XRD, Conductivity and FTIR Studies on $LiI-Li_2WO_4-Li_3PO_4$ Prepared by Low Temperature Sintering

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Abstract. Different amounts of Li_3PO_4 were mixed to a fixed ratio of $LiI:Li_2WO_4$, ground and pelletised before subjected to sintering at 70°C for 7 days. XRD shows that the product formed after sintering process is most likely $Li_6P_4W_8O_{32}$ due to peaks present at 10.6°, 22.4°, 24.0°, 24.4, 26.2°, 32.4° and 34.0°. Conductivity studies show that the sample with 25 wt.% Li_3PO_4 exhibits the highest room temperature conductivity of 3.42×10^{-3} Scm^{-1}. Conductivity is expected to occur through channel-like structures which could have formed due to corner or edge sharing of polyhedra. FTIR studies have shown the existence of WO_4 tetrahedra and WO_6 octahedral at 850 cm^{-1} and 952 cm^{-1}, and phosphate tetrahedral at 564 cm^{-1}, 700 cm^{-1}, 890 cm^{-1} and 1030 cm^{-1}.

1. Introduction

Lithium ion conductors are prepared by melt quenching technique [1,2,3]. In cases where lithium iodide is one of the chemical components, melting is done under vacuum and quenched in liquid nitrogen [4,5]. These materials can exhibit at room temperature electrical conductivity as high as 10^{-3} Scm^{-1}. For example $LiI-Li_2O-B_2O_3$ has been shown to exhibit conductivity of 10^{-2} Scm^{-1} at 300 °C [6]. Most of the materials produced by the rapid quenching method are glasses. However, these are also crystalline compounds that exhibit high electrical conductivity at room temperature and various methods of preparation are ballmilling, solid state reaction and sol-gel technique [7,8,9].

In this work, Li_3PO_4 has been added to $LiI-Li_2WO_4$. The three components were ground and thoroughly mixed. The mixture was then pelletised and calcined at 70 °C to initiate the reaction and maintained at that temperature for 7 days. The product was analyzed by X-ray diffraction (XRD) and by Fourier Transform Infrared Spectroscopy (FTIR). The electrical conductivity was determined by impedance spectroscopy.

2. Experimental Description

2.1. Preparation of Solid $LiI-Li_2WO_4-Li_3PO_4$ Electrolyte. The sample 0.2 wt.% LiI-0.8 wt.% Li_2WO_4 system was found to exhibit the highest electrical conductivity in the $LiI-Li_2WO_4$ family. Different amounts of Li_3PO_4 was added to the binary system. The three components were mixed and ground thoroughly and the finely mixed powder was pelleized, put on a glass slide and finally placed in a test-tube plugged with glass wool. The pelletized samples were calcined at 70 °C for 7 days. For each composition of $LiI-Li_2WO_4-Li_3PO_4$, three test samples were prepared.

2.2. X-Ray Diffraction. X-ray diffraction measurements were performed using the X-ray Phillip Expert Diffraction system. The diffractograms were taken at 2θ angles between 10° to 70°.

2.3. Measurement of Electrical Conductivity. The electrical conductivity of the sample was measured by the acimpedance technique. Complex impedance was measured using the HIOKI 3520-01 LCR HI Tester that was interfaced to a computer. The measurements were carried out at room temperature in the frequency range 42 to 10^6 Hz.

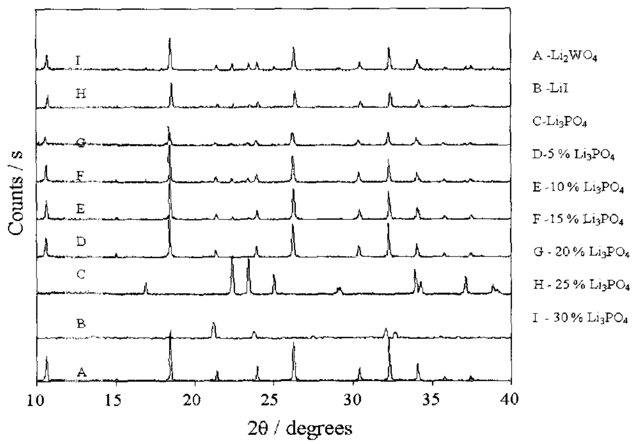

Fig. 1. XRD pattern of LiI-Li_2WO_4-Li_3PO_4 solid electrolyte for 2θ = 10-40°.

2.4. Fourier Transform Infrared Spectroscopy. FTIR measurement was done using the Perkin Elmer FT-IR Spectrometer SPECTRUM 2000, and was performed using the KBr method. The spectrum was obtained in the 400 to 4000 cm^{-1} region at 1 cm^{-1} wave number resolution.

3. Results and Discussion

The XRD diffractogram of the various LiI-Li_2WO_4-Li_3PO_4 (Fig. 1) samples showed peaks at 10.6°, 18.5°, 21.5°, 22.4°, 23.5°, 24.0°, 25.0°, 26.2°, 30.3°, 32.4°, 34.0°, 35.5° and 37.0°. The peaks at 10.6°, 22.4°, 24.0°, 24.4°, 26.2°, 32.4° and 34.0° are also found in the diffractogram of $Li_6P_4W_8O_{32}$ (JCPDS pattern: 40-1061). The peaks at 10.6°, 24.0°, 26.2°, 32.4° and 34.0° are also peaks observed to pure Li_2WO_4. The peak at 22.4° is also found in the Li_3PO_4 diffractogram. Hence after 7 days of sintering at 70°, it can be deduced that the compound $Li_6P_4W_8O_{32}$ has formed but with some Li_3PO_4 and Li_2WO_4 leftovers. Within this 2θ range peaks attributed to LiI are not observed. It may be possible that the iodine component in LiI has vaporized during sintering.

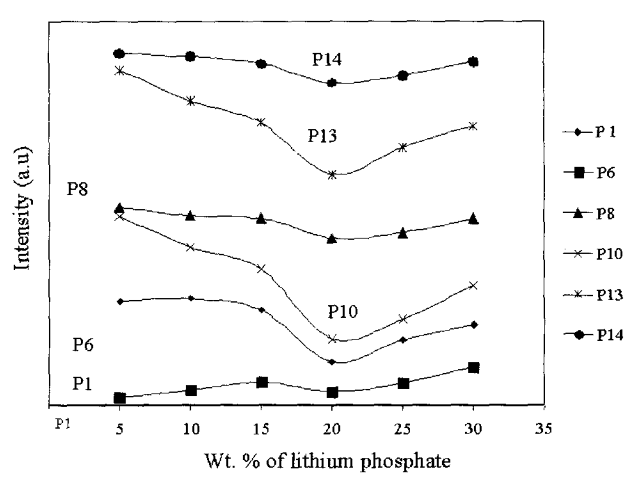

Fig. 2. Intensity of the peaks versus wt.% Li_3PO_4.

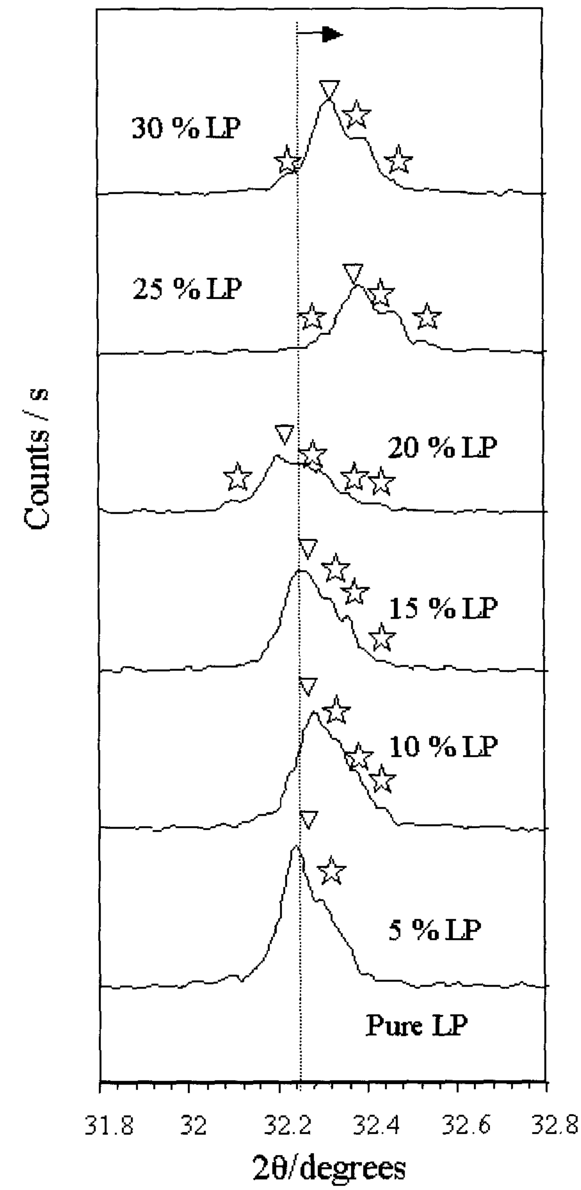

Fig. 3. XRD pattern to show the splitting of the peaks or the appearance of new peaks and the shifting of the peak to higher angle as the amount of lithium phosphate (LP) is increased.

In order to justify that the peaks at 10.6°, 24.0°, 26.2°, 32.4° and 34.0° are representative of $Li_6P_4W_8O_{32}$, the intensity of the peaks was plotted with respect to Li_3PO_4 content (Fig. 2). If these peaks are representative of Li_2WO_4 then the intensity of the peaks should continue to decrease

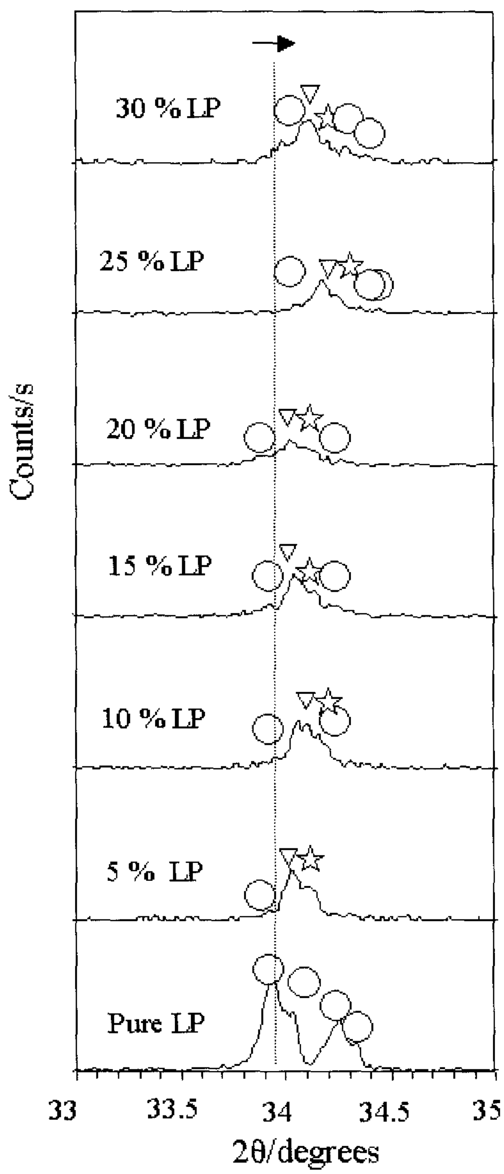

Fig. 4. XRD pattern to show the splitting of the peaks or the appearance of new peaks and the shifting of the peak to higher angle as the amount of lithium phosphate (LP) is increased.

as the Li_3PO_4 content increases. However, upon examination of Fig. 2, it can be observed that after addition of more than 20 wt.% Li_3PO_4 the intensity of the peaks increases again. The decrease in intensity can be understood because with the increase in Li_3PO_4 content, for the same quantity of LiI-Li_2WO_4-Li_3PO_4 the actual amount of Li_2WO_4 has decreased. The increase in intensity is attributed to the formation of $Li_6P_4W_8O_{32}$ and therefore the peaks which showed an increase in intensity must also be that of $Li_6P_4W_8O_{32}$. It can also be inferred that $Li_6P_4W_8O_{32}$ is formed when at least 20 wt.% of Li_3PO_4 has been added.

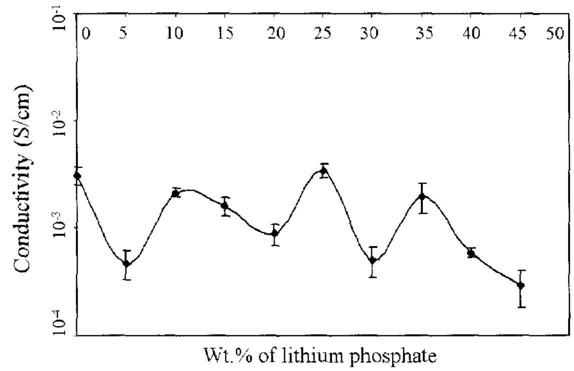

Fig. 5. Conductivity versus wt.% Li_3PO_4.

The intensity of the peak at 22.4° shows abrupt increase in intensity when 25 wt.% of Li_3PO_4 was added to the binary system. This peak is the 100 % intensity peak of $Li_6P_4W_8O_{32}$ according to JCPDS pattern: 40-1061.

Figure 3 shows the peak at around $2\theta = 32.0°$. It can be observed that this peak has shifted to a higher 2θ angle after more than 20 wt.% Li_3PO_4 has been added to the binary system. The peak at 33.9° has also shifted to a higher 2θ angle on addition of Li_3PO_4. In the diffractogram of pure Li_3PO_4 the peak at about 34° is part of doublet but upon adding Li_3PO_4 and sintering at 70° for 7 days, the doublet has merged until a single peak is formed in the diffracogram of a sample containing 30 wt.% Li_3PO_4 (Fig. 4).

It is not an easy task to explain the variation in con-

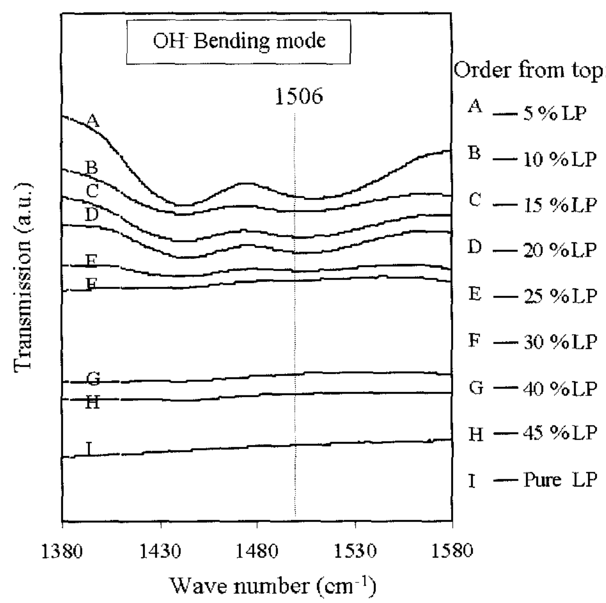

Fig. 6. FTIR spectra of pure Li_3P0_4 and samples with various wt. % of Li_3P0_4 with wave number in the range 1380-1580 cm^{-1}.

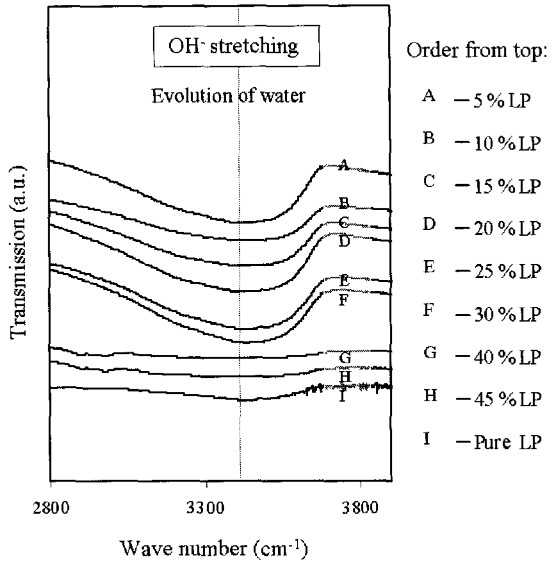

Fig. 7. FTIR spectra of pure Li_3P0_4 and samples with various wt. % of Li_3P0_4 with wave in the range 2800-3900.

ductivity shown in Fig. 5. From IR studies OH^- bending and stretching modes [10] are observed until the Li_3PO_4 content exceeds 30 wt.%. At such concentration of Li_3PO_4 (40 and 45 wt.%) the FTIR spectrum showed the absence of OH^- bending mode between 1380 and 1580 cm^{-1} (Fig. 6). Likewise the OH^- stretching mode is also absent within the 2800-3800 cm^{-1} region (Fig. 7). The existence of OH^-

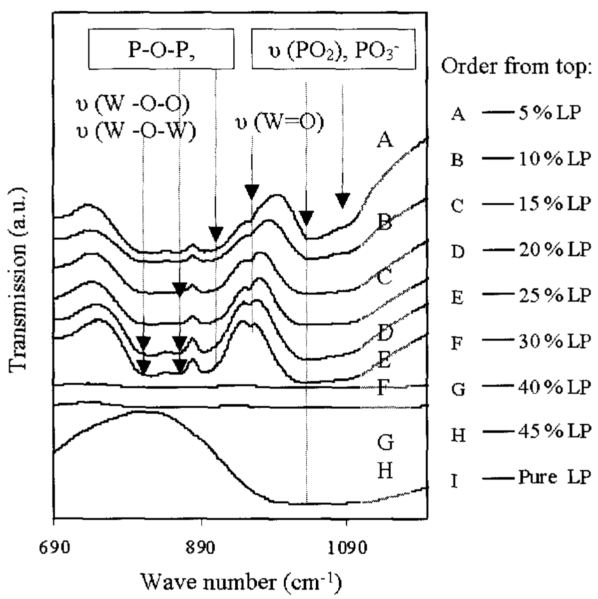

Fig. 8. TIR spectra of pure Li_3PO_4 and samples with various wt. % of Li_3PO_4 with wave number in the range 690-1200 cm^{-1}.

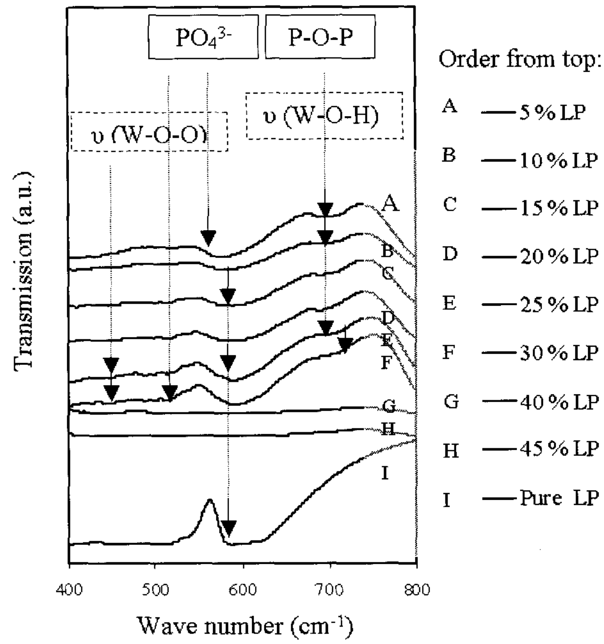

Fig. 9. FTIR spectra of pure Li_3PO_4 and samples with various wt. % of Li_3PO_4 with wave number in the range 400-800 cm^{-1}.

stretching and bending modes is evident of physiosorbed water. Hence the variation in conductivity for samples containing less than 35 wt.% of Li_3PO_4 could be due to the different amounts of free proton and lithium ions available for conduction. Since samples containing 40 and 45 wt.% of Li_3PO_4 do not show the presence of OH^- bending and stretching, it is possible that these samples are pure lithium ion conductors.

The band in the region 850-960 cm^{-1} (Fig. 8) is assigned to the stretching vibration of the W-O bond associated with WO_6 octahedra [11,12,13]. The band at 580 cm^{-1} (Fig. 9) and 910 cm^{-1} (Fig. 8) are assigned to the vibration modes in PO_4^{3-} tetrahedral ions [14]. The presence of phosphate (PO_4^{3-}) ions and octahedral WO_6 ions implies that ionic conductivity could have taken place via channel like structures that could have formed as a results of corner or edge-sharing polyhedral [11,15,16,17,18,19]. Table 1 and Table 2 show the W-O and P-O stretching vibration found in the literature. However, in samples containing wt.% 40 and 45 Li_3PO_4, bands due to these units are absent. Thus, it is possible that such channel like structures are also not present giving rise to blocking effects that reduce the conductivity of the material as observed in Fig. 5.

4. Conclusions

Sintering of LiI-Li_2WO_4-Li_3PO_4 at 70 °C for 7 days, produced the $Li_6P_4W_8O_{32}$ phase with probably some leftover

Table 1. Stretching vibration involving tungsten and oxygen.

	Stretching vibration	Wavenumber (cm^{-1})	Reference
1.	ν (W-O)	800-900	Naquis and Kagel, 1971
2.	ν (W=O) polycrystalline WO_3	950 680-700, 800	Mercier et al., 1983
3.	ν (W-O) associated with WO_6 octahedra ν (W-O-W) ν (W=O)	857 625-850 1006	Sekiya et al., 1994
4.	WO_3 ions	900	Radhakrishna, 1996
5.	ν (W-O-O)	800-890	Sammes et al., 1997
6.	ν (W=O) ν (W-O-W)	950 797-844	Orel et al., 1999
7.	ν (W-O) associated with WO_6 octahedra ν (W-O)	880, 730(sh), 670(sh), 770(sh), 950, 880,820	Chowdari et al., 2000
8.	ν (W-O-O) ν (W-O-H) ν (W-O-W)	566, 830 690 715, 806	Krasovec et al., 2001
9.	ν (W=O) WO_3 spectra	950 680, 780 810	Cazzanelli et al., 2001
10.	ν (W-O)	820	Vijayalakshmi et al., 2003

unreacted components. The presence of $Li_6P_4W_8O_{32}$ is implied by the presence of the peaks at 10.6°, 22.4°, 24.0°, 24.4°, 26.2°, 32.4° and 34.0°. Conductivity is contributed by proton and lithium ions for Li_3PO_4 content less than 30 wt.%. The existence of protons is exhibited by the OH^- stretching and bending modes. Conduction in samples containing more than 35 wt.% Li_3PO_4 does not occur through channel like structures since the FTIR spectrum of these materials do not exhibit bands due to octahedral and tetrahedral units which when share-corners or edges can form channel-like conducting pathways.

Table 2. Stretching vibration of P-O.

	Stretching vibration	Wavenumber (cm^{-1})	Reference
1.	ortho phosphate ions PO_4^{3-} meta phosphate ions PO_3^-.	940-1120, 540-650 1200-1350, 1040-1150	Naquis. and Kagel, 1971
2.	ν (PO_2) bridging P-O-P units	1080, 1030 and 960 710 and 890	Znasik and Mika, 1991
	ν (PO_4^{3-}) tetrahedral ions	920 and 560	Gopalakrishna n et al, 1991
3.	ν (PO_2) ν (POP)	1150 650	Swenson et al., 2000
4.	ν (PO_2)	1120	Garbarczyk et al., 2000
5.	ν (P-O) stretching	1008, 966 and 910	Hirankumar et al., 2001
6.	ν (P=O) ν (P-O) in PO_3^{2-} ions ν (P-O$^-$)	1250-1280 990-1000 1100-1300	Kim et al., 2002

6. References

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