

Short communication

Structural and ionic transport properties of $\text{Li}_2\text{AlZr}[\text{PO}_4]_3$

T. Savitha^a, S. Selvasekarapandian^{a,*}, C.S. Ramya^a, M.S. Bhuvaneshwari^a,
G. Hirankumar^a, R. Baskaran^a, P.C. Angelo^b

^a Solid State and Radiation Physics Laboratory, Department of Physics, Bharathiar University, Coimbatore 641 046, Tamil Nadu, India

^b Department of Metallurgical Engineering, P.S.G. College of Technology, Coimbatore 641004, Tamil Nadu, India

Received 5 May 2005; accepted 26 July 2005

Available online 17 November 2005

Abstract

The fast ionic conductor $\text{Li}_2\text{AlZr}[\text{PO}_4]_3$ has been prepared by the solid state reaction method. The formation of the compound is confirmed by XRD and FTIR analysis. The system has been subjected to ac conductivity measurements in the temperature range 523 to 623 K with aluminium as blocking electrodes over a frequency range of 42 Hz to 5 MHz. The conductivity is found to be $1 \times 10^{-5} \text{ S cm}^{-1}$ at 623 K. The activation energy calculated from the Arrhenius plot is 0.83 eV. The conductance spectrum reveals a d.c. plateau and a dispersive region that suggest the correlated hopping motion of ions. Thus, the conduction mechanism in $\text{Li}_2\text{AlZr}[\text{PO}_4]_3$ may be due to the hopping of charge carriers.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Solid electrolyte; a.c. impedance; Arrhenius plot; Conductance spectra, Lithium-ion battery, Lithium zirconium phosphate

1. Introduction

The standard lithium-ion battery has been the leading energy-storage device since the mid 1990s. This is because it has a specific energy and long cycle life. Lithium transition metal phosphates are emerging as cathode materials of interest for rechargeable lithium batteries due to their low material cost, safety, and non-toxicity. These compounds have good lithium ion mobility, but suffer from extremely low electron conductivity. Among these materials Li-based NASICON materials exhibit high Li^+ ion conductivity at ambient temperature on account of the presence of mobile Li^+ ions in the interstitial sites [1]. Phosphates with the general formula $\text{A}_x\text{M}_2(\text{PO}_4)_3$, built up by corner-sharing MO_6 octahedra and PO_4 tetrahedra [2], form a class of candidate solid electrolytes for batteries of high specific energy since their physical and chemical properties are considered to be both thermally and chemically very stable due to their tetrahedral oxyanions [3].

The solid electrolytes $\text{LiTi}_2(\text{PO}_4)_3$ [1], $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ [4], $\text{LiZr}_2(\text{PO}_4)_3$ [5] with structures analogous to that of NASICON structure have been reported. Among these electrolytes, the con-

ductivity of $\text{LiTi}_2(\text{PO}_4)_3$ is not regarded as sufficiently high for practical applications. Aono et al. [1] reported that the partial substitution of Al^{3+} for Ti^{4+} improves the density of $\text{LiTi}_2(\text{PO}_4)_3$ and enhances the Li^+ ion conductivity ($\sigma = 7 \times 10^{-4} \text{ S cm}^{-1}$). Despite its high conductivity, Ti^{4+} undergoes reduction by lithium [6]. For electrolyte application Ti^{4+} in the material should be replaced by other metal ions that are stable with respect to lithium. Many researchers are attempting to replace Ti^{4+} with transition metal ions. In the present work, titanium (0.67 Å) has been substituted by the homovalent cation Zr (0.72 Å). The compound $\text{Li}_2\text{AlZr}[\text{PO}_4]_3$ has been prepared by the solid-state reaction method and characterized by X-ray diffraction (XRD), Fourier Transform Infra Red Analysis (FTIR) and a.c. conductivity studies.

2. Experimental

The compound $\text{Li}_2\text{AlZr}[\text{PO}_4]_3$ has been prepared by the solid state reaction method. The raw materials were Li_2CO_3 , $(\text{NH}_4)_2\text{HPO}_4$, ZrO_2 and Al_2O_3 . One of the raw materials, namely ZrO_2 , was prepared by a co-precipitation method [7]. The reagents were taken in a stoichiometric ratio and ground with a mortar and a pestle. The homogenized powder was heated to 850 °C and kept for 2 h at this temperature. X-ray diffraction phase analysis were conducted to confirm the formation of sam-

* Corresponding author. Tel.: +91 422 242222x422; fax: +91 422 2422387.
E-mail address: sekarapandian@yahoo.com (S. Selvasekarapandian).

ple with the desired phases, by using Philips X-ray diffractometer, Model PW 1830. The IR spectrum was recorded for each sample in the range of 400 to 2000 cm^{-1} at room temperature by means of a SHIMADZU-8000 FTIR Spectro-Photometer. The sample was crushed into a fine powder placed in a die, and subjected to a pressure 4000 kg cm^{-2} . The resulting pellet had a thickness of 1 mm and a diameter of 1.0 cm. The pellet was sintered at 450 $^{\circ}\text{C}$ for 2 h. The pellet was mounted between two aluminium blocking-electrodes and impedance measurements were conducted over the frequency range 42 Hz to 5 MHz at temperatures from 523 to 623 K.

3. Results and discussion

3.1. XRD analysis

The XRD pattern of $\text{Li}_2\text{AlZr}[\text{PO}_4]_3$ is shown in Fig. 1. The three strong intensity peaks at $2\theta = 23.3749^{\circ}$, 20.0917° and 19.6228° indicate the formation of the sample. Some traces of ZrO_2 , Al_2O_3 are observed in the XRD pattern. A peak at $2\theta = 13.992^{\circ}$, which corresponds to the secondary phase, lithium zirconium phosphate (JCPDF 44 - 0010) is also presented. Thus, the pattern reveals the polycrystalline nature of the sample. The particle size (D) is estimated using the Debye Scherrer formula, i.e.,

$$D = \frac{0.94\lambda}{\beta_{2\theta} \cos \theta} \quad (1)$$

where λ is the wavelength of the X-ray and $\beta_{2\theta}$ is the full width at half maximum of the corresponding peak in the XRD pattern. The particle size for the sample is of the order of 38 nm. This confirms the formation of nanocrystalline phases.

3.2. FTIR analysis

Vibrational spectroscopy is a valuable analytical tool. The appearance or non-appearance of certain vibrational frequencies can provide important information on the structure of a particular molecule. The IR spectrum of $\text{Li}_2\text{AlZr}[\text{PO}_4]_3$ is given in Fig. 2. Some bands associated with the stretching and bend-

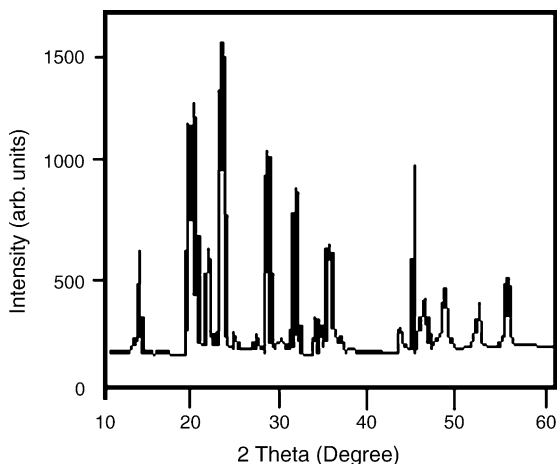


Fig. 1. XRD pattern of $\text{Li}_2\text{AlZr}[\text{PO}_4]_3$.

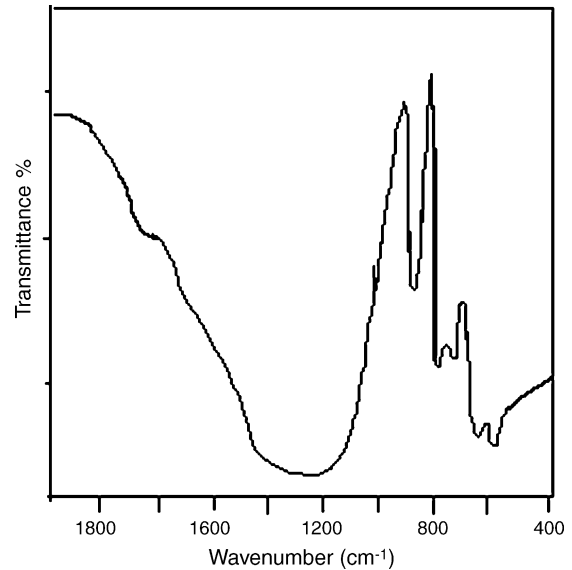


Fig. 2. FTIR spectrum of $\text{Li}_2\text{AlZr}[\text{PO}_4]_3$.

ing vibrations of PO_4^{3-} anions have been found to be active in infra-red region. The band appearing at about 450 cm^{-1} can be attributed to symmetric stretching (γ_2) of (PO_4^{3-}), whereas the bands at around 600 and 1050 cm^{-1} can be attributed to asymmetric stretching (γ_4 and γ_3) of (PO_4^{3-}) [8]. Vibrations of PO_4 tetrahedra that correspond to two bending modes have been observed, i.e., bands at 430 cm^{-1} (γ_2) and 590 cm^{-1} (γ_4) can be attributed to PO bending [9]. In the present study, all the characteristic bands for PO_4 vibrations are observed in the expected regions. This indicates that the anion ring has not been distorted due to its co-ordination with cations of greater electronegativity.

3.3. Impedance measurements

An impedance investigation of the ionic conductors over a wide frequency range has an advantage in that it allows the identification of charge transport processes in the grains and grain boundaries of ceramics over a wide temperature range [10]. Cole-Cole plots for $\text{Li}_2\text{AlZr}[\text{PO}_4]_3$ at 523, 573 and 623 K are presented in Fig. 3. The data show a high-frequency semicircle at all the temperatures. The bulk capacitance at the maximum of the semicircle can be determined using the relation:

$$\omega R_b C_b = 1 \quad (2)$$

The values are in the range of pF, and indicates that the conductivity is due to the bulk of the material. The bulk resistance, R_b , can be determined from the intercept of the low frequency part of the arc with the real Z' -axis. As the temperature increases, the R_b value shifts towards a lower impedance value. It is of the order of $10^4 \Omega$ at 623 K. The d.c. bulk electrical conductivity can be obtained from:

$$\sigma_b = \left(\frac{l}{A}\right) \times \left(\frac{1}{R_b}\right) \quad (3)$$

where l and A are the thickness and cross-sectional area of the pellet, respectively. The conductivity is found to be $1 \times 10^{-5} \text{ S cm}^{-1}$.

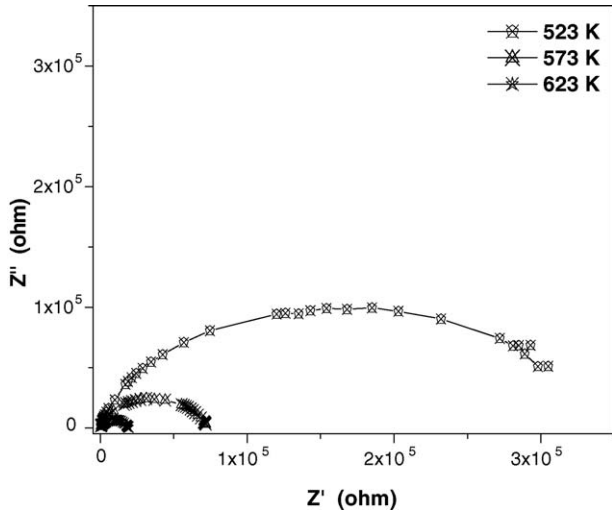


Fig. 3. Cole-Cole plot of $\text{Li}_2\text{AlZr[PO}_4\text{]}_3$ at various temperatures.

The temperature dependence of the d.c. electrical conductivity of $\text{Li}_2\text{AlZr[PO}_4\text{]}$ is shown in Fig. 4. The activation energy E_a of the bulk conductivity is calculated according to the Arrhenius equation, namely:

$$\sigma_b T = \sigma_0 \text{Exp} \left(\frac{-E_a}{kT} \right) \quad (4)$$

where σ_0 is pre-exponential factor and k is the Boltzmann constant. The conductivity increases linearly with temperature, which is associated with a decrease in the bulk resistance as indicated by the Cole-Cole plot. The activation energy calculated from the slope of the graph is found to be 0.83 eV.

3.4. Frequency dependent conductivity

The frequency-dependent conductivity spectrum shown in Fig. 5 displays a low-frequency d.c. plateau and a high frequency dispersive regions. The d.c. conductivity value determined by extrapolating the plateau on the Y-axis is $1 \times 10^{-5} \text{ S cm}^{-1}$ at 623 K. The results at all three temperatures are shown in Table 1. When the temperature increases, the transition from the d.c.

Table 1
Conductivity parameters at various temperatures

Temperature (K)	σ_{dc} (S cm^{-1})	ω_p (Hz)	n	K ($\text{S cm}^{-1} \text{ kHz}^{-1}$)
523	6.7×10^{-7}	3.1×10^4	0.99	9.9×10^{-9}
573	3×10^{-6}	1.7×10^5	0.94	8.5×10^{-9}
623	1×10^{-5}	6.8×10^5	0.91	9.3×10^{-9}

plateau to a.c. conductivity dispersion region shifts towards the higher frequency range. The dispersion region is characterized by the random hopping of mobile ions [11]. The general formulation of the real part of the complex electrical conductivity is given by [12]:

$$\sigma'(\omega) = \sigma(0) + A\omega^n \quad (5)$$

where $\sigma(0)$ is the d.c. conductivity of the sample, A is a constant; n is the power law exponent which represents the degree of interaction between the mobile ions. The parameter n is a temperature-dependent function, which decreases with increase in temperature (Table 1). At high frequencies, the conductance spectra at different temperatures converge. This indicates that the a.c. conductivity is independent of temperature at high frequencies (Fig. 5).

Using the Almond and West formalism [13], the ionic hopping rate, ω_p , can be obtained directly from a.c. conductivity data using the formula:

$$\sigma(\omega) = 2 \sigma(0) \quad (6)$$

Ionic hopping rates have been found to be thermally activated and can be described by:

$$\omega_p = \omega_e \exp \left(\frac{-H_m}{kT} \right) \quad (7)$$

where ω_e is an effective attempt frequency which includes the entropy term and H_m is the activation enthalpy for hopping or migration of ions. The linear character of $\log \omega_p$ with temperature is demonstrated in Fig. 4. The value of H_m can be deduced from the slope of the straight line and is found to be 0.81 eV. This value is very close to the activation energy determined

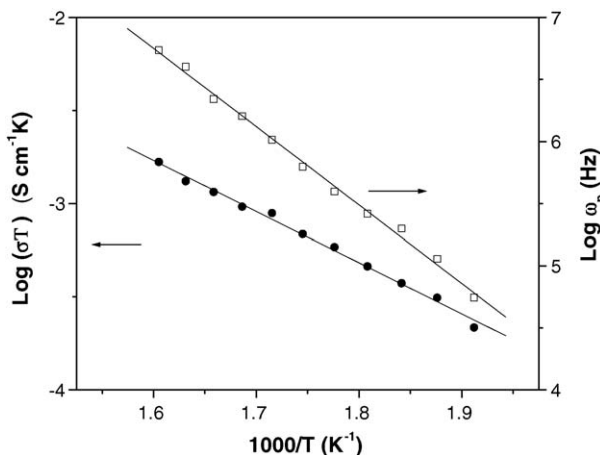


Fig. 4. Arrhenius plot of $\text{Li}_2\text{AlZr[PO}_4\text{]}_3$.

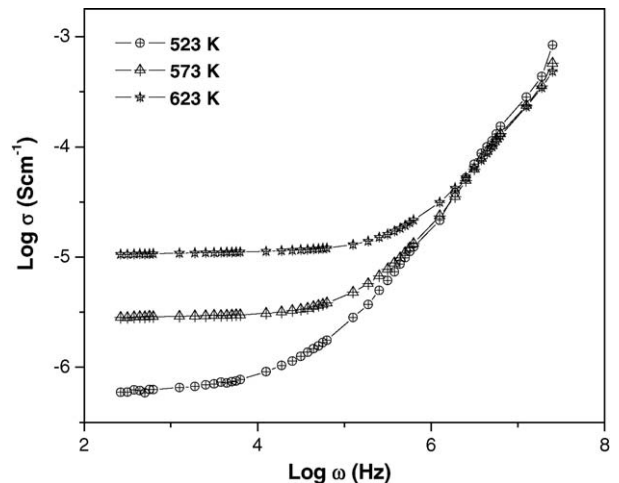


Fig. 5. Conductance spectra of $\text{Li}_2\text{AlZr[PO}_4\text{]}_3$.

above from d.c. conductivity measurements. The magnitude of the carrier-concentration term K can be obtained from the formula [13]:

$$K = \frac{\sigma T}{\omega_p} \quad (8)$$

In the present study, K remains almost constant over the chosen temperature range (Table 1). This reveals that all the ions are in a mobile state and support the ‘strong electrolyte’ model [14]. Hence, the conduction mechanism in $\text{Li}_2\text{AlZr}[\text{PO}_4]_3$ is probably due to the hopping of charge carriers.

4. Conclusion

Lithium-based, NASICON structured, $\text{Li}_2\text{AlZr}[\text{PO}_4]_3$ has been prepared by the solid-state reaction method and has been characterized by structural and conductivity studies. The XRD pattern confirms the formation of a nanocrystalline phase in the sample. The FTIR spectrum reveals the identity of the functional groups. Cole-Cole plots demonstrate the contribution of mobile ions to the bulk conductivity. The compound is found to obey the Arrhenius law and the activation energy is found to be 0.83 eV. From conductance spectra conductivity parameters such as hopping frequencies, the mobile ion concentration and the activation enthalpy of hopping has been calculated using the Almond and West formalism. The ionic hopping frequency has been found to be thermally activated with an activation energy

0.81 eV, which is close to that found from d.c. conductivity studies and suggests that the conduction mechanism may involve the hopping of charge carriers.

References

- [1] K. Takada, M. Tansho, I. Yanase, T. Inada, *Solid State Ionics* 139 (2001) 241–247.
- [2] E.R. Losila, S. Bruque, M.A.G. Aranda, L. Moreno-Real, E. Morin, M. Quarton, *Solid State Ionics* 112 (1998) 53.
- [3] J. Isasi, A. Daidouh, *Solid State Ionics* 133 (2000) 303.
- [4] A.K. Ivanov-Schitz, A.V. Nistik, N.G. Chaba, *Solid State Ionics* 139 (2001) 153–157.
- [5] M. Catti, N. Morgante, R.M. Ibberson, *J. Solid State Chem.* 152 (2000) 340–347.
- [6] V. Thangadurai, A.K. Shukla, J. Gopalakrishnan, *J. Mater. Chem.* 9 (1999) 739.
- [7] M. Vijayakumar, S. Selvasekarapandian, M.S. Bhuvanewari, G. HiranKumar, G. Ramprasad, R. Subramanian, P.C. Angelo, *Physica B* 334 (2000) 3390.
- [8] N. Zouari, M. Ben Amor, T. Mhiri, A. Daoud, J.M. Reau, *J. Alloys Compd.* 240 (1996) 70–75.
- [9] J. Xu, I.S. Butter, D.F.R. Gilson, *Spectrochim. Acta Part A* 55 (1999) 2801–2809.
- [10] A. Orilukas, A. Dindune, Z. Kanepe, J. Ronis, E. Kazakevicius, A. Kezionis, *Solid State Ionics* 157 (2003) 177.
- [11] J.-M. Le Meins, O. Bohnke, G. Courbion, *Solid State Ionics* 11 (1998) 167.
- [12] A.K. Jonsher, *Nature* 267 (1977) 673.
- [13] D.P. Almond, A.R. West, *Solid State Ionics* 9–10 (1983) 277–282.
- [14] E.F. Hairetdinov, N.F.L. Uvarov, *Phys. Rev. B* 50 (13) (1994) 259.