Low temperature synthesis of NASICON NaZr$_2$(PO$_4$)$_3$ powders with the assistance of in situ formed mineralizer

Tao Wang$^{1}$, Jianmin Liu$^{2,*}$, Feng Jiang$^{2}$, Guo Feng$^{2}$, Jian Liang$^{2}$, Lifeng Miao$^{2}$, Qian Wu$^{2}$, Xinbin Lao$^{2}$, Mengting Liu$^{1}$, Weihui Jiang$^{1,2,*}$

$^{1}$School of Material Science and Engineering, Jingdezhen Ceramic University, Jingdezhen, Jiangxi 333403, China
$^{2}$National Engineering Research Center for Domestic and Building Ceramics, Jingdezhen, Jiangxi 333001, China

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Abstract

A new approach was developed to prepare NaZr$_2$(PO$_4$)$_3$ (NZP) powders at low temperature of 330°C. The effect of different molar ratios of ZrO(NO$_3$)$_2$·xH$_2$O to NaH$_2$PO$_4$·2H$_2$O on the synthesis of NZP powders was systematically investigated by XRD, FEM-SEM, TEM, EDS and Raman spectroscopy. The mineralizer NaNO$_3$ was formed in situ due to the mechanochemical reaction between raw materials ZrO(NO$_3$)$_2$·xH$_2$O and NaH$_2$PO$_4$·2H$_2$O during the grinding process. When the optimal molar ratio of Zr: P = 2:6 was used, the NZP powders with high crystallinity, good dispersity and particle sizes in the range of 500–700 nm were obtained. The dense NZP ceramics was obtained by sintering at 1100 °C for 3 h with 2 wt.% ZnO as the sintering aid. The relative density and Vickers hardness of the sintered ceramics reached 93.4% and 704 MPa, respectively.

Keywords: NaZr$_2$(PO$_4$)$_3$, mineralizer, mechanochemical, formation mechanism

I. Introduction

In recent years, the NASICON-type materials (Natrium SuperIonic CONductors) have received growing attention due to their special 3D framework suitable for fast Na$^+$ mobility [1–4]. Rhombohedral NaZr$_2$(PO$_4$)$_3$ (NZP) is the prototype of all the NASICON-type materials, and its structure consists of PO$_4$ tetrahedra and ZrO$_6$ octahedra sharing corners, where Na$^+$ ions are located in the holes between the ZrO$_6$ octahedra. Based on this open 3D framework and multiple ionic sites that can be replaced, NaZr$_2$(PO$_4$)$_3$ is endowed with high ionic conductivity, low thermal expansion, a host for radioactive waste, a fairly large surface area and the ability to accommodate ions in the lattice. These features make NZP one of the most valuable material in the field of sodium batteries, substrate material for electronic packaging, braze fixtures for aircraft engines and for nuclear waste immobilization [5–8].

To date, several methods have been developed to fabricate NaZr$_2$(PO$_4$)$_3$ powders, including the hydrothermal procedure [9], modified thermal decomposition method [8], traditional solid-state method [5,10] and sol-gel synthesis [11,12]. Although hydrothermal procedure can be used to prepare NaZr$_2$(PO$_4$)$_3$ powders at approximately 200 °C [9], some limitations such as long processing time (more than three days), strict preparation conditions (e.g. high pressure) and high pollution (by-product HCl) make it difficult to achieve the mass production. Ordóñez-Regi et al. [8] utilized a modified thermal decomposition method to prepare NaZr$_2$(PO$_4$)$_3$ powders at 800 °C. The whole process required two days and certain hazardous substances such as HF were used to promote the synthesis of intermediate product. In contrast, both sol-gel synthesis and traditional solid-state methods show facile preparation conditions, but a reaction temperature higher than 600 °C and long processing time (≥16 h) are still required in both methods. Especially, a temperature higher than 900 °C is generally demanded in traditional solid-state method although it is advantageous as a solvent-free and has
simpler preparation process than other methods. Thus, it is challenging to develop a facile and solvent-free route to achieve the low temperature synthesis of fine NaZr$_2$(PO$_4$)$_3$ powders with good dispersity and crystallinity. In view of these demands, we have developed a facile and solvent-free solid state reaction to reduce the calcination temperature from 900 to 810 °C with the assistance of in situ formed mineralizer NaCl [13,14]. Importantly, it was found that the declined calcination temperature was greatly dependent on the mechanochemistry process and in situ formed mineralizer, which provided a liquid environment for fast mass transfer at desired temperature.

In this work a new approach was developed to fabricate NaZr$_2$(PO$_4$)$_3$ powders at low temperature of 330 °C. To the best of our knowledge, it is the first attempt to prepare NaZr$_2$(PO$_4$)$_3$ powders at such a low temperature in the absence of solvent. In situ formed mineralizer NaNO$_3$ during the grinding process was found to be essential for the synthesis of high quality powders at low temperature. The effects of molar ratio of Zr to P on the preparation of NaZr$_2$(PO$_4$)$_3$ powders were systematically studied and the formation mechanism of NaZr$_2$(PO$_4$)$_3$ powders at low temperature was also discussed. Furthermore, the as-prepared powders were used to obtain sintered ceramic material and the corresponding properties were determined.

II. Experimental

Zirconium oxyxinate hydrate (ZrO(NO$_3$)$_2$·xH$_2$O, with Zr mass fraction of 26 wt.%) and sodium dihydrogen phosphate dihydrate (NaH$_2$PO$_4$·2H$_2$O) of analytical grade were purchased from Shanghai Aladdin Co. Ltd. and used as starting materials without further purification. In a typical synthesis of NaZr$_2$(PO$_4$)$_3$ powders, 10 mmol ZrO(NO$_3$)$_2$·xH$_2$O and 5 mmol NaH$_2$PO$_4$·2H$_2$O (molar ratio Zr:P = 2:n, n = 3−8) were mixed and ground homogenously in an agate mortar for 15 min. During the mechanical grinding process, the mechanochemistry took place and NaNO$_3$ was formed in situ. Then the precursor mixture was transferred into a corundum crucible with a lid and calcined at 330 °C for 5 h (heating rate 5 °C/min). After natural cooling to room temperature within the shut off furnace, the final NaZr$_2$(PO$_4$)$_3$ powders were obtained by washing the mass 3 times with deionized water and drying at 80 °C for 5 h. According to the previous reports [15,16], impurities such as monoclinc zirconia (m-ZrO$_2$) are easily observed due to the slight volatilization of Na and P elements during calcination, which will result in a declined performance of NZP materials. Thus, excess amounts of NaH$_2$PO$_4$·2H$_2$O are added by design for the preparation of NaZr$_2$(PO$_4$)$_3$ powders (stoichiometric ratio of Zr:P in NaZr$_2$(PO$_4$)$_3$ is 2:3) powders and all the compositions of the reactants are listed in Table 1. The sintered NZP ceramics were obtained by regrinding 1 g of the as-prepared powders with 2 wt.% of ZnO (used as sintering aid) in an agate mortar for 15 min. The milled powders were uniaxially pressed into pellets (ϕ18 × 2 mm) under pressure of 20 MPa and finally sintered at 1100 °C for 3 h in a resistance furnace.

The phase composition of the samples was examined by X-ray diffraction (XRD, DX-2700 B, 40 kV, 30 mA) using Cu Kα radiation. The Rietveld refinements were carried out to attain detailed structure parameters by using the software package GSAS [17,18] and the experimental data were collected in the 5−120° 2θ angular range with a step of 0.02° and counting time of 4 s. The microstructure and chemical composition of the samples were characterized by transmission electron microscope (TEM, JSM-2010) and field-emission scanning electron microscopy (FE-SEM, SU8010) equipped with energy dispersive spectrometry (EDS). The particle size and distribution range of the as-prepared samples were recorded on a Malvern Mastersizer 3000 (UK) dynamic light scattering laser particle size analyser, where $D_{10}$, $D_{50}$, and $D_{90}$ represent the particle sizes corresponding to the cumulative particle size distributions of 10%, 50% and 90%, respectively. Raman spectra in the frequency range of 90–1200 cm$^{-1}$ were obtained on a Ramanspectrometer (Renishaw in Via) using 532 nm incident photons from an Ar ion laser. The bulk densities of the sintered samples were acquired by the Archimedes method. Then the relative density was calculated according to the formula of $\rho/\rho_0 \times 100\%$, where $\rho$ and $\rho_0$ are the bulk density and theoretical density of NZP ($\rho_0 = 3.198$ g/cm$^3$), respectively. The Vickers hardness (HV) of polished specimens was determined by the indentation fracture technique via a Vickers diamond indenter (HV-1000, Shanghai Yanrun Light Machine Co. Ltd, China) with a load of 4.9 N for 10 s. The HV measurements for each sample were performed for three times, and then the average value was calculated.

III. Results and discussion

The phase composition of the samples synthesized with different NaH$_2$PO$_4$·2H$_2$O ratios was examined by XRD. As shown in Fig. 1, a single phase NaZr$_2$(PO$_4$)$_3$ (JCPDS No. 33-1312, space group of R3c) can be observed in the sample P$_3$, whereas the secondary ZrP$_2$O$_7$ and NaPO$_3$ phases were detected in the samples P$_0$–P$_2$ and P$_2$–P$_3$, respectively. It is worth noting that the peak intensity of ZrP$_2$O$_7$ is reduced while the peak intensity of NaZr$_2$(PO$_4$)$_3$ is maintained.

Table 1. Composition of reactants for all prepared samples

<table>
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<tr>
<th>Sample</th>
<th>Zr/P molar ratio</th>
<th>$W_z$ [g]</th>
<th>$W_n$ [g]</th>
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<td>2.340</td>
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<td>2:4</td>
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<td>3.120</td>
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<td>P$_2$</td>
<td>2:5</td>
<td>3.508</td>
<td>3.900</td>
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<tr>
<td>P$_3$</td>
<td>2:6</td>
<td>3.508</td>
<td>4.680</td>
</tr>
<tr>
<td>P$_4$</td>
<td>2:7</td>
<td>3.508</td>
<td>5.460</td>
</tr>
<tr>
<td>P$_5$</td>
<td>2:8</td>
<td>3.508</td>
<td>6.240</td>
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$W_z$ - weight of ZrO(NO$_3$)$_2$·xH$_2$O
$W_n$ - weight of NaH$_2$PO$_4$·2H$_2$O
tensity of NaZr$_2$(PO$_4$)$_3$ get promoted with increasing amount of NaH$_2$PO$_4$·2H$_2$O. This result suggests that the occurrence of ZrP$_2$O$_7$ favours the crystal growth of NaZr$_2$(PO$_4$)$_3$ by providing building blocks of Zr and P. Noticeably, the Zr:P molar ratio in ZrP$_2$O$_7$ is 2:4, which is smaller than that of 2:5 (P$_0$) in NaZr$_2$(PO$_4$)$_3$. In view of the hypothesis that ZrP$_2$O$_7$ is directly generated by the reaction between ZrO(NO$_3$)$_2$·xH$_2$O and NaH$_2$PO$_4$·2H$_2$O, it is necessary to adopt excess amount of NaH$_2$PO$_4$·2H$_2$O for the further synthesis of NaZr$_2$(PO$_4$)$_3$ as shown in Eq. 1. Moreover, the increasing amount of NaH$_2$PO$_4$·2H$_2$O will lead to the formation of the impurity NaPO$_4$ phase (the samples P$_4$ and P$_5$), which is produced by the decomposition of NaH$_2$PO$_4$·2H$_2$O and the decomposition process can be divided into two steps: Eq. 2 at 212–224°C and Eq. 3 at 260–360°C [19]. Interestingly, the amounts of NaH$_2$PO$_4$·2H$_2$O in the samples P$_1$ and P$_2$ are larger than P$_0$, which means that residual NaH$_2$PO$_4$·2H$_2$O will be decomposed into NaPO$_4$ during calcination process. However, no NaPO$_4$ phase is observed in the samples P$_1$ and P$_2$ except for NaZr$_2$(PO$_4$)$_3$ and ZrP$_2$O$_7$ phases. This may be caused by the reaction between ZrP$_2$O$_7$ and NaPO$_4$, and corresponding reaction can be deduced as Eq. 4. In this case, 1 mol NaZr$_2$(PO$_4$)$_3$ can be formed by the reaction of 2 mol ZrP$_2$O$_7$ and 1 mol NaPO$_4$. Furthermore, the intuitive reaction equation for the formation of NaZr$_2$(PO$_4$)$_3$ by ZrO(NO$_3$)$_2$·xH$_2$O and NaH$_2$PO$_4$·2H$_2$O can be obtained by doubling Eq. 1 and then adding it to Eqs. 2 and 3. As shown in Eq. 5, it is clear that the appropriate molar ratio of Zr:P is 2:6, which is also consistent with XRD results.

$$\text{ZrO(NO}_3)_2\cdot x\text{H}_2\text{O} + 2 \text{NaH}_2\text{PO}_4\cdot 2\text{H}_2\text{O} \rightarrow 2 \text{NaNO}_3 + + \text{ZrP}_2\text{O}_7 + (x + 6) \text{H}_2\text{O}$$  

(1)

$$2\text{NaH}_2\text{PO}_4\cdot 2\text{H}_2\text{O} \rightarrow \text{Na}_2\text{H}_2\text{P}_2\text{O}_7 + 5\text{H}_2\text{O}$$  

(2)

$$\text{Na}_2\text{H}_2\text{P}_2\text{O}_7 \rightarrow \text{NaPO}_4 + 2\text{H}_2\text{O}$$  

(3)

$$2\text{ZrP}_2\text{O}_7 + \text{NaPO}_4 + \text{H}_2\text{O} \rightarrow \text{NaZr}_2(\text{PO}_4)_3 + 2\text{HPO}_3$$  

(4)

$$2\text{ZrO(NO}_3)_2\cdot x\text{H}_2\text{O} + 6 \text{NaH}_2\text{PO}_4\cdot 2\text{H}_2\text{O} \rightarrow \text{NaZr}_2(\text{PO}_4)_3 + 4 \text{NaNO}_3 + 5 \text{H}_2\text{O} + (2x + 17) \text{H}_2\text{O}$$  

(5)

To further understand the formation mechanism of NaZr$_2$(PO$_4$)$_3$ at low temperature, the whole reaction process and related equations are discussed. Figure 2 shows the XRD pattern of the P$_3$ precursor mixture dried at 80°C for 5h after the mechanical grinding process. The strongest diffraction peak located at 29° (2θ) is assigned to crystalline NaNO$_3$ (JCPDS No. 85-0850), where Na$^+$ and NO$_3^-$ originate from NaH$_2$PO$_4$·2H$_2$O and ZrO(NO$_3$)$_2$·xH$_2$O, respectively. This result indicates the occurrence of a mechanochemistry combined with the in situ formation of NaNO$_3$ during mechanical grinding. The secondary NaH$_2$PO$_4$ phase (JCPDS No. 70-0954) can be observed due to the dehydration of excess NaH$_2$PO$_4$·2H$_2$O during the drying process [19]. In addition, a phase of Zr(HPO$_4$)$_2$·H$_2$O is also detected, confirming again the occurrence of a mechanochemical reaction during the mechanical grinding. As an inorganic ion exchanger, crystalline Zr(HPO$_4$)$_2$·H$_2$O is easy to be formed at low temperature, even at room temperature [20,21]. Moreover, Zr(HPO$_4$)$_2$·H$_2$O can be decomposed into ZrP$_2$O$_7$ at about 146°C [14]. Thus, it can be deduced that the first reaction between ZrO(NO$_3$)$_2$·xH$_2$O and NaH$_2$PO$_4$·2H$_2$O is to generate Zr(HPO$_4$)$_2$·H$_2$O and NaNO$_3$. As reported in the previous papers about the mechanochemistry of solids [22,23], when crystal hydrates are utilized as raw materials, especially acids and bases, the reaction can be accelerated during the mechanochemical process. Therefore, the mechanochemistry reaction can take place and in situ produces NaNO$_3$ when ZrO(NO$_3$)$_2$·xH$_2$O and NaH$_2$PO$_4$·2H$_2$O are used as raw materials. According to above analysis and our previous investigations of NaZr$_2$(PO$_4$)$_3$ synthesis by ZrOCl$_2$·8H$_2$O and NaH$_2$PO$_4$·2H$_2$O [13,14], all reaction steps for the formation mechanism of NaZr$_2$(PO$_4$)$_3$ with ZrO(NO$_3$)$_2$·xH$_2$O and NaH$_2$PO$_4$·2H$_2$O as starting materials can be described by Eqs. 6–11:

$$\text{ZrO(NO}_3)_2\cdot x\text{H}_2\text{O} + 2\text{NaH}_2\text{PO}_4\cdot 2\text{H}_2\text{O} \rightarrow 2\text{NaNO}_3 + + \text{Zr(HPO}_4)_2\cdot \text{H}_2\text{O} + (x + 4) \text{H}_2\text{O}$$  

(6)
Furthermore, the theoretical reaction of NaZr
\[ \text{Na}_2\text{Zr}_2\text{O}_4 \cdot \text{H}_2\text{O} \rightarrow \text{ZrP}_2\text{O}_7 + 2\text{H}_2\text{O} \]  
(7)

2 NaH\text{H}_2\text{P}_2\text{O}_7 \rightarrow \text{Na}_2\text{H}_2\text{P}_2\text{O}_7 + 5\text{H}_2\text{O} \]  
(8)

2 ZrP\text{O}_7 + \text{Na}_2\text{H}_2\text{P}_2\text{O}_7 \rightarrow \text{NaZr}_2(\text{PO}_4)_3 + \text{NaPO}_3 + 2 \text{H}_2\text{O} \]  
(9)

\[ \text{Na}_2\text{H}_2\text{P}_2\text{O}_7 \rightarrow 2\text{NaPO}_3 + \text{H}_2\text{O} \]  
(10)

2 ZrP\text{O}_4 + \text{NaPO}_3 + \text{H}_2\text{O} \rightarrow \text{NaZr}_2(\text{PO}_4)_3 + 2 \text{HPO}_3 \]  
(11)

Furthermore, the theoretical reaction of NaZr\text{PO}_4\text{H}_4\text{S}_3 synthesis by using ZrO(\text{NaO})\text{H}_2 + \text{NaH}_2\text{PO}_4 \text{H}_2\text{O} as raw materials can be given as Eq. 12:

\[ 2\text{ZrO(\text{NaO})H}_2 \cdot \text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{NaZr}_2(\text{PO}_4)_3 + 4\text{NaNO}_3 + \text{NaPO}_3 + \text{HPO}_3 + (2x + 17)\text{H}_2\text{O} \]  
(12)

where the mass transfer process can be effectively promoted by the intermediate ZrP\text{O}_7 and the liquid environment formed by the molten NaNO\text{O}_3. More importantly, all reaction steps can be conducted at low temperature. For instance, Eq. 6 can happen at room temperature, Eq. 7 can be conducted at about 146 °C, Eq. 8 in the range 212–224 °C and Eq. 10 at 260–360 °C. Equation 9 can be carried out at about 220 °C, and the final Eq. 11 can be conducted at about 340 °C. On the basis of these investigations, the low-temperature synthesis of NaZr\text{PO}_4\text{H}_4\text{S}_3 powders can be realized at 330 °C.

Figure 3 shows the FE-SEM images of the samples P_0–P_5 obtained at 330 °C. The dramatic morphological changes from irregularly-shaped particles (particle size 10–400 nm) to cube-like particles (particle size 500–700 nm) can be found with the increasing ratio of NaH\text{H}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}. In addition, the uniformity and dispersivity of the as-prepared powders are improved from the P_0 to P_4 samples, whereas the uniformity of the sample P_5 decreases. This suggests that the ratio of NaH\text{H}_2\text{PO}_4 \cdot 2\text{H}_2\text{O} plays an important role in the morphology and size control by influencing the crystal growth of NaZr\text{PO}_4\text{H}_4\text{S}_3. It is worth noting that rhombohedral-structured NaZr\text{PO}_4\text{H}_4\text{S}_3 (JCPDS No. 33–1312, space group of R3c) generally crystallize in cube-like shape according to its crystal preference [8,9] and the edges of this shape will be sharper with improving crystallinity. According to this, the morphological and particle size changes of the samples P_0–P_5 can be described in combination with their XRD results. When added amount of NaH\text{H}_2\text{PO}_4 \cdot 2\text{H}_2\text{O} is insufficient (the samples P_0), the precursors cannot be fully dissolved and homogeneously dispersed in the limited flux formed by NaNO\text{O}_3, resulting in the occurrence of unexpected ZrP\text{O}_7 (see Fig. 1) and an inefficient mass transfer. In this case, the obtained sample P_0 shows a low crystallinity and presents irregular shapes composed of small and aggregated particles. With the increase of NaH\text{H}_2\text{PO}_4 \cdot 2\text{H}_2\text{O} addition (the samples P_1 and P_2), the crystallinity of NaZr\text{PO}_4\text{H}_4\text{S}_3 is greatly improved by the reaction between ZrP\text{O}_7 and NaPO\text{O}_3, and more cube-like NaZr\text{PO}_4\text{H}_4\text{S}_3 particles with sharper edges can be observed (Fig. 3b,c). When a superfluous amount of NaH\text{H}_2\text{PO}_4 \cdot 2\text{H}_2\text{O} is used (the sample P_5), the crystal growth of NaZr\text{PO}_4\text{H}_4\text{S}_3 is significantly promoted due to the extensive dissolution of precursors in NaPO\text{O}_3-NaNO\text{O}_3 flux, resulting in the abnormal grain growth of NaZr\text{PO}_4\text{H}_4\text{S}_3. In this case, NaZr\text{PO}_4\text{H}_4\text{S}_3 crystals with various particle sizes will appear in the sample P_5, of which the irregularly-shaped and small particles are assigned to residual NaPO\text{O}_3 phase. In summary, NaZr\text{PO}_4\text{H}_4\text{S}_3 with high crystallinity and good dispersion (the samples P_1 and P_3) can only be achieved when appropriate amount of NaH\text{H}_2\text{PO}_4 \cdot 2\text{H}_2\text{O} is adopted, and the optimum molar ratio of Zr:P is determined to be 2:6 because of the detected impurity phase (NaPO\text{O}_3) in the sample P_4.

Figure 4 shows the corresponding particle size distribution of the samples P_1, P_3 and P_5. It is clear that the Zr:P molar ratio has great influence on the particle size distribution. When the amount of NaH\text{H}_2\text{PO}_4 \cdot 2\text{H}_2\text{O} is insufficient (Fig. 4a) or superfluous (Fig. 4c), the size distribution of the samples is inhomogeneous. When
the molar ratio of Zr:P is 2:6 (Fig. 4b), the as-prepared P3 powders show a sharp peak corresponding to a narrow size distribution, of which $D_{50}$ is 0.63 $\mu$m, $D_{10}$ is 0.39 $\mu$m and $D_{90}$ is 2.52 $\mu$m. These data are consistent with the FE-SEM results and the narrow particle size distribution will ensure a good sintering behaviour of the as-prepared NaZr$_2$(PO$_4$)$_3$ powders.

Figure 5a shows the FE-SEM images and EDS mappings of the sample P3 obtained at 330 °C. The samples are composed of well-distributed cube-like particles with a particle sizes ranging from 400 to 600 nm. In addition, all elements including Na, Zr, P and O show a homogeneous distribution in the crystal particles, and the corresponding EDS spectrum (Fig. 5b) clearly reveals that the molar ratio of Na:Zr:P is approximately 1:2.2:2.5 close to the stoichiometric ratio in NaZr$_2$(PO$_4$)$_3$, indicating that all the elements are homogeneously distributed in the liquid flux without segregation during the crystal growth of NaZr$_2$(PO$_4$)$_3$. As shown in Figs. 6a,b, the obtained NaZr$_2$(PO$_4$)$_3$ powders present a cube-like structure with the average particle size of 500 nm. A clear SAED (selected area electron diffraction) pattern (Fig. 6e) recorded along [110] axis indicates the high crystallinity of the powders, and the three adjacent spots are indexed as (003), (110) and (113) planes, which is in accordance with NaZr$_2$(PO$_4$)$_3$ crystal structure (JCPDS No. 33-1312).

In order to discuss the advancement of this work, synthesis conditions of NaZr$_2$(PO$_4$)$_3$ powders by several methods are listed in Table 2. It is clear that the synthesis conditions of hydrothermal procedure are much stricter than other methods although its reaction temperature is the lowest one. In contrast, synthesis conditions of this work are more suitable for the mass production of NaZr$_2$(PO$_4$)$_3$ powders owing to its low reaction temperature, short processing time, solvent-free and ambient reaction environment. Noticeably, there is a huge breakthrough in this work when compared with our previous work that the reaction temperature is significantly reduced from 810 to 330 °C without the other changes in synthesis conditions. Meanwhile, the resulting products in this work keep having a good dispersity and crystallinity even at such a low temperature.

Figure 7a shows the XRD patterns of the P3 powders and sintered P3 ceramics. Both samples exhibit almost the same diffraction peaks of NaZr$_2$(PO$_4$)$_3$ (JCPDS No. 33-1312) and no other peaks are observed, indicating that the addition of ZnO does not affect the crystal structure of NZP after sintering. To further determine the phase composition, Raman spectra of the P3 powders and sintered P3 ceramics are shown in Fig. 7b. The Raman bands located at 125 ($A_{1g}$), 192 ($A_{1g}$), 261 ($E_g$),
Table 2. Synthesis conditions of NaZr$_2$(PO$_4$)$_3$ powders obtained by several methods

<table>
<thead>
<tr>
<th>Methods</th>
<th>Reaction temperature</th>
<th>Processing time [h]</th>
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292 (A$_{1g}$), 325 (E$_g$), 421 (E$_g$), 434 (A$_{1g}$), 484 (A$_{1g}$), 637 (E$_g$), 1026 (E$_g$), 1061 (E$_g$) and 1083 cm$^{-1}$ (A$_{1g}$) are assigned to typical vibration modes of NaZr$_2$(PO$_4$)$_3$. The bands in range 326–1084 cm$^{-1}$ are attributed to the internal vibrations of PO$_4^{3-}$ where the strongest band at 1026 cm$^{-1}$ arise from the symmetric stretching vibration of PO$_4^{3-}$ unit. The bands at 261, 292 and 325 cm$^{-1}$ are assigned to Zr–O stretching vibration mode. In addition, the bands below 261 cm$^{-1}$ arise from the translations of the Zr and the translations and librations of the PO$_4^{3-}$ [11,26]. Meanwhile, two different Raman bands (697 and 1156 cm$^{-1}$) marked with asterisks are ascribed to O–P–O bonds in NaPO$_3$ [19]. Besides, no other Raman bands such as Zn–O band [27] are observed in the sintered P$_3$ ceramics, which may be attributed to the relatively low content of ZnO adopted in this work. The NaPO$_3$ phase detected by Raman spectroscopy instead of XRD suggests that only a small amount of NaPO$_3$ is contained in the P$_3$ powders. However, the sintered P$_3$ ceramics shows a single phase of NaZr$_2$(PO$_4$)$_3$ without NaPO$_3$, indicating that Na and P elements may be volatile in the form of NaPO$_3$ phase.

Figure 8 shows the typical Rietveld plots of the P$_3$ powders and sintered P$_3$ ceramics, and the corresponding Rietveld refinement results are listed in Table 3. The $R_{wp}$ values for all samples are found to be below 15%, suggesting a good fitting between experimental and theoretical patterns. Obviously, all the sam-
Figure 8. Refinement patterns of: a) \( \text{P}_3 \) powders and b) sintered \( \text{P}_3 \) ceramics obtained with the Rietveld software GSAS.

Table 3. Structural properties of synthesised powder and sintered \( \text{P}_3 \) ceramics

<table>
<thead>
<tr>
<th>Sample</th>
<th>( a = b ) [Å]</th>
<th>( c ) [Å]</th>
<th>Volume [Å³]</th>
<th>Space group</th>
<th>( R_w )</th>
<th>( R_p )</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>JCPDS No. 33-1312</td>
<td>8.8048</td>
<td>22.7572</td>
<td>1527.88</td>
<td>( \text{R}3\text{c} )</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>( \text{P}_3 ) powders</td>
<td>8.8333</td>
<td>22.7912</td>
<td>1540.08</td>
<td>( \text{R}3\text{c} )</td>
<td>7.43%</td>
<td>5.70%</td>
<td>2.263</td>
</tr>
<tr>
<td>( \text{P}_3 ) ceramics</td>
<td>8.8063</td>
<td>22.7608</td>
<td>1528.64</td>
<td>( \text{R}3\text{c} )</td>
<td>7.50%</td>
<td>5.74%</td>
<td>1.907</td>
</tr>
</tbody>
</table>

\( \text{P}_3 \) powders and sintered \( \text{P}_3 \) ceramics crystallize in a rhombohedral structure with space group of \( \text{R}3\text{c} \). However, there is a significant difference of the lattice constants in the \( \text{P}_3 \) powders and sintered \( \text{P}_3 \) ceramics, and the latter one is closer to the standard sample (JCPDS No. 33-1312). This difference may be caused by the insertion of Na\(^+\) into the NaZr\(_2\)(PO\(_4\))\(_3\) structure. Wang et al. [5] have utilized first-principles to investigate the XRD patterns and the relaxed atomic structures of NaZr\(_2\)(PO\(_4\))\(_3\). They found that more Na\(^+\) in a molecule (from 1 to 3) can be inserted into the NaZr\(_2\)(PO\(_4\))\(_3\) structure without destroying it. In this work, when the sample was heated at 330 °C, the \textit{in situ} formed NaNO\(_3\) forms liquid ionic state where a small amount of Na\(^+\) may be inserted into the NaZr\(_2\)(PO\(_4\))\(_3\) structure and leads to an increase in lattice constants. However, the sodium-rich NZP structure such as Na\(_2\)Zr(PO\(_4\))\(_2\) has been proved to be unstable at high temperature (above 900 °C) and easy to transform into stable NaZr\(_2\)(PO\(_4\))\(_3\) phase [28]. Based on this phenomenon, the reduced lattice constants of the sintered ceramics can be explained as following. During sintering process, the slight volatilization of Na and P elements at high temperature (1100 °C) will lead to the disappearance of NaPO\(_3\) phase as discussed in Fig. 7. Meanwhile, the volatilization of the Na\(^+\) will result in the reduced lattice constants of the sintered \( \text{P}_3 \) ceramics, making it close to the more stable phase (JCPDS No. 33-1312).

Figure 9a shows the FE-SEM image of the fractured surface of the sintered \( \text{P}_3 \) ceramics with 2 wt.%

Figure 9. FE-SEM image (fractured surface) with EDS mappings (a) and EDS spectrum (b) of the \( \text{P}_3 \) sintered at 1100 °C.
ZnO addition. It is clear that the sample presents a well-densified microstructure with little porosity, and the grain sizes are obviously increased when compared with the P₃ powders after sintering. In addition, the NZP crystals in the sintered ceramics remain uniform in size as with the P₃ powders (Fig. 3d). In general, NZP bulk ceramics are hard to densify even when fired at a higher temperature (1200–1250 °C) due to the poor sintering activity of the as-prepared NZP powders [29]. It is well known that the mass transfer of liquid-phase sintering is faster than that of solid-phase sintering due to the improved dissolution and migration of the reactants. Thus, the addition of ZnO can act as a sintering aid and effectively promote the densification of NZP materials by forming an eutectic liquid phase of Zn₃(PO₄)₂ with PO₄³⁻ at approximately 1000 °C [29,30]. EDS mappings of the fractured surface indicate that all the elements are homogeneously distributed without segregation during the sintering process. In addition, the EDS spectrum (Fig. 9b) shows that the determined molar ratio of Na:Zr:P = 1:2.1:2.7 is close to the stoichiometric ratio in NaZr₂(PO₄)₃, confirming again that the sintered P₃ ceramics possesses a uniform chemical composition similar to that of the obtained P₃ powders. Moreover, a reduced O content in the sintered P₃ ceramics (Fig. 9b) can be found when compared with the P₃ powders (Fig. 5b). Since the slight volatilization of Na and P elements during sintering process is conducted in the form of NaPO₃ phase, the O content in the sintered P₃ ceramics will get reduced at the same time, resulting in a lower O content in sintered ceramics than in the powders. The sintering properties of the sintered P₃ ceramics are listed in Table 4. The sintered ceramics shows a single phase NaZr₂(PO₄)₃ and its relative density is calculated to be approximately 93.4 %TD, corresponding to a high Vickers hardness up to 704 MPa. These properties are comparable with previous reports [29,30] and suggest that the as-prepared NZP powders in this work are good candidates for preparing sintered ceramics.

### IV. Conclusions

This work developed a new approach to prepare NaZr₂(PO₄)₃ powders at a low temperature of 330 °C. It was found that NaNO₃, essential for the low-temperature synthesis of NaZr₂(PO₄)₃ powders, was produced in situ by mechanochemistry during the grinding process. The optimum molar ratio of Zr:P was 2:6 and an excess amount of NaH₂PO₄·2 H₂O is beneficial to the crystal growth of NZP through the formation of intermediate products. The as-prepared NZP powders with particle sizes of 500–700 nm show a high crystallinity and good dispersity. The relative density of the sintered ceramics with 2.0 wt.% ZnO addition can reached 93.4 %TD by sintering at 1100 °C for 3 h and its Vickers hardness was approximately 704 MPa. Furthermore, this work provides a facile route for the low-temperature synthesis of other compounds.

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**References**


<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase composition</th>
<th>Bulk density (ρ) (g/cm³)</th>
<th>Theoretical density (ρ₀) (g/cm³)</th>
<th>Relative density (ρ/ρ₀)</th>
<th>Vickers hardness (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sintered P₃</td>
<td>NaZr₂(PO₄)₃</td>
<td>2.986</td>
<td>3.198</td>
<td>93.4 %TD</td>
<td>704</td>
</tr>
</tbody>
</table>

Table 4. Properties of the sintered P₃ ceramics


