

Synthesis and Thermal Characterization of NZP Compounds $\text{Na}_{1-x}\text{Li}_x\text{Zr}_2(\text{PO}_4)_3$ ($x=0.00-0.75$)

Ahmadu U. and Yusuf A.S.

Department of Physics, Federal University of Technology, Minna, Nigeria

**corresponding author: u.ahmadu@yahoo.com*

Abstract

NZP composition $\text{Na}_{1-x}\text{Li}_x(\text{PO}_4)_3$, $x=0.00-0.75$ has been synthesized by the method of solid state reaction from $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, Li_2CO_3 , ZrO_2 and $\text{NH}_4\text{H}_2\text{PO}_4$, sintering at 1050-1250°C for 8 hours only in order to determine the effect on thermal and other properties, such as the phase formation of the compound. The materials have been characterized by TGA and DTA thermal analysis methods from room temperature to 1000°C. It was observed that the increase in lithium content of the samples increases thermal stability of the samples and the DTA peaks shifted towards higher temperatures with increase in lithium content. The thermal stability regions for all the samples is observed to be above 640°C. The sample with the highest lithium content, $x=0.75$ exhibited the greatest thermal stability over the temperature range.

Keywords: thermal analysis; sodium zirconium phosphate; NASICON

1. Introduction

One of the most important materials that is being presently studied in materials science is sodium Zirconium Phosphate, $\text{NaZr}_2(\text{PO}_4)_3$, otherwise popularly known as NASICON or NZP. The material has been found to have very unique properties such as being the only substance that can accommodate atoms of different sizes in its various lattice sites [1]. The Na, Zr and Phosphorus can all be substituted, except oxygen, resulting in compositions with varying physical and chemical properties suitable for diverse applications. Several studies have been undertaken reflecting the various potential applications such as its use as substrate material for oxide-coating [1-2], for demobilisation of nuclear wastes [3], applications in zero or negative thermal expansion materials [4-6] and as electrode for rechargeable lithium battery applications [7] and gas sensors [8], among others.

We are carrying out series of characterizations on the NZP, beginning with thermal analysis of lithium substituted composition $\text{Na}_{1-x}\text{Li}_x(\text{PO}_4)_3$ ($x=0.00-0.75$), with the ultimate objective of

determining their suitability for applications as electrolytes for energy applications. Many studies have been carried out on NZP materials that were synthesized through various routes in order to obtain materials of good thermal and electrical characteristics, in particular by appropriate configuration of the sintering times and temperatures. This has ultimately led to the synthesis of pure phase and good crystalline materials with enhanced properties. Studies have shown that the minimum sintering temperature required for the formation of NASICON is about 1100°C [9] at different sintering times which may be as low as possible, but generally varying from 16 hours [10] to as much as 20 hours [11], aside from other intermediate and higher values. The authors in ref. [12] in their study of two different NASICON compositions have examined the balance between these two factors on the formation of the phases of the NASICON compound and found that there is indeed a particular balance that exists between them for the formation of NASICON to ensue. The present study is therefore expected to elucidate this further by using a sintering time of only 8 hours for both the sintering and other preliminary steps in the solid state synthesis of the materials, making the aggregate time to be much less than had hitherto been reported in literature. By maintaining a high temperature at the expense of the sintering time and improving on sample preparation through thorough grinding and regrinding of sample for many hours, we wish to determine whether NZP of good crystallinity and phase purity could be formed within this period at a sintering temperature of 1050-1250°C. Thus we studied four compositions that to our knowledge have not been systematically analysed and thermally examined their stability with respect to increasing lithium content between room temperature and 1000°C using DTA and TGA thermal analysis methods. We are interested particularly in structural transformations that may take place and how this will affect the other parameters to be determined ultimately. Moreover, we also observe the systematic degradation of the compound with temperature and the reasons behind them. Here we report the results of the thermal characterizations while the ongoing research on XRD, among others, is taking place to determine the phases and other relevant parameters relating to the materials.

2. Experimental

2.1 Synthesis

The preparation of these samples was carried out at the Centre for Energy Research and Development (CERD), O.A.U. Ile-Ife. Basic starting materials of analytical grade (>99%) were used, that is, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, ZrO_2 , Li_2CO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$. Stoichiometric amounts of these materials were

mixed and thoroughly ground in an agate mortar for about five hours in each case. The solid solution was then dried in air for about four (4) hours. Acetone was added in appropriate quantity to homogenize the mixture. Pellets of discs of 13mm diameter and 6mm thickness were prepared for sintering purposes under pressure of $7.42 \times 10^6 \text{N/m}^2$. The sintering was carried out at the National Metallurgical Development Centre (NMDC), Jos. All the samples were placed inside a gas-heated furnace for eight (8) hours at successive temperatures 200, 500, 1050, 1100, 1150, 1200 and 1250°C, respectively. Between each temperature, the samples were allowed to furnace-cool to room temperature and the samples were thoroughly ground, re-mixed, pelletized and placed back into the furnace for the next round of heating. The maximum sintering temperature was 1250°C.

2.2. Thermal characterization

Specimens of the virgin powder samples were used for the measurement on DTA machine NETZCHDTA404PC in air, at the Centre for Energy Research and Development (CERD), O.A.U. Ile Ife. The readings were conducted between room temperature and 1000°C at heating rate of 20.0K/min. The results are shown in fig.2 (a-d). The TGA was performed on virgin powder specimens from room temperature to about 1000°C on an TGA Shimadzu DT-30 thermal analyser in air at a heating rate of 20.0K/min at the University of Witwatersrand, South Africa. The plot of Weight (Wt %) versus Temperature (T°C) of the samples are shown in fig.3 (a-d) together with the composite plot, fig.4.

3. Results and Discussions

For the sample $x=0.00$, there is only one exothermic peak at 188.9°C which began from 140-220°C in the DTA plot. This can be attributed to the loss of water and water of hydration. The absorbed heat continued to increase until it reached a plateau between 680-760°C, showing the establishment of equilibrium. This shows that the sample is stable in this region, fig.1 and is confirmed by the TGA plot in fig.5 where the sample showed stability from 600°C to 1000°C.

Similar work by the authors [13] on the sample, for example, has about eight peaks in the DTA plots, three are endothermic and the rest are exothermic. They attributed the endothermic (largest) peak which they found at 120°C to the elimination of water from the mixture. Their work and others showed that using different precursors of the starting materials leads to different results, particularly, the peaks and their positions. The area of the peak in this sample is the smallest,

comparatively, showing that the reaction involving the evolution of water released the least amount of heat. In the system $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$ ($0.5 < x < 0.9$) the DTA did not show any structural changes on heating, though melting was observed above 800°C [14]. Similarly, [15] observed the DTA peaks in a temperature region different from the TGA in $\text{Li}_{1+x}\text{GaTi}_{2-x}(\text{PO}_4)_3$ with $x=0.1-0.9$.

Ref. [16] studied NZP $x=0.00$ by sol-gel preparation and had one exothermic peak in the DTA at 270°C from 220--280°C and overall weight loss is 29%, RT--1000°C and it similarly, had approximately four temperature regions and shows stability around 600°C upwards.

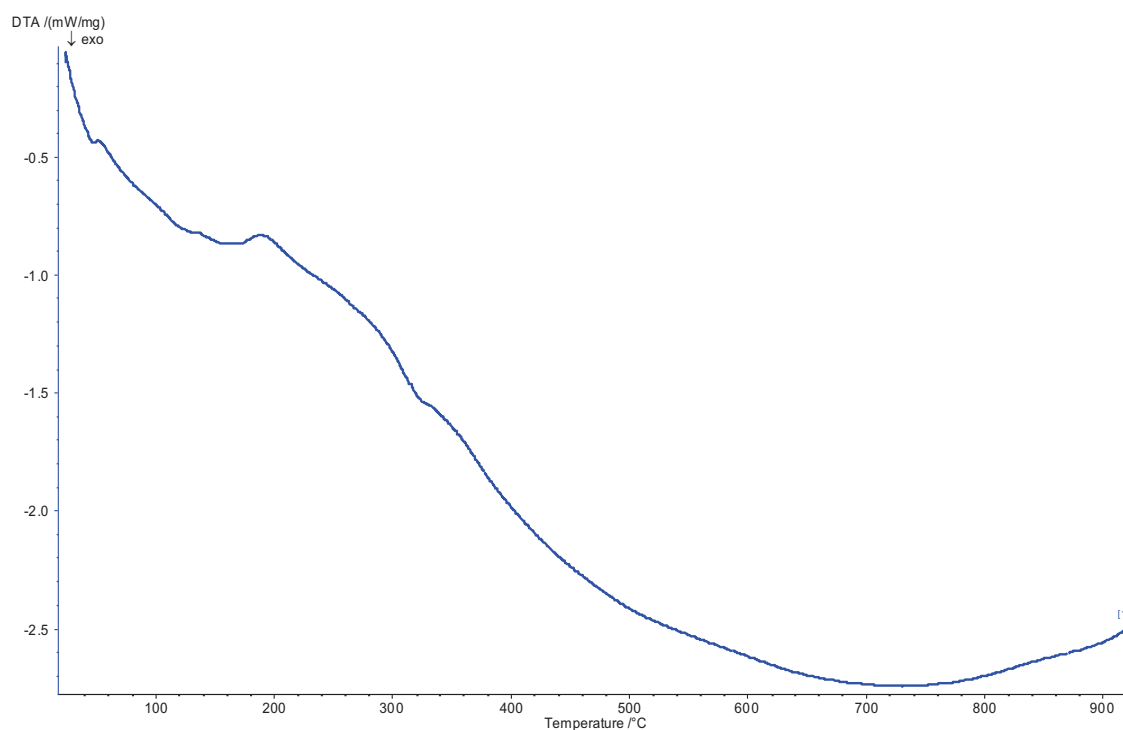


Fig.1. DTA plot of sample $x=0.00$ showing the exothermic peak at 188.9°C.

The sample $x=0.25$ showed one sharp exothermic peak at 200°C, starting from 180-250°C which is also ascribed to the loss of water and water of hydration. A plateau exists from 670-760°C showing that the stability region for this sample began at an earlier temperature, fig.2. This means that the increment of lithium content in the sample has increased the thermal stability of the compound compared to the $x=0.00$ sample.

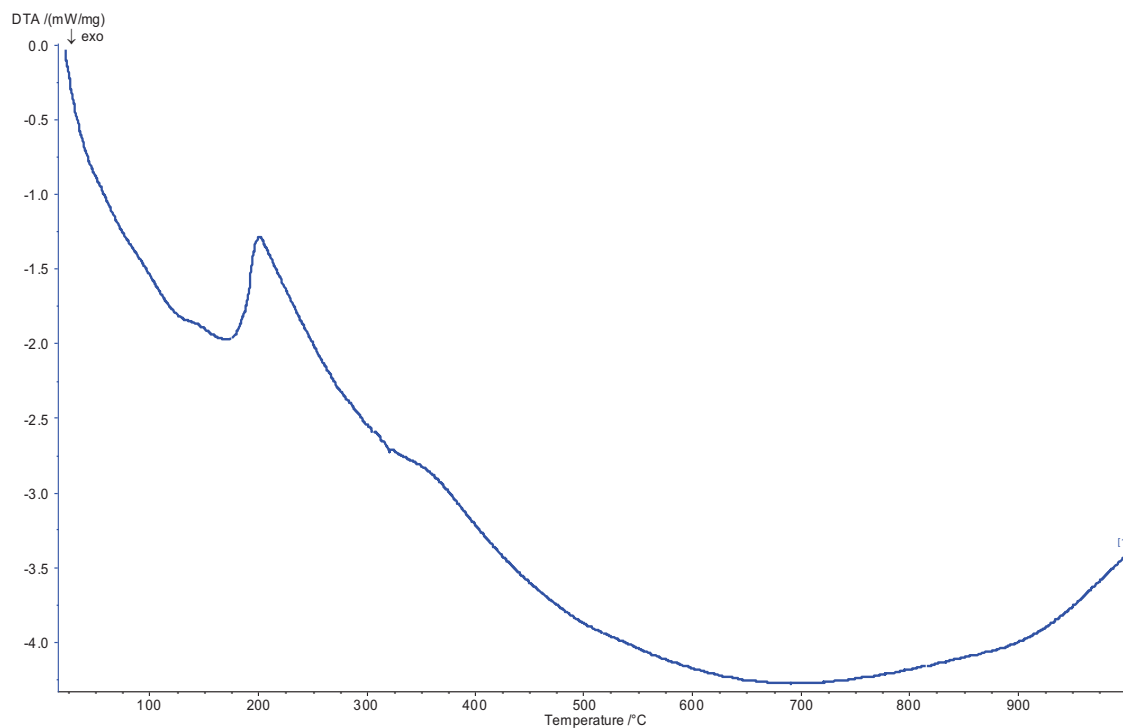


Fig.2. DTA plot of sample $x=0.25$ showing the exothermic peak at 200.0°C.

In the case of $x=0.50$ sample, there is a sharp exothermic peak at 196.4°C from 163-250°C is also attributed to the loss of water of hydration and moisture. A plateau is observed between 580-700°C, fig.3 which is wider than the previous samples. There is a broad exothermic peak at about 800°C which may point to the beginning of crystallization process.

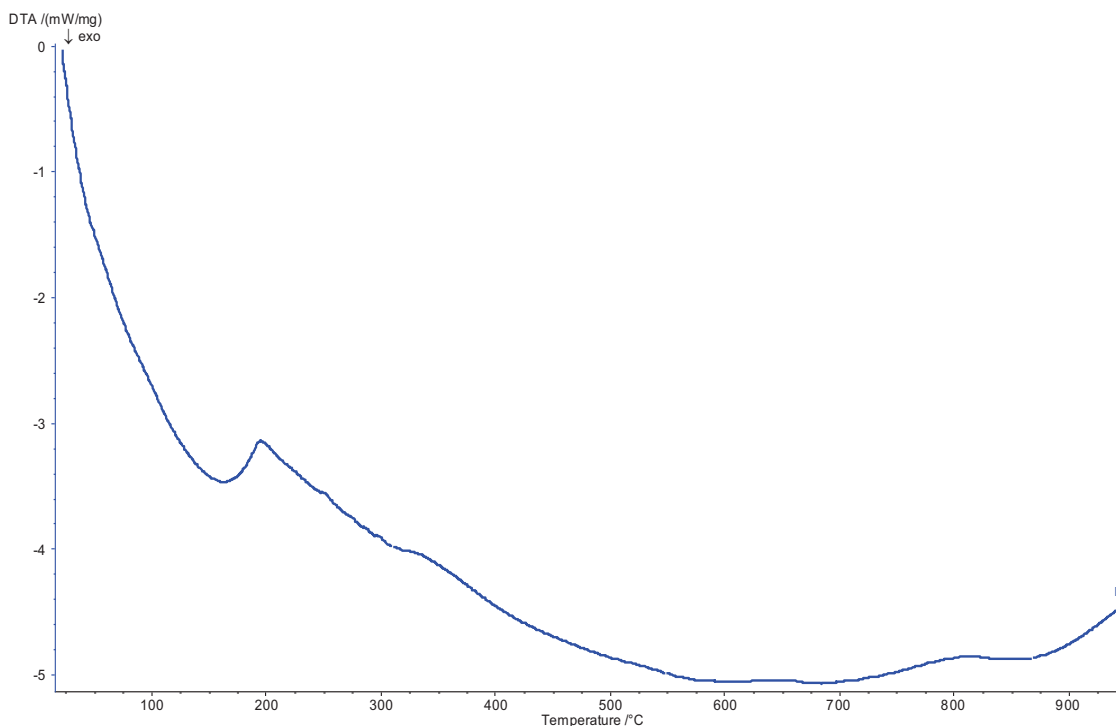


Fig.3. DTA plot of sample $x=0.50$ showing the exothermic peak at 196.4°C .

The last sample, $x=0.75$ showed the largest and broadest exothermic peak at 202.6°C between $140\text{-}250^{\circ}\text{C}$ showing the loss of water and water of hydration. Similarly, a plateau at $650\text{-}720^{\circ}\text{C}$ is observed which is the widest region of stability compared to the others, fig.4. This is a confirmation of the fact that increasing lithium content brings about thermal stability of the sample, by decreasing the rate of loss of weight of the sample, as confirmed by the TGA results below. Also the positions of the exothermic peaks are shifted towards higher temperatures with increasing lithium contents.

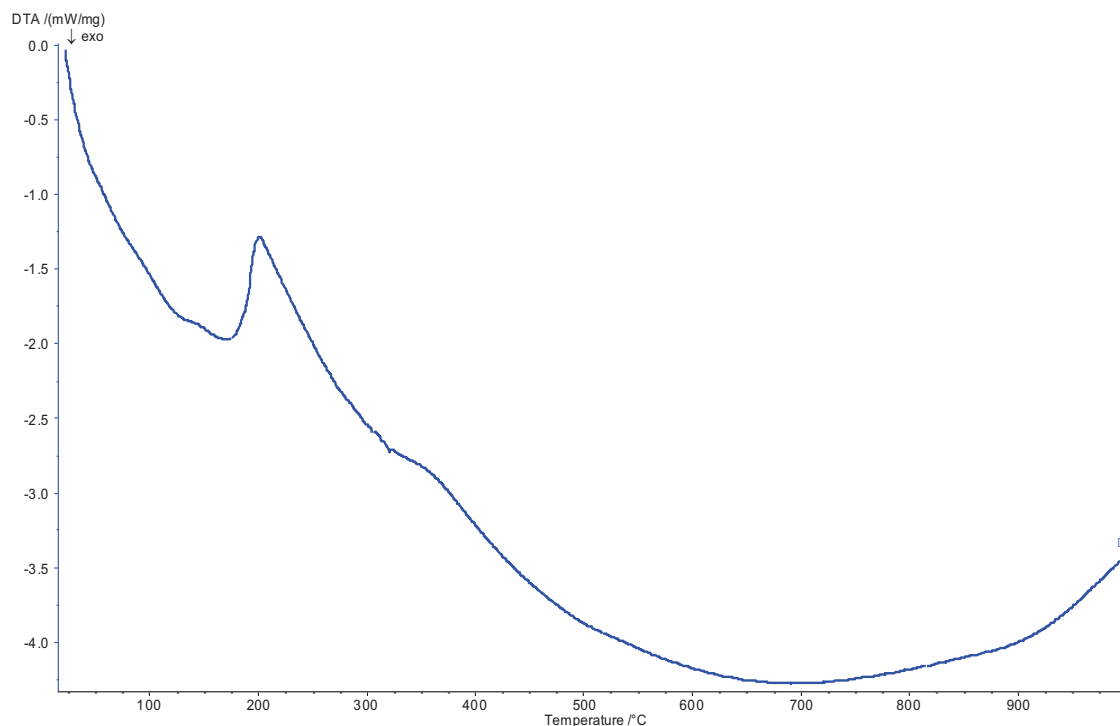


Fig.4. DTA plot of sample $x=0.75$ showing the exothermic peak at 201.7°C.

The position of the peaks is shifting with increased lithium content, implying that the lithium increases the thermal stability of the samples, delaying the temperature at which these losses occur. This is confirmed by the TGA plot. The TGA for all the samples show the same character and can be approximately broken into four temperature ranges: 1) RT- 60°C, 2) 60-180°C, 3) 180-360°C and 4) 360-1000°C, with the first range being the smallest almost invisible in the $x=0.50$ and 0.75 samples. In all the samples 600-1000°C is the thermal stability region, as the weight loss is about 1% only. The rate of mass loss decreases with increasing temperature through the regions, until it becomes virtually constant from above 600°C upwards in all the samples. The TGA plot is not shown beyond 800°C because of the limitation of the EXCEL PROGRAM which was used to plot the data, as it is limited to 32,000 data points only (OFFICE 2007 PROGRAM) and becomes unstable beyond this range. Nevertheless, the weight loss is virtually constant beyond this temperature range. The composite TGA plot is shown to 600°C.

Thus for sample $x= 0.00$, the weight loss is 7% in the first region, approximately 5% in the second region, 15% weight in the third and 2% in the fourth region. The weight loss is greatest in the third and is within the region of the exotherm, as observed in the DTA. Overall there was a weight

loss of about 29% from room temperature to about 1000°C, fig.5. The TGA shows that the sample is stable from around 600°C and this is in agreement with that of [13] and the general characteristics of the plots are the same in terms of mass losses in the various regions. This implies the formation reaction of the product is complete at this temperature. This is also in agreement with the DTA results discussed above for the sample. In their study of $\text{Li}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$ ($0.5 < x < 0.9$) ref. [14] did not observe any mass losses in the TGA from room temperature up to 800°C.

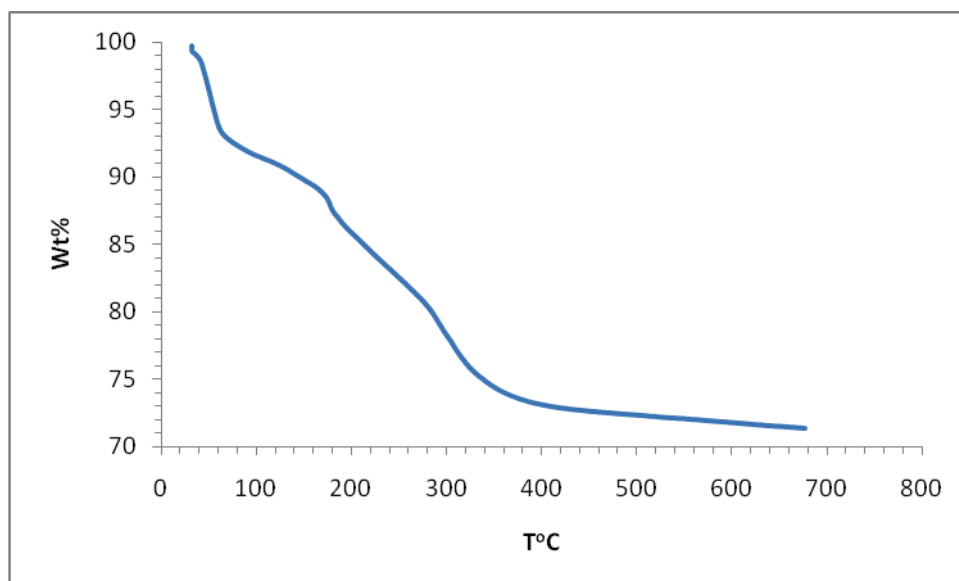


Fig. 5. TGA Plot of sample $x=0.00$ showing the four temperature regions of weight losses

In the same region for sample $x=0.25$, the weight loss are 6%, 4%, 16% and 2.5% respectively. Similarly, the weight loss is the greatest in the third region, almost the same amount with the $x=0.00$ sample. Overall weight loss is approximately 29%, fig.6, as in the sample $x=0.00$ and correlates with the sample $x=0.00$ in terms of the greatest amount of mass loss in the third region. Similarly, the rate of weight loss with changing temperature has now decreased, showing that the material has become more stable with increase in lithium content.

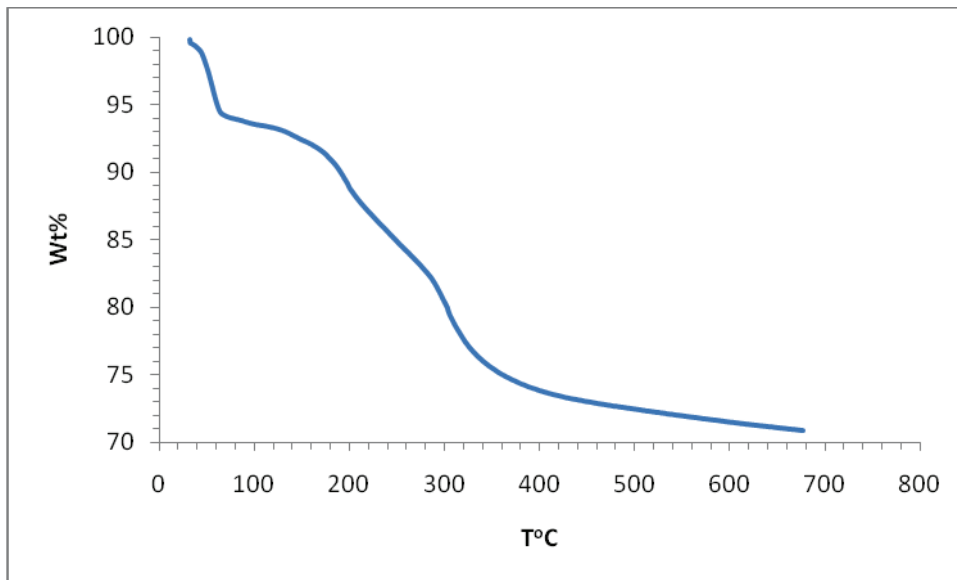


Fig. 6. TGA Plot of sample $x=0.25$ showing the four temperature regions of weight losses

Similarly, for $x= 0.50$ respective weight losses in the regions are 5%, 3%, 13% and 2% confirming further the activity in the exothermic region, i.e. , third region. Again there is a slight decrease in the rate of weight loss with changing temperature compared to the earlier samples. Overall weight loss is 23%., fig.7, and further evidence of the comparative stability of this sample.

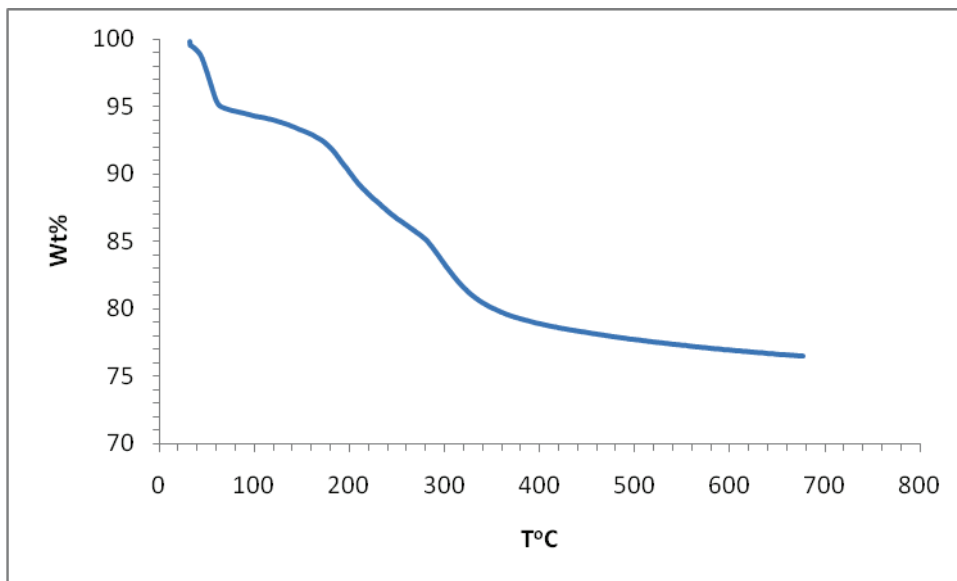


Fig.7. TGA Plot of sample $x= 0.50$ showing the four temperature regions of weight losses

The last sample, $x=0.75$ has respectively, 2%, 2.5% and 5% in the regions with overall weight loss of 25%, fig.8. The weight loss has drastically reduced in the third region to only 5% and beyond, showing that the lithium content at this level has dramatically increased the stability of the sample with the rate of weight loss with increased temperature being the lowest. The results show an increasing stability of the samples with increased lithium content.

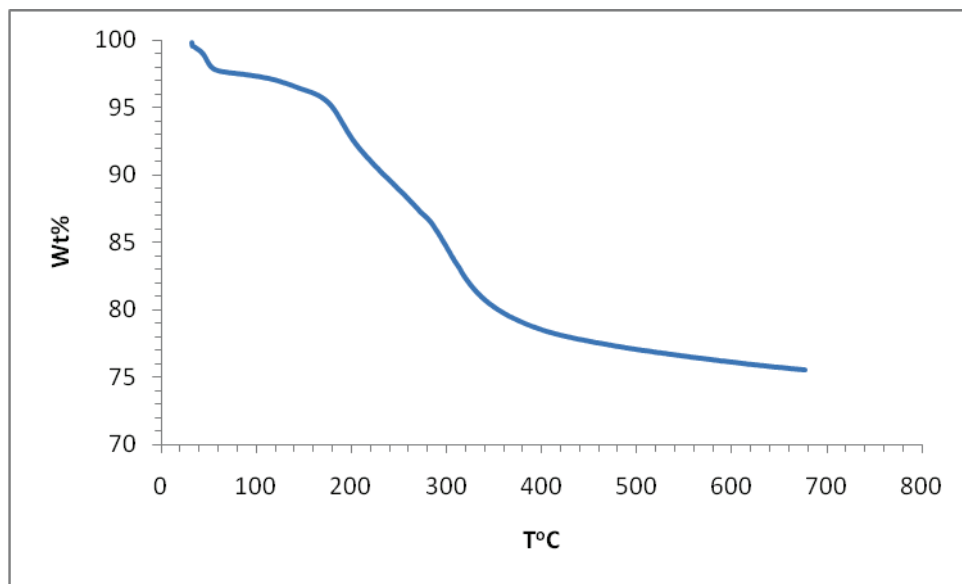


Fig. 8. TGA Plot of sample $x=0.75$ showing the four temperature regions of weight losses

The composite TGA plot is shown in fig.9 for comparison and it is clear that the samples exhibited the same characteristics, with the four temperature domains clearly visible and weight losses occurring at about the same temperature range. Within the temperature range RT-60°C, $x=0.00$ showed the highest weight loss of about 30%, with $x=0.75$ being the least. Similarly, between RT-360°C, the plots maintained a particular order in terms of weight loss with $x=0.75 < 0.50 < 0.25 < 0.00$. The weight loss decreases with increasing lithium content. Beyond this temperature the weight loss for the $x=0.00 > x=0.25$ up to about 500°C, thereafter they maintain virtually the same weight loss. Whereas the $x=0.50$ sample became more stable, with less loss in weight than $x=0.75$ and beyond 360°C. The $x=0.50$ and 0.25 have the same weight loss from RT-170°C, about 5%. The fourth region has the least loss in weight in all the samples and almost the same magnitude. The composite plot is shown in fig.9.

The small weight loss from RT-60°C, visible in all samples except $x=0.75$, may be attributed to loss of the homogenizer acetone. Moreover, loss of Ammonia and water can also be attributed to

the weight loss at up to 150°C whereas weight loss of CO₂ takes place at 260-428°C [17]. The fact that no weight increase was observed throughout, except very small bulges at 81.17, 82.61, 85.70 and 87.61°C in increasing order of sample concentration, which may point to slight increments in weight in the compositions, indicates that the material is stable in air to oxidation [18]. It seems reasonable to say that the decomposition of Na₂CO₃ at 831°C and Li₂CO₃ at 723°C to produce the Na and Li respectively, imply that the latter, although decomposes earlier, is thermally more stable owing to the higher melting (181°C) and boiling points (1342°C) of the elemental substituent (Li) and hence when the substitutions take place in the $x \neq 0.00$ samples, the composition becomes increasingly more thermally stable. The dehydration of the Na₂CO₃.H₂O is expected between 100-150°C [19]. This is also certainly helped by the high reactivity of lithium and thus its bonding within the framework becomes stronger. This therefore explains why the sample $x=0.00$ (no lithium) is the least stable from the composite TGA plots.

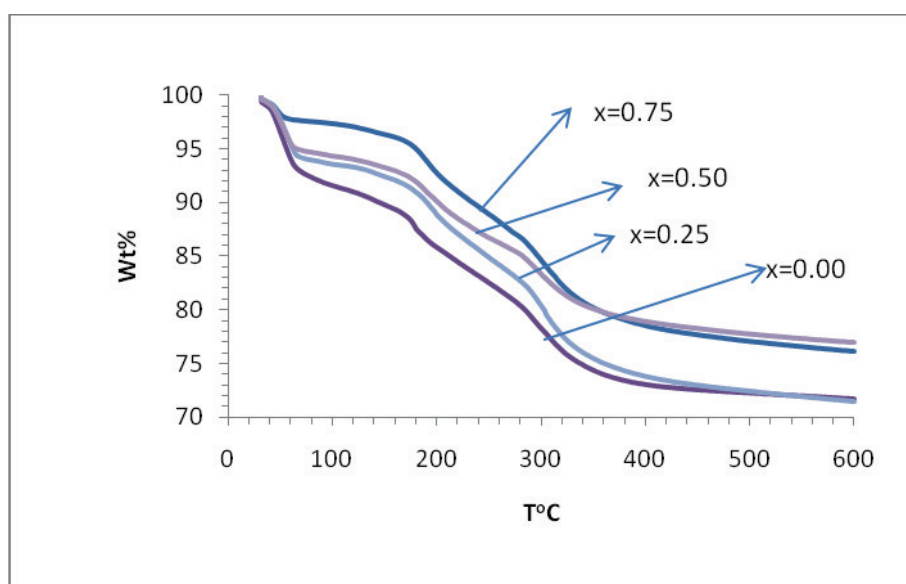


Fig. 9. Composite TGA Plot of Na_{1-x}Li_xZr₂(PO₄)₃ showing the compositions.

4. Conclusion

The systematic Increase in the lithium content of the samples increases the thermal stability of the compounds in particular from 50°C to 350°C owing to the greater thermal stability of lithium. However, $x=0.50$ and 0.75 are more stable throughout the temperature range, as they are clearly separated from the $x=0.00$ and $x=0.25$ and are on the upper side indicating lower weight loss. The samples $x=0.00$ and 0.25 remained clearly distinguished in their thermal behaviour from 69°C until

425°C when they became indistinguishable. Whereas $x=0.50$ and 0.75 had a shorter period of distinguishable thermal behaviour from 69 to 317°C before they became closer. It may be concluded that the threshold for increased thermal stability for the compositions is when the composition is $x=0.50$, as the compositions appear clearly separated into two. The exothermic peaks were observed to shift towards higher temperatures with increased lithium content just as the process itself shifted towards higher temperatures from its lower limits in agreement with the TGA results. Consequently, the thermal stability regions become wider with increased lithium content. There were no peaks observed that could be attributed to any form of structural transformation in the compositions since the NZP is not expected to begin to form until far above 1050°C, beyond the temperature limit of the TGA/DTA. This is very important for electrical conductivity measurements and for structural analyses purposes. It was also possible to establish the sintering temperature for the compositions, which are similar, for the solid state synthesis of these materials. Work is ongoing to characterize the phase and other properties of the compositions before conclusive deductions can be made, though the materials seem to exhibit the typical NZP character from the thermal point of view.

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