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Synthesis and crystal structure of $Na_4Sn_3O_8$

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A new ternary Na–Sn–O compound, $Na_4Sn_3O_8$, has been synthesized from a mixture of Na_2CO_3 and SnO_2 by heating at 1270–1400 °C for 6–24 h in air using a powder bed. The crystal structure of $Na_4Sn_3O_8$ has been refined by the Rietveld analysis of the powder X-ray diffraction data. $Na_4Sn_3O_8$ crystallizes in the cubic system ($a = 9.1815(2)$ Å, $Z = 4$) with the space group of either $P4_332$ or $P4_132$. The unit cell contains twelve SnO_6 and four NaO_6 octahedra connecting by edge-sharing and additionally twelve sodium atoms distributed in octahedral holes.

Introduction

For the past several decades, sodium ion conductors have received great interest. Sodium β-alumina is the most remarkable of these due to its important application in advanced sodium–sulfur batteries.[1] The discovery of NASICON accelerated the consideration of the relationship between crystal structure and ionic conduction.[2,3]

Tin double oxides, *e.g.* $CdSnO_3$, Cd_2SnO_4[4] and Zn_2SnO_4,[5] which are n-type semiconductors, have been studied as promising transparent conducting oxides due to their transparency and relatively high electrical conductivity. Therefore, Na–Sn–O ternary system compounds are very interesting because their transport properties may show either ionic or electronic conduction.

Recently, $Ag_4Hf_3S_8$[6] and $Ag_{3.8}Sn_3S_8$,[7] which exhibit relatively high ionic conductivity, have been discovered. Single crystals of both sulfides were grown, and it was established that both compounds crystallize in the cubic system with the space group of $P4_332$ for $Ag_4Hf_3S_8$ and $P4_132$ for $Ag_{3.8}Sn_3S_8$. Here, mobile silver ions are located at tetrahedral sites in $Ag_4Hf_3S_8$ and octahedral sites in $Ag_{3.8}Sn_3S_8$.

We have synthesized the previously unreported $Na_4Sn_3O_8$, which appears to have a crystal structure related to $Ag_4Hf_3S_8$ and $Ag_{3.8}Sn_3S_8$. We report here the synthesis and the crystal structure of $Na_4Sn_3O_8$. The preliminary data of the electrical conduction in $Na_4Sn_3O_8$ are also given.

Experimental

Powders of SnO_2 and dried Na_2CO_3 were mixed in appropriate proportions (Na : Sn = 1–1.5 : 1). A part of the mixture was pressed into pellet form (6 mm in diameter and 4 mm in thickness) by uni-axial pressing at 2 MPa. The powder mixture (*ca.* 2 g, as powder bed) and pellet sample were put into an alumina crucible, and covered with an alumina lid to restrict vaporization. The sample was calcined at 1200–1400 °C for 6–48 h in air.

For characterization, powder X-ray diffraction analysis (Rigaku, Co. Ltd., RINT 2000 PC) was performed for phase identification. The crystal structure was refined by the Rietveld analysis of the powder X-ray diffraction data using the RIETAN-2000 program.[8] The density of the powdered sample was determined by displacement in *o*-xylene using a pycnometer. The electrical conductivity of the sample was measured by the impedance method (Yokokawa Hewlett Packard Ltd., LH4192A) at 400–800 °C.

Results and discussion

Fig. 1(A) shows the XRD pattern of the mixture of Na_2CO_3 and SnO_2 (Na : Sn = 1.33 : 1) calcined at 1300 °C for 6 h using the powder bed. These diffraction peaks cannot be indexed on any known Sn–O and Na–Sn–O compounds, and we describe it here as the 'α-phase'. The single phase of the α-phase was obtained when the nominal composition was Na : Sn = 1.33 : 1 (=4 : 3). Na_2SnO_3 was detected in addition to the α-phase when the nominal composition of Na : Sn was over 1.33, and SnO_2 was detected when it was under 1.33. The color of the α-phase is white. The role of the powder bed was to restrict the vaporization of the Na component. Otherwise, SnO_2 was detected in the sample exposed directly to air under the same calcining conditions [Fig. 1(B)].

The relationship between the products and calcining conditions was examined. The nominal composition was fixed to Na : Sn = 4 : 3. The X-ray diffraction analysis detected Na_2SnO_3, $Na_2Sn(OH)_6$, and SnO_2 if the heating temperature was below 1260 °C (for 6–48 h), while the single phase of the α-phase was obtained with a temperature of 1270–1400 °C (for

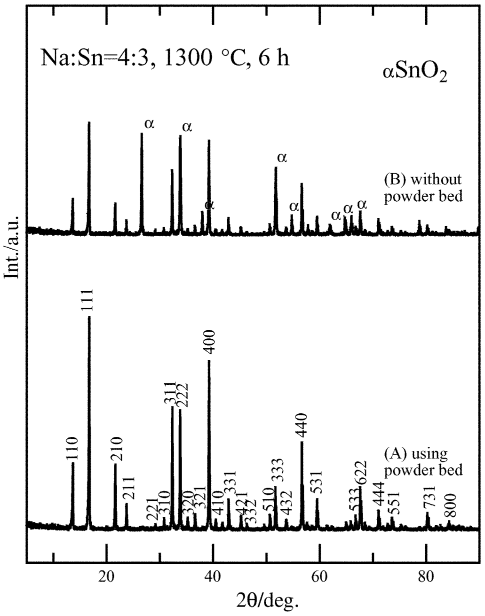

Fig. 1 XRD patterns of Na_2CO_3 + SnO_2 (Na : Sn = 4 : 3) calcined at 1300 °C for 6 h: (A) using the powder bed and (B) without the powder bed.

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Table 1 Powder X-ray Rietveld refinement for $Na_4Sn_3O_8$

Chemical formula	$Na_4Sn_3O_8$
Formula weight	576.06
Space group	$P4_132$ (no. 213)
a/Å	9.1815(2)
V/Å^3	774.00(3)
Z	4
$D_c/10^3$kg m^{-3}	4.94
Powder color	White
X-Ray radiation	CuKα
Monochromator	Graphite
2θ Range/°	10.00–130.00
Step width/°	0.03
No. of data points	4001
Counting time/s step^{-1}	5
T/°C	20
No. of reflections	656
No. of refined parameters	36
No. of structual parameters	16
Reliability factors:	
R_{wp}/%	18.21
R_P/%	12.76
R_I/%	6.80
R_F/%	4.49
S	1.575

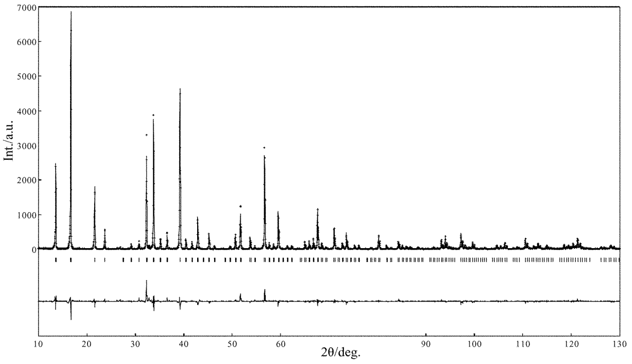

Fig. 2 Observed, calculated and difference profiles resulting from the Rietveld analysis of the powder X-ray diffraction data collected on $Na_4Sn_3O_8$.

6–24 h). A long heating period (for 48 h) at 1270 °C caused partial decomposition of the α-phase to Na_2SnO_3 and SnO_2. Thermal stability of the α-phase was also examined by heating the single phase sample again for 3 h in air without the powder bed. The α-phase decomposed to Na_2SnO_3 and SnO_2 when heated at 900 °C or higher for a long period, but the decomposition did not occur when the sample was heated below 800 °C.

The crystal system, lattice parameters and possible space group of the α-phase were determined as follows. All reflections could be completely indexed in the cubic system [Fig. 1(A)]. Using the indexed reflection lines, a = 9.1813 Å was obtained. The possible space group was either $P4_132$ (no. 213) or $P4_332$ (no. 212) because of the reflection condition: h 0 0 with $h = 4n$. The pycnometric density of the powder sample was determined to be 4.92(3) × 10^3 kg m^{-3}. On the basis of the measured density and the nominal composition, it was supposed that the unit cell contains 16 Na, 12 Sn and 32 O atoms and the chemical formula is $Na_4Sn_3O_8$ (Z = 4).

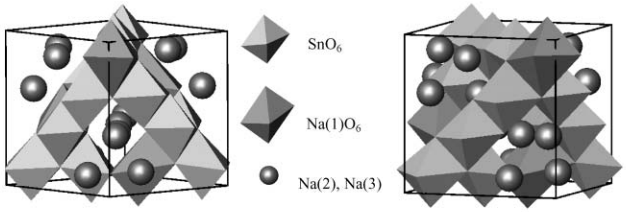

Fig. 3 Crystal structure of $Na_4Sn_3O_8$.

Table 3 Selected interatomic distances (Å) in $Na_4Sn_3O_8$

Sn–O(1)	2.135(8) (×2)
Sn–O(2)	2.057(8) (×2), 2.075(9) (×2)
Na(1)–O(2)	2.432(8) (×6)
Na(2)–O(2)	2.568(7) (×6)
Na(3)–O(1)	2.588(12) (×2)
Na(3)–O(2)	2.240(8) (×2), 2.448(10) (×2)

The Rietveld analysis was carried out to refine the crystal structure. Table 1 shows the data collection and the refinement conditions. The positions of oxygen and tin atoms were derived from those of sulfur and tin atoms, respectively, in $Ag_{3.8}Sn_3S_8$[7] because of the similarity of the powder XRD patterns. It is noted that two enatiomorphous space groups (such as $P4_132$ and $P4_332$) cannot be distinguished using the powder X-ray diffraction technique.[9] Here we chose $P4_132$ as the space group of $Na_4Sn_3O_8$ for the Rietveld analysis. The number of possible positions for sodium atoms is 32 for tetrahedral and 20 for octahedral coordination. We assigned all sodium atoms to the octahedral coordination; *i.e.* 4a, 4b, and 12d sites. Attempts to refine the structure with tetrahedral coordination of sodium atoms did not give good results. At first, the occupancies of these possible sodium sites were decided roughly using the Rietveld method. During calculation, it was found that the 4b site needed to be fully occupied by sodium atoms. The remaining 12 sodium atoms were assigned to the 4a and 12d sites equally (occupancy; 0.75). Isotropic atomic displacement parameters (B) were kept at the same values within all oxygen atoms, and sodium atoms occupying the 4a and 12d sites. Fig. 2 shows the result of the Rielveld refinement. Reliability factors of R_I and R_F were 6.80 and 4.49%, respectively. The lattice parameter was refined to be a = 9.1815(2) Å. The calculated density (4.94 × 10^3 kg cm^{-3}) is in good agreement with the experimental data. The refined atom coordinates are given in Table 2. Fig. 3 shows the crystal structure of $Na_4Sn_3O_8$. Twelve SnO_6 and four NaO_6 octahedra connect with edge-sharing in the unit cell and 12 sodium atoms are distributed in the octahedral holes. Selected interatomic distances for $Na_4Sn_3O_8$ are given in Table 3. As seen in Table 3, SnO_6 and $Na(3)O_6$ octahedra are distorted. A similar situation can be seen in the single crystal data of $Ag_{3.8}Sn_3S_8$.[7] Relatively high R_I and/or R_{wp} values suggest high levels of conduction ion delocalization and diffuse scattering around the Bragg peaks.[10] These results suggest the validity of the proposed crystal structure to a certain degree, but there is room for further consideration

Table 2 Atom coordinates for $Na_4Sn_3O_8$

Atom	Position	Occupancy	x	y	z	B/Å^2
Sn	12d	1.0	0.61572(9)	0.86572(9)	5/8	0.47(3)
Na(1)	4b	1.0	7/8	7/8	7/8	2.3(2)
Na(2)	4a	0.75	3/8	3/8	3/8	3.1(2)
Na(3)	12d	0.75	0.3540(8)	0.6040(8)	5/8	3.1(2)
O(1)	8c	1.0	0.1159(10)	0.1159(10)	0.1159(10)	0.42(13)
O(2)	24e	1.0	0.1363(9)	0.9023(8)	0.9093(9)	0.42(13)

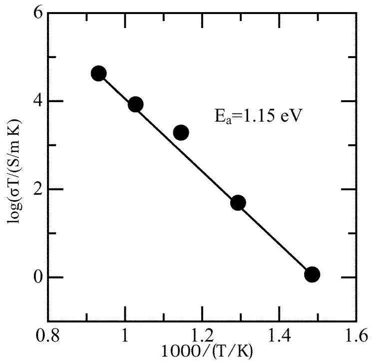

Fig. 4 Electrical conductivity of $Na_4Sn_3O_8$ as a function of inverse temperature.

about the occupation by the sodium ions. It is also possible that the site occupied partially by the sodium ion is divided into two or more crystallographic sites.[6,7,11] A fully satisfying refinement should be done by the four-circle X-ray analysis method using a single crystal. In the present study, we have not succeeded in obtaining single crystals of $Na_4Sn_3O_8$ because of the thermal instability as mentioned above.

Fig. 4 shows the electrical conductivity of $Na_4Sn_3O_8$ as a function of inverse temperature. The activation energy for the electrical conduction in $Na_4Sn_3O_8$ was estimated to be 1.15 eV. It is comparable with that of the Na^+-ionic conductor of $Na_{6.10}Mn_{4.95}(P_2O_7)_4$ where Na^+ ions are also distributed statistically,[11] while higher than those of superionic conductors such as sodium β-alumina[1] and NASICON.[2,3] The difference in the activation energy indicates lower mobility of sodium ions in $Na_4Sn_3O_8$ than compared with those of these superionic conductors. Measuring the transport number of the sodium ion in $Na_4Sn_3O_8$ is now in progress.

In conclusion, we have discovered a new compound in the Na–Sn–O ternary system. The chemical formula is $Na_4Sn_3O_8$ and this compound belongs to the cubic system with a space group of either $P4_332$ or $P4_132$. The crystal structure of $Na_4Sn_3O_8$ is proposed using powder X-ray diffraction data. All the sodium ions in $Na_4Sn_3O_8$ are located in octahedral sites. Detailed transport properties of $Na_4Sn_3O_8$ will be reported in the near future.

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