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Puckered Hexagonal Nets in $^{2}_{\infty}[Sn_{3/3}As^{-}_{3/3}]$ and $^{2}_{\infty}[Sn_{3/3}Sb^{-}_{3/3}]$

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The new compounds KSnAs and KSnSb have been prepared and their crystal structures have been determined from X-ray powder diffraction patterns. Both compounds crystallize in hexagonal systems (space group $P6_3mc$; a = 4.1032(5) Å, c = 12.845(2) Å for KSnAs and a = 4.359(1) Å, c = 13.150(3) Å for KSnSb). The structures contain puckered sheets, with the Sn and As (or Sb) segregated on opposite sides of each sheet and with the potassium cations between the sheets.

1. Introduction

Both α-As and α-Sb adopt the interesting layer structure which consists of puckered hexagonal sheets of covalently bonded As or Sb layers. In the structures of $CaSi_2$ (*1*) and $CaGe_2$ (*2*), the Si^- and Ge^- nets are isosteric to the As nets. Although in $BaSi_2$ (*3*), KSn (*4*), and $SrSi_2$ (*5*) the anionic species exhibit the same electronic configuration as As, the first two compounds consist of Si_4^{4-} or Sn_4^{4-} tetrahedra and the third one contains a three-dimensional network formed by three-bonded Si^- atoms. In the ternary compound $BaGe_2As_2$ (*6*) the Ge atoms are coordinated tetrahedrally by two Ge and two As atoms. These tetrahedra are linked to each other such that a three-dimensional framework results. To our knowledge, compounds with these puckered sheets containing two different elements have not been reported. In this paper we present the syntheses and crystal structures of KSnAs and KSnSb which consist of puckered sheets with the potassium cations between the sheets.

2. Experimental and Results

2.1 Preparation

All manipulations were performed under a He atmosphere. Potassium metal (99.95%), tin metal (99.999%), and antimony metal (99.5%) were obtained from Cerac. Arsenic powder (99%) was obtained from AESAR. The compounds KSnAs and KSnSb were prepared in two steps. First, KSn was prepared by reacting potassium metal with tin metal (1.03 : 1.00 mole ratio) in an alumina crucible at about 280°C for 1 h under 1 atm He. The product was checked for purity by means of an X-ray powder pattern. The compound KSnAs was prepared by heating a mixture of KSn and As (1 : 1 mole ratio) in an alumina crucible at 590°C for 24 h under 1 atm He. The compound KSnSb was prepared by heating a pressed pellet containing a stoichiometric amount of KSn and Sb in an alumina crucible lined with tungsten foil at 530°C for 24 hr under 1 atm He. Both compounds crystallized as shiny metallic plates. However, single crystals suitable for single crys-

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TABLE I

THE UNIT CELL PARAMETERS OF KSnAs AND KSnSb

KSnAs	KSnSb
Hexagonal	Hexagonal
$P6_3mc$	$P6_3mc$
a = 4.1032(5) Å	a = 4.359(1) Å
c = 12.845(2) Å	c = 13.150(3) Å
V = 187.30(6) Å^3	V = 216.4(2) Å^3

tal X-ray diffraction work could not be isolated from the reaction products. Therefore, the crystal structures were determined from their X-ray powder patterns.

The synthesis of KSnBi was also accomplished, but this compound was found to be isostructural with KBi_2 (*7, 8*).

2.2 X-ray Powder Investigations

X-ray powder patterns of the products were obtained using a Philips powder diffractometer and Cu$K\alpha$ radiation in the range from 2θ = 5 to 80° at 0.25°/min in 2θ. The sample was contained in a specially designed vacuum-tight cell which was fitted with a Be window. The effect of preferred orientation was largely reduced, but not eliminated, by thoroughly mixing a finely powdered sample (ca. 400 mesh) with MgO powder. The integrated intensities were estimated by measuring the peak areas. Silicon powder was mixed with all samples as an internal standard for calculating the observed d-spacings and unit cell parameters. Both samples gave very sharp diffraction peaks, suggesting well-ordered crystal structures.

Both powder patterns were completely indexed on the basis of a hexagonal unit cell. The unit cell parameters for both compounds are listed in Table I. The crystal structure refinement was carried out with a computer program originally written by Wiseman (*9*). The atomic scattering factors for neutral atoms were taken from the "International Tables for X-ray Crystallography" (*10*). The scale factor and positional parameters were refined using the observed intensities. A fixed isotropic temperature factor (1.5 Å^2) was initially used for all atoms. The initial atomic positions were assigned the same values as those for $Ca_{0.9}Li_{0.13}Ge_{1.97}$ (*11*) because they showed comparable unit cell parameters. In the refinement of KSnAs, the tin and aresenic atoms were assumed to be at $2a$ and $2b$ special positions of the space group $P6_3mc$ (No. 186), respectively. The refinement quickly converged to $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 9.59\%$. The sample still showed the effect of preferred orientation since I(obsd) for all $00l$ reflections were significantly greater than the corresponding I(calc). However, the enhancement factor ($E = 100 \times (I_o - I_c)/I_c$ for the $00l$ reflections largely varies: 8% for 002, 70% for 004, 200% for 006, and 90% for 008, which is unexpected. A least-squares refinement including the scale factor, positional, and thermal parameters resulted a very poor agreement factor probably because of the correlation between the scale factor and thermal parameters. The refinement with alternately fixed scale factor and thermal parameters very slowly converged to a slightly lower R factor (9.27%). The thermal parameter for Sn decreased to 0.87 Å^2, while all other parameters remained essentially the same. Since $I_o(00l) > I_c(00l)$ and the $00l$ reflections have a large effect on the atom at the $2a$ special position, the decrease in the thermal parameter for Sn is expected. Accordingly, the considerably smaller thermal parameter for Sn may not be physically meaningful, and a fixed isotropic thermal parameter (1.5 Å^2) was used for all atoms in the subsequent refinements. Several different models were also tested. A few cycles of least-squares refinement with the Sn and As positions being exchanged, randomly occupied, or partially

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR KSnAs

d-spacings (Å)		Intensities		
Observed[a]	Calculated	Observed	Calculated	*hkl*
6.41(1)	6.422	821	762	002
3.551(3)	3.554	124	139	100
3.423(3)	3.425	209	255	101
3.209(3)	3.211	201	118	004
3.109(3)	3.109	1000	969	102
2.734(2)	2.734	386	404	103
2.383(2)	2.382	530	488	104
2.142(1)	2.141	75	25	006
2.051(1)	2.052	347	427	110
1.954(1)	1.954	135	189	112
1.7130(7)	1.712	179	136	202
1.6056(6)	1.606	57	30	008
1.5550(6)	1.555	122	108	204
1.3664(4)	1.367	101	86	206

[a] Cu$K\bar{\alpha}$ (λ = 1.5418 Å) was used for calculating the observed *d*-spacings.

disordered ($\frac{3}{4}$ Sn + $\frac{1}{4}$ As at 2*a* position, $\frac{3}{4}$ As + $\frac{1}{4}$ Sn at 2*b* position, or $\frac{2}{3}$ Sn + $\frac{1}{3}$ As at 2*a* position, $\frac{2}{3}$ As + $\frac{1}{3}$ Sn at 2*b* position) yielded considerably poorer refinement results. Therefore, the model giving $R(F) = 9.59\%$ was assumed to be essentially correct.

In the crystal structure refinement of KSnSb, the initial tin and antimony atoms were assumed to be at the same positions as the corresponding atoms in KSnAs. The refinement yielded a considerably lower agreement factor ($R(F) = 4.90\%$). In contrast to KSnAs, $I_c(002)$ for KSnSb is greater than the corresponding I_o. No other 00*l* reflections were included in the structure refinement, because they overlapped either with a strong peak (102) from KSnSb or with the reflection from the sample cell. The exact reason why KSnAs had a relatively higher *R* factor is not clear to us. However, it should be noted that tin and antimony are nearly isoelectric so that any (dis)order in KSnSb would not affect the intensity fit.

TABLE III

X-RAY POWDER DIFFRACTION DATA FOR KSnSb

d-spacings (Å)		Intensities		
Observed[a]	Calculated	Observed	Calculated	*hkl*
6.59(1)	6.575	857	942	002
3.778(3)	3.775	34	54	100
3.628(3)	3.628	609	653	101
3.277(3)	3.274	1000	985	102
2.861(2)	2.860	708	702	103
2.481(1)	2.479	765	719	104
2.068(1)	2.069	333	268	112
1.8950(8)	1.895	288	240	106
1.6818(6)	1.682	108	88	107

[a] Cu$K\bar{\alpha}$ (λ = 1.5418 Å) was used for calculating the observed *d*-spacings.

The indexing results and the calculated intensities for KSnAs and KSnSb are listed in Tables II and III, respectively. The atomic positions and some selected interatomic distances are given in Tables IV and V, respectively.

3. Discussion

Figure 1 shows a stereographic view of the unit cell of KSnAs, together with a projection onto the $(11\bar{2}0)$ plane. The tin and arsenic atoms form puckered sheets which are separated by potassium atoms. The principal building units of the puckered sheets can be regarded as the chair form of

TABLE IV

POSITIONAL PARAMETERS FOR KSnAs AND KSnSb

KSnAs				KSnSb			
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
K	$\frac{1}{3}$	$\frac{2}{3}$	0	K	$\frac{1}{3}$	$\frac{2}{3}$	0
Sn	0	0	0.2742	Sn	0	0	0.2990
As	$\frac{1}{3}$	$\frac{2}{3}$	0.6709	Sb	$\frac{1}{3}$	$\frac{2}{3}$	0.6885

TABLE V

SELECTED INTERATOMIC DISTANCES IN KSnAs AND KSnSb[a]

KSnAs		KSnSb	
Sn–As	2.715 Å	Sn–Sb	2.925 Å
K′–Sn	3.745 (3×)	K′–Sn	3.650 (3×)
K–As	3.230 (3×)	K–Sb	3.505 (3×)
K′–As	4.227	K′–Sb	4.135
K′–Sn′	4.245	K′–Sn′	4.668

[a] The atom labels refer to Fig. 1.

the six-membered rings, i.e., $[\mathrm{Sn}_{3/3}\mathrm{As}^{-}_{3/3}]$. The X-ray powder investigations indicate that the tin and arsenic atoms in KSnAs are ordered. Although tin and antimony have nearly the same X-ray scattering factors, one can speculate the structure of KSnSb on the basis of the interatomic distances (vide infra). As shown in the projection diagram the sequence of layers is ABaCBcABaCBcA . . . , where the lowercase letters denote the potassium layers. However, the sequence in α-As is ABCABC. . . .

According to the 8 − N rule the charge distributions are as follows: $\mathrm{K^+Sn^-As}$ and $\mathrm{K^+Sn^-Sb}$. The observed bond lengths d(Sn–As) (2.715 Å) and d(Sn–Sb) (2.925 Å) can be successfully estimated based on the following distances: d(Sn–Sn) (in $\mathrm{K^+Sn^-}$) = 2.98 Å (*4*), d(As–As) (in α-As) = 2.517 Å (*12*), and d(Sb–Sb) (in α-Sb) = 2.908 Å (*12*). The potassium atoms are coordinated by three Sn and three As(Sb) in a distorted octahedral geometry. Since the radius for $\mathrm{Sn^-}$ is greater than the radii for As and Sb, the distance $d(\mathrm{K^+–Sn^-})$ is expected to be longer than d(K–As) and d(K–Sb). Accordingly, the interatomic distances 3.650 and

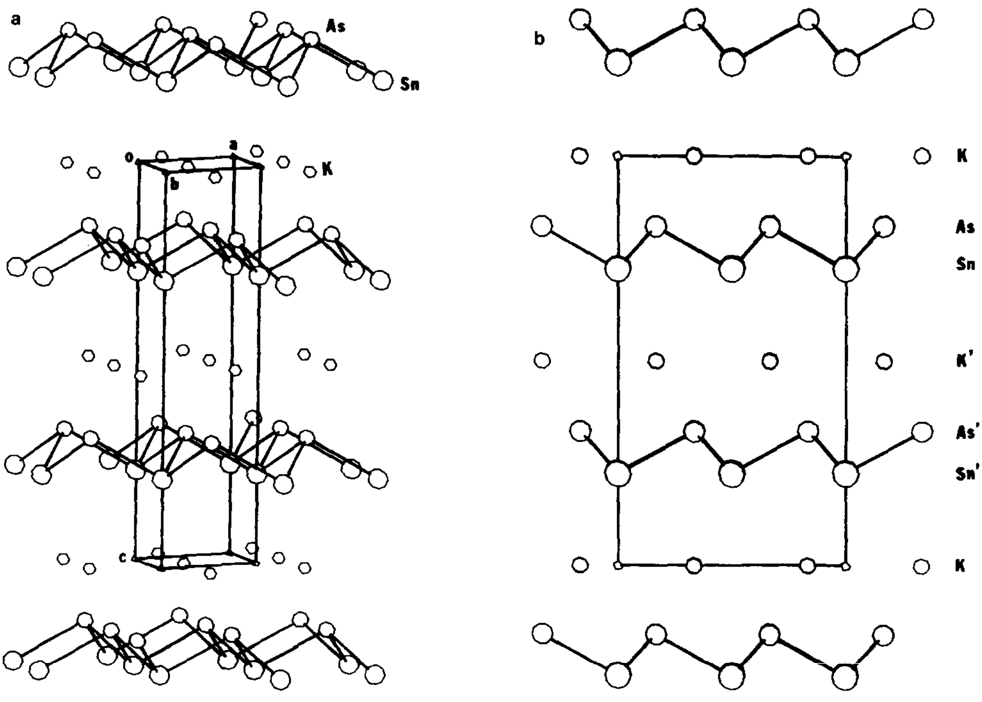

FIG. 1. (a) A perspective view of the KSnAs structure. (b) A projection of the KSnAs structure onto the (11$\bar{2}$0) plane with the unit cell outlined.

3.505 Å in KSnSb correspond to *d*(K–Sn) and *d*(K–Sb), respectively.

Since Sn and Sb are Mössbauer elements, Mössbauer spectroscopy measurements of KSnAs and KSnSb along with KSn, Sn, and Sb references would be very informative either on the problem of (dis)-order or in obtaining the experimental evidence of the oxidation states of Sn and Sb in these two compounds. On the other hand, our resistivity measurements on a pressed pellet of KSnSb showed nonmetallic behavior between 320 and 4 K. A preliminary analysis of KSnAs using photothermal deflection spectroscopy suggests that it is a semiconductor at room temperature. Further research on these materials is in progress.

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