC conductivity measurements for both the samples were carried out at different frequencies in the temperature range of 300– 463K and results are plotted along log (σ_{ac}) vs 1000/T (K) (Table 1 and Fig.7-8). From AC conductivity studies, it is observed that the ionic conductivity (σ_{ac}) is by and large unrepentant of frequency and hence conductivity at 5 KHz is considered for detailed analysis. σ_{ac} at room temperature (RT) for both the samples exhibit relatively low values. As the temperature (360-400K) boasted to the samples, the σ_{ac} values sharply increased to more than one to two fold exponentially (table.1).This is because of liberation of adsorbed water molecules and/or breakdown of O-H^{-1} molecules which facilitated dilation of conducting paths, resulted relatively easy path for conducting alkali ions . It is more prominent in Na_2O - Cr_2O_3 - P_2O_5 material because of relatively smaller and ideal ionic radii of Na^+ ion which is prerequisite for a solid electrolyte. However,further boast of temperature to the samples, resulted sharp fall of σ_{ac} values. It is attributed due to the higher thermal strain resulted rapid haphazard movements of ions within the electrolytes and resulted obstruction to the conduction ions.

The activation energy (E_{ac}) for AC conductivity was calculated by fitting the conductivity data to the Arrhenius relations:

$$\sigma_T = \sigma_0 \exp(-E_{ac}/k_bT)$$

Where σ_0 is a pre-exponential factor and $E_{ac,}$ k_b and Tare activation energy for AC conduction, Boltzmann's constant and the absolute temperature respectively. The E_{ac} is relatively small for both the samples at RT (Table 1.). As temperature increases, E_{ac}also increases this is due to the high haphazard thermal vibration, resulted blocking the path of conducting ions.

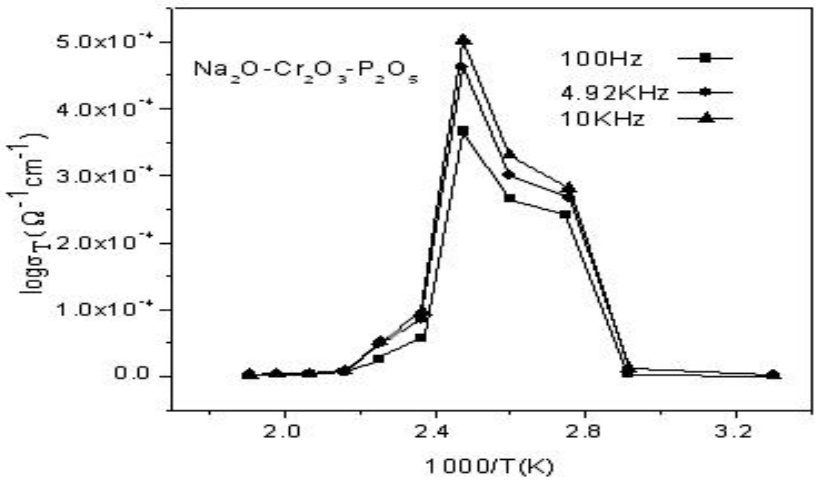

Fig 7. log σ_{ac} ($\Omega^{-1}cm^{-1}$) v/s 1000T (K) of Na_2O - Cr_2O_3 - P_2O_5

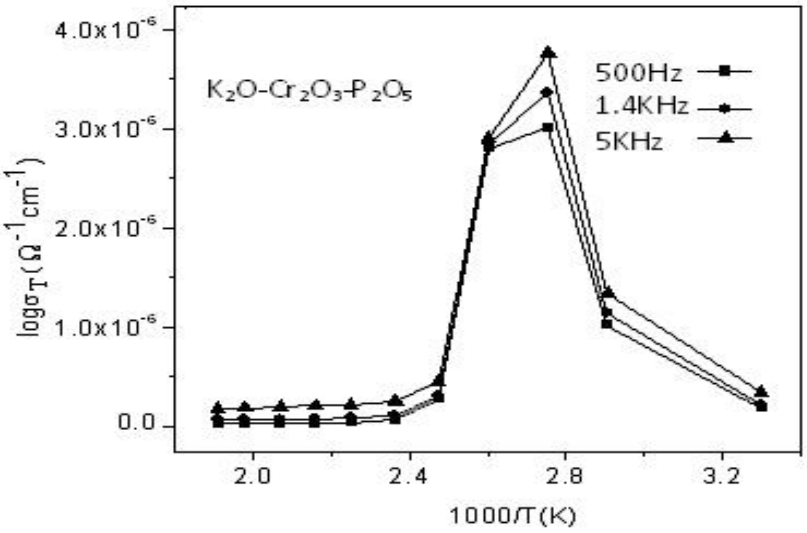

Fig 8. log σ_{ac} ($\Omega^{-1}cm^{-1}$) v/s 1000T (K) of K_2O - Cr_2O_3 - P_2O_5

Table1. AC conductivity and activation energy

Material	T° K	σ_{ac} ($\Omega^{-1}cm^{-1}$)	$E_{a\,(ac)}$ev
Na_2O - Cr_2O_3 - P_2O_5	303	$1.71X\ 10^{-6}$	0.066
	404	$4.62X10^{-4}$	0.125
	523	$1.93X10^{-06}$	0.058
K_2O - Cr_2O_3 - P_2O_5	303	$3.46X10^{-07}$	0.050
	363	$3.76X10^{-06}$	0.017
	523	$1.81X10^{-07}$	0.040

5. Conclusion

$M^{+}{}_2O$ - Cr_2O_3 - P_2O_5 materials were synthesized as fine materials by hydrothermal method. Powder XRD results revealed Na_2O - Cr_2O_3 - P_2O_5 and K_2O - Cr_2O_3 - P_2O_5 materials were crystallized in orthorhombic and monoclinic systems respectively.FTIR studies revealed 4 bands vibrations and exhibited the polymerization of $[PO_4]^{3-}$ tetrahedral. AC conductivity analysis revealed, the conductivity of both the materials is relatively low at room temperature. However both the materials exhibited relatively high conductivity when thermal energy boasted (363-404 T° K). It is more prominent in Na_2O - Cr_2O_3 - P_2O_5 material.

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