

THERMAL BEHAVIOR OF Al SUBSTITUTED $\text{LiTi}_2(\text{PO}_4)_3$ NASICON COMPOUNDS

Tasiu Zangina^{1,3}, Jumiah Hassan¹, Raba'ah Syahidah Azis¹,
Khamirul Amin Matori¹, Umaru Ahmadu²,
Chifu Ebenezar Ndikilar³ and Makiyyu Abdullahi Musa¹

¹ *Department of Physics, Faculty of Science,
Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia*

² *Department of Physics, Faculty of Science,
Federal University of Technology Minna, Nigeria*

³ *Department of Physics, Faculty of Science,
Federal University Dutse, Jigawa, Nigeria*

*Corresponding: tasiuzangina@gmail.com

ABSTRACT

The compounds lithium aluminum titanium phosphates $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$ (LATP) with various compositions $0 < x < 1$ have been synthesized using solid-state method. The as-prepared sample has been characterized using various techniques. From TGA result, it has been observed that as x -content increases into the reaction mixture the integral temperature of decomposition decreases. Similarly, the temperature at which the materials become stable also decreases this indicated that phase stability is affected by increasing x content into basic compound. For structural analysis; the samples were successfully synthesized with $R\text{-}3c$ space group assuming a hexagonal crystal axis with ICSD database 98-006-9677. The finding showed that single phase is only observed with lower x -value substitution. As Al content increases the number of secondary phases were observed to increase with various aluminum phosphate (AlPO_4).

Keyword: NASICON-type; Thermal behavior; structural property

INTRODUCTION

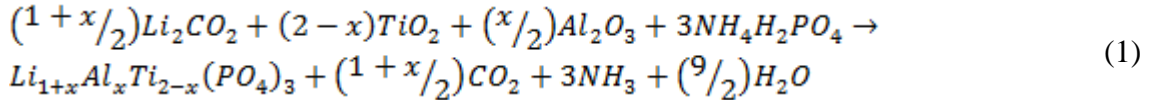
The material with NASICON-type structure (Sodium (Na) SuperIonic CONductor), Lithium Titanium Phosphate $\text{LiTi}_2(\text{PO}_4)_3$ (LTP) has been the most studied material due to the attention received for battery application [1]. The crystal structure consist of network arrangement in three dimension, 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]. The substitution of trivalent cation such as Al^{3+} was reported by many workers to

enhanced the material densification and lead to better sinterability which resulted high ionic conductivity [5]. Knowledge of thermal behaviour and thermodynamic properties of certain material is essential before put into application[6].The present studydescribes the effect of *Al*substitution in *LTP* on thermal stability, phase composition/transformation and basic structure of the as-prepared sampleswith various compositions $Li_{1+x}Ti_{2-x}Al_x(PO_4)_3$ where $x = 0, 0.2, 0.25, 0.3, 0.4, 0.5, 0.75$ and 1.0 .

EXPERIMENTAL

Synthesis

The crystalline material, lithium aluminum titanium phosphate ($Li_{1+x}Ti_{2-x}Al_x(PO_4)_3$, $0 < x < 1$) were 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), and Al_2O_3 (96% Strem). 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 °C for 2 h at heating rate 2°C/min in air and then finally sintered at 1100 °C. The overall chemical reaction is illustrated in Eq.1



Measurement and characterization techniques

Thermal analysis of the reaction mixtures was carried out using TGA machine, Metler Toledo Brand, (Model number *TGA/DSC HT*). The measurement was conducted in air from room temperature to 1200 °C. The structural compositions and various phases of ($Li_{1+x}Ti_{2-x}Al_x(PO_4)_3$) was studied and confirmed using the x-ray diffraction (*XRD*) machine, Philips X'pert diffractometer model 7602 EA Almelo with Cu $K\alpha$ radiation source with $\lambda = 1.5418 \text{ \AA}$. The functional groups of *LATP* were confirmed from the spectra of *FTIR*. The modes of vibrations of PO_4 were given in the intervals of the standard group vibrations by considering the literature. The machine Perkin Elmer Spectrum 100 Series spectrophotometer (Waltham MA) was employed for the analysis.

RESULTS AND DISCUSSION

Figure 1 shows the thermal property of the reaction mixture $Li_{1+x}Ti_{2-x}Al_x(PO_4)_3$ with various compositions $x = 0, 0.2, 0.25, 0.3, 0.4, 0.5, 0.75$ and 1.0 . It can be seen from the entire plots that the mass decreases as temperature increases this is ascribed to the decomposition of the reactant mixtures that lead to the loss of mass. The curves were divided into five temperature regions as shown in the figure. The major percentage mass loss occurred in the region I to IV which is associated with the decomposition of $NH_4H_2PO_4$, AlO_2 and Li_2CO_3 to evolve water moisture (H_2O), ammonia (NH_3) and carbon dioxide (CO_2). As temperature increases through the regions the rate of mass loss decreased and become constant along region V. The thermal stability was observed to vary in all the samples ranging from 482-400 °C depending on the stoichiometry of the

mixtures as shown in Table 1. Similar trend was reported by [7] and also in the preparation of $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ using co-precipitation method by [8]. Figure 2 indicates the derivative thermo-gravimetric (DTG) ($-dm/dt$) data the figure describes the rate of mass loss as temperature changes which has advantages of providing higher resolution and better specific temperature behavior.

The total mass loss, the residue and the temperature at which each composition (x) becomes stable is shown in Table 1. It is seen from the table that the total mass loss increases as the x -content ($(1+x)Li_2CO_3$) increased in the *LTP* compound from 0 to 1.0 see Eq.1 and the systematic increase in x -value in the *LATP* compound lead to sample formation towards low temperature. This probably attributed to the decrease in the molecular weight of the samples when a smaller radius and less atomic weight material are introduced into the system.

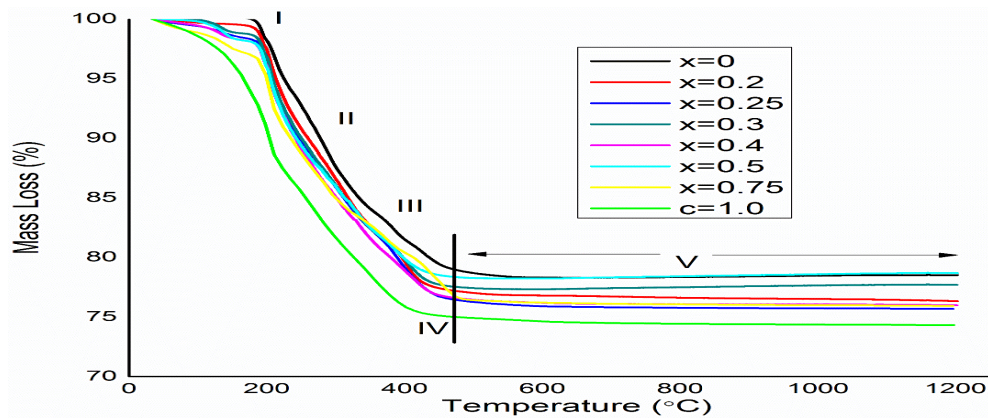


Figure 1: TGA of various stoichiometry (x) of $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ LATP

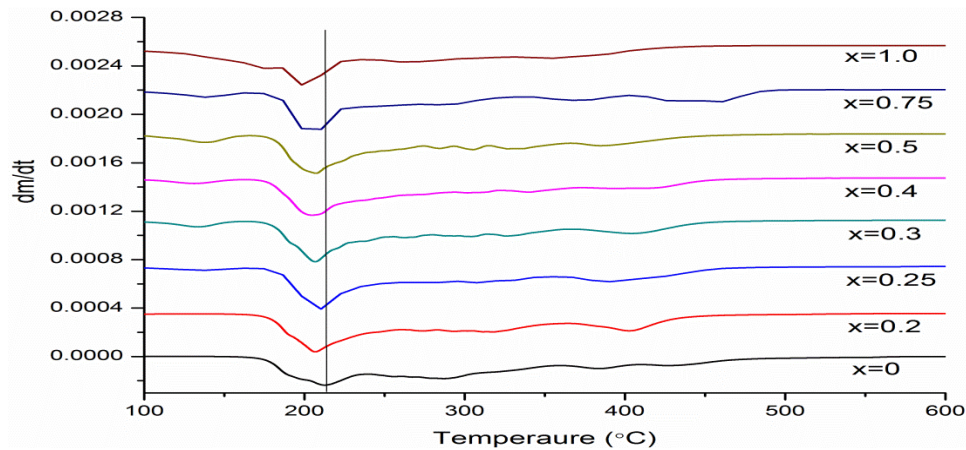


Figure 2: DTG of various stoichiometry (x) of $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ LATP

The XRD pattern of Al substituted *LATP* is illustrated in Fig 3. The figure shows the phase compositions and effect of Al substitution into the basic compound *LTP*. The typical peaks reflect and match the standard *ICSD* database with reference code 98-006-9677. It is observed the samples exhibit hexagonal crystal structure system belonging to *R-3c* space group. Single phase structure was observed for the compositions $x = 0, 0.2$ and 0.25 . But secondary phases were detected for samples with high Al substitution. For sample $x = 0.3$ we noticed the presence of unreacted Rutile (TiO_2) with *ICSD* card no.98-001-7744. Berlinite ($AlPO_4$) with little percentage in $x = 0.4$. The presence of two secondary phases were identified for sample $x = 0.5$ which include; Berlinite ($AlPO_4$)

Table 1: Illustrates the percentage mass loss, residue and the stability temperature of $Li_{1-x}Al_xTi_{2-x}(PO_4)_3$ *LATP* samples with various compositions

Sample [x]	$Li_{1+x}Ti_{(2-x)}Al_x(PO_4)_3$ <i>LATP</i>	Molecular weight of <i>LATP</i> [g/mol]	Total mass Loss [%]	Residue [%]	Stability temperature [°C]
0	$LiTi_2(PO_4)_3$	387.584	21.49	78.51	481.80
0.2	$Li_{1.2}Ti_{1.8}Al_{0.2}(PO_4)_3$	384.800	23.27	76.73	436.96
0.25	$Li_{1.25}Ti_{1.75}Al_{0.25}(PO_4)_3$	384.100	24.30	75.70	439.43
0.3	$Li_{1.3}Ti_{1.7}Al_{0.3}(PO_4)_3$	383.400	22.30	77.67	434.76
0.4	$Li_{1.4}Ti_{1.6}Al_{0.4}(PO_4)_3$	382.000	24.02	75.98	433.15
0.5	$Li_{1.5}Ti_{1.5}Al_{0.5}(PO_4)_3$	380.610	23.67	76.33	430.57
0.75	$Li_{1.75}Ti_{1.25}Al_{0.75}(PO_4)_3$	377.125	23.50	76.50	457.70
1.0	$Li_2TiAl(PO_4)_3$	373.638	25.70	74.30	400.80

card no. 98-000-5212 and Berlinite ($AlPO_4$) card no. 98-000-4649. Meanwhile, for $x = 0.75$ and $x = 1.0$ additional number of impurities increased which include; Zeolite ($AlPO_5$) with *ICSD* card no. 98-005-8629, Zeolite ($AlPO_{.53}$) with *ICSD* card no. 98-005-8635, $AlPO_{.31}$ with *ICSD* card no. 98-002-9743 and some unidentified peaks. These secondary phases ($AlPO_4$) are sometime difficult to be avoided when sintering at high temperatures [9]. However, the present analysis indicated that the impurities or secondary phases can be avoided when substitution is carried out with little Al content as observed in the XRD analysis of the compositions with $x = 0.2$ and 0.25 .

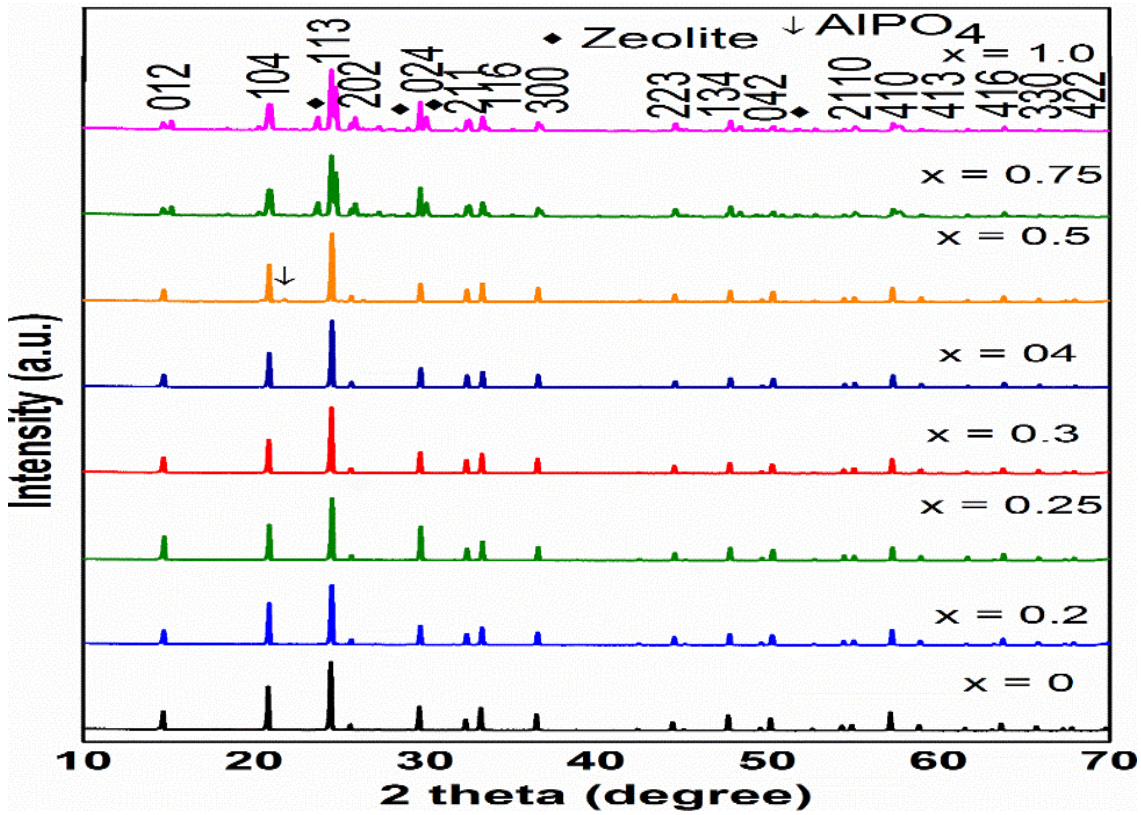


Figure 3: X-ray diffraction patterns of $\text{Li}_{x+1}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ with various compositions

Table 2: Effect of Al substitution on lattice parameters, unit cell volume and density of LATP

x-value	Unit cell parameters			Experimental density [g/cm ³]	Theoretical density [g/cm ³]
	a = b(Å)	c(Å)	V(Å ³)		
0	8.51183	20.84517	1307.92	2.75530	2.95253
0.2	8.50352	20.81085	1303.22	2.68513	2.94189
0.25	8.50330	20.80592	1303.84	2.67623	2.93515
0.3	8.49882	20.79212	1300.61	2.66810	2.93707
0.4	8.49359	20.77403	1297.88	2.59724	2.93251
0.5	8.49924	20.79299	1300.60	2.59810	2.91573
0.75	8.48436	20.77183	1294.92	2.59770	2.90174
1.0	8.48430	20.77115	1294.86	2.58767	2.87502

The Effect of Al substitution on lattice constant and unit cell volume in the *LTP* structure is listed in Table 2. It can be seen from the table that as *Al* content (substitution) increases, the unit cell parameters and unit cell volume were observed to decreased this is attributed to the smaller size (atomic radius) of *Al* ion as compared to

that Ti cation[10,11]. The unit cell is possible to shrink along c-axis due to smaller radius of Al ion[3]. The present result confirm that XRD peaks always shift from their position to a slightly higher or lower 2θ when substitution or doping causes changes in lattice parameters[10]. Table 2 also shows that the experimental density is more than 90% of the theoretical density for all the samples. Both the theoretical and experimental densities were observed to decrease due to the higher content of Al in the crystal structure. This may be associated to the reduced molecular mass of Ti ions by Al ion substitution.

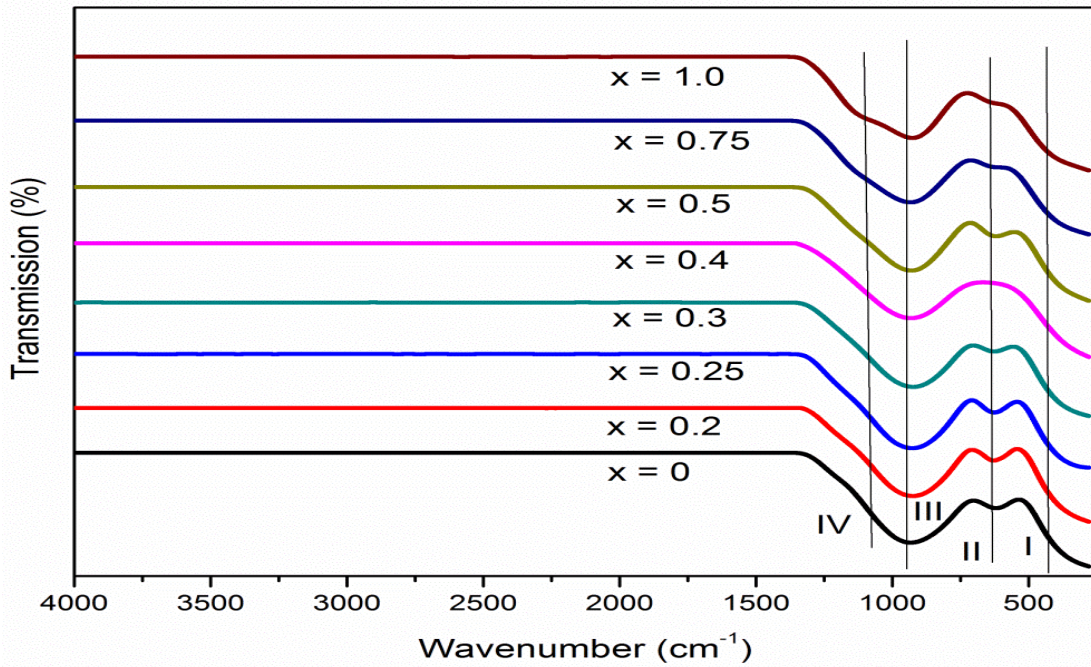


Figure 4: FTIR spectra of Al substituted LTP with different composition

Figure 4 illustrates the FTIR spectra of the $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ with various compositions. The strong vibration band in region (III) within the range 900 cm^{-1} to 985 cm^{-1} represents the symmetry stretching vibration of PO_4^{3-} . The bands in the region (II) 560 cm^{-1} to 670 cm^{-1} correspond to asymmetry bending vibration modes of O-P-O. A weak vibration bands were observed in region (IV) which are assigned to the asymmetry stretching vibration bands within the range 1100 cm^{-1} to 1250 cm^{-1} . Another weak vibration band was also indicated in region I within the range 300 cm^{-1} to 420 cm^{-1} . The partial substitution of titanium Ti^{4+} ions with aluminium Al^{3+} ions in all the compositions do not show any influence in the FTIR absorption bands. In a similar finding N. Y. Kosova showed the same behaviour in the FTIR analysis of LATP[12,13].

CONCLUSION

The present analysis shows that thermal stability is generally affected by increasing the Al substitution in lithium aluminum titanium phosphate (LATP) which leads to sample

formation toward lower temperatures. The XRD analysis indicated that increase in the Al content in the sample increases the number of secondary phases. It is seen from the analysis that the samples with composition $x = 0, 0.2$ and 0.25 exhibited single phases. But, secondary phases with various $AlPO_4$ phases were observed as the content of Al is increased. The vibrational and stretching modes of PO_4 of all the samples were observed and confirmed by the FTIR spectra.

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