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PREPARATION AND CHARACTERIZATION OF $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ CONDUCTING ELECTROLYTE

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ABSTRACT

The $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ glass ceramic with NASICON-type phase has been synthesized. Ionic conductivity identification of the pelletized powder was carried out by electrochemical impedance spectrometer (EIS). The highest ionic conductivity obtained for $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ is 1.22×10^{-5} S cm^{-1} after being annealed at 800ºC for 3 hours in air.

Keywords: LATP; sol-gel method; EIS; XRD; FESEM

INTRODUCTION

Solid lithium-ion conducting materials have been studied to avoid the usage of flammable liquid-based compounds to develop solid state batteries of high safety and incomparable performance [1]. There are two types of solids; crystal and glass. Studies by Minami et al. [2] show that the ionic conductivity of glassy materials is higher than that of its corresponding crystals. The structure of glass, which is similar to the corresponding melt with high conductivity and low activation energy, contributes to its high ionic conductivity. Glass ceramics is a category of dense material of great potential as solid electrolytes [3]. It has been transformed into mostly crystalline form through heat treatment. The advantages of glass ceramics compared to sintered polycrystalline are that they are easily manufactured into desired shape and size, have dense microstructure, possesses negligible grain boundary effects and also known to exhibit good chemical stability [4-7]. Lithium aluminium titanium phosphate (LATP), consists of $LiTi_2(PO_4)_3$ which is analogous to a NASICON (Na Super Ionic CONductor) type, is among the most promising group of oxide based solid lithium conductors [7-9]. LATP is known to be one of the most highly conductive, air stable lithium based ceramic electrolytes investigated in recent years [10- 11]. Nasicon structure referring to the two polyhedral; TiO_6 octahedra and PO_4 tetrahedra, whereby they are linked together by their corners forming $[Ti_2(PO_4)_3]^-$ rigid skeleton that provides a three dimensional network structure allowing the mobile ion, Li^+ to migrate through it [12-17]. The ionic conductivity, as reported by previous studies, can be improved by the addition of a smaller trivalent cation, Al^{3+} [4,9-13]. The partial substitution of Ti^{4+} by Al^{3+} in the structure of $LiTi_2(PO_4)_3$ compound contributes to the increment of ionic conductivity [9,14-15]. Starting from that on, much attention has been done to the studies of $Li_{1+X}Al_XTi_{2-X}(PO_4)_3$ for possible use as electrolyte. In the present work, $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ solid electrolyte by sol-gel technique is prepared. The prepared samples were analyzed using thermogravimetry analysis (TGA) to obtain the suitable sintering temperature, X-ray diffraction was carried out to learn the samples' phase and the ionic conductivity was determined by impedance spectroscopy studies on the sample.

EXPERIMENTAL DETAILS

The vitreous sample $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ was prepared by mixing a stoichiometric amount of $Al(NO_3)_3$ (Bendosen) and TiO_2 (QReC), $LiC_2H_3O_2$ (Sigma) as well as $NH_4H_2PO_4$(Sigma-Aldrich) by sol-gel method. The mixture is dissolved ethanol and kept magnetically stirred for about 10 hours while being heated at ≈70°C and 15 drops of acetic acid is added. The obtained sample was grounded and sintered at temperature range 600ºC-900ºC for 3 hours. The structure parameter of powders was obtained using X-ray diffraction (Cu Kα radiation, λ=1.54056Å, at room temperature in air). The data were collected by a step-scanning method in the 2θ range between 10º and 90º with step width of 0.02º/min. Sample was pelletized to measure its electrical conductivity which was done by complex impedance technique (HIOKI 3531-01 LCR Hi-Tester) in a frequency range between 100Hz and 1MHz at temperature varies from 30ºC to 100ºC. Microstructures of the glass ceramic of the glass ceramic after the heat treatment were carried out by Fourier emission scanning electron microscopy (FESEM).

RESULTS AND DISCUSSION

Thermal analysis.

Figure 1 illustrates the TGA curve of the prepared powder fired in air with heating rate 10°C/min measured with temperature range of 100°C - 800°C. The TGA shows that the samples undergo three stages of weight loss before it becomes constant at 550°C. The sample experience first weight loss at around 94°C which can be caused by the volatilization of the solvent [18]. The mass loss between approximately 250°C and 500°C corresponds to the residual surfactant decomposition and combustion of organic components and the elimination of residual carbons. Results indicate that to obtain desired product, samples should be calcined at a minimum temperature of 550°C [19-22].

Phase characterization.

Increasing the value of x gradually increase the diffraction XRD peaks intensity due to the growth of the $LiTi_2(PO_4)_3$-type phase, as shown in Figure 2 below. A maximum intensity was obtained for the $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ sintered at 900°C, whereby the peaks of $AlPO_4$ phase progressively decrease at the same time indicating that the added Al^{3+} were beginning to incorporate into the $LiTi_2(PO_4)_3$-type structure, replacing the Ti^{4+} ions. Increasing $Al(NO_3)_3$ into the system increases the conductivity and keeps it at x10^{-}

^{4} Scm^{-1}, while further addition decreases the conductivity. Second phase peaks of TiP_2O_7 can also be observed in all samples. TiP_2O_7 peaks are expected as according to below Eq. 1, which is due to the loss of Li_2O:

$$2LiTi_2(PO_4)_3 \rightarrow 3TiP_2O_7 + TiO_2 + \uparrow Li_2O \qquad (1)$$

The constant ascending and dominant peaks of $LiTi_2(PO_4)_3$, however, shows that the major conducting phase can be expressed as $Li_{1+X}Al_XTi_{2-X}(PO_4)_3$ [4].

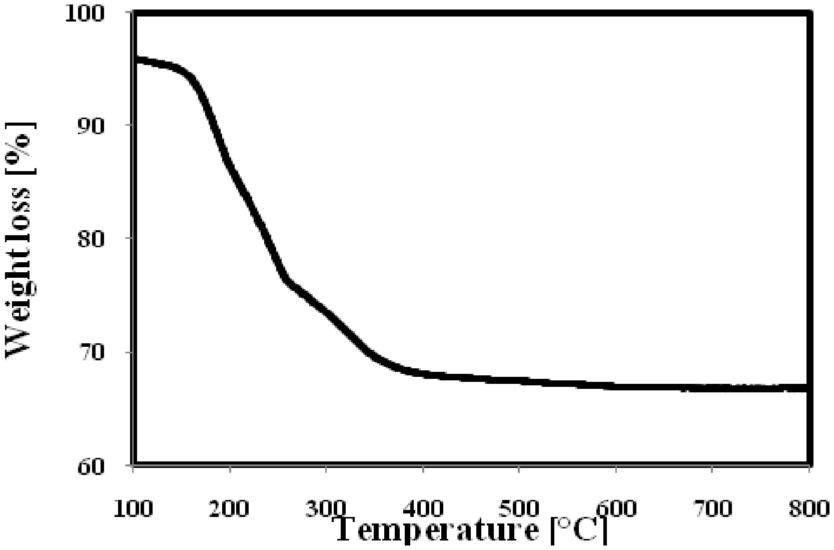

Figure 1: TGA curves of the $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ powder obtained in air with heating rate 10°C/min

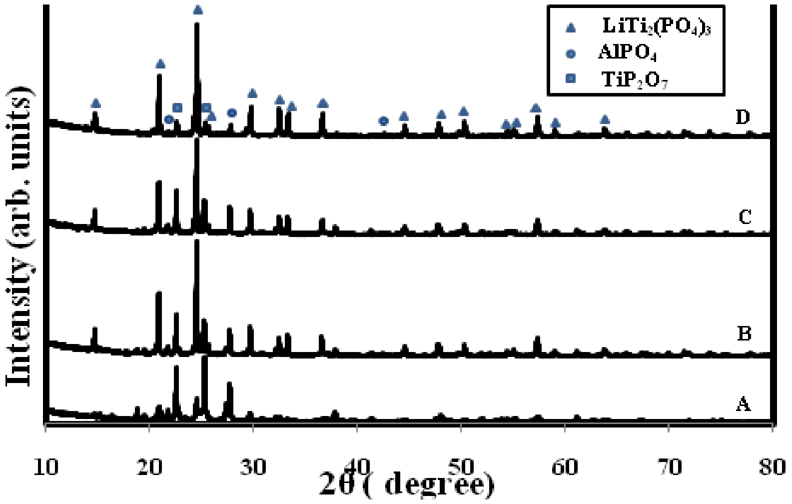

Figure 2: XRD plots of $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ glass ceramic specimens crytallized at (A) 600°C, (B) 700°C, (C) 800°C and (D) 900°C for 3 hours

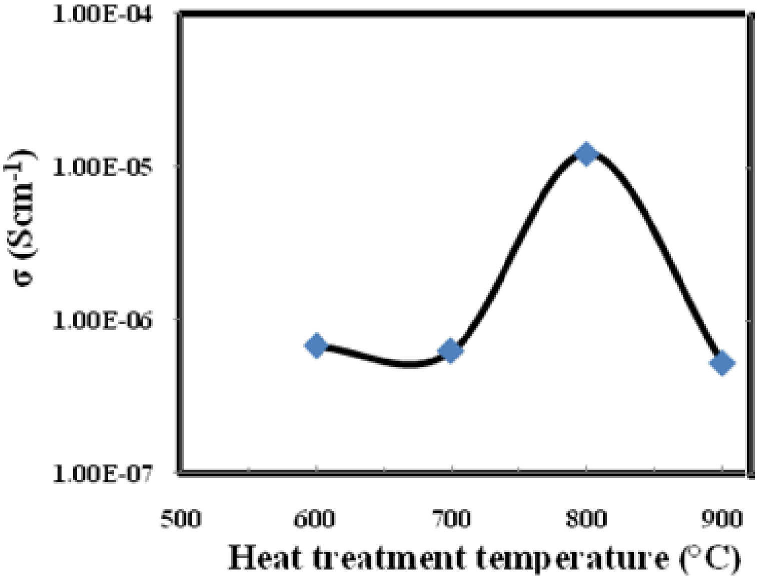

Figure 3: Impedance spectroscopy plots for the specimen heated for 3h as a function of heating temperature, ranging between 600°C to 900°C

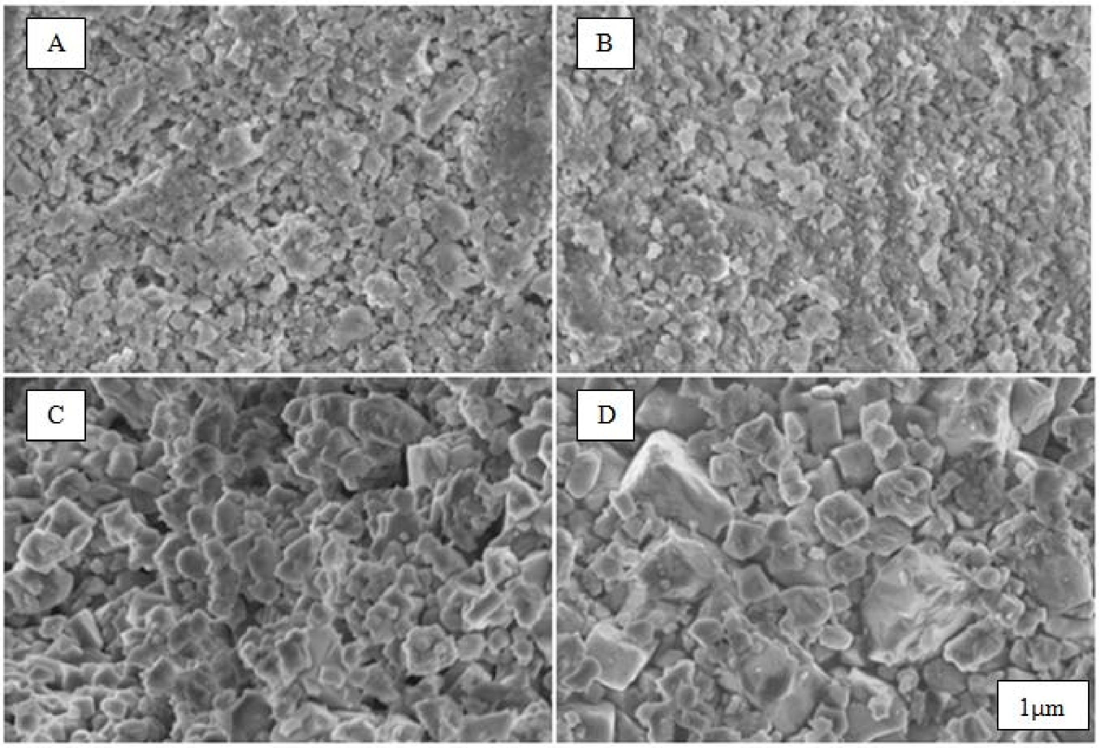

Figure 4: FESEM micrograph of the fracture surfaces of $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ glass ceramics treated at, (A)600°C, (B)700°C, (C)800°C and (D)900°C, for 3h

Morphology of $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ powders.

Figure 4. (A) – (D) show the FESEM micrograph of the $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ powders calcined at 600°C to 900°C for 3h in air. The as-prepared powder heat treated at 600°C and 700°C gives fine grain particles, but increased in size when the latter temperature was given. Further increment of the treating temperature leads to an increase in grain size due to impurity and contains a uniform grains with tight contact. Specimen treated at 900°C shows an obvious agglomeration and not uniform grains, these may lead to the decrease of ionic conductivity. The morphological surface obtained for the specimen treated at 800°C should be the main reason of its high conductivity [4-6].

Electrical properties.

The ionic conductivities of the specimen were determined from the impedance spectroscopy at ambient temperature. Figure 3 shows the impedance spectroscopy plots of $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ as a fuction of heating temperature in the range 600°C to 900°C. It can be seen that the ionic conductivity of specimen treated at 800°C increased drastically to 1.22×10^{-5} S cm^{-1} approximately two order of magnitude compared to those heated below this temperature. Increasing the heating temperature decreases the ionic conductivity to 5.24×10^{-7} S cm^{-1}.

CONCLUSION

Glass ceramic phase of $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ has been succesfully prepared. The XRD peaks show that the major conducting crystalline phase is $LiTi_2(PO_4)_3$-type phase. The ionic conductivity obtained at room temperature is 1.22×10^{-5} S cm^{-1}. The high ionic conductivity and ease of fabrication suggests that they are a suitable solid electrolyte for electrical devices.

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