

Hydrothermal synthesis and characterization of LiHMgP₂O₇

A M Sunitha^{*}, G S Gopalakrishna, K Byrappa, and M S Bhargavaram
Department of Studies in Earth science, University of Mysore, Manasagangotri, Mysore 570 006, India,

Abstract: A series of LiHMgP₂O₇-material was synthesized by hydrothermal method. The resultant material was characterized by powder X-ray diffraction, FTIR, SEM and Impedance measurement. The powder XRD studies revealed that the material has tetragonal system with cell parameters $a = b = 7.744 \text{ \AA}$, $c = 12.09 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$. Repetitive hydrothermal treatment yielded improved crystalline materials.

PACS Nos.: 81.10.Dn, 61.10.Nz, 81.70.Pg, 78.30.Hv

Keywords: hydrothermal synthesis, SEM, Powder XRD, FTIR, Impedance measurement

I. Introduction:

Alkali transition metal phosphates have been extensively studied owing to their wide application as prospective electrolytes, sensors, laser materials, piezoelectric, luminescence, optoelectronics, ceramics, and as magnetic materials [1-6]. Since the interest is focused on the preparation of polycrystalline material which drastically enhances their physical and chemical properties. These materials are mainly dependent on the size, shape and surface morphologies of the particles [7-9]. The hydrothermal synthesized particle size has an inverse relationship with the temperature [10-11]. The alkaline metal phosphates have shown superconductivity at low temperature [12-13] and also good diamagnetic, semiconductors [14-16]. Here we have reported the hydrothermal synthesis and characterization of a group of phosphate material: LiHMgP₂O₇ and also discussed the electrical impedance spectroscopy analysis of this material.

II. Hydrothermal Synthesis Of Lihmgp₂o₇:

2.1 Experimental procedure:

The phosphate material has been synthesized using hydrothermal method at moderate temperature and pressure conditions. Synthesis of phosphate materials by hydrothermal technique is one of the best method compared to other methods, owing to its advantages like synthesis at a relatively low temperature and it is a closed system; hence, gaseous fugacity play an important role in the synthesis process. The chemical reagents were used as per the annular grade of LiOH (99.5%), Mg(NO₃)₂ (99%) and H₃PO₄ (98%) from Raghu chemicals without further purification. A known amount of LiOH and Mg(NO₃)₂ were taken in a Teflon – lined stainless-steel autoclave with a capacity of 50ml (Morey type autoclaves). Later known quantity of H₃PO₄ were added to it and thoroughly stirred till homogeneity was attained. The crystallization was formed by spontaneous nucleation and rate of nucleation was controlled by the rate of heating. The experiments were carried out 3 days continuously at a temperature of 150°C and followed by sudden quenching to the ambient conditions. The resultant product was thoroughly washed with distilled water, absolute Ethanol and dried at 80°C for 45 mints. LiHMgP₂O₇ fine crystalline material was obtained under the following ratio (in grams):

LiOH: Mg(NO₃)₂:H₂O:H₃PO₄

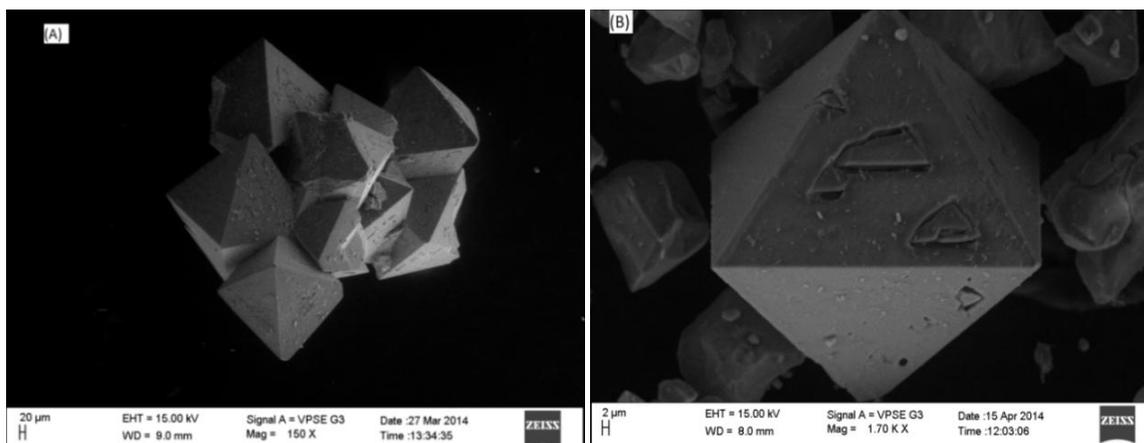
3.0-3.5:1.5-2.5:4-5ml

$\text{LiOH} + \text{Mg}(\text{NO}_3)_2 + 2\text{H}_3\text{PO}_4 \rightarrow \text{LiHMgP}_2\text{O}_7 + 2\text{H}(\text{NO}_3)\uparrow + 2\text{H}_2\text{O}\uparrow$

III. Results 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 are of good quality and exhibited smooth surface, sub transparent, sub vitreous luster, with a size of μm (Fig:1).



(A) Octahedral form of Polysynthetic twinning crystal (B) Octahedral form of single crystal
Fig.1 SEM photograph of LiHMgP₂O₇

3.2. Powder XRD:

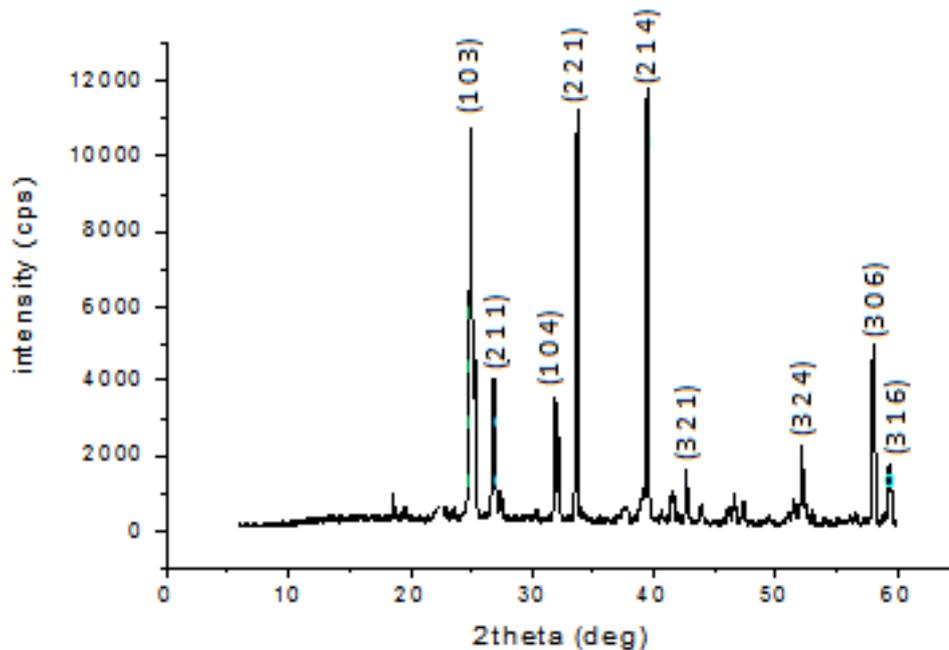


Fig: 2 Powder XRD patterns of LiHMgP₂O₇

Powder X-ray diffraction (XRD) measurements were recorded using RigakuMiniFlex 2 Diffractometer with Ni filtered CuK α radiation of wavelength 1.5406Å and a graphite monochromator. The specifications used for the recording were 30kV and 15mA. The product was scanned in the continuous mode in the 2θ range of 6-60 degree with scanning speed 5 degree/min.

The data analyzed using an XRD software MDI jade 5.0 represented a tetragonal system in octahedral form (tetragonal system $\alpha=\beta=\gamma=90^\circ$, $a=b=7.744\text{Å}$ and $c=12.09\text{Å}$).

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

FTIR spectrum was measured by an Origin Jasco spectrometer with the KBr pellet technique ranging from 400-4000 cm^{-1} .

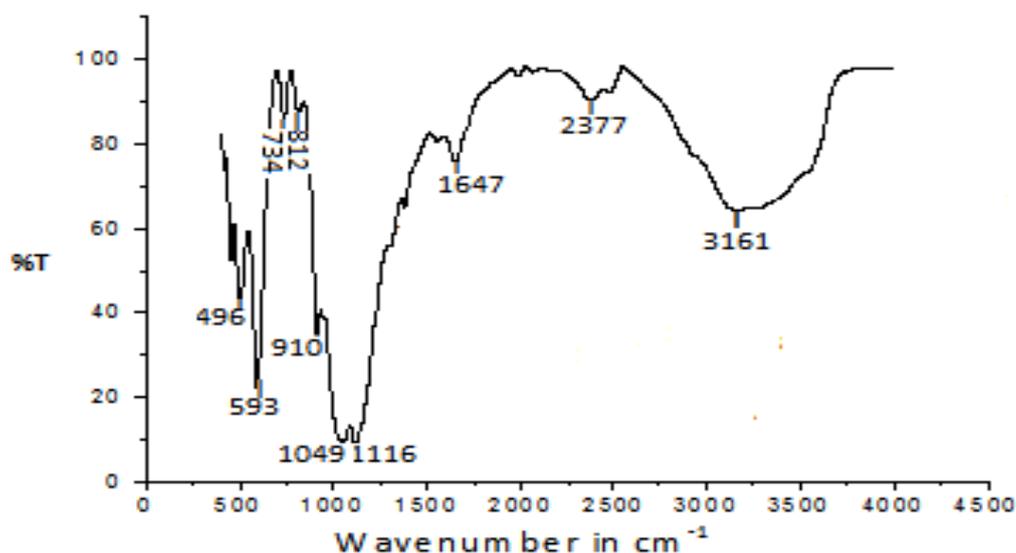


Fig: 3 FTIR spectra of LiHMgP₂O₇ material

FTIR spectra exhibited a number of prominent broad and narrow multiple vibration bands especially in four frequency regions at $\nu_1 = 3161 \text{ cm}^{-1}$, $\nu_2 = 2375 \text{ cm}^{-1}$, $\nu_3 = 1647 \text{ cm}^{-1}$ and $\nu_4 = 1116 - 416 \text{ cm}^{-1}$ as shown in figure. The vibrational band ν_1 represent O-H molecules. The vibrational stretching of ν_2 represent Mg-O and ν_3 represent Li-O-Li banding. The vibrational band ν_4 represent P-O-P molecules. The multiplication and fineness in the vibrational bands of phosphates, especially in the lower frequency region were due to the complexity and polymerization of $[\text{PO}_4]^{3-}$ to $[\text{P}_2\text{O}_5]$ tetrahedron [17, 20]. These were more prominent in the materials containing higher concentration of phosphorus ions.

3.4 Impedance measurement:

Impedance spectroscopy has been measured using a IM6 ZAHNER electric in the frequency range of 1Hz to 1MHz, at room temperature. Pellet was prepared from the polycrystalline powder at a pressure of 7 kg/cm² pressed for 6 mints.using tungsten carbide dies, plungers, and a hydraulic press. The pellet was 1cm in diameter and 0.12cm in thickness. Impedance spectroscopy measurement has been carried out at room temperature in the frequency range of 1Hz - 400 kHz using Zahner impedance analyzer (Model - IM6). The measured impedance data was analyzed using Zeeman 2.0 software and equivalent circuit was obtained along with various parameters as illustrated

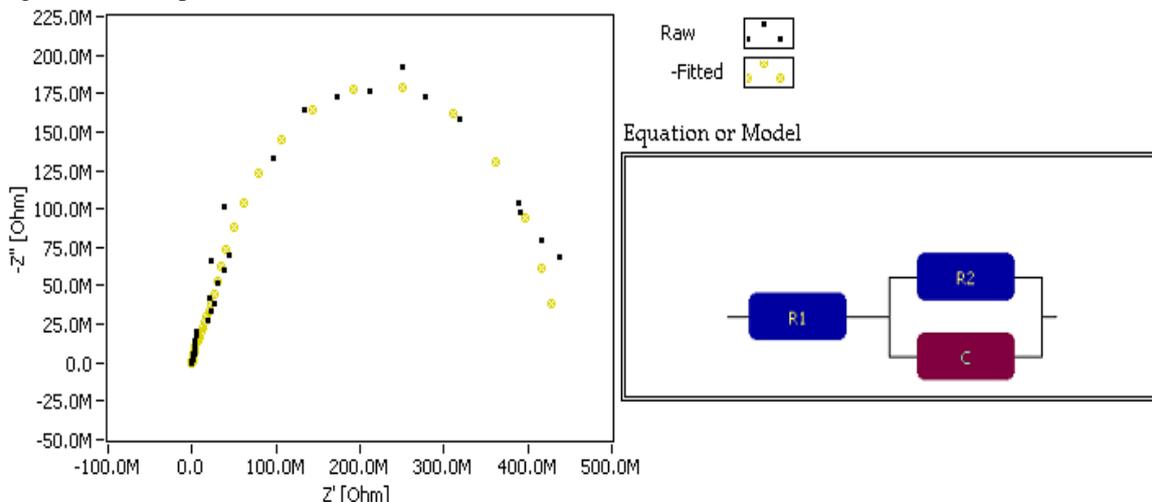


Fig:4 cole- cole plot and equivalent circuit

Complex impedance diagram of Z' vs Z'' i.e. Cole- Cole plots are given in fig.4. In samples at room temperature, the impedance at low frequencies significantly higher than at high frequencies. This behavior may explain the fact that LiHMgP₂O₇ act as an insulator at low frequencies, because of capacitance. When the low frequency 1Hz applied to the material the impedance value is 400M Ω , the main AC current flows through the electrode to electrolyte and the material is bypassed from the resistance and reactance as shown in an equation or model, in this sense, the material act as an insulator.

Equivalent circuit represent the cole-cole plot theory cole- cole plot represent on single arc these arc represent parallel connection between resistance and capacitance (R_2 and C) . R_1 be the homoc resistance (or grain boundary effect) exhibit between electrode and electrolyte, these R_1 series connection of R_2 and C,

IV. Conclusion:

LiHMgP₂O₇ product has been synthesized by hydrothermal method at moderate temperature and pressure. Powder XRD result have revealed the degree of crystallinity and size of the crystallites increased manifold due to the hydrothermal treatment and these exhibited a tetragonal system of octahedral form. LiHMgP₂O₇ material cannot be used as a good conducting material is an insulator at low frequencies because presence of capacitance, impedance value at low frequencies is in the order of 10⁸ Ω

Acknowledgments:

The authors would like to express thanks to UPE, Government of India for financial assistance under the project UPE.

Reference:

- [1]. H.G. Danielmeyer, G. Huber, W.W. Kruhler, *J.F. Jesser, Appl. Phys*, 2 (1973) 335.
- [2]. H.P. Weber, T.C. Damen, H.G. Danielmeyer, C.C. Tofield, *Appl. Phys. Lett*, 22 (1973) 534.
- [3]. H.Y.P. Hong, *Mater. Res. Bull*, 11 (1976) 173.
- [4]. J.B. Goodenough, H.Y.P. Hong, J.A. Kafalas, *Mater. Res. Bull*, 11 (1976) 203.
- [5]. C. Delne, R. Olazcuage, G. Le Flem, P. Hagenmuller, F. Cherkaoue, R. Brochu, *Mater. Res. Bull*, 16 (1981) 285.
- [6]. K. Byrappa, G.S. Gopalakrishna, *Prog. Cryst. Growth Charact*, 11 (1985) 89.
- [7]. H.T. Zhang, Y.M. Xiong, X.G. Luo, C.H. Wang, S.Y. Li, X.H. Chem, *J. Crystal Growth*, 242 (2002) 259.
- [8]. M.A. Kastner, *Phys. Today*, 46 (1) (1993) 24.
- [9]. J.F. Smyth, *Science*, 258 (1990) 247.
- [10]. T. Zhu, C.H. Yan, Z.M. Wang, H.W. Zhao, J.R. Sun, B.G. Shen, *Solid State Commun*, 117 (2001) 471.
- [11]. R.D. Sanchez, J. Rivas, C. Vazquez-Vazquez, A. Lopez- Quintela, M.T. Causa, M.S. Tovar Oseroff, *Appl. Phys. Lett*, 68 (1996) 134.
- [12]. I. Shirovani, M. Takaya, I. Kaneko, C. Sekine, T. Yagi, *Solid. State. Commun*, 116 (2000) 683.
- [13]. T. Sakon, A. Kobayashi, M. Kubotam, Y. Nakanishi, H. Nojiri, S. Mitsudo, S. Takagi, S. Suzuki *Physica B*, 300 (1999) 259.
- [14]. Yi Xie, Huilan SU, Bin LI, Yitai Qian, *Mat. Res. Bull*, 35 (2000) 675.
- [15]. K. Kuriyama, K. Kushida, R. Taguchi, *Solid. State. Commun*, 108 (1988) 429.
- [16]. I. Shirovani, Takafumi Adachi, Kenji Sakae Todo, Kiyokazu Nozawa, Takehiko Yagi, Minoru Kinoshita *J. Phys. Chem. Solids*, 57 (1996) 211.
- [17]. M.J. Mahesh, G.S. Gopalakrishna, K.G. Ashamanjari, J. Shashidhara Prasad, *Indian J. Phys*, 79 (2005) 37.
- [18]. A. Rabenau, *Angew. Chem. Int. Ed. Eng.*, 24 (1985) 1026.
- [19]. R. Shirley, *The Crysfire 2002 System for Automatic Powder Indexing: User's Manual*, The Lattice Press, 41 Guildford Park Avenue, Guildford, Surrey GU2 7NL, England, 2002.
- [20]. M. Mahendra, S.P. Madhu, B.H. Doreswamy, G.S. Gopalakrishna, M.A. Sridhar, J. Shashidhara Prasad, K.G. Ashamanjari, *Mater. Res. Bull*, 38 (2003) 1309.

Figure Captions:

- Fig.1 SEM photograph of LiHMgP₂O₇
 Fig.2 Powder XRD patterns of LiHMgP₂O₇
 Fig.3 FTIR spectra of LiHMgP₂O₇ material
 Fig.4 cole- cole plot and equivalent circuit