The initial study on the synthesis and characterization of NaZr$_2$(PO$_4$)$_3$ from West-Borneo ZrSiO$_4$

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Abstract. Due to its excellent electrical properties, NaZr$_2$(PO$_4$)$_3$-type sodium superionic conductor is a preferred material for the application in energy storages such as sodium ion batteries. Here, the initial study on the synthesis of NaZr$_2$(PO$_4$)$_3$ from Indonesian West-Borneo Zircon is reported. The synthesis was conducted using our facile technique of a sodium carbonate sintering method. Zircon and the carbonate were mixed at a stoichiometry ratio approach and sintered at 1000°C. The sintered product was leached with water to dissolve the silica compound and continued by filtration and washing to obtain the zirconia compound, followed with phosphoric acid blending until pH 5 to get a precipitate. It was calcined at 800°C. The mineralogy, chemical composition, and particle sizes of the calcined product were evaluated. The synthesized sodium superionic conductor consists of NaZr$_2$(PO$_4$)$_3$ with a trigonal structure as the main phase and SiO$_2$ as a minor phase. The SiO$_2$ content is accounting 6% of the total. Particle size analysis measured 90% of the total particle size distribution of the calcined NZP is less than 18.283 µm in sizes, while the average particle size is about 5.633 µm. The present study unveils a facile technique in the synthesis of NaZr$_2$(PO$_4$)$_3$ from Indonesian West-Borneo ZrSiO$_4$.

1. Introduction
Sodium zirconium phosphate known as NZP is an interesting inorganic material due to its unique crystalline structure and properties, such as low thermal expansion, fast and high ionic conductivity, great chemical stability, and high radiation resistance [1-5]. Thus, NZP based material finds application in superionic conductors, the immobilization of radioactive wastes, sensor, and catalysis [3,4,6-8]. In addition, NZP is also a parent compound of sodium superionic conductor (NASICON) comprising no Si [9-11], a ceramic ion conductor that has a general formula of Na$_{1+x}$Zr$_2$P$_3$O$_{12}$ [12-14].

Many methods have been introduced to synthesize NZP materials, such as a conventional solid-state method, solution routes, molten salts, sol-gel processing [3], a microwave technology [1,2,6], hydrothermal synthesis [7], a chemical solution deposition technique [10] and so on. Nevertheless, most of those synthesis methods are commonly used high chemical grades of salts and organometallic compounds for NZP precursor materials and specific instruments, which are less economic and may show some drawbacks when the technologies are applied in a large-scale.

In this paper, the initial study on the synthesis and characterization of NZP from Indonesian West-Borneo zircon (ZrSiO$_4$) is reported using a low-cost, facile technique of a sodium carbonate sintering method. Our previous works demonstrated the method accomplishment in the preparation of...
nanomaterial ZrO$_2$ from ZrSiO$_4$ [15-18]. A low-cost, facile technique of sodium carbonate sintering method basically is the alkaline disintegration process of ZrSiO$_4$ compound in a solid form through sintering process at high temperatures. Meanwhile, ZrSiO$_4$ is a valuable and potential material as a ZrO$_2$ source with its content achieving ~ 65wt.% [15-16]. Thus, the present work focuses on the synthesis of NaZr$_2$(PO$_4$)$_3$ from local ZrSiO$_4$ as the ZrO$_2$ precursor and other technical grade chemicals via a sodium carbonate sintering method. The initial characteristics including crystalline phases, chemical composition, and particle sizes of the synthesized NZP are presented in this paper.

2. Experimental Methods

2.1. Materials

The main chemical as the ZrO$_2$ source used in this initial study was the micronized Indonesian West Borneo zircon (ZrSiO$_4$) obtained from PT. Monokem Surya Indonesia. The chemical composition of zircon consisted of 64.51% of ZrO$_2$, 31.31% of SiO$_2$, and 0.95% of HfO$_2$ as major components. Meanwhile, other chemicals used were technical grade sodium carbonates (Na$_2$CO$_3$), phosphoric acid, carboxyl methyl cellulose (CMC) obtained from a local-chemical market. All chemicals were used without further purification.

2.2. Synthesis of NZP from ZrSiO$_4$

Sodium zirconium phosphate (NZP) was synthesized from ZrSiO$_4$ via a low-cost, facile technique of sodium carbonate sintering method. Zircon was combined with sodium carbonate in solid mass at stoichiometry ratio approach assisted with an organic binder of CMC. Solid mixtures were then sintered at 1000°C in a furnace. The sintered product was then leached by water to dissolve the silica compound, leaving a zirconium compound in residues. The residues were then mixed with phosphoric acid until the pH 5, resulting in white precipitates. The products were filter-pressed, washed several times, dried in an oven, and then calcined at 800°C. The final product was characterized including crystalline phases, chemical composition, and particle sizes.

2.3. Characterization

The mineralogy of the calcined product was investigated by powder X-ray diffraction (XRD) instrument (XRD, D/teX Ultra 250 detector, Rigaku) at 40 Kv and 30 mA with Cu/Kα radiation source. The diffraction patterns were scanned from 2.0000 to 65.0000 (2θ) with an angular step of 0.0100. Furthermore, a Thermo ARL 9900 X-ray fluorescence system was used to analyze chemical compositions of the synthesized NZP. Then, the particle sizes distribution of the synthesized NZP was measured applying a Malvern mastersizer.

3. Results and Discussion

In the synthesis of NaZr$_2$(PO$_4$)$_3$ from Indonesian West-Borneo Zircon through a sodium carbonate sintering method, ZrSiO$_4$ was initially mixed with the alkaline of Na$_2$CO$_3$ in a solid mass. This product was then sintered at 1000°C in a furnace, resulting in a mixture of Na$_2$ZrO$_3$ and Na$_2$SiO$_3$ compounds (as given in the equation 1) [15,17].

\[
\text{ZrSiO}_4 + 2\text{Na}_2\text{CO}_3 \overset{\text{at } 1000^\circ\text{C}}{\rightarrow} \text{Na}_2\text{SiO}_3 + \text{Na}_2\text{ZrO}_3 + 2\text{CO}_2
\]  

(1)

However, the separation of Na$_2$ZrO$_3$ and Na$_2$SiO$_3$ compounds was conducted by water-leaching because of a water-soluble compound of Na$_2$SiO$_3$. This process led to the formation of the aqueous solution of Na$_2$SiO$_3$ and left residual of Na$_2$ZrO$_3$, as shown in the equation 2 [15,17].

\[
\text{Na}_2\text{SiO}_3 + \text{Na}_2\text{ZrO}_3 \overset{\text{H}_2\text{O}}{\rightarrow} 2\text{Na}^+\text{SiO}_2^{2-} \text{aq} + \text{Na}_2\text{ZrO}_3\_\text{s}
\]  

(2)

The products in the equation 2 were then separated through a filtration technique. The residue of Na$_2$ZrO$_3$ was further reacted with phosphoric acid at approximately pH 5 to give white fine materials.
precipitates such as Balm-like solids. The precipitates were washed with aquadest for several times to remove the existing silica compound that attached on the precipitate surfaces and then dried in an oven. The final product was the calcined at 800°C. The calcined product was characterized including mineralogy, chemical composition, and particle sizes.

3.1. The result of XRD investigation of the calcined product

The XRD investigation result on the as-synthesized ZrSiO₄-NZP based after calcination at 800°C was demonstrated in figure 1. As according to PDF2 No.00-033-1312, sodium zirconium phosphate (NaZr₂(PO₄)₃) with a trigonal crystal system was detected by the appearance of its main peaks at the diffraction angles, 2θ, of 19.38°, 20.07°, 23.27°, and 31.04°, corresponding to the (104), (110), (211), (116) crystal planes of the NaZr₂(PO₄)₃ structure. Meanwhile, the minor crystalline phase of SiO₂ in the form of cristobalite polymorph was found at a diffraction angle, 2θ, of 21.86°, corresponding to the (101) crystal plane of the tetragonal cristobalite structure. The SiO₂ finding was based on PDF2 No.00-076-0939.

Based on the XRD result in figure 1, it could be concluded that NaZr₂(PO₄)₃ NASICON-type was successfully synthesized from local ZrSiO₄ through a sodium carbonate sintering method. The residue of Na₂ZrO₃ in the equation 2 was completely reacted with phosphoric acid (H₃PO₄) which resulted a new compound of sodium zirconium phosphate (NaZr₂(PO₄)₃) after calcination process at 800°C, as indicated by equation 3.

\[
2\text{Na}_2\text{ZrO}_3(s) + 6\text{H}_3\text{PO}_4(l) + \text{pH} 5 \rightarrow \text{NaZr}_2(\text{PO}_4)_3 + 3\text{NaH}_2\text{PO}_4 + 6\text{H}_2\text{O} \quad (3)
\]

Figure 1. The XRD identification results on the as-synthesized NZP after calcination at 800°C.

However, the SiO₂ existence in NZP was probably caused during removing a soluble silica compound from a sintered product in the preparation of NZP from ZrSiO₄. Since the sintered product was leached by water to dissolve the silica compound, there should not have been the material in the surface of the zirconium compound especially after water-washing treatment. Nevertheless, when the
silica compound exhibited very fine particles, it would infiltrate into a solid residue of zirconia compound, so the silica compound removing was slightly difficult to be controlled from the zirconia compound. Therefore, the infiltrated silica compound inside the zirconia compound would have transformed to cristobalite in the next calcination process at a higher temperature. Nevertheless, the NZP synthesized from the local raw materials in this work was obtained at a relative low temperature of 800°C.

In addition, our result seems to be different from the finding of Luo et al. [1]. They reported that pure NZP phase had been successfully prepared at 1100 °C. They used sodium carbonate (Na2CO3), ammonium dihydrogen phosphate (NH4H2PO4), and zirconyl nitrate hydrate (ZrO(NO3)2⋅xH2O) as NZP precursors and a microwave-assisted solid-state reaction technique. The issue of the different crystallization temperature of the NZP phase commonly should be governed by the particular synthesis conditions, such as the precursor types, pH and media, temperature, etc.

3.2. Chemical compositions of NZP

The chemical compositions of the synthesized NZP from ZrSiO4 were analyzed using a Thermo ARL 9900 X-ray fluorescence system whose result is presented in table 1. The chemical analysis in table 1 shows the SiO2 presence in NZP sample after calcination at 800°C. It is accounted 6% of the total. This result corroborates the XRD investigation result in the calcined NZP.

| Compound  | m/m (%) | Std.Err. | Element | m/m (%) | Std.Err. |
|-----------|---------|----------|---------|---------|----------|
| P2O5      | 39.93   | 0.24     | Px      | 17.43   | 0.11     |
| ZrO2      | 34.14   | 0.24     | Zr      | 25.27   | 0.18     |
| Na2O      | 13.21   | 0.17     | Na      | 9.80    | 0.13     |
| SiO2      | 6.07    | 0.12     | Si      | 2.84    | 0.06     |
| SO3       | 1.37    | 0.06     | Sx      | 0.547   | 0.023    |
| HfO2      | 0.420   | 0.021    | Hf      | 0.356   | 0.018    |
| Al2O3     | 0.372   | 0.019    | Al      | 0.198   | 0.010    |
| MgO       | 0.144   | 0.007    | Mg      | 0.0867  | 0.0043   |
| MoO3      | 0.135   | 0.010    | Mo      | 0.0898  | 0.0065   |
| Y2O3      | 0.0890  | 0.0044   | Y       | 0.0701  | 0.0035   |
| Fe2O3     | 0.0676  | 0.0034   | Fe      | 0.0473  | 0.0024   |
| CaO       | 0.0667  | 0.0033   | Ca      | 0.0477  | 0.0024   |
| K2O       | 0.0261  | 0.0014   | K       | 0.0217  | 0.0011   |
| TiO2      | 0.0258  | 0.0014   | Ti      | 0.0155  | 0.0008   |
| Am2O3     | 0.0247  | 0.0041   | Am      | 0.0225  | 0.0037   |
| La2O3     | 0.0158  | 0.0022   | La      | 0.0135  | 0.0018   |
| Yb2O3     | 0.0140  | 0.0019   | Yb      | 0.0123  | 0.0017   |
| Sc2O3     | 0.0046  | 0.0010   | Sc      | 0.0030  | 0.0006   |
As previously mentioned, after having leached a sintered product wisely by water solvent, a soluble silica compound of the sintered product was dissolved in the solution and some of its particles attached in a residue of zirconia compound surface. After purification of the residue by water-washing and filter-press treatment were done, there should be no silica in zirconia compound. However, some of the soluble silica compound particles still persisted inside the zirconia compound residue. This phenomenon was proven by silica yield after calcination process on the as-synthesized NZP at 800°C (table 1). Thus, a soluble silica compound is proposed consisting of fine particles, which may infiltrate into a zirconia compound.

3.3. Particle size measurement
Figure 2 demonstrates a particular particle size distribution of the NZP calcined at 800°C, exhibiting a size range of 0.12 –50 µm with an average particle size (D50) of 5.633 µm. In addition, according to the presented volume density curve in figure 2, the calcined NZP consists of particles sizes below 1.481 µm with the population of 10%. Meanwhile, 90% of the total particle size distribution of the calcined NZP is less than 18.283 µm in sizes. According to figure 2, the particle sizes of NZP calcined at 800°C shows a quite wide distribution range, indicating that the NZP particles exhibit dissimilarity.

![Figure 2](image_url)

**Figure 2.** Particle size distribution measured by a Malvern mastersizer of the as-synthesized NZP calcined at 800°C.

4. Conclusion
Sodium zirconium phosphate NASICON-type, NaZr2(PO4)3, was successfully synthesized from Indonesian West-Borneo Zircon via a facile technique of a sodium carbonate sintering method. The initial study shows that the synthesized NASICON consisted of NaZr2(PO4)3 (NZP) with a trigonal
structure as the main phase and SiO$_2$ as the minor phase. Besides, the SiO$_2$ content is accounting 6% of the total. Meanwhile, particle size analysis measured 90% of the total particle size distribution of the final product of NZP is less than 18.283 µm in sizes, while the average particle size is about 5.633 µm.

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