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SYNTHESIS AND ELECTRICAL CONDUCTIVITY STUDY OF $LiGdP_2O_7$ FAST IONIC CONDUCTOR

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ABSTRACT

The electrical conductivity of solid electrolyte $LiGdP_2O_7$ prepared by wet chemical method has been found to be 2×10^{-5} S cm^{-1} at 400°C. The transport properties such as hopping frequency, charge carrier concentration have been studied. The activation energy for hopping (E_ω) is in good agreement with the bulk activation energy (E_σ) suggesting the independent nature of carrier concentration with temperature.

Key words: Rare earth phosphates, FTIR Analysis, Impedance spectroscopy, Transport parameters.

INTRODUCTION

Fast ion conductors characterized by their high ionic conductivity have attracted a great deal of attention because of their potential applications in solid state high energy density batteries, sensors and fuel cells[1-3]. Mono and Double phosphates have received considerable attention in developing new ionic conducting material due to their tri-dimensional framework of $P_2O_7^{4-}$ polyhedra, which gives rising tunnels along the c direction[4]. The conductivity of the monovalent cation is higher than that of the divalent and trivalent ion due to its small atomic radius. Among the monovalent cationic conductors, alkali metal ions such as Na and Li were especially well known for their high ionic conduction in solid electrolytes. Among them, Li based systems are particularly attractive due to their high energy densities and high open circuit potentials. The present work explores the ion dynamics of $LiGdP_2O_7$ electrolyte using the analysis of frequency dependent conductivity obtained from complex impedance measurements.

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EXPERIMENTAL

Polycrystalline sample of $LiGdP_2O_7$ has been prepared by Wet Chemical method. $LiOH.H_2O$, $Gd(NO_3)_3.6H_2O$, $(NH_4)_2HPO_4$ are used as starting materials. The starting materials are dissolved in doubly distilled water separately and the solution are mixed and stirred well. Aqueous solutions of the raw materials were prepared separately by dissolving them in doubly distilled water. The solutions are mixed and stirred well. The observed snow white precipitate is filtered and dried at 100^{o}C. The dried sample is ground and subjected to heat treatment at 650^{o}C for 3 hrs in air. The resultant sample is crushed into powder and spread in a die. The pellets with 1.0 cm diameter having a thickness of 0.24 cm are sintered at 500^{o}C for 2 hrs in air. The silver coated on both sides acts as electrode. An impedance analyzer HIOKI 3532, controlled by a computer is used to obtain the impedance data with a frequency range between 42 Hz and 1 MHz in the temperature range between 300 and 400^{o}C in air is used. FTIR spectrum has been used to confirm the formation of P_2O_7 by using Shimadazu-8000 Spectrophotometer.

RESULTS AND DISCUSSION

FTIR analysis

The FTIR spectrum of $LiGdP_2O_7$ in the wave number range 400-2000 cm^{-1} is shown in Fig. 1.b. The FTIR spectrum indicates the presence of characteristic vibrational bands $P_2O_7^{-4}$ indicating the formation of diphosphate. The $P_2O_7^{-4}$ ion (Fig. 1.a) consists of 2 PO_4 tetrahedra sharing a common oxygen atom. Hence, the assignment of the $P_2O_7^{-4}$ modes is carried out in terms of PO_3 and P-O-P vibration. The band assignments have been tabulated in Table 1. The bands appearing between 400-650 cm^{-1} can be assigned to PO_3 bending mode. The band at 418 cm^{-1} is assigned to δ PO_3 mode of vibrations. The band at 494 cm^{-1} is assigned to δ_s PO_3 vibrations.

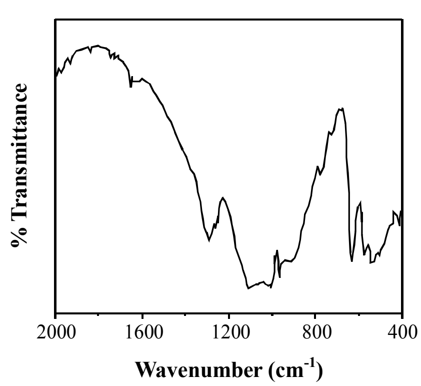

Fig. 1(a): FTIR spectrum of $LiGdP_2O_7$

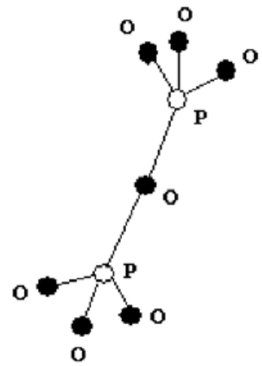

Fig. 1(b): $P_2O_7^{-4}$ ion consists of 2 PO_4 tetrahedra sharing a common oxygen atom

Table 1

Wave number (cm^{-1})	**Assigned modes of vibration**	**Wave number (cm^{-1})**	**Assigned modes of vibration**
1294	υ_{as} PO_3	725	υ_s P – O – P
1008	υ_s PO_3	652	–
963	–	576	δ_{as} PO_3
910	δ_{as} P – O – P	494	δ_s PO_3
783	υ_s P – O – P	418	δ_s PO_3

The band at 576 cm^{-1} is assigned to asymmetric bending vibrations of PO_3. The band at 725 & 783 cm^{-1} is assigned to symmetric stretching of PO_3 mode of vibrations. The bands at 910 cm^{-1} and 1008 cm^{-1} can be assigned to the asymmetric bending vibrations of P-O-P bond and υ_s vibrations of PO_3 modes, respectively. The vibrational band of symmetric stretching of PO_3 has been observed at 1294 cm^{-1}. The intensity ratio of υ_s P – O – P to υ_s PO_3 can be taken as a criterion for studying the configration of $P_2O_7^{-4}$ ion in a compound. Mahadevan pillai et al.[5] reported the eclipsed configuration of $P_2O_7^{-4}$ ions in $Rb(VO_3)(P_2O_7)_2$. In this compound the ratio is ≈ 0.3, which explains the eclipsed configuration of $P_2O_7^{-4}$ in $LiGdP_2O_7$ compound.

Impedance analysis

Fig. 2 shows the complex impedance diagram of $LiGdP_2O_7$ at two different temperatures. The data fall on a single semicircle whose center lies below the real axis. The conductivity has been found by using the equation $\sigma_b = l / R_bA$, where l is the thickness of the sample and A is the electrode area. The associated capacitance is calculated from the relation ωRC = 1, which is measured at arc maximum and is of the order of pF and related to the bulk response i.e., for the motion of ions within the grains.

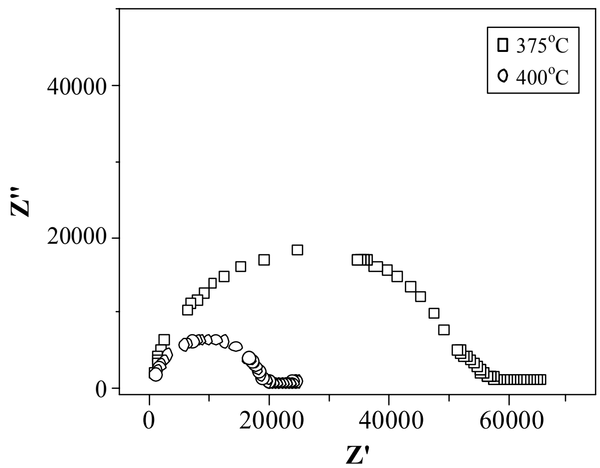

Fig. 2: The complex impedance diagram of $LiGdP_2O_7$ for 375^0 C & 400^0 C

The temperature dependance of the bulk conductivity obeys the Arrhenius relation:

$$\sigma_b (T) = \sigma_o \exp (-E_\sigma / kT) \qquad \ldots(1)$$

where σ_o is the pre-exponential factor of the bulk conductivity and E_σ the activation energy for the mobile ions. From the plot of 1000/*T* vs log σ_b (T) (Fig. 4)), the activation energy of the electrolyte can be obtained from the slope of the straight line and has been found to be 0.76 eV.

Ac conductivity analysis

The ac conductance spectrum of the sample at different temperatures is shown in Fig. 3. The spectrum consists of two different regions. At low frequency, the frequency independent conductivity plateau is observed which is equal to the dc conductivity.

The dc plateau characterizes the conduction, which is caused mainly by the hopping motion of the mobile ions. At higher frequencies, the conductivity dispersion follows the power law dependence as expected for most of the hopping type ionic conductor. According to Jonscher[6,7], the power law exponent is given by –

$$\sigma (\omega) = \sigma_o + A \omega^n \qquad \ldots(2)$$

where A represents the ac conducting part and n is a temperature dependent parameter.

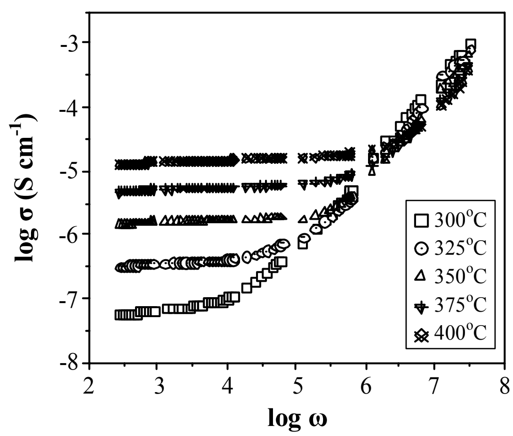

Fig. 3: The conductance spectrum for $LiGdP_2O_7$ for various temperatures

The high frequency dispersion could be attributed to cooperative event involving many neighboring ions. In the lithium Gadolinium phosphate, the "n" value is found to be greater than one and it is decreased with increase of temperature in the temperature range studied. The calculated values of n have been tabulated in Table 1. The hopping frequency ω_p, has been extracted from the Almond and West formalism[8].

$$\omega_p = (\sigma_o/A)^{1/n} \quad \ldots(3)$$

The hopping frequency ω_p has been calculated from the conductivity spectra at different temperatures and fitted to the following equation,

$$\omega_p = \omega_e \exp(-E_\omega/kT) \quad \ldots(4)$$

with

$$\omega_e = \omega_o \exp(-S_\omega/k) \quad \ldots(5)$$

where ω_e is the effective attempt frequency and E_ω is the activation energy for hopping of migration of ions, ω_o is the true attempt frequency of ions, and S_m is the activation entropy for hopping or migration of ions. The true attempt frequency ω_o are obtained from the harmonic potential well expression,

$$\omega_o = (E_\omega/2ma^2)^{1/2} \quad \ldots(6)$$

where m is the mass of the mobile ion and a is the jump distance and it is taken as 3°Å for the sample. From the infinite temperature intercept, the effective attempt frequencies have been calculated. The ω_e value is found to be 2.15×10^{19} Hz. True attempt frequency ω_o is equal to 7.6×10^{12}. The quantization of ion hopping also assists in the estimation of the mobile ion concentration of a conductor. The magnitude of ionic conductivity for a particular material is effectively determined by the product of the ion hopping rate ω_p and a carrier concentration term, K

$$\sigma_o = K\omega_p T^{-1} \qquad \ldots(7)$$

where the magnitude of the constant. K is largely a measure of the mobile ion concentration. It has been found in the present study that the K value is 3.97×10^{-9} S cm^{-1} K Hz^{-1} while the value of K for Na β-alumina is of the order of 1.5×10^{-12} S cm^{-1} K Hz^{-1}. This indicates that the compound under investigation have relatively high mobile ion concentrations.

Table 1: Transport parameters of $LiGdP_2O_7$

Temp. (°C)	σ_{dc}	n	A	β	ω_p
300	7.24×10^{-8}	1.29 ± 0.02	2.13×10^{-13}	0.56	1.94×10^{4}
325	3.89×10^{-7}	1.21 ± 0.02	6.62×10^{-13}	0.71	5.86×10^{4}
350	1.66×10^{-6}	1.26 ± 0.02	2.04×10^{-13}	0.72	3.1×10^{5}
375	5.62×10^{-6}	1.20 ± 0.03	3.93×10^{-13}	0.74	9.2×10^{5}
400	2.00×10^{-5}	1.17 ± 0.03	5.02×10^{-13}	0.77	3.1×10^{6}

Activation energy for hopping	E_ω (eV) = 0.74
Activation energy	E_σ (eV) = 0.76
Effective frequency	ω_e (Hz) = 2.15×10^{19}
True attempt frequency	ω_o (Hz) = 7.6×10^{12}
S_ω / k	= 6.45
Carrier concentration	K (S cm^{-1}K Hz^{-1}) = 3.97×10^{-9}

The close value of E_ω and E_σ implies that the charge carriers have to overcome the same energy barrier while conducting as well as relaxing.

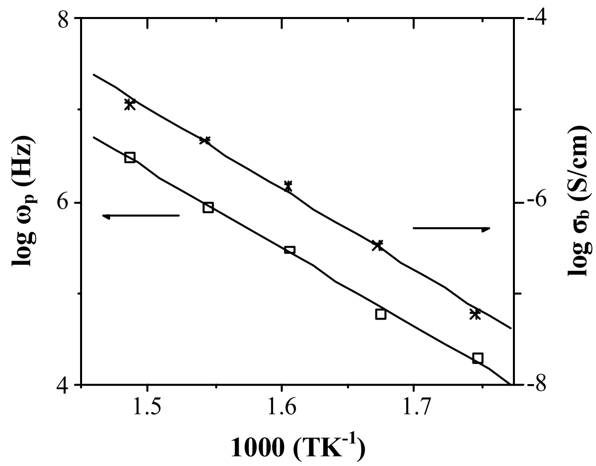

Fig. 4: The temperature dependence of both σ_b and ω_p of $LiGdP_2O_7$

CONCLUSION

The polycrystalline sample of $LiGdP_2O_7$ has been prepared by wet chemical method. The FTIR spectra show the presence of characteristic vibrational bands of $P_2O_7^{4-}$ ion. From the conductance spectrum, it has been found that $LiGdP_2O_7$ have relatively high mobile ion concentrations.

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