The Crystal Structure and Ionic Conductivity of the Ilmenite Polymorph of NaSbO$_3$

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Single crystals of NaSbO$_3$ with the ilmenite structure have been grown. The crystal structure has been determined by single crystal X-ray diffraction measurement. The ilmenite phase of NaSbO$_3$ crystallizes in the trigonal system with hexagonal symmetry, space group $R\bar{3}$ (No. 148), and $Z = 6$. The hexagonal unit cell parameters are $a = 5.2901(3)$ Å, $c = 15.926(2)$Å, and $V = 385.98(4)$ Å^3. The structure of ilmenite NaSbO$_3$ is built up from layers of edge-sharing SbO$_6$ octahedra with sodium ions located between the layers in octahedral sites. The ionic conductivity of the ilmenite analog of NaSbO$_3$ was investigated by ac complex impedance measurements and the results are discussed in terms of the structural dimensionality, the Na$^+$–oxygen bond strength, the sodium occupancy, and the bottleneck size. © 1994 Academic Press, Inc.

1. INTRODUCTION

The crystal structure of the antimony compounds A_4Sb$_4$O$_8$(X_4O$_{12}$) (A = K, Rb, Cs, Tl; X = Si, Ge) was recently studied by Pagnoux *et al.* (1). The structure of these compounds is built up from layers of cross-linked infinite chains of corner-sharing SbO$_6$ octahedra running along the a and b axes, which are held together, via corner sharing, by four-membered rings of corner-sharing SiO$_4$ tetrahedral (Si$_4$O$_{12}$). This three-dimensional (3D) structural network creates intercrossing octagonal and pentagonal tunnels running parallel to [100] and [010], where the A cations are located. The open framework of [Sb$_4$O$_8$(X_4O$_{12}$)]$^{4-}$ allows ion exchange and fast ionic transport (1).

Many framework structures containing sodium ions are good ionic conductors. For example, solid solutions of NASICON (Na$_{1+x}$Zr$_2$P$_{3-x}$Si$_x$O$_{12}$) with 3D framework structure exhibit exceptionally high ionic conductivities (2). In an attempt to prepare the sodium analog of A_4Sb$_4$O$_8$(X_4O$_{12}$), single crystals of NaSbO$_3$ with the ilmenite structure have been grown. The structure of this compound is different from that of metastable cubic NaSbO$_3$, which was prepared from the high-pressure cubic phase

of KSbO$_3$ by ion exchange in molten NaNO$_3$ (3). High sodium ion conductivity has been observed in the metastable cubic NaSbO$_3$ phase (4).

A preliminary structural report of the NaSbO$_3$ ilmenite phase based on film data provides no detailed description of the structure (5). In this work, we report the crystal structure and the ionic conductivity of the ilmenite polymorph of NaSbO$_3$.

2. EXPERIMENTAL

Synthesis

In a reaction intended to grow single crystal of Na$_4$Sb$_4$O$_8$(Si$_4$O$_{12}$), crystals of NaSbO$_3$ with the ilmenite structure were grown from a mixture containing NaNO$_3$ (Fisher, ACS certified grade), Sb$_2$O$_5$ (Aldrich, 99.995%), and SiO$_2$ (Aldrich, 99.8%) in a molar ratio of 2 : 1 : 1. The mixture was preheated in an alumina crucible in air at 500°C for 3 hr to decompose NaNO$_3$ and then held at 1300°C for 3 hr. The temperature was then slowly cooled from 1300 to 600°C at the rate of –5°C/hr and from 600°C to room temperature at the rate of –15°C/hr. The crystals obtained were colorless irregular thin platelets.

Single Crystal X-Ray Crystallographic Study

The crystals were ultrasonically washed in ethanol solvent for a few hours to remove any adhering flux. A crystal having approximate dimensions of 0.36 × 0.27 × 0.01 mm^3 was selected for the single crystal X-ray crystallographic study. The intensity data were collected with an Enraf–Nonius CAD4 diffractometer at room temperature. Graphite-monochromated MoKα radiation was employed to collect data with $4° \le 2\theta \le 60°$. A scan mode of $\omega - 2\theta$ was used. Lattice parameters obtained from a least-squares refinement of 25 accurately centered reflections with $10.2° \le 2\theta \le 31.1°$ indicated a trigonal system with hexagonal symmetry and unit cell dimensions $a = 5.2901(3)$ Å, $c = 15.926$ (2) Å, and $V = 385.98(4)$ Å^3. No apparent decay of the intensities of three standard reflections was observed in the course of data collection.

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Intensity data were corrected for Lorentz polarization effects. A correction for secondary extinction was also applied during the structural refinement. The linear absorption coefficient for $MoK\alpha$ is 105.52 cm⁻¹. An empirical correction of the data for absorption, based on the azimuthal ψ scans of three reflections with transmission factors in the range 0.35 –1.00, was applied. Data collected in the quadrant $(h, \pm k, l)$ were averaged to give a total of 257 unique reflections of which 239 with $I > 3\sigma(I)$ were considered as observed and were used in the subsequent structural solution and refinement.

The intensity statistical test and the systematic absences of $hkil$, $-h + k + l \neq 3n$; $h\bar{h}0l$, $h + l \neq 3n$; $hh\overline{2h}l$, $l \neq 3n$; and $000l$, $l \neq 3n$ suggested that the space group is acentric $R3$. Both centrosymmetric $R\bar{3}$ and noncentrosymmetric $R3$ models were tested. The structure could not be solved with space group $R3$. The space group $R\bar{3}$ was then chosen for the structure refinement. The structure was solved by direct methods (SHELXS-86) (6) and refined on $|F|$ using the full-matrix least-squares techniques in the MoLEN program package (7). A θ-dependent absorption correction following the DIFABS procedure (8) was applied to the isotropically refined structure. The maximum and minimum correction factors were 0.5743 and 1.0343, respectively. The structure was then refined anisotropically to $R = 0.025$ and $R_w = 0.036$, with a secondary extinction coefficient of 1.238×10^{-6}. The final electron

TABLE 1
X-Ray Crystallographic Data for Ilmenite NaSbO₃

Empirical formula	NaSbO₃
Formula weight	192.74
Crystal system	Trigonal (h)
Space group	$R\bar{3}$ (No. 148)
a (Å)	5.2901(3)
c (Å)	15.926(2)
V (Å³)	385.98(4)
Z	6
Calculated density (g/cm³)	4.975
Crystal size (mm)	0.36 × 0.27 × 0.01
μ (MoKα) (cm⁻¹)	105.52
Diffractometer	Enraf–Nonius CAD4
λ (Å), graphite-monochromated	0.71069
2θ range (°)	4–60
Scan mode	$\omega - 2\theta$
No. reflections collected	257
No. observations $(I > 3\sigma(I))$	239
No. variables	17
Quality-of-fit indicator[a]	1.54
Largest peak in final diff. map $(e^-/\text{Å}^3)$	1.463
Transmission coefficient	0.35–1.00
R^b, $R_w{}^c$	0.025, 0.036

[a] Quality-of-fit = $[\Sigma\omega(|F_o|-|F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.
[b] $R = \Sigma| |F_o| - |F_c| |/\Sigma|F_o|$.
[c] $R_w = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$; $\omega = 1/(\sigma^2|F_o|)$.

TABLE 2
Atomic Coordinates and $B_{eq}{}^a$ for NaSbO₃

Atom	x	y	z	B_{eq} (Å²)
Sb	0.00	0.00	0.16096(3)	0.458(6)
Na	0.00	0.00	0.3605(3)	1.01(4)
O	0.3444(6)	0.2878(8)	0.0963(2)	0.78(5)

$^aB_{eq} = 8\pi^2/3\ \Sigma U_{ij}a_i^*a_j^*\mathbf{a}_i \cdot \mathbf{a}_j$, where the temperature factors are defined as $\exp(-2\pi^2\ \Sigma h_i h_j a_i^* a_j^* U_{ij})$.

density difference map was flat with a maximum of 1.463 $e^-/\text{Å}^3$ near Sb and a minimum of $-0.504\ e^-/\text{Å}^3$ near the symmetry related Sb.

Details of the data collection and refinement of the ilmenite analog of NaSbO₃ are presented in Table 1. Final positional parameters are listed in Table 2 and selected bond distances and angles are given in Table 3. The anisotropic thermal parameters of atoms (1 page), the full lists of interatomic bond distances (1 page) and bond angles (1 page), and the observed and calculated structure factors (2 pages) are available as supplementary materials.

Ionic Conductivity Measurements

Single crystals of ilmenite NaSbO₃ were ground, pelletized, and sintered at 600°C for a few hours. The faces of the disk sample were coated with platinum paste. Ionic conductivities were measured by an ac complex impedance technique with a Solartron Model 1250 frequency analyzer and an 1186 elctrochemical interface that were programmed by a Hewlett–Packard 9816 desktop computer for data collection and analysis. The frequency range applied was from 10–65 kHz. The heating rate was controlled at 2°C/min in the temperature range 150–400°C.

TABLE 3
Selected Interatomic Distances and Angles for NaSbO₃

Distances (Å)			
Sb–O	1.981(4)	Na–O	2.313(5)
Sb–O	2.005(3)	Na–O	2.535(5)
Sb···Sb	3.05965(5)[a]	Na···Na	3.175(2)[a]
Angles (°)			
O–Sb–O	79.7(2)	O–Na–O	66.2(2)
O–Sb–O	95.4(1)	O–Na–O	157.1(2)
O–Sb–O	98.8(2)	Sb–O–Na	120.1(2)
O–Sb–O	87.3(2)	Sb–O–Na	142.4(2)
O–Sb–O	165.3(1)	Sb–O–Na	124.9(2)
O–Na–O	98.3(1)	Sb–O–Na	88.1(1)
O–Na–O	99.2(2)	Na–O–Na	81.7(1)
O–Na–O	92.5(2)	Sb–O–Sb	100.3(2)

[a] Nonbonding distance.
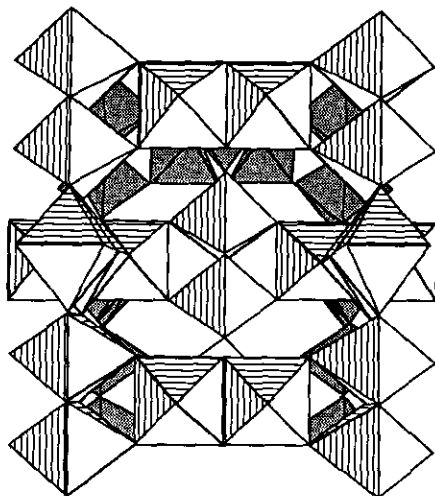
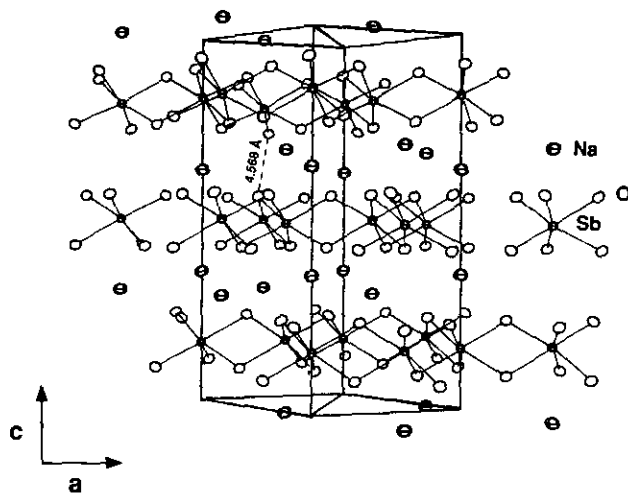FIG. 1.   The SbO$_3^-$ array of cubic KSbO$_3$ (cited from Ref. (9)).

FIG. 2.   ORTEP drawing (50% thermal ellipsoids) of the unit cell of ilmenite NaSbO$_3$ showing the layers of edge-sharing SbO$_6$ octahedra and the Na$^+$ ions between layers.

3. RESULTS AND DISCUSSION

Crystal Structure

In the structure of the cubic phase of NaSbO$_3$, which was prepared from the high-pressure cubic phase of KSbO$_3$ by ion exchange in molten NaNO$_3$, pairs of SbO$_6$ octahedra share common edges to form Sb$_2$O$_{10}$ clusters (2, 3). As shown in Fig. 1, these clusters share corners to form a 3D network structure with tunnels running along the ⟨111⟩ directions and intersecting at the origin and the body-center positions. The Na$^+$ ions are randomly distributed over two positions within these tunnels.

Unlike the skeleton structure of the metastable cubic NaSbO$_3$, the structure of the ilmenite polymorph of NaSbO$_3$ contains alternating layers of edge-sharing SbO$_6$ and NaO$_6$ octahedra. The Na$^+$ ions are located between layers of edge-sharing SbO$_6$ octahedra as shown in the unit cell structure (Fig. 2). Figure 3 depicts how the SbO$_6$ octahedra share common edges to form six-membered rings of Sb$_6$O$_{24}$ units. These six-membered rings intersect each other to form triangular Sb$_4$O$_{18}$ clusters with four edge-sharing SbO$_6$ octahedral in the same layer. As shown in Table 2 and Fig. 4, the Na$^+$ ions are located right above and below the Sb positions in octahedral sites. Thus the NaO$_6$ octahedra have an arrangement similar to that of the SbO$_6$ octahedra, forming six-membered rings of Na$_6$O$_{24}$ units and Na$_4$O$_{18}$ clusters in the same layer. This structural framework creates empty hexagonal tunnels running along [001] and through the Sb$_6$O$_{24}$ and Na$_6$O$_{24}$ units (Fig. 4).

Ionic Conductivity

Figure 5 shows a typical ac impedance spectrum of the sample at 182°C. The bulk (electrolyte) and the elec-

trode–electrolyte effects are evident from the presence of a semicircle at higher frequencies and an inclined straight line at lower frequencies.

The Arrhenius plot of the ionic conductivity of ilmenite NaSbO$_3$ in Fig. 6 shows linear behavior in the temperature range measured (150–400°C). The highest conductivity observed by ac impedance is 3.0×10^{-5} S · cm^{-1} at 400°C with $E_a = 0.66$ eV.
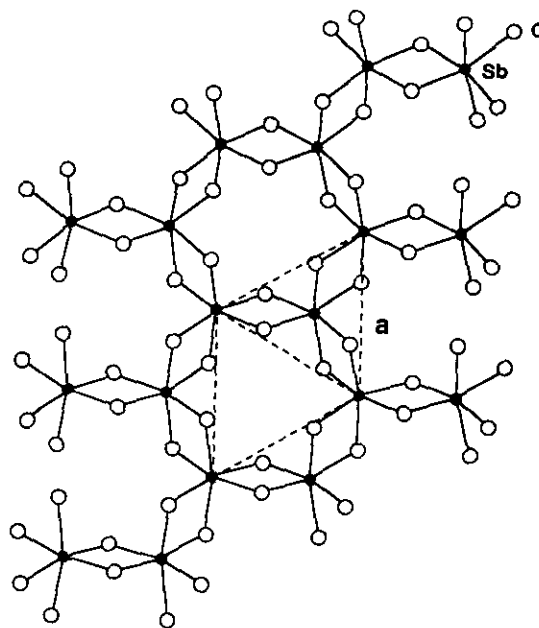

FIG. 3.   A perspective view of the edge-sharing SbO$_6$ octahedra in ilmenite NaSbO$_3$ along [001] showing the six-membered rings of Sb$_6$O$_{24}$ units and the Sb$_4$O$_{18}$ clusters.
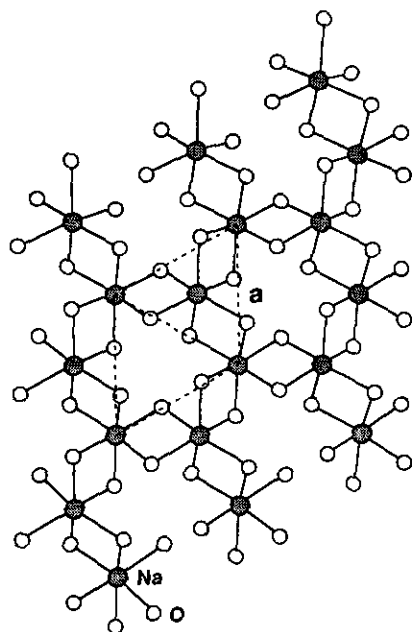
FIG. 4. A perspective view of the structure of ilmenite NaSbO₃ along [001] showing the similar arrangement of NaO₆ octahedra as that of SbO₆ octahedra.

FIG. 6. Arrhenius plot of conductivity of ilmenite NaSbO₃.

The relatively low conductivity of the ilmenite NaSbO₃ phase compared to that of the metastable cubic NaSbO₃ analog ($\sigma_{300°C} = 5.6 \times 10^{-2}$ S·cm⁻¹, (4)) may be attributed to their structural differences. We compare the ionic conductivity of the ilmenite and cubic NaSbO₃ phases in terms of several interrelated factors: (1) the dimensionality of the structure, (2) the strength of the Na⁺–oxygen bonds, (3) the occupancy of the available Na⁺ sites, and (4) the size of the bottleneck for Na⁺ diffusion.

As discussed above, in the 3D framework structure of cubic NaSbO₃, the Na⁺ ions are randomly distributed over two octahedral sites (Na(1), Na(2)) in the three-
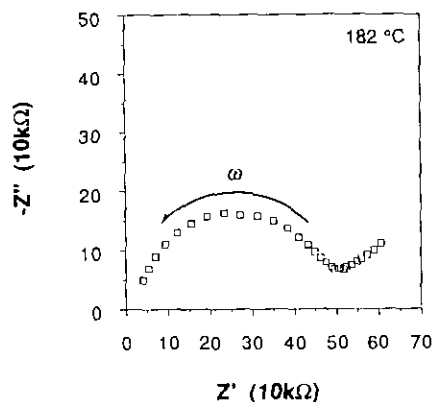

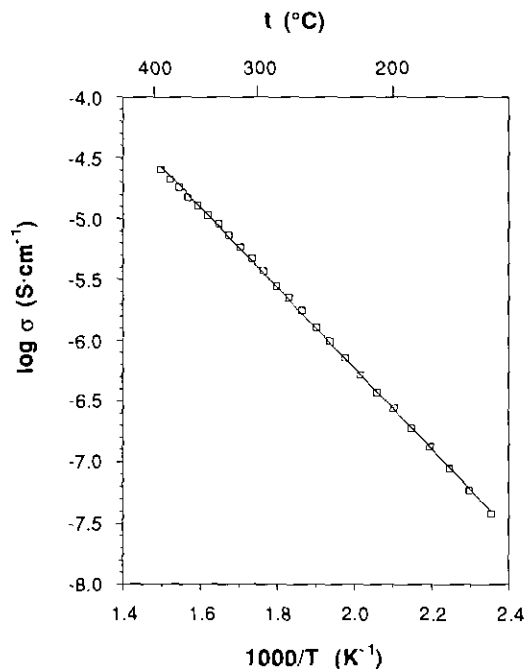FIG. 5. The ac complex impedance spectrum of ilmenite NaSbO₃.

dimensionally interconnected tunnels. In ilmenite NaSbO₃, the Na⁺ ions are ordered in octahedral sites between layers of edge-sharing SbO₆ octahedra. Thus, Na⁺ movement is expected to be three dimensional in cubic, but only two dimensional in ilmenite NaSbO₃.

In ilmenite NaSbO₃, the Na–O bond distances (2.313(5) and 2.535 (5) Å; average, 2.424 Å, Table 3) are comparable to the covalent bond distance of Na–O (Na(VI), 1.16 Å; O(VI), 1.26 Å) (10) and significantly shorter than those in cubic NaSbO₃ (2.760, 2.730, and 2.650 Å; average, 2.70 Å) (3). Consequently, the Na⁺–oxygen bond in ilmenite NaSbO₃ is stronger than in cubic NaSbO₃ and results in the observed decrease of ionic conductivity. Moreover, the Na(1)–Na(1) separation is only 2.30 Å in cubic NaSbO₃ but 3.175(2) Å in the ilmenite analog (Table 3). These considerations explain why the activation energy of cubic NaSbO₃ ($E_a = 0.29$ eV) (4) is much lower than that of the ilmenite phase ($E_a = 0.66$ eV).

Another factor that may have a significant influence on the ionic conductivity is the occupancy of the mobile ions. In fast ionic conductors the mobile cations usually have only partial occupancy of their sites. The low fractional occupancy (0.82, 0.29) of Na⁺ ions in cubic NaSbO₃ (3) in contrast to their full occupancy in the ilmenite phase partly explains the higher ionic conductivity of the cubic polymorph.

The "bottleneck" size, i.e., the minimum opening in the structure that the mobile ions must pass through, also plays an important role in conductivity. As suggested by Hong (11), the optimum bottleneck size for Na⁺ ions is

4.58 Å. The bottleneck in cubic $NaSbO_3$ is larger than 5.0 Å (3), which is partly responsible for the low activation energy (0.29 eV). In the ilmenite analog, the bottleneck for Na^+ ion diffusion in the *ab* plane, i.e., the narrowest region between the layers, is calculated to be 4.568 Å between two oxygen atoms (Fig. 2). This bottleneck size is comparable to the optimum for Na^+ ions as discussed above. Thus, the significantly higher activation energy of ilmenite $NaSbO_3$ compared to that of cubic $NaSbO_3$ appears to be due to the other factors discussed above.

4. CONCLUSIONS

The crystal structure of the ilmenite polymorph of $NaSbO_3$ has been determined by single crystal X-ray diffraction measurement. The structure contains alternating layers of edge-sharing SbO_6 and NaO_6 octahedra. The lower ionic conductivity of the ilmenite phase (3.0×10^{-5} $S \cdot cm^{-1}$ at 400°C) compared to that of the metastable cubic $NaSbO_3$ ($5.6 \times 10^{-2} S \cdot cm^{-1}$ at 300°C) is attributed to its structural low dimensionality, strong Na^+–oxygen bond, and high sodium occupancy factor.

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