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A New Cubic $KSbO_3$ Derivative Structure with Interpenetrating Networks. Crystal Structure of $Bi_3GaSb_2O_{11}$

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A new family of compounds structurally related to cubic $KSbO_3$ has been synthesized. Crystals of one of them, $Bi_3GaSb_2O_{11}$, have been prepared, and the structure has been determined. Intensity data were collected from the powder using a diffractometer, and the final R was 0.051. The structure may be regarded as three interpenetrating networks. Two networks are identical and have the composition Bi_3O_2. The other network is found in all the cubic $KSbO_3$-related structures and is based on metal-oxygen octahedra which share edges and corners.

Introduction

During our investigation of mixed oxides of the post transition metals, a cubic phase was discovered in the Bi-Ga-Sb-O system. Although this new phase appeared to be structurally related to cubic $KSbO_3$,[1] its composition was not of the AMO_3 type. The composition and structure of this new compound have now been determined, and this has led to the discovery of a new family of structurally related phases.

Experimental Section

Single crystals of the new mixed oxide in the Bi-Ga-Sb-O system were prepared from a Bi_2O_3 flux. Reagent grade oxides were mixed in the rather arbitrary molar ratios of 12:1:1 Bi_2O_3-Ga_2O_3-Sb_2O_3 since an accurate formula of the desired phase was not known. This mixture was heated in air to 1060° in an open Pt crucible, cooled at 6°/hr to 800°, and then furnace cooled. After washing the product with nitric acid, only transparent yellow crystals remained. Precession photographs were taken of these single crystals using Mo radiation. An X-ray powder pattern was obtained at 25° using a Hagg-Guinier camera with Cu $K\alpha_1$ radiation and an internal standard of high-purity KCl (a = 6.2931 Å at 25°).

X-Ray intensity data were collected on a Picker automatic powder diffractometer using Cu $K\alpha$ radiation and a graphite monochromator. The sample was ground and passed through a 400-mesh screen. This powder was packed into a sample holder which was sufficiently large to intercept all X-rays over the entire θ range scanned. The sample was also thick enough to absorb essentially all X-rays. The pattern was step scanned from 10 to 90° 2θ. The stepping increments were 0.01° in the region of peaks and 0.05° in background regions. The counting time at each step was 1.8 sec. Of the 60 possible peaks which could have been observed, 49 were judged to be observed. Resolution problems were not encountered since the sample has a cubic structure. Background corrections were made by linear interpolation between regions judged to be true background.

Least-squares refinement of the intensity data used the full-matrix program[2] SFLS6 adapted for powders. σ values were taken to be $\sqrt{I_o} + 100$, and the function $w(I_o - I_c)^2$ was minimized. Intensities of unobserved peaks were set at 2.0 for the initial stages of the refinement, but these unobserved reflections were rejected in the final cycles of refinement. Atomic scattering factors were taken from Cromer and Waber.[3] Real and imaginary anomalous dispersion corrections were made using Cromer's[4] values.

Results

Single-crystal X-ray photographs unambiguously showed a space group of $Pn3$ for this Bi-Ga-Sb oxide. A least-squares refinement of the Guinier data gave a cell edge of 9.4907 ± 0.0002 Å. Cubic $KSbO_3$ has a cell edge of 9.56 Å, and it also has a space group of $Pn3$. Thus, it seemed very likely that our new cubic phase was structurally related to cubic $KSbO_3$. Consequently, a least-squares refinement of our intensity data was initiated with 4 Bi in position b, 8 Bi in position e ($x = 0.16$), 6 Ga + 6 Sb in position g ($x = 0.34$), 12 O in position f ($x = 0.34$), and 24 O in position h ($x = 0.34, y = 0.27, z = 0.97$). The refinement was encouraging, but the thermal parameter for Ga-Sb went negative. Therefore, the ratio of Ga to Sb at this site was refined. This became 1:2 within experimental error, and this ratio was subsequently confirmed by other experiments. The formula at this point was $Bi_3GaSb_2O_9$. This would be possible if Sb were trivalent. However, it seemed more likely that Sb was pentavalent and that the formula should be $Bi_3GaSb_2O_{11}$. Since Z is 4, this would imply 8 more oxygens in the cell. Positions b + c cannot be considered since Bi already occupies position b. Positions d + a seemed extremely unlikely because an oxygen in position d would give rise to completely unreasonable interatomic distances. Thus, the only possibility appeared to be the placing of an oxygen in position e with $x \approx 0.15$. This structure readily refined to an R of 5.1%.

A listing of the final observed and calculated relative intensities is available.[5] The actual observed intensities were larger by a factor of 18. The first two reflections were rejected in the final refinement since low-angle peaks are frequently too weak due to extra absorption caused by roughness of the sample surface. The final refined parameters are given in Table I. The thermal parameters are somewhat larger than expected. This is probably due in part to Ga and Sb occupying the same crystallographic site which causes static statistical displacements. Although the standard deviations for the oxygen thermal parameters are very high, it is still significant that the oxygen thermal parameters are well behaved. Table II gives the metal-oxygen distances which might be considered as bonding.

Several methods of cation analyses were attempted on $Bi_3GaSb_2O_{11}$, but none was successful due to interferences between ions. However, using 3:1:2 Bi:Ga:Sb reactant ratios resulted in a single-phase powder pattern identical with the X-ray powder pattern of the single crystals prepared with excess Bi_2O_3. Furthermore, other compositions such as Bi_2GaSbO_7, $Bi_3Ga_{1.25}Sb_{1.75}O_{10.75}$, and $Bi_5GaSb_5O_{21.5}$ gave cubic patterns with a cell edge of 9.49 Å plus other impurity lines.

Oxygen was analyzed by the inert-gas fusion method which gave 15.4% O as compared to 15.76% calculated for $Bi_3GaSb_2O_{11}$. The observed density was 8.66 g/cm^3 compared to 8.67 g/cm^3 calculated for 4 formula units per cell.

The characterization of $Bi_3GaSb_2O_{11}$ suggested other possible phases with the same structure. Some other successful preparations are listed in Table III which shows that rare earths can partially substitute for bismuth and a variety of

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[1] P. Spiegelberg, *Ark. Kemi,* **14A**, No. 5, 1 (1940).

[2] C. T. Prewitt, unpublished computer program.

[3] D. T. Cromer and J. T. Waber, *Acta Crystallogr.,* **18**, 1041 (1965).

[4] D. T. Cromer, *Acta Crystallogr.,* **18**, 20 (1965).

[5] See paragraph at end of paper regarding supplementary material.

Table I. Positional and Thermal Parameters[a] for $Bi_3GaSb_2O_{11}$

	Position	x	y	z	B, Å^2
Bi(1)	8e; $\underline{3}$	0.3816 (7)	0.3816	0.3816	2.8 (0.2)
Bi(2)	4b; $\bar{3}$	0.0	0.0	0.0	2.0 (0.2)
$Ga_{1/3}Sb_{2/3}$	12g; 2	0.594 (1)	0.75	0.25	0.8 (0.2)
O(1)	8e; 3	0.136 (8)	0.136	0.136	2.7 (2.7)
O(2)	12g; 2	0.601 (9)	0.25	0.25	2.4 (2.4)
O(3)	24h; 1	0.594 (7)	0.530 (14)	0.248 (6)	3.1 (2.2)

[a] Numbers in parentheses are esd's in the last significant digits.

Table II. Some Interatomic Distances[a] for $Bi_3GaSb_2O_{11}$

Bi(1)-O(1)	2.34 (3×)	O(1)-Bi(1)	2.34 (3×)
O(2)	2.73 (3×)	Bi(2)	2.24 (1×)
O(3)	2.77 (3×)	O(2)-Bi(1)	2.73 (2×)
Bi(2)-O(1)	2.24 (2×)	Ga(Sb)	2.05 (2×)
O(3)	2.53 (6×)	O(3)-Bi(1)	2.77 (1×)
Ga(Sb)-O(2)	2.05 (2×)	Bi(2)	2.53 (1×)
O(3)	2.09 (2×)	Ga(Sb)	1.89 (1×)
O(3)	1.89 (2×)	Ga(Sb)	2.09 (1×)

[a] The numbers in parentheses after the distances indicate the number of such bonds per central atom. The errors estimated from standard deviations are about ±0.08 Å.

Table III. New Compounds with the $Bi_3GaSb_2O_{11}$ Structure

Compd	a, Å	T,[a] °C	Compd	a, Å	T,[a] °C
$Bi_3GaSb_2O_{11}$	9.49	1000	$Bi_3Ru_2SbO_{11}$	9.42	1100
$Bi_2LaGaSb_2O_{11}$	9.51	1000	$Bi_3RhSb_2O_{11}$	9.51	1100
$Bi_2GdGaSb_2O_{11}$	9.46	1000	$Bi_3FeSb_2O_{11}$	9.52	900
$Bi_3AlSb_2O_{11}$	9.45	1100	$Bi_3Fe_{1.67}Te_{1.33}O_{11}$	9.47	800

[a] Temperature of preparation.

cations can substitute for Ga-Sb. Weak impurity lines were present in some of these X-ray patterns so that slight deviations from the listed formulas may be indicated.

Discussion

The structure of $Bi_3GaSb_2O_{11}$ is probably best viewed as interpenetrating networks. One network is characteristic of all cubic $KSbO_3$-related structures and has a composition MO_3 where M is octahedrally coordinated by oxygen. These octahedra each share one edge forming pairs, and these pairs are linked by sharing corners to form the three-dimensional network shown in Figure 1. There are several possibilities for insertions into this framework. In cubic $KSbO_3$ there are simply K^+ cations within the SbO_3^- framework. In $La_4Re_6O_{19}$ (or $La_4O\cdot 6ReO_3$) there are La_4O tetrahedra within the octahedral ReO_3 framework.[6,7]

For $Bi_3GaSb_2O_{11}$ we find a third method of insertion into the octahedral framework. This formula can be written as $Bi_3O_2\cdot(GaSb_2)O_9$ or $Bi(2)_4O(1)_4Bi(1)_{4/2}\cdot 2GaSb_2O(2)_6O(3)_{12}$. The second part of this formula ($2GaSb_2O_9$) is the octahedral network characteristic of all cubic $KSbO_3$-related structures. There is no bonding of O(1) to Ga-Sb since the closest distance of this type is 3.84 Å. The first part of this formula ($Bi_4O_4Bi_2$) is actually two identical interpenetrating networks which interpenetrate the octahedral network. Thus, there are three interpenetrating networks! This description ignores bonding of Bi to O(2) and O(3). Table II shows that both Bi(1)-O and Bi(2)-O distances are much shorter for O(1) than for O(2) or O(3). Thus, there is some justification for ignoring Bi-O(2) and Bi-O(3) bonding as a first approximation. The Bi-O(1) bonds could be considered as the strong covalent *intra*network bonds, and the Bi-O(2) and Bi-O(3) bonds could be considered as *inter*network ionic bonds. This manner of depicting the structure is shown in Figure 2.

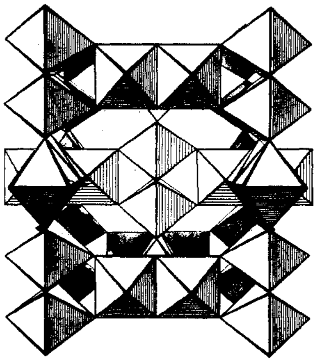

Figure 1. The octahedral network common to all cubic $KSbO_3$-type structures.

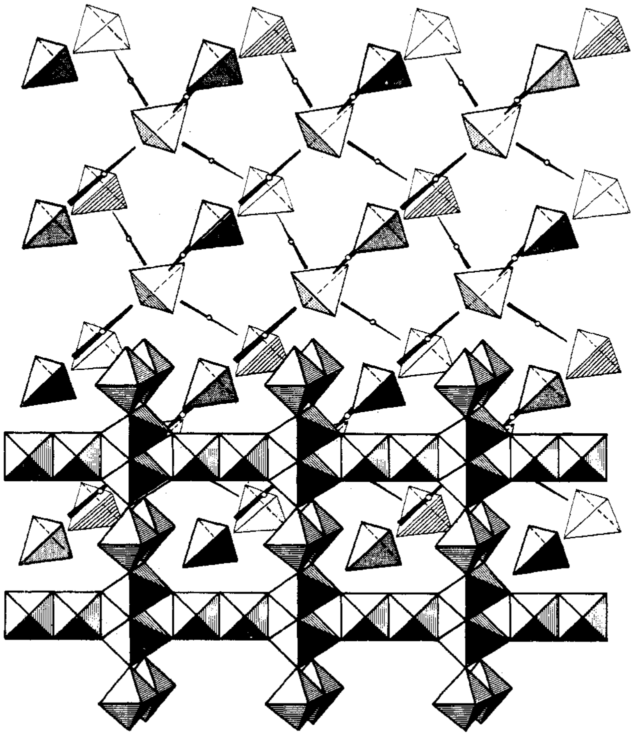

Figure 2. The three interpenetrating networks of $Bi_3GaSb_2O_{11}$. Bismuth atoms are at the corners of the tetrahedra and at the midpoints of the lines connecting the tetrahedra. Oxygen atoms are at both ends of the lines connecting the tetrahedra; thus, there is an oxygen at every face of the tetrahedra. The tetrahedra of one network are shaded with lines and those of the other with dots. The octahedra have oxygen atoms at their corners and Ga-Sb atoms at their centers. The top of the figure shows the two tetrahedral networks only, and the octahedral network is shown alone at the bottom. The octahedral network is basically at $z = 1/4$, but the tetrahedra are centered at three levels: heavy shading for $z = 1/4$, medium shading for $z = 3/4$, and light shading for $z = 5/4$.

Four Bi(2) atoms form a tetrahedron centered at position a with Bi-Bi distances of 3.53 Å. An analogous tetrahedron of La atoms is found in $La_4Re_6O_{19}$, and then there is an oxygen at the center, *i.e.*, $La_4O\cdot 6ReO_3$. However, in $Bi_3GaSb_2O_{11}$ there is instead an oxygen on every face of the tetrahedron of Bi(2) atoms. These oxygens are also each bonded to one Bi(1) atom in addition to three Bi(2) atoms of the Bi(2) tetrahedron. Thus, O(1) is in approximate tetrahedral coordination to Bi. The Bi(1) atom is shared between two tetrahedral $Bi(2)_4O(1)_4$ units; thus, we may write $Bi(2)_4O(1)_4Bi(1)_{4/2}$.

The two $Bi_4O_4Bi_2$ networks are equivalent to each other and are analogous to the two identical interpenetrating net-

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(6) J. M. Longo and A. W. Sleight, *Inorg. Chem.*, **7**, 108 (1968).

(7) N. Morrow and L. Katz, *Acta Crystallogr., Sect. B*, **24**, 1466 (1968).

works in Cu_2O. (Cu_2O also has the *Pn*3 space group with 4 Cu in b and 2 O in a.) The linearly coordinated Cu becomes Bi(1) which is also linearly coordinated to oxygen in the first approximation. The tetrahedrally coordinated O in Cu_2O becomes the $Bi(2)_4O(1)_4$ tetrahedron in $Bi_3GaSb_2O_{11}$. The pyrochlore structure has also been described as interpenetrating networks[8] where one of the networks is analogous to that found in Cu_2O.

The bonding of Bi(2) is typical of a lone-pair cation such as Bi^{3+}. In $Bi_4Si_3O_{12}$, for example,[9] Bi is also on a threefold axis with three oxygens at 2.15 Å, three at 2.62 Å, and three at 3.55 Å. The bonding of Bi(1) is less common for a lone-pair cation, but an essentially identical coordination of Bi is found in pyrochlores such as $Bi_2Ru_2O_7$ and $Bi_2Ir_2O_7$. In $Bi_2Ru_2O_7$, for example,[10] Bi is again on a threefold axis with two oxygens at 2.23 Å and six oxygens at 2.53 Å.

The coordination of the Ga-Sb "atom" is very close to octahedral. The average metal-oxygen distance of this octahedron is 2.01 Å; this compares favorably to 1.99 Å which is the sum of the radii.[11] The metal-metal distance across the shared edge is 2.96 Å. For two perfect octahedrons sharing an edge, this distance would be 2.84 Å for metal-oxygen distances of 2.01 Å. Thus, the metals are displaced away from each other as would be expected from electrostatic repulsion. This is in contrast to the situation found in $La_4Re_6O_{19}$ where the Re-Re distance is only 2.42 Å and metal-metal bonding is assumed.[6]

All the oxygens in the $Bi_3GaSb_2O_{11}$ structure are in approximate tetrahedral coordination if *intra*network and *inter*network bonds are taken into account. Thus, there are no metal-oxygen-metal angles close to 180°. Such angles tend to be avoided in post transition metal oxides as was first pointed out by Blasse.[12,13] The π interaction between the filled cation d orbitals and the filled oxygen p orbitals is, of course, strongly antibonding for 180° M-O-M linkages. However, this unfavorable interaction can be largely avoided by oxygen sp^3 hybridization which results in M-O-M angles closer to 109° and tends to eliminate the π interaction.

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Registry No. $Bi_3GaSb_2O_{11}$, 39322-88-8.

Supplementary Material Available. A listing of observed and calculated relative intensities for $Bi_3GaSb_2O_{11}$ will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2314.

(8) A. W. Sleight, *Inorg. Chem.*, 7, 1704 (1968).

(9) D. J. Segal, R. P. Santoro, and R. E. Newnham, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, 123, 73 (1966).

(10) A. W. Sleight and R. J. Bouchard, to be submitted for publication.

(11) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, 25, 925 (1969).

(12) G. Blasse, *J. Inorg. Nucl. Chem.*, 26, 1191 (1964).

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Helical Coordination. Structure and Bonding of the Five-Coordinate Complex Bis(2-thiobenzaldimino)-2,6-diacetylpyridinezinc(II)

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The crystal and molecular structure of a helical five-coordinate zinc complex of bis(2-thiobenzaldimino)-2,6-diacetylpyridine has been determined from three-dimensional single-crystal X-ray diffraction data. The complex crystallized with the monoclinic space group $P2_1$ ($C_2{}^2$; No. 4) with cell dimensions $a = 9.267$ (8) Å, $b = 13.174$ (13) Å, $c = 8.172$ (7) Å, and $\beta = 105.00$ (4)°. There are two molecules of the complex per unit cell ($\rho_{\mathrm{exptl}} = 1.50$ (2) g/cm³, $\rho_{\mathrm{calcd}} = 1.519$ (3) g/cm³ for $Z = 2$). The intensities were obtained on a Picker automatic diffractometer (Mo Kα raidation, λ 0.71069 Å); least-squares refinement of positional and thermal parameters for all the nonhydrogen atoms converged to a discrepancy index of $R = 5.68\%$ ($R_w = 5.05\%$) for 1769 independent reflections. The ligand has a helical conformation arising from intramolecular steric interactions. The zinc(II) ion is coordinated to three nitrogen atoms and two sulfur atoms forming a five-coordinate complex with an approximate C_2 axis passing through the zinc atom and the nitrogen atom of the pyridine moiety. The average Zn-S distance is 2.335 (3) Å and the average of Zn-N distances is 2.17 (1) Å. There is little evidence for electron delocalization in the potentially highly conjugated ligand system.

Introduction

Pentacoordination has been found to be rather common among transition metal complexes in recent years.[1] Most five-coordinate complexes have been synthesized by using branched polydentate chelate ligands, especially the tripod type with large bulky substitutents which force a five-coordinate donor arrangement for steric reasons.[2] However, a considerable number of five-coordinate complexes containing only unidentate ligands have been prepared in which electronic rather than steric factors predominate in influ-

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