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# Hydrothermal Synthesis and Comparative Study of Impedance Properties of $M^+HMgP2O7$ ($M^+$ =$Li^+$, $Na^+$ and $K^+$)

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## ABSTRACT

A series of $M^+$-HMg-$P_2O_7$ ($M^+$= $Li^+$, $Na^+$ and $K^+$) materials have been synthesized by soft hydrothermal technique at moderate P-T conditions. Observation through a Scanning Electron Microscope shows that microstructures of the resultant materials. The resultant powder X-ray diffraction confirms that, the $LiHMgP_2O_7$ material has tetragonal system, $NaHMgP_2O_7$ material has monoclinic system and $KHMgP_2O_7$ material has tetragonal system. FTIR studies revealed that the presence of O-H molecules and minute structural variations of synthesized materials. Impedance measurement revealed that the materials have relatively good ionic conductance at frequencies (solid electrolytes). Repetitive hydrothermal treatment yielded improved crystalline materials.

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**Keywords:** Hydrothermal synthesis, SEM, Powder XRD, FTIR, Impedance measurement.

## 1. INTRODUCTION

Material science is a very good field of research in hydrothermal synthesis of many metal phosphate materials. Recently, metal phosphate has been an increasing demand for higher performance and cheaper rechargeable batteries in different electronics devices. Phosphate materials have been extensively studied for their wide potential applications as electronics devices and as solid electrolyte for batteries of high specific energy, due to the stable physical and chemical properties with high thermal resistance[1-8]. Phosphates are also widely used in the ceramics, paint – industry and as luminescence pigments[9-10], has high

oxidation activity, as catalyst support and optical coating materials[11-12] and as electronic and magnetic materials[13-17]. The properties of fine phosphate materials are mainly dependent on the size, shape and surface morphologies of particles[18-19].

## 2. EXPERIMENTAL

A series of $M^+$-HMg-$P_2O_7$ ($M^+$= $Li^+$, $Na^+$ and $K^+$) materials have been prepared by hydrothermal method at relatively low temperature and pressure condition. The reagents of annular grade (99.99% purity) from Glaxo chemicals were used without further purification. A number of experiments were carried out using different ratios of $M^+OH$, $Mg(NO_3)_2$, and 98% of $H_3PO_4$ at constant temperature. The starting reactance were thoroughly mixed at room temperature to get a homogenous, relatively less viscous mixture and were transferred to a Teflon lined stainless steel autoclaves of 50 mL capacity. The synthesis of $M^+$-HMg-$P_2O_7$ ($M^+$= $Li^+$, $Na^+$ and $K^+$) crystals were carried out at temperature range of $150^0$C. The nucleation was spontaneous and it was minimized through slow rate of heating. At this temperature the experiments were run continuously for 3days and followed by instant quenching to ambient conditions. The resultant product was in semisolid condition. The product was thoroughly washed several times with double distilled water and ethanol using ultrasonic cleaner and final product was filtered and dried under vacuum at $90^0$c for 2 hours. The study crystals were obtained under following molar ratios in grams.

$M^+OH$: $Mg(NO_3)_2$ : $H_3PO_4$ : 3.0-3.5 :1.5-2.5 :4.0

The synthesis of $M^+$-HMg-$P_2O_7$ materials to confirmed the reproducibility of the crystals.

## 3. RESULT AND DISCUSSION

### 3.1 SEM

The morphology and size of the product was observed using Scanning Electron Microscope (SEM-ZEISS-Mysore). Crystals obtained by the hydrothermal method were of good quality and exhibited smooth surface, sub transparent and sub vitreous luster (Fig:1).

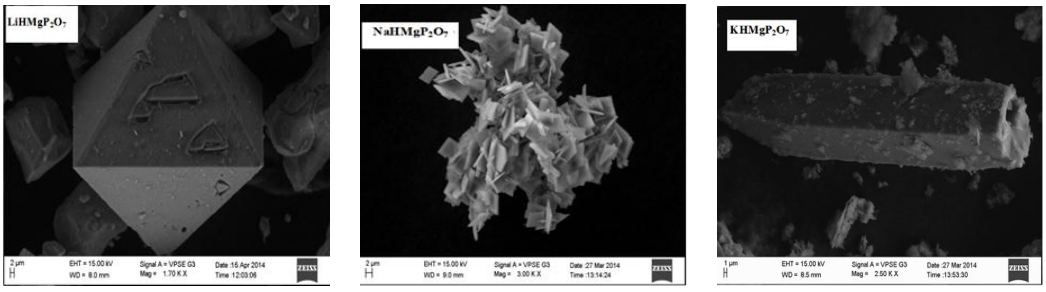



**Fig.1: SEM photograph of $M^+$-HMg-$P_2O_7$ ($M^+$= Li, Na and K) materials**

$LiHMgP_2O_7$ material has octahedral like crystal of 0.2mm to 0.5mm, $NaHMgP_2O_7$ material have rectangular plate like crystal of thickness less than 1μm, size ranging 2μm to 10μm. $KHMgP_2O_7$ material has rad like crystal of size 0.1mm to 5mm. The SEM micrograph of the specimen had well developed randomly oriented grains.

### 3.2. Powder XRD

Powder X-ray diffraction (XRD) measurements were recorded using Rigaku Mini Flex 2 Diffractometer with Ni filtered $CuK_\alpha$ radiation of wavelength 1.5406A$^o$ and a graphite monochromator. The specifications used for the recording were 30kVand 15mA.The products were scanned in the continuous mode at 2θ range of 6-60$^0$ with scanning speed of 5$^0$\min. X-ray diffraction pattern showed a single phase in all trials. The peaks have been indexed using the *d*-values and the lattice parameters were also calculated.

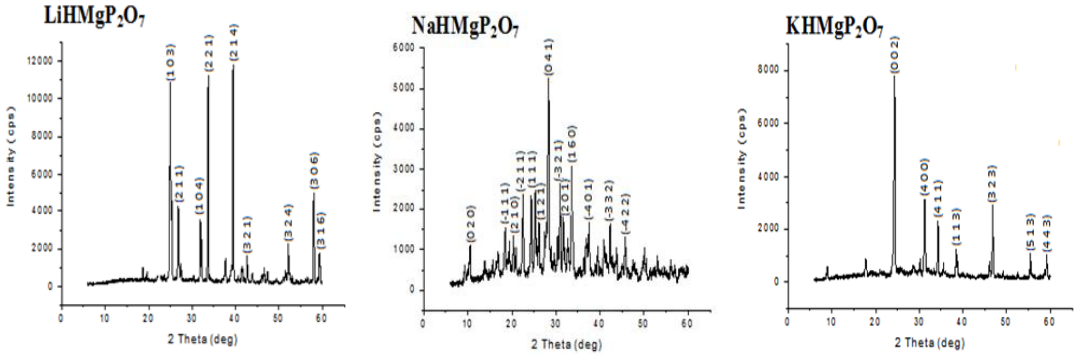



**Fig.2: Powder XRD patterns**

The XRD data were analyzed using XRD software MDI jade 5.0. $LiHMgP_2O_7$ crystallized material represent a tetragonal system in octahedral form with α=β=γ=90$^o$, a=b=7.744Å and c=12.09Å).

$NaHMgP_2O_7$ crystallized in monoclinic system with α=γ=90$^o$,β≠90$^0$ a=9.66 Å, b=16.81Å and c=5.112Å and $KHMgP_2O_7$ crystallized in tetragonal system with a=b=11.48 Å c=7.313Å and α=β=γ=90$^o$

### 3.3. Fourier Transformer Infrared Radiation (FT-IR)

FTIR spectrum was measured by a resolution JASCO FTIR-460 plus Spectrophotometer with the KBr pellet technique FT-IR spectra are recorded in the ranging from 400-4000cm$^{-1}$.

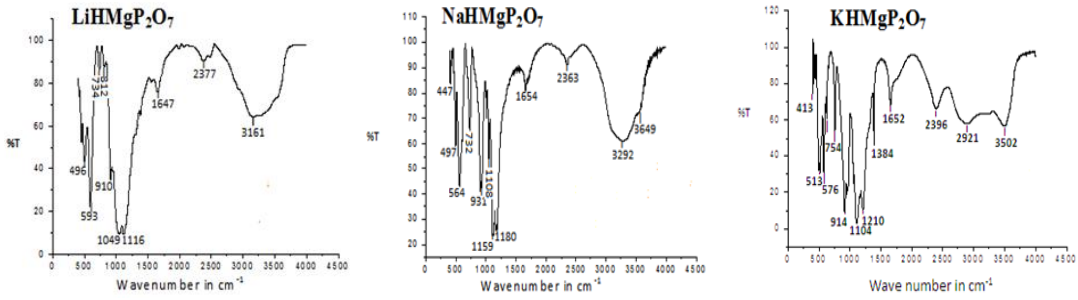
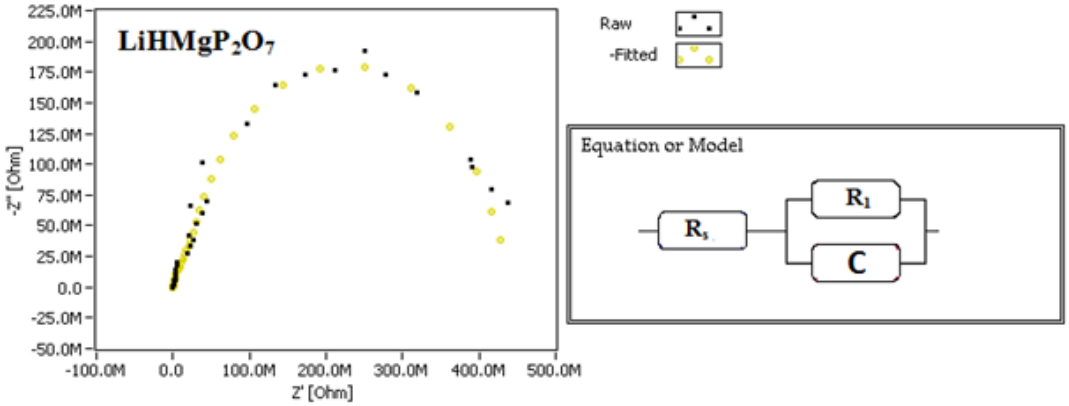



**Fig.3: FT-IR spectrums**

The spectra of $M^+HMgP_2O_7$ ($M^+$ =$Li^+$,$Na^+$ and $K^+$) compounds have exhibited prominent and narrow multiple vibration bands in four frequency regions (fig.5). The vibration regions of $LiHMgP_2O_7$ compound are at $\nu_1$=3161cm$^{-1}$, $\nu_2$=2377cm$^{-1}$, $\nu_3$=1647cm$^{-1}$, and $\nu_4$=1116 - 496cm$^{-1}$, the $NaHMgP_2O_7$ compound are at $\nu_1$=3649cm$^{-1}$ -3292cm$^{-1}$, $\nu_2$=2363cm$^{-1}$, $\nu$3=1654cm$^{-1}$ and $\nu_4$=1180 - 447 cm$^{-1}$, and the $KHMgP_2O_7$ compound are at $\nu_1$=3502cm$^{-1}$ - 2921cm$^{-1}$, $\nu_2$=2396cm$^{-1}$, $\nu$3=1652cm$^{-1}$ -1384cm$^{-1}$ and $\nu_4$=1210cm$^{-1}$ - 413 cm$^{-1}$. The vibration bands in higher region at 3161cm$^{-1}$, 3649cm$^{-1}$ and 3502cm$^{-1}$ – 2921cm$^{-1}$ have clearly indicated the presence of O-H molecule. The vibrations stretching at 2377cm$^{-1}$, 2363cm$^{-1}$ and 2396cm$^{-1}$ are due to the presence of Mg - O molecules and the bands at 1647cm$^{-1}$, 1654cm$^{-1}$ and 1652cm$^{-1}$ -1384cm$^{-1}$ are attributed due to the stretching of alkali metallic ions bonding respectively. The strong vibration bands in the range of 1116cm$^{-1}$ – 496cm$^{-1}$ ,1180cm$^{-1}$ -447cm$^{-1}$ and1210cm$^{-1}$-413cm$^{-1}$ are due to the stretching of P - O - P bonding. It has been reported that, the degree of multiplication and fineness in the spectra of phosphates increases as the degree of polymerization increases in the [$PO_4$] tetrahedral [15-16]. It is clearly noticed that, the study compounds have exhibited more number of splitting and sharpness, especially in the low frequency regions indicating the polymerization of $[PO_4]^{3-}$ to $[P_2O_7]^{4-}$.

### 3.4 Impedance measurement

Impedance spectroscopy data taken has a series of $M^+$-HMg-$P_2O_7$ ($M^+$= $Li^+$, $Na^+$ and $K^+$) materials were measured using Zahnar impedance analyzer (Model – IM6) at room temperature, in the frequency range from 100Hz to 1MHz. Pellet was prepared by using a tungsten carbide dies, plungers, and a hydraulic press. Pellet was prepared form series of $M^+$-HMg-$P_2O_7$ ($M^+$= $Li^+$, $Na^+$ and $K^+$) polycrystalline powder materials at a pressure of 7 kg/cm$^2$ pressed for 4-5 mints. The measured impedance data was analyzed using Zeeman 2.0 software and equivalent circuit was obtained along with various parameters as illustrated in the figure.




data was analyzed using Zeeman 2.0 software and equivalent circuit was obtained along with various parameters as illustrated in the figure.

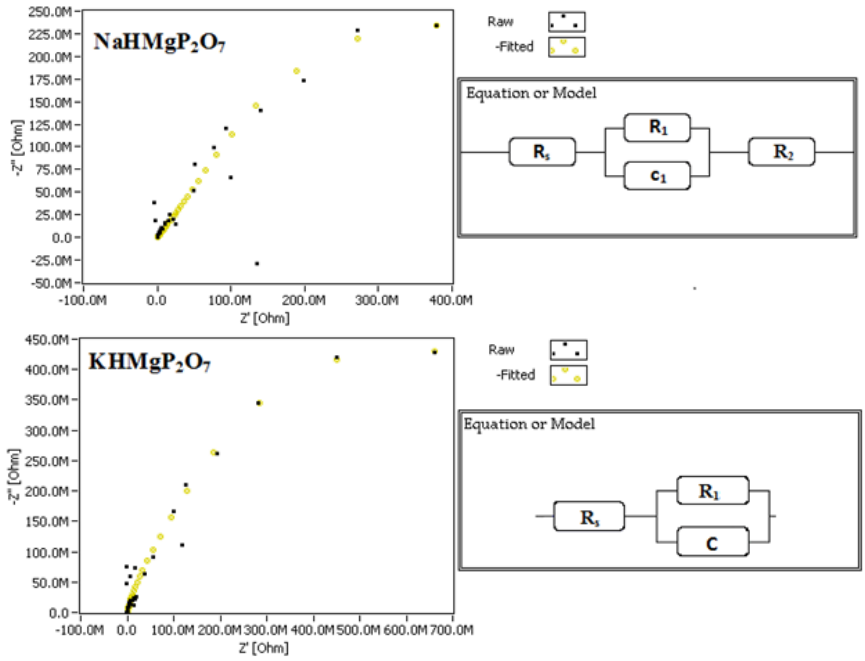



**Fig.4: cole- cole plot and equivalent circuit**

Complex impedance plots of Z' vs. Z'' were made using Cole- Cole plots of various frequency at room temperature as shown in the fig.4. Equivalent circuits justify the proposed concordance between the calculated (Fitted lines) and experimental data (Raw lines).

The frequency range and applied voltage at room temperature (RT) were in the range of 100Hz – 1MHz and 2V respectively. Complex impedance plots of Z' vs. Z'' were made using Cole- Cole plots, given in fig.4. The impedance spectra of $M^+$-$HMgP_2O_7$ samples represent an arc. The experimental plots are well fitted to the theoretical equivalent circuits along with various parameters as illustrated in Fig (4). Equivalent circuit modeling attributes to grain, grain boundary and electrode effects[20-21]. The impedance results at RT for $LiHMgP_2O_7$ fit to a series array of $R_s$ and one sub circuit (sub circuit consists of parallel $R_1$-C combination). $R_s$ are due to the inter phase between electrode and electrolyte (homic resistance). C is due to the capacitance. $NaHMgP_2O_7$, fit to series array of $R_s$ and a sub circuit (parallel $R_1$-$C_1$ combination) followed with a resistor $R_2$ . $KHMgP_2O_7$ fit to a series array of $R_s$ and one sub circuits (sub circuit consists of parallel $R_1$-C combination). As the frequency of $M^+$-$HMgP_2O_7$ materials increases impedance value decreases and conductance values increases. Comparatively the conductance of $LiHMgP_2O_7$ material was high compared to $NaHMgP_2O_7$ and $KHMgP_2O_7$ because $Li^+$ ionic radii is small compared to $Na^+$ and $K^+$ ionic radii. The impedance of $NaHMgP_2O_7$ sample decreased and conductance increased when compared to $KHMgP_2O_7$ sample. As the frequency of $M^+$-$HMgP_2O_7$ sample was increased, impedance decreased and conductance increased. This shows that $M^+$-$HMgP_2O_7$ is relatively good ionic conductance materials at high frequency.

## 4. CONCLUSIONS

$M^+$-$HMgP_2O_7$ crystals were synthesized by hydrothermal technique in the form of fine crystalline materials. FTIR results revealed the presence of O-H molecule in $M^+$-$HMgP_2O_7$ material. Impedance spectroscopy analysis indicated that these materials have positive correlation with AC conductivity with the room temperature and hence these are prospective moderate ionic conductors for high frequency.

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