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Stretching hydrolysis in LiI-Li_2WO_4-Li_3PO_4 by infrared spectroscopy

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Abstract

Infrared spectroscopy is a useful tool to probe the formation of polyhedral structures in alkali halide-oxysalts. LiI-Li_2WO_4-Li_3PO_4 is an example of alkali halide-oxysalt. These materials have been proposed as superionic materials for use as electrolytes in electrochemical devices. One of the pertinent problems in lithiated superionic materials is their hygroscopic property that can seriously affect the conductivity of the materials. In the present work, LiI-Li_2WO_4- Li_3PO_4 has been prepared by the sintering method in order to ensure removal of water from the samples. Fourier Transform Infrared (FTIR) spectra show that the band at 1634 cm^{-1} due to lithium tungstate, the band at 1628 cm^{-1} due to lithium iodide has overlapped to form a single band at around 1640 cm^{-1}. The two bands at 1050 and 590 cm^{-1} are assigned to pure lithium phosphate. The FTIR spectrum of the ternary system is almost similar to that of the binary system and they are quite similar to the spectrum of lithium tungstate. FTIR shows there is a strong broad band centered at 3400 cm^{-1} in the binary sample but the band decreases in width on addition of Li_3PO_4. This band is an indication of stretching hydrolysis. A medium band is also observed at 1505 cm^{-1}, which is due to H-O-H bending motion This band almost disappears as the amount of Li_3PO_4 is increased to 30 wt.%. These results indicate that with further treatment the sample LiI-Li_2WO_4- Li_3PO_4 has potential for use in lithium batteries.

***Keywords**: Infrared spectroscopy, alkali-halide, oxysalt, tungstate, phosphate*

1. Introduction

Tungstate glasses could form channel like conducting pathways through corner sharing of tetrahedral structures [1,2]. Structural studies of WO_3-TeO_2 glasses by Sekiya[3] showed that W=O bonds were present and the glasses contain clusters composed of corner-shared WO_6 octahedra. Channel-like frameworks have also been observed in the ternary and quartenary compounds such as $Li_9B_{19}S_{33}$ and $Li_{4-2x}Sr_{2+x}B_{10}S_{19}$ which have a distinguished structure providing an extended sublattice of partially unoccupied lithium sites[4]. This structure of tetrahedral found either in tungstate or thioborate compound is good for ionic motion.

The system Li_2O-Al_2O_3-GeO_2-P_2O_4 contains a $LiGe_2(PO_4)_3$ phase[5].This phase consists of both GeO_6 octahedra and PO_4 tetrahedra. Both units are linked by their corners to form a three dimensional structure which results in cavities and bottlenecks where the mobile lithium ions can pass through.

In the literature[6-10], adding a doping salt to a binary glass system always helped to enhance the ionic conductivity of the electrolyte and make the system more stable. In a glassy material containing “superionic” conductors (LiI or LiBr) the ionic conductivity of the glassy system [9,10] is enhanced. Enhancement of ionic conductivity of LiI mixed with inorganic oxides (Al_2O_3) to form a polyphase electrolyte has already been observed[11].

The conductivity of pure lithium phosphate, Li_3PO_4 at 100°C reported in the literature is 1.3 x 10^{-14} Scm^{-1}. When Li_3PO_4 was added to Li_4SiO_4 ionic conductivity was increased to 1.0 x 10^{-4} Scm^{-1}. This material has the advantage of being stable in air and can be easily fabricated into dense bodies[12].

$Li_{14}Zn(GeO_4)_4$ and $Li_{12}Zn_2(GeO_4)_4$ are polycrystalline electrolytes in the LISICON family. Despite having very high conductivity (1.3x10^{-1} Scm^{-1}) it was reported that these compounds were sensitive to moisture and CO_2 [13]. Solid solutions in the Li_4GeO_4-Li_2ZnGeO_4 system containing Li_3PO_4 has conductivity of 7.5 x10^{-5} S/cm at 27 ºC and increased to about 10^{-2} Scm^{-1} at 190ºC [14]. Besides the enhancement in the conductivity, these electrolytes can be easily synthesized, thermodynamically stable and insensitive to atmospheric attack.

In this work, Li_3PO_4 has been added to LiI-Li_2WO_4 to stabilize the electrolyte from atmospheric attack due to moisture. The three components were ground and thoroughly mixed. The mixture was then pelletised and calcined at 70°C for seven days to initiate the reaction. Fourier transform infrared spectroscopy was used to verify the formation of the types of polyhedra and to determine the effect of Li_3PO_4 addition on the OH stretching and OH bending vibration which is expected to decrease since Li_3PO_4 is stable in air[12].

2. Experimental Technique

2.1 Preparation of Solid (LiI-Li_2WO_4) Li_3PO_4 Electrolyte

A small portion of Li_3PO_4 with various wt. fraction was added to 0.2LiI-0.8Li_2WO_4 mixture. This system was found to exhibit the highest electrical conductivity in the LiI-Li_2WO_4 family. The three components were mixed and ground throroughly and the finely mixed powder was pelletized, put on a glass slide and finally placed in a test-tube plugged with glass wool. The pelleted 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 Fourier Transform Infrared Spectroscopy

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

3. Results and Discussion

The pellet ($LiI-Li_2WO_4$) Li_3PO_4 solid electrolyte prepared by the sintering method looked more stable, easier to handle and the degree of sensitivity to moisture and air is less compared to lithium iodotungstate samples.

Infrared analysis was done on the pure samples and test samples. The spectra of pure lithium iodide, lithium tungstate, lithium phosphate and the highest conducting $LiI-Li_2WO_4$ sample are shown in Figure 1. The two peaks located at wave number 1050 and 590 cm^{-1} are assigned to pure Li_3PO_4 (LP). The peak at 1628 cm^{-1} is the fingerprint of LiI (LI) and the peak at 1635 cm^{-1} is the fingerprint of Li_2WO_4 (LT).

The FTIR spectrum of the ternary system is almost similar to that of the binary system and they are quite similar to that of lithium tungstate. The band in the region between 1600 to 1700 cm^{-1} (Figure 2) is attributed to an overlap of the fingerprint bands of LiI and Li_2WO_4. The band at 1505 cm^{-1}, which was observed earlier in $LiI-Li_2WO_4$ system, could be seen in the spectra of this ternary system and again the band has shifted to higher wave numbers. This band is an indication of the O-H in plane bending mode 15). This band can be seen in samples containing 5, 10, 15, 20, and 25 % Li_3PO_4 but the band disappeared when the amount of Li_3PO_4 was increased up to 30 % by weight [Figure 2]. This implies that this sample contained least amount of water and the problem of being attack by atmosphere is lessened.

Another evidence for the formation of OH^- groups is the broad band between 3000 and 3700 cm^{-1} as shown in Figure 3. This range of absorption is due to O-H stretching vibrational mode15). IR spectra revealed the evolution of this O-H stretching mode. As the Li_3PO_4 content increased this band becomes less broad.

Referring to the characteristic absorption list16), there is a strong band around 940-1120 cm^{-1} and a medium band around 540-650 cm^{-1} belong to ortho phosphate ions PO_4^{3-} and meta phosphate ions PO_3^-. These two bands can be seen in Figure 4 indicating the present of PO_4^{3-} and PO_3^- ions in the samples and charge neutrality must be maintained by the Li^+ or H^+ ions. From the spectra of (Li_3PO_4. ½ H_2O), lithium orthophosphate a medium peak in the range 1000-1160 cm^{-1} can be seen. Based on the work of Znasik and Mika17), vibration of PO_2 is observed at 1080, 1030 and 960 cm^{-1} and in the samples with various wt.% of Li_3PO_4 and bridging P-O-P units is observed at 710 and 890 cm^{-1} (Figure 4). These bands indicate the existence of polyhedra, which can share corners or edges to form conducting pathways

In the lithium tungstate spectrum, a peak could be seen at wave number 1634 cm^{-1}. A multiple wave could be detected in the region between 500 cm^{-1} and 900 cm^{-1}, which was assigned to tungstate (Figure 4). This multiple wave observed was quite similar to that reported by Sammes18) who reported that this band be assigned to vibrations involving tungsten and oxygen of the type ν(O-W-O). In the spectra of glasses containing WO_3 reported by Sekiya3), a sharp peak was observed at about 930 cm^{-1} and WO_4 tetrahedra and WO_6 octahedra exist in the glasses. Chowdari19) also recorded that the band at 880 cm^{-1} was assigned to the stretching vibrations of the W-O bond associated with the WO_6 octahedra.

According to Krasovec *et.al*20) the W-O absorption can be seen in this range and the modes assigned to peroxo groups (O-W-O) at 830 and 566 cm^{-1}. A weak band at 690 cm^{-1} was observed and this was assigned to out of plane deformational W-OH mode. These bands also indicate the existence of tungstate octahedral and tetrahedral, which can also form channels by sharing corners and edges.

4. Conclusions

The addition of Li_3PO_4 can stabilize the binary system composed of $LiI-Li_2WO_4$. However the stretching and bending hydrolysis bands are still observed. The bending hydrolysis band reduces in intensity as the Li_3PO_4 content in the ternary system is increased. The presence of polyhedra units could form channel-like pathways that allowed lithium ion transport through the bulk material.

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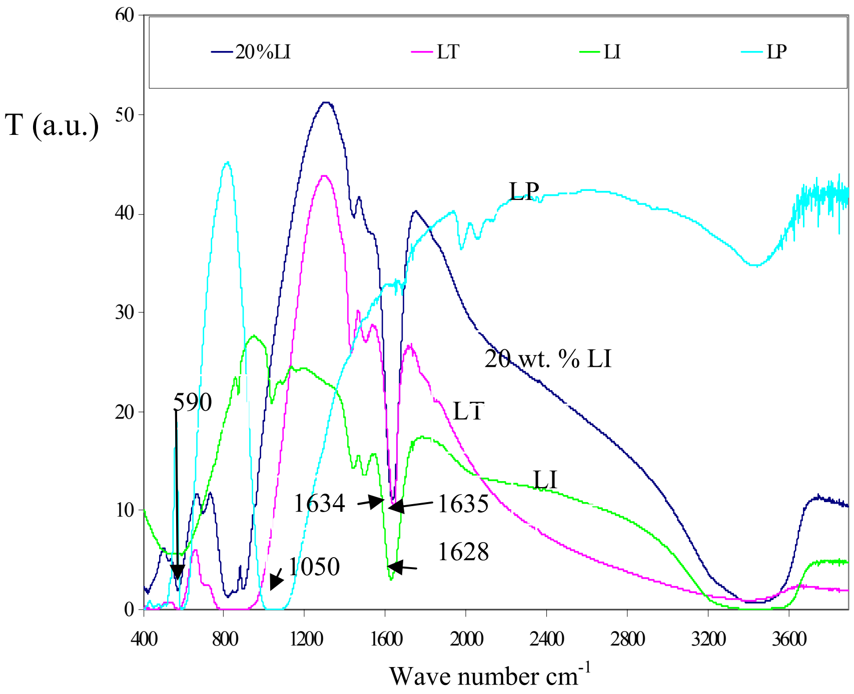

Figure 1. FTIR spectra of LiI, Li_2WO_4, Li_3PO_4 and highest conducting LiI- Li_2WO_4 that is sample with 20 wt. % LiI. (LiI=lithium iodide, LT=lithium tungstate, LP=lithium phosphate).

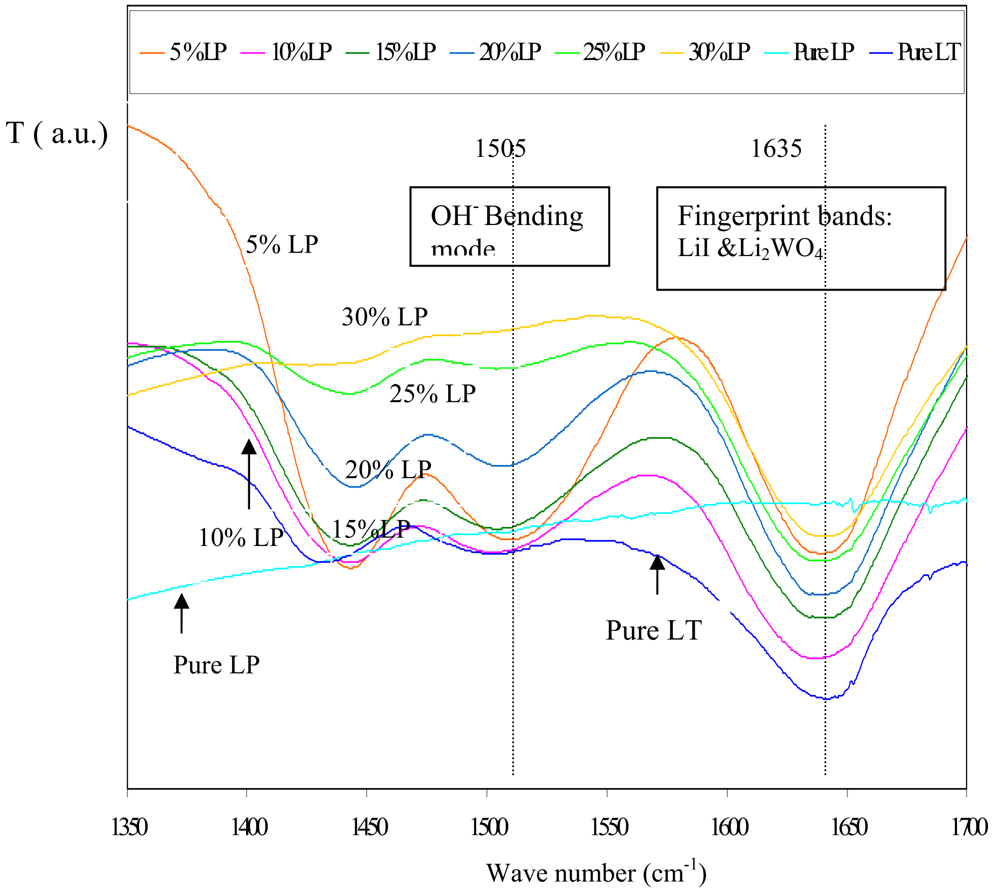

Figure 2. FTIR spectra of pure Li_3PO_4(LP), pure Li_2WO_4 (LT) and samples with various wt. % of Li_3P0_4 with wave number in the range 1350-1700 cm^{-1}

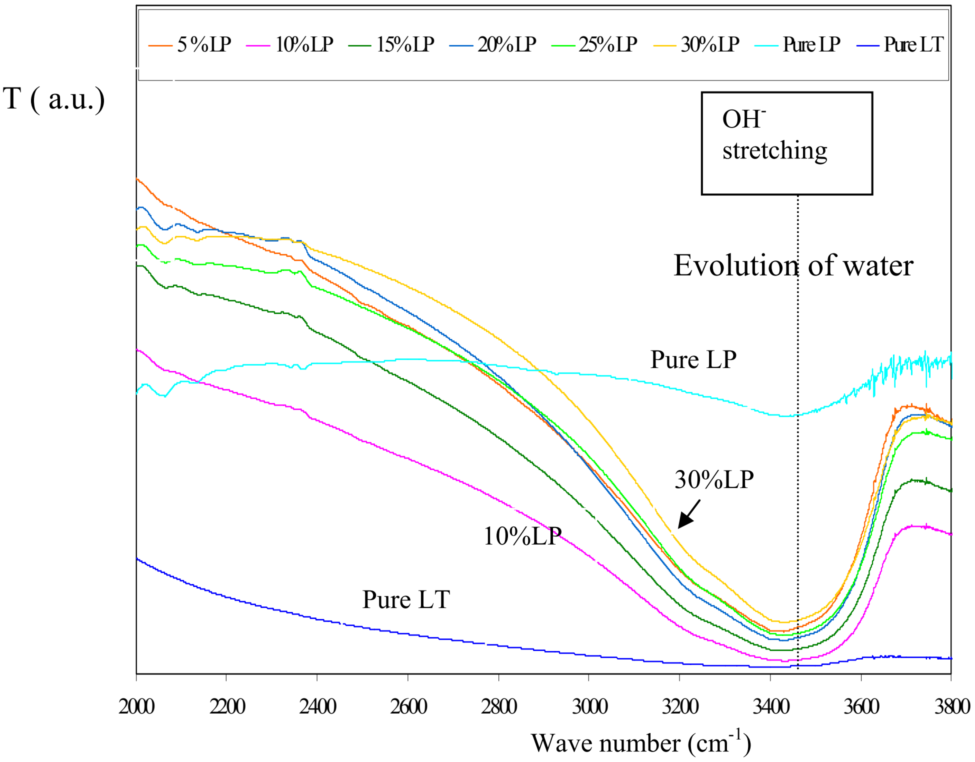

Figure 3. FTIR spectra of pure Li_3PO_4 (LP), pure Li_2WO_4 (LT) and samples with various wt. % of Li_3P0_4 with wave number in the range 2000-3800 cm^{-1}

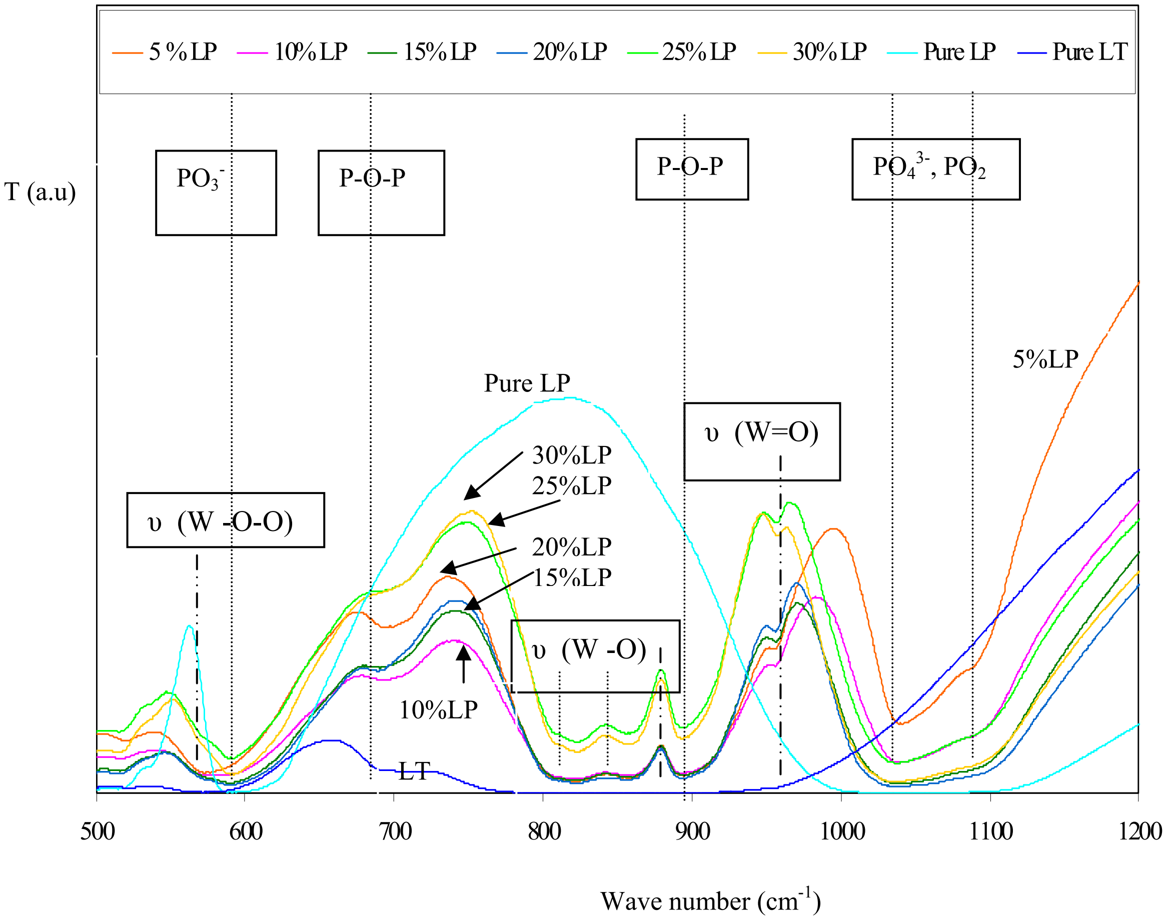

Figure 4. FTIR spectra of pure Li_3PO_4, pure Li_2WO_4 and samples with various wt. % of Li_3P0_4 with wave number in the range 500-1200 cm^{-1}