

# Crystal structure and electric conductivity of the NASICON-related solid solution $\text{NaTi}_2\text{P}_{3-x}\text{As}_x\text{O}_3$ synthesized hydrothermally

R. SHIMANOUCI-FUTAGAMI, M. NISHIMORI, H. NISHIZAWA  
 Kochi University, 2-5-1 Akebono-cho, Kochi City, Kochi 780, Japan  
 E-mail: rfuta@cc.kochi-u.ac.jp

$\text{NaTi}_2(\text{PO}_4)_3$  (NTP) has a NASICON-type crystal structure belonging to the space group  $R\bar{3}c$ . It consists of a three-dimensional network made up  $\text{TiO}_6$ -octahedra sharing the corners with  $\text{PO}_4$ -tetrahedra. Since Goodenough *et al.* [1] first reported the high conductivity of NASICON, much work has been devoted to synthesis of the analogous compounds [2–5]. This crystal structure is one of the most suitable structures for cation conduction. It is recognized that the preparation of solid solutions between NTP and other similar compounds with different size tetrahedral units, for example  $\text{AsO}_4^{3-}$ , results in a material with a higher cationic migration and higher electric conductivity.

The preparation of well-sintered ceramics is indispensable for applying these cation-conducting materials to sensors [6, 7], solid-cell type electrodes, and other electric devices. The hydrothermal method is very suitable for preparing fine powder materials, and for easily preparing a wide range of compounds of various chemical species, especially in solid solution. In this letter, we report the hydrothermal synthesis of arsenic-substituted NTP and discuss its electric conductivity associated with the crystallographic properties of the sintered materials.

The starting material for the hydrothermal reaction was prepared by the following coprecipitation method.  $\text{TiCl}_4$  was added with stirring to distilled water cooled by ice. The resulting yellow  $\text{TiCl}_4$  aqueous solution was combined with a solution of  $\text{NH}_3$ , resulting in a thick yellowish-white precipitate. The semipermeable white gel,  $\text{Ti}(\text{OH})_4$ , was obtained by washing with distilled, deionized water and air drying. For the autogenously hydrothermal reaction, the gel-like  $\text{Ti}(\text{OH})_4$ , 85%  $\text{H}_3\text{PO}_4$ ,  $\text{H}_3\text{AsO}_4$ , and  $\text{NaOH}$  aqueous solutions were put into a Teflon-lined mini-autoclave with a capacity of  $30\text{ cm}^3$ . The ratios of these materials were controlled with constant Na concentration in the reaction vessel. The autoclave was heated in an electric furnace for 5 h at a temperature of  $250^\circ\text{C}$ . After air cooling the vessel, the powdered white product was recovered by filtration, washed with distilled and deionized water, and dried in a desiccator at room temperature.

The crystalline products were identified by means of X-ray powder diffraction (XRD) using a Rigaku RAD-2C with monochromated  $\text{Cu K}\alpha$  radiation. Chemical analysis of the elements Na, Ti, P, and As was performed on the acid solution of the powder sample

using an ICP, Seiko-Electron SPS7000A. Fine powder samples were pressed under a pressure of 200 MPa and formed into pellets of 13 mm diameter, and sintered at  $1000^\circ\text{C}$  for 6 h. Electric conductivity was measured on the sintered-pellet samples using evaporated gold electrodes. Complex impedance was measured using an LCR meter (HP4284A) in a frequency range from 20 Hz to 1 MHz, at temperatures from about 200 to  $800^\circ\text{C}$ . Refinement of the crystal structure of the sintered samples was performed by Rietveld analysis based on powder X-ray patterns. The patterns were recorded in  $0.04^\circ$  [2 $\theta$ ] steps between 10 and  $135^\circ$  [2 $\theta$ ] counting for 20 s. per point. Refinement of structure parameters was performed using the RIETAN program under the presence of the imagery atoms being partially P and partially As [8, 9].

XRD patterns of the hydrothermally synthesized samples are shown in Fig. 1. The nature of the crystalline phases in the products was shown to depend upon the ratio of P to As in the starting materials. On these as-prepared samples, a pure single phase with the NTP structure was obtained at ratios of P : As between 9 : 1 and 6 : 4. Chemical analysis by ICP indicated that

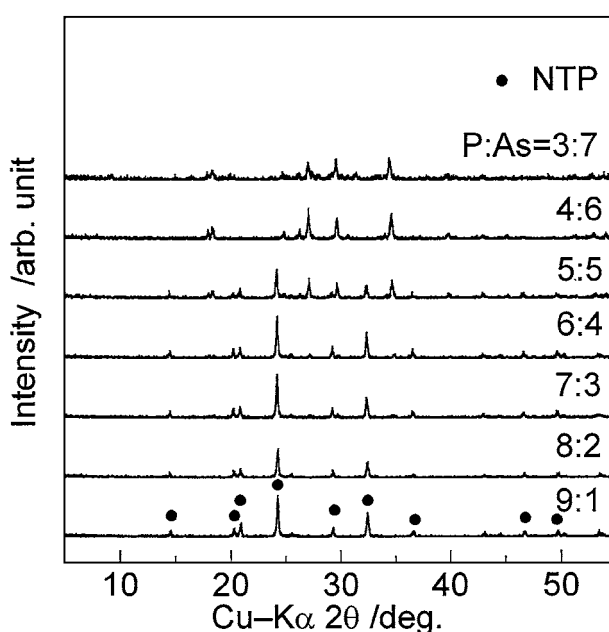


Figure 1 X-ray powder diffraction patterns of the hydrothermally synthesized crystalline samples with the ratios of P : As in the starting materials.

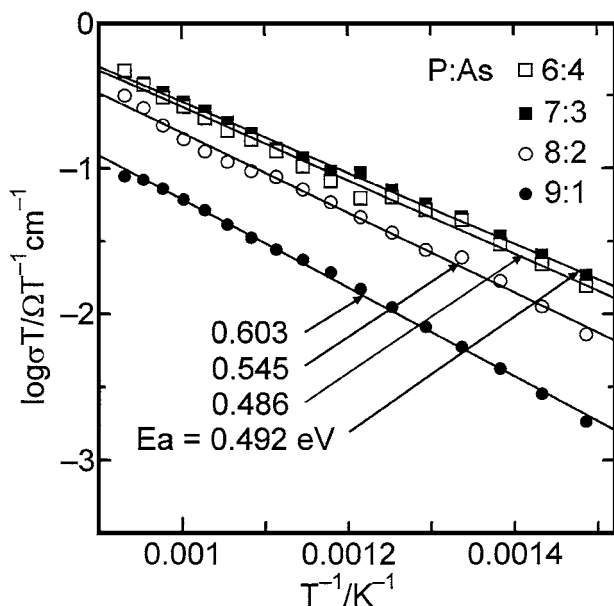


Figure 2 Arrhenius plots of the electric conductivity of the sintered samples determined by the complex impedance method.

P:As ratios in the synthesized powder samples were maintained as the same value as the starting materials ratios. These hydrothermally prepared fine crystalline powders were well sintered at 1000 °C for 6 h. Though they are sintered at a high temperature, an NTP-type single phase without impurities was obtained under the same materials ratio conditions.

Fig. 2 shows the Arrhenius plots of the conductivity of the sintered samples determined by the complex impedance method. The logarithm of the conductivity changed linearly versus  $1/T$  over a wide range of temperatures. The conductivity increased and the activation energy decreased with the substitution of As for P. A similar correlation between electric conductivity and amount of substituted element of solid solution has been

TABLE II Change of lattice parameters and bond distances of the tetrahedral unit, (P,As)-O<sub>4</sub>, in NTP structure with the ratios of P:As

P:As	9:1	8:2	7:3	6:4
Lattice parameters (nm)				
<i>a</i>	0.8501	0.8511	0.8504	0.8513
<i>c</i>	2.1762	2.1781	2.1786	2.1804
Lattice volume (nm <sup>3</sup> )				
<i>V</i>	1.3619(7)	1.3663(2)	1.3643(5)	1.3685(8)
Bond distances (degree)				
P,As-O(1)	0.1520(5)	0.1540(6)	0.1592	0.1596
P,As-O(2)	0.1540(6)	0.1578(8)	0.1590(4)	0.1620(3)

reported for boron-substituted NTP [10]. In the case of boron-substituted NTP or other related NASICON-type solid solutions [10, 11], enrichment with Na<sup>+</sup> enhanced conductivity because the concentration of charge carriers increased. Though, in the case of arsenic-substituted NTP, the amount of charge carrier Na<sup>+</sup> was kept constant when the amount of substituted element was increased. We must devote our attention to another factor causing higher electric conductivity in the system. As well as charge carrier concentration, structural properties are also important factors in determining electric conductivities.

Table I shows the crystallographic and structural parameters, and the selected bond distances obtained by Rietveld analysis for the sintered sample of the ratio of P:As = 9:1, NaTi<sub>2</sub>(P<sub>0.9</sub>As<sub>0.1</sub>)<sub>3</sub>O<sub>12</sub>. Rietveld analysis of XRD patterns provided efficient structural parameters for other samples as well as NaTi<sub>2</sub>(P<sub>0.9</sub>As<sub>0.1</sub>)<sub>3</sub>O<sub>12</sub>. Table II shows the change of the lattice parameters and the bond distances of tetrahedral unit in NTP structure with the amount of substituted arsenic. Both the *c*-parameter and lattice volume increased with the change of P:As from 9:1 to 6:4. Solid-solution type materials were considered to be formed below the 6:4

TABLE I Crystallographic and structural parameters, and selected bond distances for NaTi<sub>2</sub>(P<sub>0.9</sub>As<sub>0.1</sub>)<sub>3</sub>O<sub>12</sub> calculated by Rietveld analysis of XRD patterns

Space group	$R\bar{3}c$ (No. 167, setting 2 : hexagonal lattice)				
Unit cell parameter	$a = 0.850(1)$ nm				
	$c = 2.176(2)$ nm				
	$V = 1.3619(7)$ nm <sup>3</sup>				
	$Z = 6$				
	$D = 3.0491(8)$ g/cm <sup>3</sup>				
R factors (%)					
$R_{\text{wp}} = 9.80$	$R_{\text{p}} = 7.47$	$R_{\text{e}} = 2.15$			
Atomic parameters					
Atom	Sym. pos.	$x$	$y$	$z$	$B$
Na	6(b)	0	0	0	2.344(3)
Ti	12(c)	0	0	0.1449	0.551
P, As	18(e)	0.2863(2)	0	0.25	1.100(1)
O(1)	36(f)	0.1746(5)	−0.0245(5)	0.1925(1)	0.455(2)
O(2)	36(f)	0.1928(9)	0.1601(1)	0.0886(7)	0.283
Selected atomic distances and angles					
Distances (nm)	Angles (deg.)				
Na-O(2) = 0.2456(2)	O(2)-Na-O(2) = 64.801				
Ti-O(1) = 0.1905(6)	O(1)-Ti-O(1) = 93.240				
	O(2)-Ti-O(2) = 84.837				
	O(1)-Ti-O(2) = 89.334				
P,As-O(1) = 0.1520(5)	O(1)-P,As-O(1) = 112.478				
P,As-O(2) = 0.1540(6)	O(2)-P,As-O(2) = 112.387				
	O(1)-P,As-O(2) = 110.195				

value because the lattice parameters changed continuously with the ratio of the chemical species. This indicates a change of lattice parameters to conform to the size of a new tetrahedral unit, (P,As)-O<sub>4</sub>. The larger cell-volumes in these NASICON-type structures with higher arsenic-substitutions must be a result of the different ionic radii of P<sup>5+</sup> and As<sup>5+</sup>. Bond distances between the imagery atom, being partially P and partially As at each ratio, and coordinated O at the tetrahedral unit, (P,As)-O<sub>4</sub>, are also shown in Table II. The distances obviously increase with an increase in arsenic-substitution, and this natural characteristic of the crystal structure may cause a decrease in the activation energy of ionic migration.

In the present work, the NASICON-type solid solution NaTi<sub>2</sub>P<sub>3-x</sub>As<sub>x</sub>O<sub>3</sub> was obtained as a fine powder by means of a hydrothermal method. For this material, the electric conductivity increases with increases in the As content of the chemical composition. The reason for the enhancement of electric conductivity is confirmed to be the change of crystal structure, especially the size of (P,As)-O<sub>4</sub> tetrahedra, as determined by Rietveld analysis.

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