New Process of Solidification under Low Temperature of Cation Conductive NaSn\(_2\)(PO\(_4\))\(_3\) Synthesized Hydrothermally

R Shimanouchi\(^1\)\(^2\), R Okubo\(^1\) and H Sato\(^1\)

\(^1\)Faculty of Science and Technology, Kochi University, 2-5-1, Akebono-cho, Kochi 780-8520, Japan

Email: rshima@kochi-u.ac.jp

**Abstract.** NaSn\(_2\)(PO\(_4\))\(_3\) hard bulk materials were successfully obtained by low-temperature calcination (~600 °C) from hydrothermally synthesized sols without a powder-press or sintering at high temperature. A hydrothermal reaction was performed at 250 °C for 5 h using an aqueous solution of NaOH, an aqueous solution of SnCl\(_4\), and H\(_3\)PO\(_4\) as starting materials. The ratio of the starting materials was changed, and the range in which NaSn\(_2\)(PO\(_4\))\(_3\) was formed was investigated. As a result, the sample hydrothermally synthesized under the synthesis conditions of Na: Sn: P = 2.75: 0.50: 1.75 was produced as a white sol in a Teflon container. In order to remove Cl from this sol, an immersion treatment with deionized water was performed. After immersion treatment for 3 h, and calcination at 600-900 °C, it was possible to obtain the target substance NaSn\(_2\)(PO\(_4\))\(_3\) as a hard bulk material.

1. Introduction

Ionic conductors are used extensively in modern society. However, in order for these materials to be used in electronics, it is often essential to solidify the powdered material via sintering. NASICON-type compounds are well known as materials with high sodium ionic conductivity and applications in a wide range of functional devices, such as gas sensors and batteries. In order to obtain hardened NASICON ceramics, conventional sintering methods often use temperatures in excess of 1000 °C and long dwelling times to achieve high relative density [1-5].

However, high-temperature sintering processes are energetically disadvantageous because of the high costs associated with high-temperature sintering processes, therefore low-temperature sintering processes are favored. In addition, the production of high-density materials, which is often the aim of high-temperature sintering, is not important for materials intended to be used in gas sensors or batteries. In fact, some porosity of the sensor surface required, as it facilitates reactivity with sensing gases and electrolyte diffusion into the electrode well [6, 7].

Recent reports have detailed techniques for the solidification of inorganic powders to obtain porous bulk materials at low temperatures. Liang et al. reported the preparation of porous NaTi\(_2\)(PO\(_4\))\(_3\) sodium-ion battery anodes by annealing of precursor after immersed in oleic acid, with a well discharge capacity of 201 mAh.g\(^{-1}\) [8]. Miyake et al. have reported the preparation of porous zeolites via hydrothermal synthesis, that exhibit acceptable machinability [9, 10]. Reportedly, hydrothermal method is suitable for producing microcrystalline ceramic powders at lower temperatures and within shorter reaction times compared to solid-state reaction methods [11-14]. Under hydrothermal conditions, it is possible to conduct specific reactions of aqueous solutions at high temperatures (>100 °C) and pressures (>760...
mmHg). As a result, of details provided above, the hydrothermal method is more suitable for inorganic chemical reactions.

NaSn<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> are NASICON-type compounds that have been extensively reported upon regarding their synthesis, crystal structure, and properties [15-20]. However, no reports of the successful application of NaSn<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> compounds available, perhaps due to difficulties associated with the solidification and sintering of these compounds.

In this study, we report a method to obtain a bulk NaSn<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> via low-temperature calcination, and deionizing of a precursor sol.

2. Experimental
For preparation via hydrothermal synthesis, the starting materials used were SnCl<sub>4</sub>, NaOH, and H<sub>3</sub>PO<sub>4</sub>. Aqueous solutions of these compounds were placed in a Teflon-lined mini-autoclave, and then, it was filled with deionized water up to 40% of its capacity. The reaction vessel was placed in an electric furnace and heated at 250 °C for 5 h. The filtrated powder products and sol-like products, separated from the solution by decantation, were washed with deionized water, and dried in a desiccator. The obtained products were then calcined at fixed temperatures in air.

The sol-like products were immersed in deionized water (500 mL) for 1-3 h several times to remove excess ions. They were then dried at 40 °C for 12 h and calcined at a relatively low temperature of 600 – 900 °C.

Powder X-ray diffraction (XRD) measurements were performed on a Rigaku RINT-2000 X-ray diffractometer, operated at an acceleration voltage of 40 kV (20 mA) over the diffraction angle (2θ) range from 5° to 75°, using Cu-Kα radiation. The microstructures of the products were observed by scanning electron microscopy (SEM, JSM-6500F). For bulk materials, the Vickers hardness was measured using MVK-EIII (Akashi Manufacturing Co., Ltd.). The measurement was carried out by averaging the values measured ten times for one sample using a weighted 100 g for 10 seconds.

3. Results and discussion
3.1. Preparation of crystalline powders
Most of the samples hydrothermally synthesized in this study were produced as powders. However, under the synthesis conditions Na : Sn : P = 2.75 : 0.50 : 1.75 and 3.00 : 0.50 : 1.50, the samples after hydrothermal synthesis were a hydrated, sol-like, soft, and transparent material.

Figure 1. XRD patterns of samples synthesized via the hydrothermal method at various Na : Sn : P reagent ratios, and calcined at 900 °C for 24 h.
First of all, in order to investigate the relationship between the reagent ratios and the formed crystal phase, we prepared calcined crystalline powders for all the samples. The sol-like substances were taken out from a reaction vessel, dried in a desiccator, ground to a powder, and washed with deionized water using vacuum filtration. Each sample was then sufficiently dried at room temperature, and calcined at 900 °C for 24 h in an electric furnace.

Figure 1 shows the XRD patterns of the products obtained when the ratio of Na was changed. As shown in this figure, the phases formed changed according to the reagent ratios, where sodium phosphate was formed under conditions where the Na ratio was relatively high. The formation of NaSn$_2$(PO$_4$)$_3$ was confirmed when the Na ratio was low. A pure single phase of NaSn$_2$(PO$_4$)$_3$ was obtained as a powder from a reagent ratio at Na : Sn : P = 2.75 : 0.50 : 1.75 (Figure 1). Including these results, Figure 2 shows a formation diagram created by synthesizing crystalline samples at various reagent ratios. From this data it is clear that pure crystalline NaSn$_2$(PO$_4$)$_3$ powder was produced under conditions p and condition j in Figure 2.

![Figure 2. A formation diagram of samples synthesized via calcination at 900 °C for 24 h after the hydrothermal preparation at various reagent ratios of Na : Sn : P.](image)

3.2. Preparation of bulk material of NaSn$_2$(PO$_4$)$_3$

As mentioned above, a hydrothermally prepared precursor of NaSn$_2$(PO$_4$)$_3$ was a hydrated, sol-like, soft and transparent material as shown in Figure 3. After drying and calcination at 800 °C, a bulk material was obtained. However, the XRD pattern of this material was another phase that was not NaSn$_2$(PO$_4$)$_3$, due to the presence of chloride ions. In the case of a powder sample, impurities can be removed via vacuum filtration, following which crystalline NaSn$_2$(PO$_4$)$_3$ could be obtained by subsequent calcination as shown in Figure 2.
To remove the chloride ions, the bulk material was immersed in deionized water (500 mL) for 1 h, and again in fresh deionized water 1-3 times. A longer immersion treatment (3 h) without exchanging the deionized water was also attempted.

XRD patterns of each sample (Figure 4) were obtained following the immersion treatment, drying at 40 °C (12 h), and calcination at 800 °C (12 h). The immersion process of one hour and more resulted in the disappearance of the initial phase, and a single phase of the target substance NaSn$_2$(PO$_4$)$_3$ was obtained. Results obtained from the EDS analysis (Figure 5) demonstrated that the amount of chloride ions contained in the sample was reduced in proportion to the number of times the immersion treatment was performed, with their presence undetected following three 1 h treatments. Further, no difference was observed between the three 1 h treatments and one 3 h treatment.

**Figure 3.** Photograph of hydrothermally prepared sol-like material obtained under p conditions

**Figure 4.** XRD patterns of samples dried at 40 °C for 12 h and calcined at 800 °C for 12 h after immersion treatments of the sol-like materials.
Figure 5. Chloride ion content measured by EDS of samples dried at 40 °C for 12 h and calcined at 800 °C for 12 h after immersion treatments of the sol-like materials.

The bulk samples subjected to the immersion treatment for 3 h were calcined at 600-900 °C for 12 h. The SEM images of these calcined bodies are shown in Figure 6. In the sample calcined at 600 °C, the aggregation of uniform particles of approximately 1 μm (dia.) was observed, which is characteristic of powders obtained via hydrothermal synthesis. Further, after calcination at 700 °C, the reaction between the particles could be observed. Following calcination at 800 °C or 900 °C, a uniform surface of bulk material was observed.

Figure 6. SEM images of bulk materials of NaSn2(PO4)3 calcined at various temperatures for 24 h after immersion treatment for 3 h.
Conventionally, the preparation of ceramics involves powder grinding and pressure molding. In our samples, these processes were not employed. As a result, the obtained materials were expected to exhibit inferior homogeneity and hardness. To evaluate the hardness of these samples, Vickers hardness measurements of the immersed and calcined bulk materials of NaSn$_2$(PO$_4$)$_3$ were conducted (Figure 7). The Vickers hardness of the samples calcined at 600 °C was ~80 kgf.mm$^{-2}$, whereas that of the samples calcined >700 °C was ~110 kgf.mm$^{-2}$. Whilst these values are relatively low, indicating the prepared materials are not that dense or hard. However, it is sufficient as a material for sensors or batteries if it has the strength to be processed, it does not need to be harder than necessary. Miyake et al. have reported about porous ZSM-5 bulk bodies prepared by a one-pot hydrothermal method were found to exhibit acceptable machinability with some hardness. [9] We have now established a method for preparation of NaSn$_2$(PO$_4$)$_3$ materials that are hard enough to be considered sufficient for use as sensors or electrolyte materials.

**Figure 7.** Change in Vickers hardness of bulk materials of NaSn$_2$(PO$_4$)$_3$ calcined at various temperatures for 24 h after immersion treatment for 3 h.

4. **Conclusions**
From the results of this investigation, at the conditions of (Na : Sn : P, 3.00 : 0.50 : 1.50) and (Na : Sn : P, 2.75 : 0.50 : 1.75), a single phase NaSn$_2$(PO$_4$)$_3$ could be obtained by calcination of the immersed bulk material in deionized water. NASICON-type materials generally require high sintering temperatures of 1000 °C or more. In this case, a bulk material could be obtained at a low temperature and within a short time (600–900 °C and 12 h, respectively). The process of subjecting the hydrothermal-synthesized sol-like substance to an immersion treatment with deionized water, drying, and calcination, is highly advantageous, as this method involves significantly reduced energy of preparation compared to the conventional sintering method.

**Acknowledgements**
We thank the Research Laboratory of Hydrothermal Chemistry, Kochi University, for enabling the synthesis of the materials at high temperatures and measurements of Vickers hardness. We also thank the Center for Advanced Marine Core Research, Kochi University, for SEM-EDS measurements.
References

[1] Hong H Y-P, Goodenough J B and Kafalas J A 1976 Fast Na⁺-ion transport in skeleton structures
Mater. Res. Bull. 11 203–20

[2] Hong H Y-P 1976 Crystal structures and crystal chemistry in the system Na₁₋ₓZrₓSi₃P₃₋ₓO₁₂ Mater.
Res. Bull. 11 173–82

[3] Bohnke O, Ronchetti S and Mazza D 1999 Conductivity measurements on nasicon and nasicon-
modified materials Solid State Ionics 122 127–36

[4] Fuentes R O, Figueiredo F M, Marques F M B and Franco J I 2001 Influence of microstructure
on the electrical properties of nasicon materials Solid State Ionics 140 173–9

[5] Fuentes R O, Figueiredo F M, Marques F M B and Franco J I 2001 Processing and electrical
properties of nasicon prepared from yttria-doped zirconia precursors J. Eur. Ceram. Soc. 21
737–43

[6] Pašciak G, Mielcarek W, Prociów K and Warycha J 2014 Structural and electrical studies of
nasicon material for NO₃ sensing Ceram. Int. 40 12783–7

[7] Huang Z, Liu L, Yi L, Xiao W, Li M, Zhou Q, Guo G, Chen X, Shu H, Yang X and Wang X 2016
Facile solvothermal synthesis of NaTi₂(PO₄)₃/C porous plates as electrode materials for high-
performance sodium ion batteries J. Power Sources 325 474–81

[8] Liang J, Fan K, Wei Z, Gao X, Song W and Ma J 2018 Porous NaTi₂(PO₄)₃@C nanocubes as
improved anode for sodium-ion batteries Mater. Res. Bull. 99 343–8

[9] Igi E, Kameshima Y, Nishimoto S and Miyake M 2015 Separation of alcohol/water mixtures by
zsm-5 bulk bodies prepared with a one-pot hydrothermal method Microporous Mesoporous
Mater. 208 160–4

[10] Igi Y K E, Nishimoto S and Miyake M 2012 Fabrication of large porous zsm-5 bulk bodies by a
one-pot hydrothermal method J. Eur. Ceram. Soc. 32 1441–6

[11] Rendon-Angeles J C, Yanagisawa K, Matamoros-Veloz Z, Pech-Canul M I, Mendez-Nonell J
and Diaz-de la Torre S 2010 Hydrothermal synthesis of perovskite strontium doped lanthanum
chromite fine powders and its sintering J. Alloys Compd. 504 251–6

[12] Drofenik M, Ban I, Makovec D, Žnidarič I, Jagličič Z, Hanžel D and Lisjak D 2011 The
hydrothermal synthesis of super-paramagnetic barium hexaferrite particles Mater. Chem. Phys.
127 415–9

[13] Matsumoto Y and Shimanouchi R 2016 Synthesis of Al₂(MoO₄)₃ by two distinct processes,
hydrothermal reaction and solid-state reaction Procedia Eng. 148 158–62

[14] Shimanouchi R, Takatsuka A, Ozeki R and Kawano Y 2019 Preparation and electric conductivity
of Na₃Al₂(PO₄)₃ ceramic from a hydrothermally synthesized precursor Mater. Chem. Phys.
238 121927

[15] Carrasco M P, Guillem M C and Alamo J 1992 Synthesis and structural study of NaTi₂(PO₄)₃-
NaSn₃(PO₄)₃ solid solutions. I. The effect of composition on lattice parameters Mater. Res.
Bull. 27 603–10

[16] Rodrigo J L and Alamo J 1991 Phase transition in NaSn₃(PO₄)₃ and thermal expansion of NaMiv₂
(PO₄)₃; Miv = Ti, Sn, Zr Mater. Res. Bull. 26 475–80

[17] Carrasco M P, Guillem M C and Alamo J 1993 Structural study, thermal expansion and electrical
conductivity of the composition NaSnZr(PO₄)₃ Solid State Ionics 63–5 688–91

[18] Alamo J and Rodrigo J L 1992 High temperature neutron diffraction study of sodium di-tin tri-
phosphate Mater. Res. Bull. 27 1091–8

[19] Govindan Kutty K V, Asuvathraman R, Mathews C K and Varadaraju U V 1994 Effect of
variation in frame work composition on the thermal expansivity of nzp phases Mater. Res.
Bull. 29 1009–16

[20] Liu B, Xing Y, Sun X, Liu X and Hou S Y 2009 Microemulsion-mediated solvothermal synthesis
and characterization of NaSn₃(PO₄)₃ nanocubes Mater. Lett. 63 2548–51