Synthesis and Crystal Structure of a Novel Zintl Phase: K_3SbTe_3

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A ternary Zintl phase material of the formula K_3SbTe_3 has been prepared following a high temperature procedure. The material consists of an ionic lattice of potassium ions and discrete $[SbTe_3]^{3-}$ ions. K_3SbTe_3 is a poor semiconductor ($\rho = 2 \times 10^5 \Omega$-cm) and dissolves in several polar solvents (e.g., H_2O, DMF, DMSO). Crystal data for K_3SbTe_3 include the following: cubic, space group $P2_13$ (No. 198), $a = 10.306(1)$ Å, $V = 1094.6(2)$ Å^3, $Z = 4$, $D_{calc} = 3.773$ g cm^{-3} at $T = 110(5)$ K, MoK radiation, $\lambda (K) = 0.71073$ Å, $\mu = 114.7$ cm^{-1}, $M_r = 621.86$, $F(000) = 1056$, and $R = 0.023$ for 574 unique observed reflections. © 1991 Academic Press, Inc.

Introduction

Zintl materials are "valence" compounds; the metals and metalloids that comprise the material will transfer or share electrons in order to achieve an octet in the outermost electron shell (*1*). This often results in the formation of covalently bonded polyatomic anionic units, referred to as Zintl anions. The valence character of Zintl materials is often expressed as the 8-N rule (*1*). The octet valence shell of the Zintl phase arises when the more electropositive metals (i.e., alkali and alkaline-earth metals) are allowed to react with the less electropositive metals and metalloids (i.e., the posttransition main group metals). Because of the 8-N rule, Zintl phases are formally semiconductors. In practice, however, the band gap may be sufficiently large that a material may effectively be an insulator. Zintl materials lie at the boundary between intermetallic alloys and ionic salts and may have a combi-

nation of properties related to both classes of materials.

Because of the differences in the electronegativities of the elements that comprise a Zintl phase material, there is often a great deal of ionic character in the Zintl phase, and this ionic character may be sufficient to allow the solvation of salt-like ions (cations and Zintl anions) in polar solvents (e.g., KSn dissolves in liquid NH_3, and K_5InTe_4 dissolves in H_2O).

Ternary Zintl phase materials of the type A^I–B^V–X^{VI}, where A^I represents an alkali metal, B^V = As, Sb, or Bi, and X^{VI} = S, Se, or Te have been extensively studied for the past two decades (*2*). The compounds have electrical, physical, and optical properties of practical value (*3*). The synthesis and preparation of alkali metal telluroantimonides is particularly interesting for the physicochemistry and crystal chemistry of this group of compounds.

The typical methods for the preparation

of A^I–B^V–X^{VI}-type compounds consist of fusing the alkali metal chalcogenides with the chalcogenides of the group V elements or fusing together a stoichiometric mixture of the elements of groups I, V, and VI. This latter method was used by us to give the pure crystal compound K$_3$SbTe$_3$.

The phase diagrams for the A_2Te–Sb$_2$Te$_3$ mixtures of binary tellurides have been investigated to determine the range of crystallization of the compound ASbTe$_2$ (4). Despite the many investigations concerning phase diagrams for the A_2Te–Sb$_2$Te$_3$ systems, little has been done to explore the crystal structures and chemical properties of these materials. Kovba and co-workers have reported a congruently melting solid is observed with the composition of K$_3$SbTe$_3$ (4). Therefore, we have prepared a material with this stoichiometry and report on its crystal structure.

We have undertaken the synthesis of a series of A^ISb^{V}Te^{VI} from the direct synthesis method. In this paper we present the preparation, crystal structure, and properties of a I–V–VI-type ternary Zintl phase material, K$_3$SbTe$_3$ (5).

Experimental

Synthesis

K$_3$SbTe$_3$ was prepared by direct combination of the elements. A dry quartz tube was charged with 0.12 g of K(3 mmole), 0.12 g of Sb(1 mmole), and 0.38 g of Te(3 mmole). The sample quartz tube was evacuated at a pressure of approximately 5×10^{-3} Torr for 1.5 hr and then sealed under vacuum. The sample tube was placed inside a larger diameter tube, which was similarly evacuated and sealed. The outer tube was used to prevent air contamination in the event that the inner tube fractured during cooling. The sample was heated at 550°C in an automatic control furnace for 6 hr and then cooled to ambient temperature over a 28-hr period. A metallic dark gray crystalline product was obtained.

Crystallography

Single crystals of K$_3$SbTe$_3$ were separated under a protective coat of hydrocarbon oil and examined using a microscope. A rectangular crystalline plate was attached to a glass fiber using silicon grease, rapidly transferred from the oil to an Enraf–Nonius CAD-4 diffractometer, and cooled to 110(5) K using a stream of cold N$_2$ gas. Unit cell dimensions were determined by least-squares refinement of the measured setting angles of 25 reflections with $50° \leq 2\theta \leq 70°$. Systematic absences $h00$: $h = 2n + 1$; $0k0$: $k = 2n + 1$; $00l$: $l = 2n + 1$; and diffraction symmetry indicated the cubic space group $P2_13$. A total of 1856 reflections were measured from one octant to a maximum 2θ of 60° using ω: 2θ scans. Three standard reflections measured at 2-hr intervals showed a 5.8% decline in intensity during data collection, and a decay correction was applied based on a linear least-squares fit to the intensity standards. The data were corrected for Lorentz and polarization effects and for absorption by a Gaussian numerical integration using the measured dimensions of the crystal. Equivalent symmetry-related reflections were averaged, yielding a final data set of 618 reflections with an internal agreement factor of $R_i(F) = 0.022$. A total of 574 reflections in the final set had $I > 3\sigma(I)$. The crystal data and measuring conditions for K$_3$SbTe$_3$ are listed in Table I.

The structure of K$_3$SbTe$_3$ was solved by assuming that it is similar to the structure of K$_2$Mg$_2$(SO$_4$)$_3$ which also belongs to the space group $P2_13$ (6). The Te atoms were assigned the same atomic coordinates as the S atoms of K$_2$Mg$_2$(SO$_4$)$_3$. Four K atoms were assigned the coordinates of the K and Mg atoms. After two cycles of least-squares refinement, a large temperature factor indicated the incorrect K atom, and a subse-

Space group	$P2_13$ (No. 198)
$a(\text{Å})$	10.306(1)
$V(\text{Å}^3)$	1094.6(2)
Z	4
$T(\text{K})$	110(5)
$D_{calc}(\text{g cm}^{-3})$	3.773
$\lambda(\text{Mo}K)$ (Å)	0.71073
$\mu(\text{Mo}K\alpha)$ (cm^{-1})	114.7
Crystal size (mm)	$0.11 \times 0.21 \times 0.22$
Range of transmission coefficients	0.160–0.453
Range of 2θ measurements (°)	2–60
h, k, l range	0–14
Scan width in ω (°)	$1.0 + 0.35 \tan \theta$
Scan speed (° mm^{-1})	0.52–5.1
Number of structure factors	
Total measured	1856
Unique	618
Observed ($I > 3\sigma(I)$)	574
Number of variables	23
Agreement factors (on F)	
R_I	0.022
R	0.023
R_W	0.038
GOF	1.174

quent difference Fourier summation revealed the location of the Sb atom. The final model consisted of three K atoms and one Sb atom located on the three-fold axis and one Te atom in a general position. Comparison of observed and calculated structure factors indicated the presence of some secondary extinction, and an isotropic extinction parameter was included as a parameter in the refinement. The maximum extinction coefficient was 12% of F_c. Full-matrix least-squares refinement minimizing $\Sigma_w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2$ (F) and $\sigma^2(F^2) = \sigma_{cs}^2 + (0.04F^2)^2$ including anisotropic thermal parameters for all atoms, converged at $R = 0.023$ and $R_w = 0.038$ for 23 variables and 388 reflections. Atomic scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-Ray Crystallography* (7). All computer programs used for data collection, reduction, and refinement were from the CAD4-SDP package (8).

Resistivity Measurements

Resistivity measurements on pressed pellets were made using a linear four-probe method (9). The current was supplied by a Keithley Model 224 programmable current source and the voltage drop across the sample was measured using a Keithley Model 181 digital nanovoltmeter.

Results and Discussion

The fractional coordinates of K_3SbTe_3 obtained from the crystal structure determination are listed in Table II. An ORTEP (10) diagram of the contents of the unit cell is illustrated in Fig. 1. Interatomic distances are listed in Table III. The structure consists of an ionic lattice of K^+ ions and discrete $[SbTe_3]^{3-}$ ions. The $[SbTe_3]^{3-}$ anion has a trigonal pyramidal geometry and is located on a crystallographic three-fold axis in the unit cell. The Sb–Te bond distance is 2.7831 (7) Å and the Te–Sb–Te bond angle is 101.86(2)°.

The closest nonbonded contacts to the Sb atom are from three K(2) ions at 3.837(1) Å. Each Te atom makes ionic contacts with six K(1) ions, six K(2) ions, and six K(3) ions at distances ranging from 3.451 to 3.748 Å. Each K ion is surrounded by six Te atoms at distances of 3.45–3.75 Å arranged in distorted trigonal antiprisms.

Several other Zintl phase materials that we have prepared follow the basic tetrahedral electron-pair geometry of the central atom in the Zintl anion. For example, K_4SnTe_4 and K_5InTe_4 both have the tetrahedral geometry of the Zintl anion. The compound reported here also has a tetrahedral electron-pair geometry with a lone pair stabilizing the potassium position in the unit cell.

The local bonding electron structure of antimony is very similar to the electron structure of some other antimony chalcogenides. For example $BaSb_2Se_4$ contains both 3-coordinate ($SbSe_3$) and 4-coordinate ($SbSe_4$) antimony units that are bonded into a polymeric array (11).

The unusual compound $Ba_4Sb_4Se_{11}$ also has a related structure that contains two trig-

TABLE II

POSITIONAL AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS

Atom	x	y	z	$B(\text{Å}^2)$
TE	0.63774(5)	0.47379(5)	0.25076(5)	1.045(8)
SB	0.78217(5)	0.78217	0.78217	0.993(4)
K(1)	0.0745(2)	0.0745	0.0745	1.10(1)
K(2)	0.5672(2)	0.5672	0.5672	1.05(1)
K(3)	0.3273(2)	0.3273	0.3273	1.55(2)

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as $B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

onal pyramidal SbSe₃ units that are coupled together by two bridging sellenides (e.g., SeSb(μ-Se)₂SbSe) in a *cis* or *trans* configuration. The crystalline material also contains a trigonal pyramidal $SbSe_3^{3-}$ Zintl anion, as well as $Sb_2Se_4^{2-}$ and Se_2^{2-} Zintl anionic units, in addition to the barium counterions (*12*). The bonding electron distribution of K₃SbTe₃, as well as the antimony sellenides previously reported, is consistent with the predictions of the Zintl concept of bonding.

Because of the differences in the electronegativities of the elements that comprise a Zintl phase material, there is often a great deal of ionic character in the Zintl phase. This ionic character may be sufficient to allow the solvation of salt-like ions in polar solvents (*13–15*). Since some Zintl phase materials have been reported to dissolve in polar solvents, we examined the solubility of K₃SbTe₃ in several solvents. We observed the solid material to form solutions with DMSO, DMF, formamide, en, and H₂O solvents. All of the solutions were stable except the aqueous solution which was metastable and decomposed to an insoluble product after 24 hr.

Our observations concerning other Zintl phase solutions show a trend that correlates the solubility properties of the materials. We have reported reactions of $K_4SnTe_4^{13}$, $K_5InTe_4^{14}$, and $K_2Te_2^{15}$ with transition metals in solution to produce intermetallic prod-

ucts. The intermetallic product is formed because the Zintl phase precursor dissolves in a polar solvent. Each of the soluble Zintl phase materials contains isolated Zintl anions and potassium cations in the solid material. The intermetallic material forms from the metathesis reaction of the Zintl solution with a metal salt.

Other Zintl phase materials that are insoluble include $K_3Ga_3As_4$ (*16*), $K_4In_4X_6$ ($X = $ As, Sb) (*17*), and $K_2Ga_2Sb_4$ (*18*). Each of these materials has a polymeric structure; $K_3Ga_3As_4$ and $K_4In_4X_6$ ($X = $ As, Sb) are planar, and $K_2Ga_2Sb_4$ is one-dimensional. It appears that the covalent bonding network in the lattice prevents these materials from dissolving.

The results of resistivity measurements using the four-probe van der Pauw method show that the material is a poor semiconductor at room temperature, with a specific re-

TABLE III

INTERATOMIC DISTANCES (Å)

Atom 1	Atom 2	Distance
Te	Sb	3 × 2.7831(6)
Te	K(1)	3 × 3.4511(6)
Te	K(1)	3 × 3.6215(7)
Te	K(2)	3 × 3.4774(8)
Te	K(2)	3 × 3.6059(5)
Te	K(3)	3 × 3.6248(6)
Te	K(3)	3 × 3.7482(5)

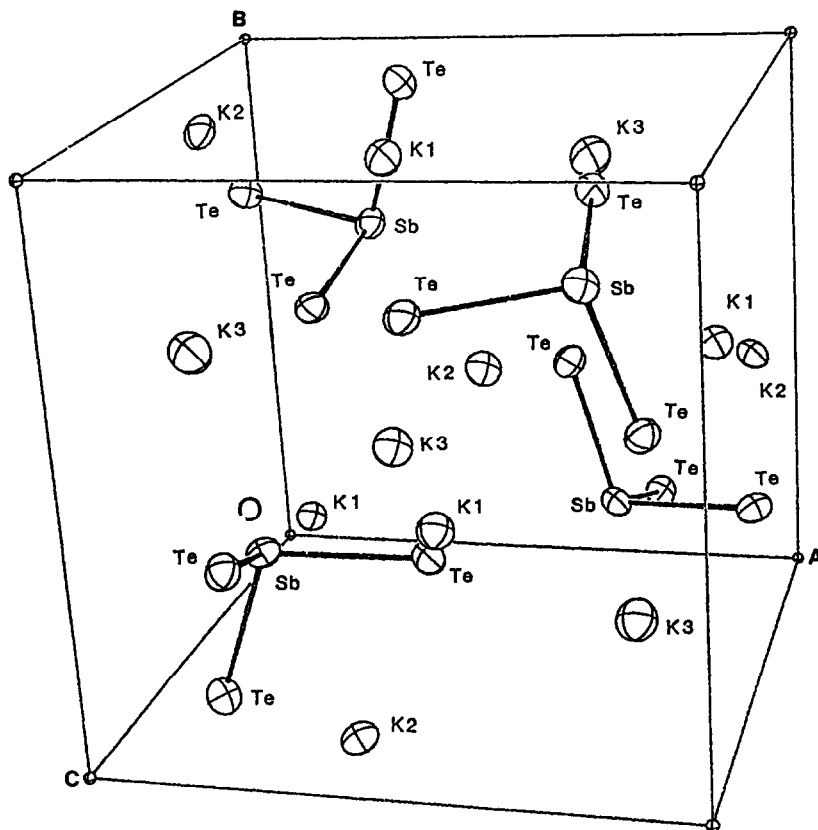FIG. 1. ORTEP diagram of the unit cell of K_3SbTe_3.

sistivity of $\rho = 2 \times 10^5$ Ω-cm. Although the material has a great deal of ionic character, K_3SbTe_3 is a better conductor than layered I–III–V materials such as $K_3Ga_3As_4^{16}$ and $K_4In_4X_6$ (X = As, Sb) (17), although the polymeric I–III–V material $K_2Ga_2Sb_4^{18}$ is a better semiconductor.

We have observed that K_3SbTe_3 reacts in solution with transition metal halide salts to produce interesting magnetic intermetallic materials (e.g., $M_5(SbTe_3)_2$, where M = Co, Ni, Fe); some of these exhibit spin glass and photomagnetic effects. We are in the process of examining the chemical properties of K_3SbTe_3 and other alkali–antimony–telluride Zintl phases and will report on this in a subsequent communication.

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