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Na_3SbSe_3: Synthesis, Crystal Structure Determination, Raman Spectroscopy, and Ionic Conductivity

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Dedicated to Professor Rudolf Hoppe on the Occasion of His 90th Birthday

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Abstract. Na_3SbSe_3 was obtained by solid state reaction of anhydrous Na_2Se, antimony, and selenium in a ratio of 3:2:3. It is air and moisture sensitive and melts at 870 K. Yellow single crystals of Na_3SbSe_3 were used for single-crystal X-ray diffraction. It crystallizes in the cubic space group $P2_13$ (No. 198) with $a = 9.0227(2)$ Å, $V = 734.53(3)$ Å^3, and $Z = 4$. Na_3SbS_3 is isotypic with Na_3AsS_3. Trigonal $SbSe_3$ pyramids therein act as mono-, bi-, and tridentate ligands to sodium. Sodium is located at three different sites, which are all coordinated by six selenium atoms, providing a strongly distorted octahedral environment. $NaSe_6$ octahedra of identical type share common vertices; in case of different sites also face sharing is observed. Na_3SbSe_3 shows temperature dependent Na^+ conductivity above 380 K, which increases to $2.9 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$ at 590 K.

Introduction

Alkali metal containing antimony chalcogenides of the general composition M_3SbQ_3 (M = Li, Na, K, Rb, Cs and Q = S, Se, Te) are well characterized. 35 years ago, *Sommer* and *Hoppe* already described the isotypic thioantimonates(III) Na_3SbS_3, K_3SbS_3, and the thioarsenates(III) Na_3AsS_3, and K_3AsS_3, respectively.[1] However, they determined only the crystal structure of Na_3AsS_3 and derived the isotypism from X-ray powder data. It should later become apparent, that almost every other known compound M_3SbQ_3 crystallizes in the cubic structure type of Na_3AsS_3,[2] which was also termed as a "stuffed variety of the $NaClO_3$-type".[1] They also discussed the structural relation of M_3SbQ_3 and the Li_3Bi structure type. Later on this structure type was described as derivative of the Th_3P_4 structure type.[3] Therein, also a group-subgroup scheme is discussed in order to describe the symmetry relations. Concerning the crystal structures of the alkali metal chalcogenoantimonates(III) Li_3SbS_3 is a solitary exception. It crystallizes orthorhombic in the space group $Pna2_1$.[4] The thioantimonates(III) M_3SbS_3 of the heavier alkali-metals rubidium and cesium are not known to date. The same situation is found for the corresponding antimony tellurides M_3SbTe_3. Na_3SbTe_3[5] and K_3SbTe_3[6] are isotypic to Na_3AsS_3, whereas similar compounds with lithium, rubidium, or cesium are not yet known. The selenides K_3SbSe_3, Rb_3SbSe_3, and Cs_3SbSe_3 were described by *Bronger*.[7] Corresponding compounds with lithium and sodium are not mentioned in literature. The latter one was also not observed in earlier investigations of the ternary system Na-Sb-Se by *Lazarev*.[8] Analogous compounds with monovalent coinage metals are also known. Nevertheless, they differ from alkali metal compounds in their structure like Ag_3SbS_3,[9] Cu_3SbS_3,[10,11] and Cu_3SbSe_3.[12] Some of them have interesting electric properties. Pyrargyrite Ag_3SbS_3, e.g., is a piezoelectric Ag^+-ion conductor,[13,14] whereas Cu_3SbSe_3 has interesting thermoelectric properties.[15]

Reports on electric features of alkali metal containing antimony chalcogenides are rather rare. Recently the ionic conductivity of Li_3SbS_3 was verified and its bandgap was calculated by DFT calculations.[4] Herein, we report on the preparation, structure, and physical properties of Na_3SbSe_3, which have not yet been described in literature.

Results and Discussion

Structure Description and Discussion

The crystal structure of Na_3SbSe_3 was determined by single-crystal X-ray diffraction. Crystallographic data are listed in Table 1. The compound crystallizes in space group $P2_13$. The cell has the lattice constant $a = 9.0227(2)$ Å, and a cell volume of $V = 734.53(3)$ Å^3 with $Z = 4$. The crystal structure was refined to $R_1 = 0.0243$ [22 parameters, 541 reflections with $I > 2\sigma(I)$] and $R_2 = 0.0475$ (all data). Atomic coordinates and equivalent isotropic displacement parameters U_{eq} are listed in Table 2, the anisotropic displacement parameters U_{ij} in Table 3.

Trigonal-pyramidal $SbSe_3$ units are observed in Na_3SbSe_3 (see Figure 1). The distance $d_{primary}$(Sb–Se) is 2.5778(6) Å,

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Table 1. Crystallographic data for the structure analysis of Na_3SbSe_3.

	Na_3SbSe_3
Formula weight /g·mol^{-1}	427.60
Color	yellow
Crystal system	cubic
Space group	$P2_13$ (No. 198)
Lattice constant a /Å	9.0227(2)
Cell volume V /Å^3	734.53(3)
Number of formula units per unit cell Z	4
Calculated density ρ_{calc} /g·cm^{-3}	3.867
Temperature T /K	123
Wavelength λ /Å	0.71073
Diffractometer	Oxford Diffraction Gemini R Ultra CCD, Mo-K_α (λ = 0.71073 Å)
Absorption coeff. μ /mm^{-1}	18.678
Absorption correction	Multi-scan[16]
2Θ-range /°	$6.38 \le 2\Theta \le 57.68$
hkl-ranges	$-7 \le h \le 12$ $-7 \le k \le 9$ $-11 \le l \le 11$
No. of reflections, R_{int}	1471, 0.0325
No. of independent reflections	559
Structure solution	SIR92[17]
Structure refinement	SHELX-97[18]
No. of parameters	22
Final R, wR [$I > 2\sigma(I)$]	0.0243, 0.0471
Final R, wR (all reflections)	0.0259, 0.0475
GooF	1.049
Largest difference peak $\Delta\rho_{\max}$ and hole $\Delta\rho_{\min}$ /e·Å^{-3}	0.593 / –0.625
Flack parameter	0.01(2)

Table 2. Atomic coordinates and equivalent isotropic displacement parameters U_{eq}[a)] for Na_3SbSe_3.

Atom	Wyck.	x	y	z	U_{eq}
Na1	4a	0.5815(3)	x	x	0.018(1)
Na2	4a	0.3218(3)	x	x	0.0136(9)
Na3	4a	0.8128(3)	x	x	0.0124(9)
Sb	4a	0.03605(4)	x	x	0.0085(2)
Se	12b	0.23652(6)	0.61312(6)	0.50125(6)	0.0100(2)

a) U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

and the angle Se–Sb–Se 99.67(2)°. In addition, the distances $d_{\mathrm{secondary}}$(Sb–Se) = 3.785 Å to next nearest neighbors shall be mentioned here. A strongly distorted octahedral environment for antimony results when these additional selenium atoms are taken into account. Systematic trends become obvious comparing these data with the analogous compounds containing the heavier alkali metals. Thus, d_{primary} decreases slightly from Na_3SbSe_3 to Cs_3SbSe_3, whereas an increase of about 1.2 Å is observed for $d_{\mathrm{secondary}}$ from the sodium containing compound to the cesium homologue. In addition, an increasing angle Se–Sb–Se changing systematically from 99.67° (Na_3SbSe_3) to 102.9° (Cs_3SbSe_3) is determined. A detailed analysis of the influence of these systematic changes on the bonding behavior within the constituting $SbSe_3$ units will be subject of a forthcoming study.

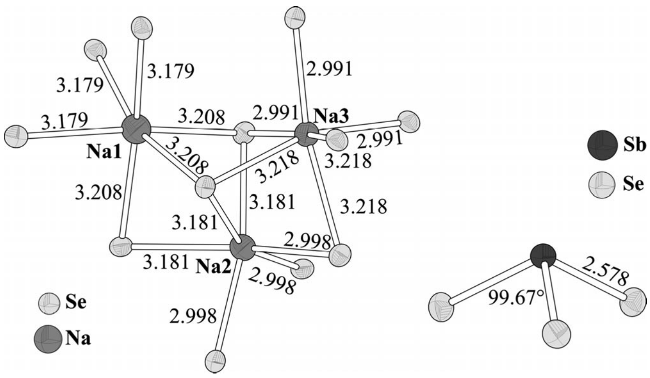

Figure 1. The distorted octahedral coordination of the three sodium sites (Na1, Na2, and Na3) is shown on the left side, distances are given in Å. $SbSe_3$ units form the well known trigonal pyramids (right).

Sodium ions occupy three different sites (Na1, Na2, and Na3) with six-fold coordination by selenium (see Figure 1). Significant deviations from an ideal octahedral surrounding of the sodium ions are observed in accordance with their site symmetry 3, confer the distances d(Na–Se) and angles summarized in Table 4.

Table 4. Selected interatomic distances /Å and angles /° for Na_3SbSe_3 at 123 K.

Sb–Se	3 ×	2.5778(6)	Se–Sb–Se	3 ×	99.67(2)
Na1–Se	3 ×	3.179(3)	Se–Na1–Se	3 ×	83.54(9)
	3 ×	3.208(3)	Se–Na1–Se	3 ×	85.73(9)
			Se–Na1–Se	3 ×	85.91(2)
			Se–Na1–Se	3 ×	107.26(1)
			Se–Na1–Se	3 ×	163.95(2)
Na2–Se	3 ×	2.998(2)	Se–Na2–Se	3 ×	79.17(2)
	3 ×	3.181(3)	Se–Na2–Se	3 ×	84.41(8)
			Se–Na2–Se	3 ×	93.08(9)
			Se–Na2–Se	3 ×	106.66(1)
			Se–Na2–Se	3 ×	159.03(4)
Na3–Se	3 ×	2.992(2)	Se–Na3–Se	3 ×	75.49(8)
	3 ×	3.218(3)	Se–Na3–Se	3 ×	86.92(2)
			Se–Na3–Se	3 ×	92.59(9)
			Se–Na3–Se	3 ×	105.90(2)
			Se–Na3–Se	3 ×	161.51(7)

Table 3. Anisotropic displacement parameters U_{ij} for Na_3SbSe_3.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na1	0.018(1)	U_{11}	U_{11}	0.000(1)	U_{23}	U_{23}
Na2	0.0136(9)	U_{11}	U_{11}	0.001(1)	U_{23}	U_{23}
Na3	0.0124(9)	U_{11}	U_{11}	0.000(1)	U_{23}	U_{23}
Sb	0.0085(2)	U_{11}	U_{11}	–0.0002(2)	U_{23}	U_{23}
Se	0.0088(3)	0.0108(3)	0.0103(3)	0.0000(2)	0.0001(2)	–0.0016(2)

The distances d(Na–Se) vary between 2.99 and 3.22 Å. This is in good accordance with effective ionic radii for Na^+ = 1.02 Å, and Se^{2-} = 1.98 Å, both for a coordination number of 6.[31] The polyhedra $[NaSe_6]$ are corner-sharing in case of equivalent types of sodium and they form a three-dimensional network. These three resulting networks formed by Na1, Na2, and Na3 are interpenetrating and the selenoantimonate(III) units are located in between. $SbSe_3$ units are separated from each other. However, they act as mono-, bi-, and tridentate ligands to sodium, respectively. Thus, the different sodium sites get a completely different environment. Na1 is coordinated by six monodentate $SbSe_3$, Na2 has three bidentate ligands, and Na3 is coordinated by one tridentate and three monodentate ligands (see Figure 2).

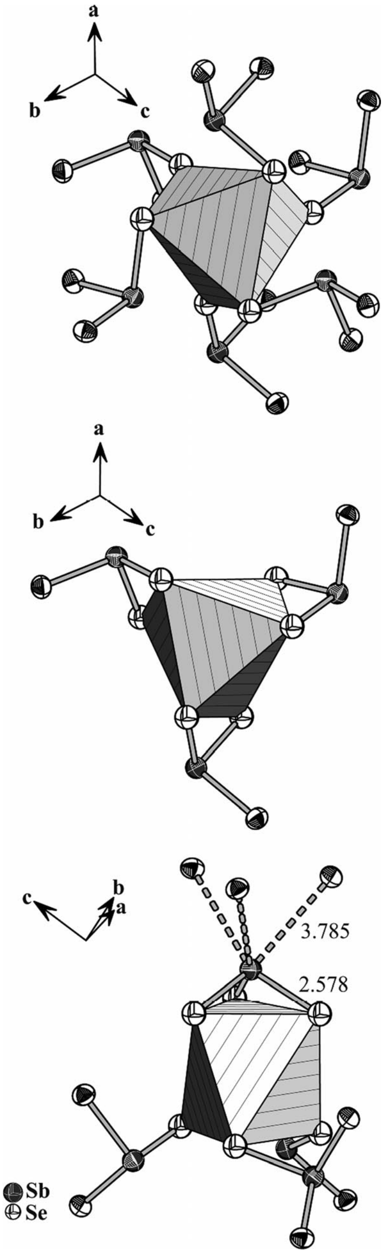

Figure 2. Coordination of Na1 (top), Na2 (mid), and Na3 (bottom) by $SbSe_3$ units in monodentate, bidentate and mixed tridentate and monodentate manner.

Powder X-ray Diffraction

Figure 3 displays the measured diffraction pattern and the pattern calculated from single crystal structural data, demonstrating the purity of the sample obtained from the solid state reaction.

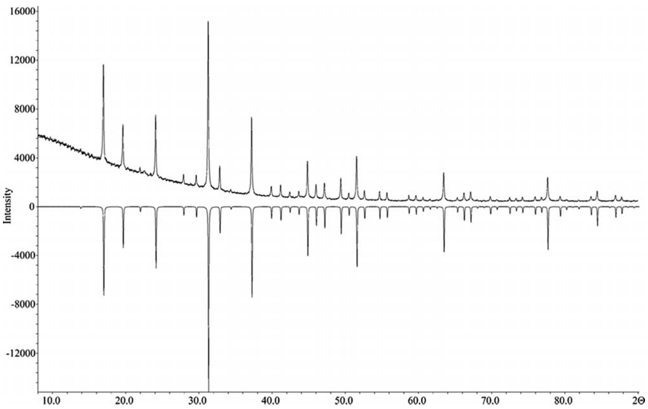

Figure 3. The sample purity becomes obvious from the measured (top) and calculated X-ray powder diffraction pattern for Na_3SbSe_3 (down, inverted intensities).

Raman Spectroscopy

Raman spectroscopy is a nice tool for the estimation of bond strengths in solid compounds, which contain molecular fragments. Thus, it was shown that the stretching modes of complex SbS_3 units reveal some insight in the bonding situation of these units. Their vibrational bands correspond to those of the thioles $Sb(SR)_3$ ($R = C_4H_9$, C_6H_5)[19] when no so called secondary bonds of the SbS_3 unit are present.[20–22] Contrary, a red-shift of the vibrational modes is observed for those cases when SbS_3 units show coordination by additional sulfur atoms in distances up to about 4 Å.[23,24] The antimony atom in the title compound has three additional selenium atoms in its coordination sphere at a distance of about 3.8 Å as depicted in Figure 2. As a consequence a slight red shift of the Raman resonances of these units is observed here in comparison to the resonances of $Sb(SeMe)_3$.[25] As shown in Figure 4 the pro-

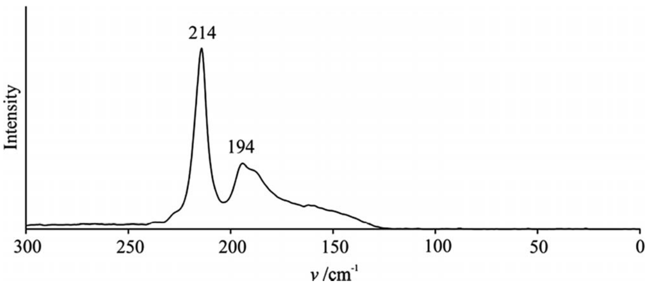

Figure 4. Raman spectrum of the title compound.

nounced bands in the Raman spectrum are situated at 214 and 194 cm^{-1}. For $Sb(SeMe)_3$ these bands were found at 237 and 204–210 cm^{-1}. Therein, antimony has also three additional selenium atoms from adjacent molecules in a similar arrangement as found in Na_3SbSe_3. However, the bonding interactions seem to be stronger in case of the ionic sodium compound.

Differential Thermal Analysis (DTA)

A pure sample of Na_3SbSe_3 was used for DTA analysis. The melting and crystallization process shows the typical feature for dystectic melting, i.e., there is only one reversible maximum, both in the melting and in the crystallization curve. The melting point of Na_3SbSe_3 is observed at 870 K, and it crystallizes at 697 K (onset temperatures).

Impedance Measurement

The total electric conductivity of the title compound was determined by frequency dependent impedance spectroscopy. Figure 5 shows a representative Nyquist-plot of Na_3SbSe_3 at 586 K. The linear arc in the low frequency regime indicates ionic conductivity. An Arrhenius plot of these conductivities is shown in Figure 6. The activation energy is 0.69 eV. The ionic conductivity increases from $5 \times 10^{-9}\ \Omega^{-1}\ cm^{-1}$ at 380 K to $3 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$ at 590 K. Some data from literature shall be given herein for comparison: a very high, strong anisotropic sodium ionic conductivity is reported for β-alumina, i.e., $1.4 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ at 298 K,[32] whereas, for example, Na_3PS_4 shows a good ionic conductivity of $4.2 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$ at 323 K.[33]

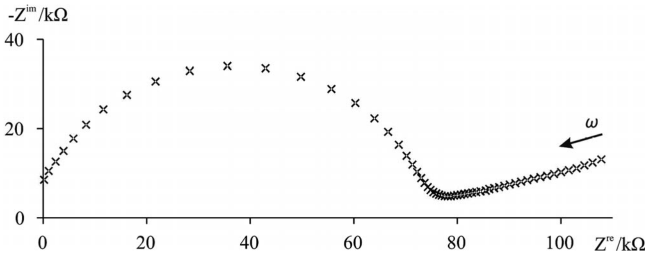

Figure 5. Impedance spectrum of Na_3SbSe_3 at 590 K. The spectrum shows the typical frequency dependency in case of an ionic conductor in case of blocking electrodes.

Experimental Section

Synthesis: Yellow single crystals of Na_3SbSe_3 were prepared by annealing a stoichiometric mixture of Na_2Se, antimony (99.9999 %, Chempur) and selenium (99.999 %, Chempur) in a 3:2:3 ratio at 723 K in evacuated silica ampoules. These were coated with graphite by pyrolysis of acetone prior to use. After 10 weeks the product was slowly cooled down to room temperature. Using anhydrous Na_2Se was essential for a successful synthesis. This was obtained by reaction of stoichiometric quantities of distilled sodium (99 %, Merck) and selenium in dry ammonia.[26] Na_2Se and Na_3SbSe_3 were handled in an atmosphere of argon in order to prevent decomposition due to their air and moisture sensitivity.

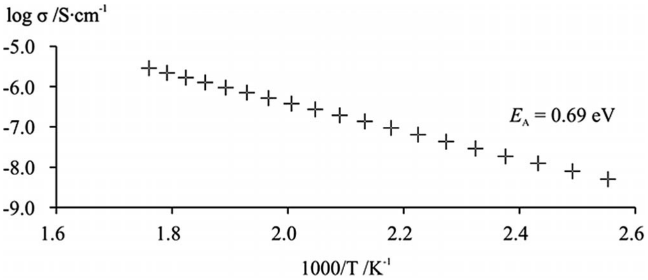

Figure 6. The Arrhenius plot shows an exponential dependency of the specific ionic conductivity on temperature.

Crystal Structure Analysis: A single crystal of Na_3SbSe_3 was transferred into a drop of mineral oil and cooled to 123 K by a stream of nitrogen. The measurement was performed with an Oxford Diffraction Gemini R Ultra CCD with Mo-K_α-radiation (λ = 0.71073 Å). Absorption was corrected by multi-scans.[16] The crystal structure was solved by direct methods with SIR92.[17] All atoms were refined with anisotropic displacement parameters. The Flack parameter of zero gave no hint for inversion twinning. An extinction parameter was introduced in the final stage of the refinement but it took no significant value and was therefore disregarded.

Powder X-ray Diffraction: X-ray diffraction patterns were measured in sealed glass capillaries (diameter 0.2 mm) at room temperature. A STOE Stadi P diffractometer with monochromatic Cu-$K_{\alpha1}$-radiation (λ = 1.540598 Å, Ge-monochromator). Diffraction data were collected in a 2Θ-range from 8.0° to 90° and analyzed with the STOE program package WINXPOW.[27]

Raman Spectroscopy: The powdered sample in a sealed glass capillary (diameter 0.5 mm) was excited by a Nd:YAG laser (λ = 1064 nm) in a Varian FTS 7000e Spectrometer coupled to a Varian FT-Raman module. A liquid nitrogen cooled germanium detector was used in back-scattering mode. Scattering intensities were finally evaluated by the software Varian resolutions Pro.[28]

Thermal Analysis: The thermal behavior was investigated by performing DTA with a Setaram DTA-TG 92–16.18. A small amount of the powdered sample was filled in a capillary tube (diameter 1.5 mm) and sealed in an argon atmosphere. The tube was heated up from 298 to 1073 K and cooled down again to room temperature with a heating/cooling rate of 10 K·min^{-1}. Al_2O_3 was used as an external standard. Onset temperatures of the melting and crystallization process are derived from the respective curves.

Impedance Spectroscopy: A powdered sample of Na_3SbSe_3 was pressed 20 min with a pressure of 7000 kg·cm^{-2} to a pellet with 92 % of the calculated density. It was inserted between thin plates of gold as blocking electrodes. Frequencies ranged from 1 Hz to 1 MHz and temperatures from 373 K to 573 K (IMd6, Zahner Elektrik). The data were evaluated with the software Thales Flink.[29] Details of the setup are given elsewhere.[30]

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request for deposited data.html) on quoting the depository number CSD-425125.

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