Journal of Basic and Applied Engineering Research
p-ISSN: 2350-0077; e-ISSN: 2350-0255; Volume 6, Issue 8; July-September, 2019, pp. 477-479
© Krishi Sanskriti Publications
http://www.krishisanskriti.org/Publication.html

Structure and Electric Relaxation Behavior of $LiTi_2(PO4)_3$ Chemical Solid Electrolyte

Nafiu Sani Abbas

Department of Integrated Science, School of Science Education,
Saadatu Rimi College of Education Kumbotso, Kano, Nigeria
E-mail: abbasnafiusani@yahoo.com

Abstract—*Relaxation and ionic conductivity behavior of conducting materials such as NASICON-types (Sodium Super Ionic CONductor) is an important area of research interest due to their potential application in electronic devices. Lithium Titanium Phosphate($LiTi_2(PO_4)_3$)was prepared by conventional solid state synthesis technique, while characterization was carried out using X-ray powder diffraction (XRD),The XRD analysis indicated the sintering behavior of the material. The synthesized $LiTi_2(PO_4)_3$ was observed to fully formed at 1000 °C. Temperature and frequency dependence of AC conductivity and dielectric relaxation behavior were obtained at different temperatures from 30to 280 °C within the frequency range of 40 Hz to 1 MHz by carrying out IS analysis. The AC conductivity was observed to be frequency-independent in the low frequency region from 40 MHz to 10 KHz and frequency-dependent at higher frequency region (10 KHz to 1 MHz). For dielectric permittivity analysis, the dielectric constant ε′ and dielectric loss ε″ were found to increase at low frequency and decrease as frequency increased at all temperatures. The calculated AC conductivity of1.44E-03$(Sm)^{-1}$ was observed at room temperature.*

Keywords: *Solid electrolyte, $LiTi_2(PO_4)_3$, Structure, Conductivity, Relaxation behavior.*

Introduction

The material with *NASICON*-type structure (Sodium (Na) SuperIonic CONductor), Lithium Titanium Phosphate$LiTi_2(PO)_4$ *(LTP)* has been the most studied material due to the attention received for battery application[1]. The crystal structure consist of network arrangement in three dimension,the octahedral TiO_6 share their corners with tetrahedra PO_4 with interstitial and conduction channel along c-axis whereas Li is located at the interstitial sites [2,3]. The un-substituted *LTP* exhibits low ionic conductivity at room temperature for practical application [4]. Other workers reported that reduction of Ti^{4+} to Ti^{3+} with Li^{+}restricts the material to be used as an electrolyte in solid state battery [5].

In this work, characterizations were carried out to analyze the sintering behavior of the material LTP from room temperature to 1200 ^{0}C and the relaxation properties of the sample.

Methodology

The crystalline material, lithium titanium phosphate was prepared by solid-state synthesis method using the materials; Li_2CO_3 (99% Alfa Aesar), TiO_2 (99.9% Alfa Aesar), $NH_4H_2PO_4$(98% Alfa Aesar). The stoichiometry mixtures were ball mixed in a process control agent (*PCA*) using methanol for 24 h then dried in oven for 12 h. The sample powder was calcined at 700 ^{o}C for 2 h at heating rate2^{o}C/min in air and then finally sintered from 500 ^{o}C to 1200 ^{o}C. The overall chemical reaction is illustrated in Eq.1

$$Li_2CO_3 + TiO_2 + 3NH_4H_2PO_4 \rightarrow Li\ \ Ti_2(PO_4)_3 + CO_2 + 3NH_3 + (9/2)H_2O$$

Measurement and characterization techniques

The structural compositions and various phases of the LTP was studied and confirmed using the x-ray diffraction (*XRD*) machine, Philips X'pertdiffractometer model 7602 EA Almelo with Cu Kα radiation source with λ = 1.5418 Å. The relaxation behaviou was observed to be frequency-independent in the low frequency region from 40 MHz to 10 KHz and frequency-dependent at higher frequency region (10 KHz to 1 MHz).

Result and Discussion

The X-ray diffraction patterns of the un-substituted powder $LiTi_2(PO_4)_3$ (LTP) with x = 0 sintered in the temperature range from 500 ºC to 1200 ºC is illustrated in **Figure 1** It shows the sintering behaviour of LTP when sintered at the various temperatures. From the Rietveld analysis, the samples exhibited hexagonal crystal structure system belonging to R3c space group with ICSD card number 98-006-9677. The powder sintered at 500 ºC is observed with additional peaks which includes Lithium Phosphide (Li_3PO_3) with ICSD card no. 98-002-2312, Titanium Phosphate (TiP_2O_7) with ICSD card no. 98-006-0110 and Titanium Oxide (TiO_2) with ICSD card no. 98-006-7825. As the sintering temperatures increases the number of phases is reduced. For the samples sintered at 600 ºC, 700 ºC and 800 ºC only Titanium Phosphate (TiP_2O_7) was observed. At 900 ºC, there is the presence of un-reacted Titanium Oxide (TiO_2) with ICSD card no. 98-010-5396. The presence of these secondary phases or impurities is attributed to the low temperature of crystallization. However, the

number of secondary phases disappeared as the temperature reaches 1000 °C, 1100 °C, and 1200 °C with only single phase of LTP. This suggests a complete chemical reaction. Meanwhile, proper crystallization is achieved at these temperatures with well-defined sharp peaks. The Rietveld analysis indicated goodness of fit of about 3.6.

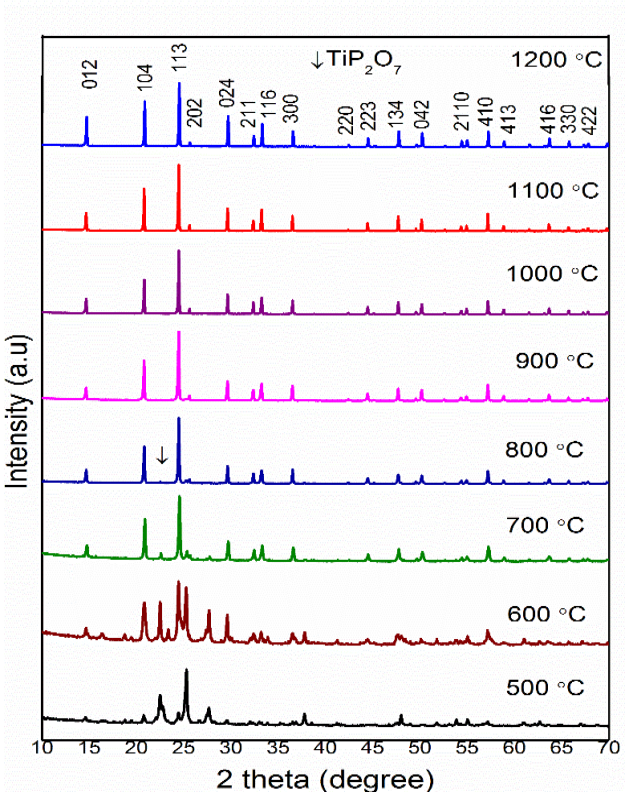

Figure 1

AC conductivity (σ_{ac}) is one of the electrical parameters used to investigate and analysed the dynamics of ions in polycrystalline materials such as NASICON compounds. The variations of AC conductivity ($\ln\sigma_{ac}$) with frequency $\ln(\omega)$ of un-substituted LTP and Al substituted LTP at different measuring temperatures from 30 °C to 280 °C and within the frequency range 40 Hz to 1 MHz are depicted in **Figures 2.** It is well known that the measured AC conductivity σ_{ac} of an ionic polycrystalline material at a certain temperature is always explained in terms of Jonscher′s power law. It can be seen from all the plots that as the measuring temperature increases, the AC conductivity also increases, this is due to the higher thermal energy acquired by the ions at higher temperatures.

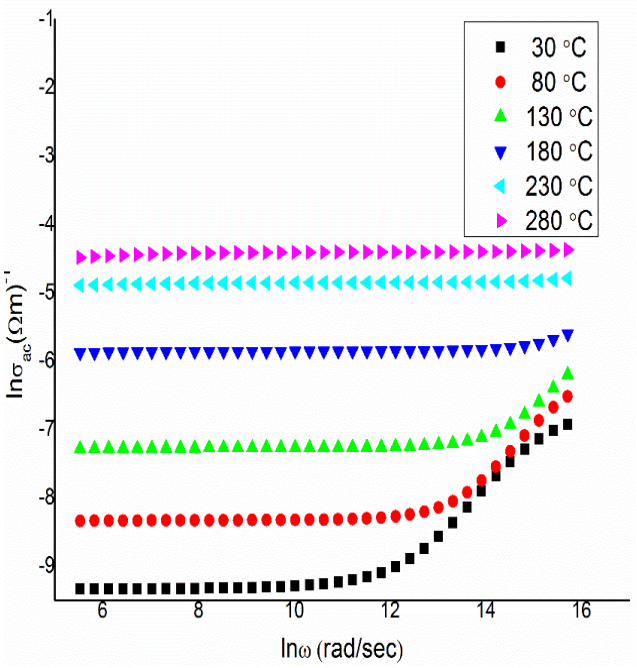

Figure 2

Figure 1 and 2 indicate the relaxation behavior of the sample LTP which is good agreement with Jonscher′s power law.

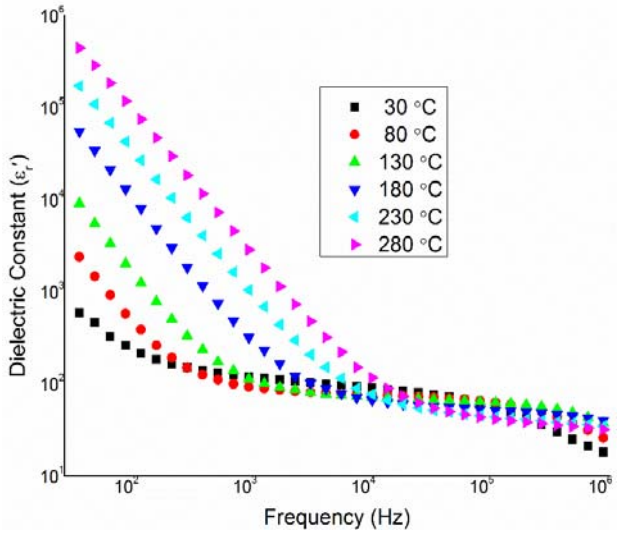

Figure 3

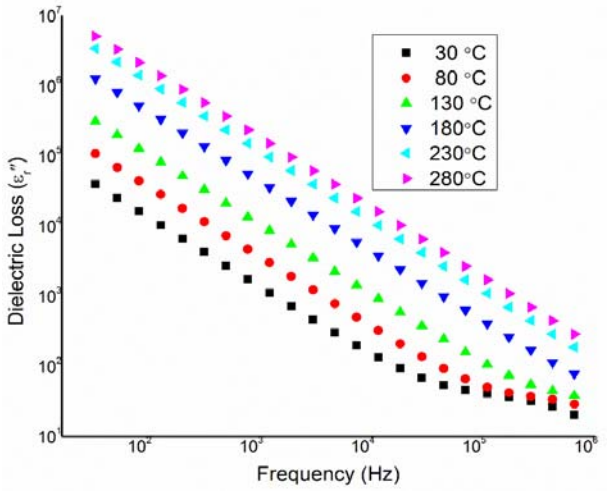

Figure 4

Conclusion

The material was successfully synthesized with ICSD card no 98-004-0755 with various compositions (secondary phases). The relaxation properties of the material was also studied.

References

[1] R. Ramaraghavulu and S. Buddhudu, "Analysis of structural, thermal and dielectric properties of LiTi2(PO4)3 ceramic powders," *Ceram. Int.*, vol. 37, pp. 3651–3656, 2011.

[2] G. X. Wang, D. H. Bradhurst, S. X. Dou, and H. K. Liu, "LiTi2(PO4)3 with NASICON-type structure as lithium-storage materials," *J. Power Sources*, vol. 124, no. 1, pp. 231–236, 2003.

[3] D. H. Kothari and D. K. Kanchan, "Study of Study of electrical properties of gallium-doped lithium titanium aluminum phosphate compounds," *Ionics 211253–1259 DOI 10.1007/s11581-014-1287-9*, pp. 1253–1259, 2015.

[4] H. Aono, "Ionic conductivity and sinterability of lithium titanium phosphate system," *Solid State Ionics*, vol. 40–41, no. 2, pp. 38–42, 1990.

[5] Savitha, T., S. Selvasekarapandian, C. S. Ramya, M. S. Bhuvaneswari, and P. C. Angelo. "Electrical conduction and relaxation mechanism in $Li_2AlZr(PO_4)_3$." *Journal of materials science* 4vol. 2, no. 14, pp. 5470-5475, 2007

[6] U. Ahmadu, A. O. Musa, S. A. Jonah, and N. Rabiu, "Synthesis and thermal characterization of NZP compounds," Journal of Thermal and Calorimetry Analysis vol. 2, pp. 175–179, 2010.

[7] B. Key, D. J. Schroeder, B. J. Ingram, and J. T. Vaughey, "Solution-based synthesis and characterization of lithium-ion conducting phosphate ceramics for lithium metal batteries," *Chem. Mater.*, vol. 24, no. 2, pp. 287–293, 2012.

[8] A. Ignaszak, P. Pasierb, R. Gajerski, and S. Komornicki, "Synthesis and properties of Nasicon-type materials," Thermochimica Acta, vol. 426, pp. 7–14, 2005.