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The Room-Temperature Structure of BaZnGeO₄

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Abstract

The room-temperature phase of $BaZnGeO_4$ shows two types of superlattice reflexions. The first appear on the $(001)^*$ reciprocal-lattice plane, giving relationships $\mathbf{a} = \mathbf{a}_{sub} - \mathbf{b}_{sub}$ and $\mathbf{b} = \mathbf{a}_{sub} + 2\mathbf{b}_{sub}$. The second type appear along the $\mathbf{c}^*$ direction, and are very weak and incommensurate with a relationship $\mathbf{c} \simeq 4\mathbf{c}_{sub}$. The superstructure has been determined neglecting the incommensurate reflexions. The space group is $P6_3$ with unit-cell dimensions $a = 9.2905$ (3), $c = 8.728$ (1) Å and $Z = 6$. The final R is 0.0464 for 306 independent reflexion data collected on a four-circle diffractometer. The crystal has a stuffed structure derived from the high-tridymite framework. Ba atoms are surrounded by nine oxygen atoms with Ba—O distances ranging from 2.55 (6) to 3.75 (8) Å. Ordering of Ge and Zn atoms is observed between two independent tetrahedral sites, giving average tetrahedral cation–oxygen distances of 1.76 (6) and 1.90 (7) Å for the respective tetrahedra.

Introduction

$BaZnGeO_4$ was first synthesized by Wallmark & Westgren (1937). This compound is one of the orthogermanates with a stuffed structure (Buerger, 1954) derived from the high-tridymite framework. It was reported to be isostructural with $BaAl_2O_4$ (Do Dinh & Durif, 1964). However, Takei, Tsunekawa & Maeda (1980) discovered the existence of a superstructure of $BaZnGeO_4$ which is different from that of $BaAl_2O_4$ reported by Von Hörkner & Müller-Buschbaum (1979). Takei & Tsunekawa (1980) studied the thermal phase transition of $BaZnGeO_4$ by differential thermal analysis and X-ray diffraction, reporting the following sequence of phase transitions; phase I (>1108 K), II (1108–522 K), III (522–234 K), IV (234–191 K) and phase V (<191 K). The high-temperature form (phase I) is free from superlattice reflexions and considered to be isostructural with the average structure of $BaAl_2O_4$, having hexagonal symmetry. All other phases show weak superlattice reflexions appearing along a and/or c axes. Similar superlattice reflexions were often reported for crystals with stuffed derivatives of the tridymite structure. In the superstructure of β-eucryptite (Winkler, 1948) and plutonic nepheline (Dollase, 1970), for example, ordering of Al and Si atoms at tetrahedral sites was observed. It is likely that the superstructure of $BaZnGeO_4$ is caused by ordering of Zn and Ge atoms as in β-eucryptite and nepheline. Structure determination of phase III at room temperature was undertaken

to supply structural knowledge on the successive phase transitions of BaZnGeO$_4$.

Experimental

Single crystals of BaZnGeO$_4$ synthesized by the Czochralski pulling method were shaped into spheres of 0.09 mm diameter. Weissenberg photographs taken at room temperature show hexagonal symmetry. The crystal gives two types of superlattice reflexions. The first appear along (001)* reciprocal-lattice planes, giving the relationships $a = a_{sub} - b_{sub}$ and $b = a_{sub} + 2b_{sub}$. The second type are very weak and incommensurate, appearing along c^* with a relationship $c \simeq 4c_{sub}$ (Fig. 1). The main diffraction spots corresponding to the subcell indicated that the structure is of the BaAl$_2$O$_4$ type, showing the symmetry $6/mmm$. However, a slight lowering of symmetry to $6/m$ was observed in the intensity distribution of superlattice reflexions. Since intensities of most of the incommensurate superlattice reflexions are below the sensitivity limit of the single-crystal diffractometry, the present study deals with only the superstructure along the plane perpendicular to the c axis. Weissenberg photographs revealed the space group to be $P6_3$ or $P6_3/m$ from the restriction $l = 2n$ for the reflexion $00l$. Since piezoelectricity had been detected, $P6_3$ was selected for the true space group. The space group of the subcell was determined to be $P6_322$. This is the same as that of the average structure of BaAl$_2$O$_4$. The cell dimensions were obtained by the least-squares method from 24 2θ values, which were measured on a four-circle diffractometer (Philips, PW1100) with Cu $K\alpha$ radiation in the 2θ range between 19 and 118°. The center of gravity of the reflexion profile was used for the 2θ value of each reflexion.

The results are shown in Table 1 together with other crystallographic data. Intensity data up to sin $\theta/\lambda = 0.63$ Å^{-1} were collected by the $\omega-2\theta$ scan technique. The intensity data were corrected for Lorentz and
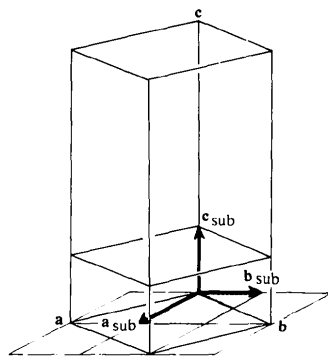
Table 1. *Crystallographic data for* BaZnGeO$_4$ *at room temperature*

The data of the subcell are in brackets.

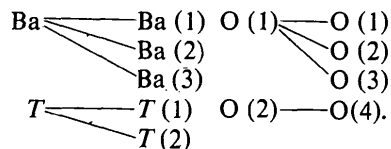Hexagonal $P6_3$ [$P6_322$]
$a = 9.2905$ (3) Å [5.3638 Å]
$c = 8.728$ (1) Å [8.728 Å]
$Z = 6$ [2]
$D_x = 5.183$ Mg m^{-3}
μ(Cu $K\alpha = 1.5418$ Å) = 83.591 mm^{-1}

polarization factors by the usual procedure. Absorption effects were corrected by the factors A^* listed in *International Tables for X-ray Crystallography* (1967). 306 independent reflexion data ($|F_o| > 3\sigma|F_o|$) were used for the structure determination of which 140 were those of the superlattice reflexions.

Structure determination

In advance of superstructure determination, the average structure was determined. The three-dimensional Patterson function was synthesized using the main reflexions. The Patterson diagrams indicate that the average structure of BaZnGeO$_4$ is essentially identical to the substructure of BaAl$_2$O$_4$ obtained by disregarding the doubling of the a axis (Perrotta & Smith, 1968). Therefore, two Ba atoms are allocated to the 2(a) sites of $P6_322$ and Zn and Ge atoms to 4(f) sites in a disordered state. The positions of the oxygen atoms were readily found by consecutive Fourier and difference-Fourier syntheses. Least-squares refinements were carried out with anisotropic temperature factors giving a final R of 0.064 for the 166 main reflexions.

The atoms in the supercell are related to those of average structure as follows:

$$Ba \begin{cases} Ba\,(1) \\ Ba\,(2) \\ Ba\,(3) \end{cases} \qquad O\,(1) \begin{cases} O\,(1) \\ O\,(2) \\ O\,(3) \end{cases}$$

$$T \begin{cases} T\,(1) \\ T\,(2) \end{cases} \qquad O\,(2){-\!-\!-}O(4).$$

Two possible types of deviation from the average structure were considered. One is the ordering of Zn and Ge atoms between $T(1)$ and $T(2)$ tetrahedral cation sites and another is the shift of atoms from the average position. The first type was supposed to give only a small contribution for intensities of the superlattice reflexions, because the difference of atomic number between Zn and Ge atoms is small. Therefore, the second type was considered at first.

It is usually very difficult to extract a small deviation of an atomic coordinate from the ordinary Patterson function. Therefore, the partial Patterson function was calculated using only the superlattice reflexions. It is clear from the average structure that all Ba–Ba and

Fig. 1. The geometrical relationships between supercell and subcell. a, b and c represent supercell and a_{sub}, b_{sub} and c_{sub} represent subcell vectors.

$T(1)$–$T(1)$ vectors are nearly on the plane $z = 0$ and its equivalents, and all $T(1)$–$T(2)$ vectors on the plane $z = 0.1$ and its equivalents. The section of the partial Patterson map through the planes $z = 0$ and $z = 0.11$ are shown in Fig. 2(a) and (b), respectively. These diagrams are interpreted fairly well by assuming the shifts $\Delta x = 0.005$, $\Delta y = -0.005$ and $\Delta z = -0.001$ for $T(1)$ and $\Delta x = -0.001$, $\Delta y = -0.006$ and $\Delta z = 0.001$ for $T(2)$. While R for the average structure was 0.2020 for all 306 observed reflexions, it was reduced to 0.1430 with these small shifts of the $T(1)$ and $T(2)$ atoms. Then the structure was refined by the least-squares method. In the course of the refinement, the O(4) atom was revealed to be triply split. Each part of the triplet has the population of one-third and is sited approximately 0.3 Å from the average position. Further, a significant difference was found between $T(1)$–O and $T(2)$–O bond lengths, indicating an ordering of tetrahedral metals. The refinements were tried for the following three models. In the first model, the Ge and Zn atoms occupy the $T(1)$ and $T(2)$ sites, respectively; in the second model the Ge and Zn atoms occupy each site
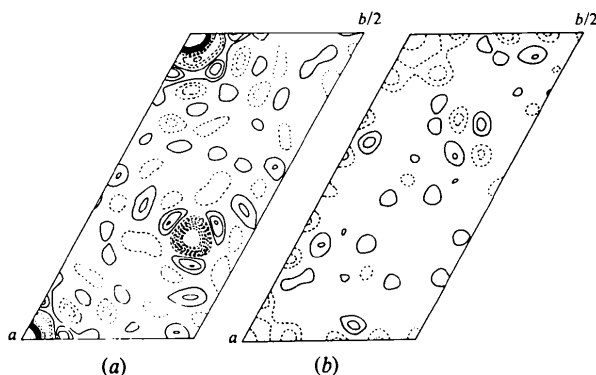

(a)   (b)

Fig. 2. The partial Patterson maps. (a) Section at $z = 0.0$ plane and (b) at $z = 0.11$ plane. Contours are at equal but arbitrary intervals, negative contours being broken.

Table 2. *Positional and thermal parameters of* BaZnGeO$_4$ *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq} (Å^2)
Ba(1)	0	0	$\tfrac{1}{4}$	0.015 (1)
Ba(2)	$\tfrac{1}{3}$	$\tfrac{2}{3}$	0.2536 (13)	0.018 (1)
Ba(3)	$\tfrac{2}{3}$	$\tfrac{1}{3}$	0.2523 (12)	0.019 (1)
$T(1)$	0.6674 (6)	−0.0049 (5)	0.4587 (11)	0.004 (1)
$T(1)$	0.6654 (8)	0.6598 (7)	0.5610 (16)	0.028 (1)
O(1)	0.780 (6)	0.895 (4)	0.488 (13)	0.040 (18)
O(2)	0.450 (3)	0.892 (3)	0.514 (5)	0.065 (24)
O(3)	0.765 (5)	0.204 (6)	0.514 (8)	0.037 (16)
O(4$_I$)†	0.750 (7)	0.697 (8)	0.780 (8)	0.007 (31)
O(4$_{II}$)†	0.656 (6)	0.675 (6)	0.755 (12)	0.016 (31)
O(4$_{III}$)†	0.624 (7)	0.583 (7)	0.768 (9)	0.019 (30)

† These oxygen atoms each have a population of $\tfrac{1}{3}$.

Table 3. *Selected interatomic distances* (Å) *and bond angles* (°)

(i) Environment of Ba atoms

Ba(1)–O(1^{I,III,VII}) ×3	2.73 (9)		Ba(2)–O(2^{0,I,VI}) ×3	2.92 (4)
O(1^{IX,XI,XIII}) ×3	2.89 (9)		O(3^{V,XII,XIII}) ×3	2.78 (7)
O(4$_I^{IX,XI,XIII}$) ×3	2.62 (5)		O(4$_I^{V,XII,XIII}$) ×3	3.08 (6)
O(4$_{II}^{IX,XI,XIII}$) ×3	3.10 (4)		O(4$_{II}^{V,XII,XIII}$) ×3	3.23 (5)
O(4$_{III}^{IX,XI,XIII}$) ×3	3.69 (5)		O(4$_{III}^{V,XII,XIII}$) ×3	2.55 (6)
mean	3.01 (6)		mean	2.91 (6)

Ba(3)–O(2^{IV,X,XIII}) ×3	2.76 (4)
O(3^{0,III,VII}) ×3	2.94 (7)
O(4$_I^{IV,X,XIII}$) ×3	3.75 (8)
O(4$_{II}^{IV,X,XIII}$) ×3	2.96 (6)
O(4$_{III}^{IV,X,XIII}$) ×3	3.16 (8)
mean	3.11 (6)

O(1^{I,III,VIII})–Ba(1)–O(1^{IX,XI,XIII}) ×3	114 (2)
O(1^{IX,XI,XIII}) ×3	114 (2)
O(2^{0,I,VI})–Ba(2)–O(3^{V,XII,XIII}) ×3	114 (1)
O(3^{V,XII,XIII}) ×3	112 (1)
O(2^{IV,X,XIII})–Ba(3)–O(3^{0,III,VII}) ×3	113 (1)
O(3^{0,III,VII}) ×3	111 (1)

(ii) $T(1)$O$_4$ tetrahedron

$T(1)$–O(1^{II})	1.73 (6)	O(1^{II})–$T(1)$–O(2^{II})	119 (2)
O(2^{II})	1.81 (3)	O(3^0)	116 (3)
O(3^0)	1.75 (3)	O(4$_I^{IV}$)	77 (5)
O(4$_I^{IV}$)	1.68 (8)	O(4$_{II}^{IV}$)	102 (5)
O(4$_{II}^{IV}$)	1.79 (11)	O(4$_{III}^{IV}$)	111 (5)
O(4$_{III}^{IV}$)	1.79 (7)	O(2^{II})–$T(1)$–O(3^0)	109 (2)
mean	1.76 (6)	O(4$_I^{IV}$)	113 (2)
		O(4$_{II}^{IV}$)	108 (2)
		O(4$_{III}^{IV}$)	84 (2)
		O(3^0)–$T(1)$–O(4$_I^{IV}$)	119 (4)
		O(4$_{II}^{IV}$)	100 (3)
		O(4$_{III}^{IV}$)	113 (4)
		mean	106 (3)

(iii) $T(2)$O$_4$ tetrahedron

$T(1)$–O(1^{IV})	2.00 (5)	O(1^0)–$T(2)$–O(2^I)	112 (2)
O(2^I)	1.84 (4)	O(3^{III})	110 (2)
O(3^{III})	1.89 (8)	O(4$_I^0$)	99 (4)
O(4^0)	2.03 (7)	O(4$_{II}^0$)	104 (4)
O(4$_I^0$)	1.70 (10)	O(4$_{III}^0$)	127 (4)
O(4$_{II}^0$)	1.91 (8)	O(2^I)–$T(2)$–O(3^{III})	120 (2)
mean	1.90 (7)	O(4$_I^0$)	122 (2)
		O(4$_{II}^0$)	100 (2)
		O(4$_{III}^0$)	92 (2)
		O(3^{III})–$T(2)$–O(4$_I^0$)	90 (3)
		O(4$_{II}^0$)	109 (3)
		O(4$_{III}^0$)	95 (3)
		mean	107 (3)

Symmetry codes

(0)	$x,$	y, z	(vii)	$1 - x + y,$	$1 - x, z$
(i)	$y - x,$	$1 - x, z$	(viiii)	$x - 1,$	$y - 1, z$
(ii)	$x,$	$y - 1, z$	(ix)	$y - 1,$	$y - x, z - \tfrac{1}{2}$
(iii)	$1 - y,$	$x - y, z$	(x)	$1 + x - y,$	$x, z - \tfrac{1}{2}$
(iv)	$y,$	$y - x, z - \tfrac{1}{2}$	(xi)	$x - y,$	$x - 1, z - \tfrac{1}{2}$
(v)	$x - y,$	$x, z - \tfrac{1}{2}$	(xii)	$y, 1 - x + y, z - \tfrac{1}{2}$	
(vi)	$1 - y, 1 + x - y, z$		(xiii)	$1 - x,$	$1 - y, z - \tfrac{1}{2}$

with equal population; and in the third Ge atoms are at $T(2)$ and Zn at $T(1)$. The R values for the respective refinements were 0·0464 ($R_w = 0·0593$), 0·0482 ($R_w = 0·0619$) and 0·0503 ($R_w = 0·0670$). The R values as well as $T–O$ distances suggested that the first model represents the correct atomic configuration. Final atomic parameters are listed in Table 2.* Selected bond distances and bond angles are listed in Table 3.

The refinements were carried out with the modified version of the full-matrix least-squares program *LINEX* including the extinction correction after Becker & Coppens (1974a,b, 1975). The atomic scattering factors and anomalous-dispersion correction terms for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974).

Description of the structure and discussion

The structure of $BaZnGeO_4$ viewed along the c axis is shown in Fig. 3. Fundamentally the structure is isomorphous with $BaAl_2O_4$. The TO_4 tetrahedra are corner linked to form layers normal to the c axis. These layers are connected to form a three-dimensional framework by sharing O(4) atoms. There are two independent tetrahedra in this structure. One of the two tetrahedral sites is occupied mainly by Ge and the other by Zn. This framework encloses three crystallographically independent cavities. These cavities are filled by Ba atoms. The large Ba atoms are surrounded by nine oxygen atoms. Each coordination polyhedron of the Ba atoms consists of six oxygen atoms arranged to form a trigonal antiprism with three additional coordinating oxygen atoms. Ba(1) is surrounded by six

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36558 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
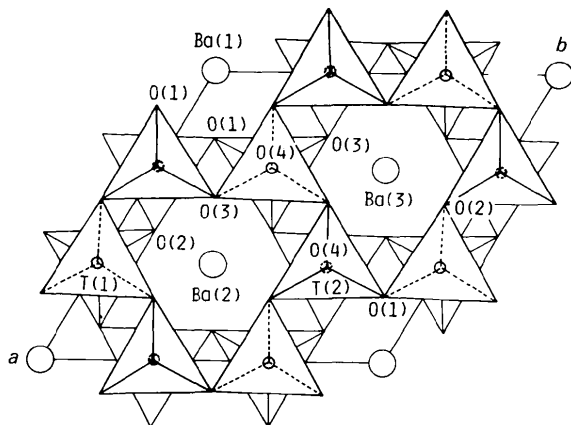

Fig. 3. The structure of $BaZnGeO_4$ projected along the c axis. The oxygen atoms are at the corners of the tetrahedra.

O(1) and three O(4) atoms. Ba(2) and Ba(3) are enclosed by three O(2), three O(3) and three O(4) atoms. The Ba atoms are nearly on the midplane of the two adjacent tetrahedral layers.

Ba–O distances range widely, as seen in Table 3, with the average distances of 3·01 (6) for Ba(1), 2·91 (6) for Ba(2) and 3·11 (6) Å for Ba(3). These values are consistent with the Ba–O distances in $BaAl_2O_4$, which range from 2·616 to 3·464 Å (Von Hörkner & Müller-Buschbaum, 1979). The exact coordination of the Ba atoms is complicated by the statistical arrangement of the O(4) atom. Similar situations are often found in stuffed derivatives of the high-tridymite framework, e.g. in plutonic nepheline (Dollase, 1970), in $BaAl_2O_4$ (Perrotta & Smith, 1968), etc. If the O(4) atom occupies the center of the three atomic sites of the split atoms, Ba–O(4) distances are about 3·11 Å for three Ba atoms. In the split oxygen model, the shortest Ba–O(4) distances decrease to 2·62 (5) Å for Ba(1), 2·55 (6) Å for Ba(2) and 2·94 (7) Å for Ba(3). The remaining Ba–O(4) distances increase to 3·10 (4) and 3·69 (5) Å for Ba(1), 3·08 (6) and 3·23 (5) Å for Ba(2), and 3·17 (8) and 3·75 (8) Å for Ba(3). The shortest distances for the respective Ba atoms are close to the average value of 2·89 Å for typical Ba–O bonds (Shannon, 1976).

In the average structure, $T(1)O_4$ and $T(2)O_4$ tetrahedra are equivalent and the Zn and Ge atoms are in a completely disordered arrangement. The observed average $T–O$ bond lengths are 1·76 (6) and 1·90 (7) Å for $T(1)$ and $T(2)$ tetrahedra, respectively. This difference obviously indicates significant ordering of the Ge and Zn atoms in the tetrahedral sites.

The magnitude of the displacements from the average structure are 0·09 (5) Å or less for the metal atoms. Therefore, it may be concluded that the deviation from the average structure is primarily due to the ordering of the tetrahedral metals with concomitant movements of the coordinating oxygen atoms.

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Disorder in the Structure of Trisodium Phosphorothioate Dodecahydrate*

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Abstract

Na$_3$PO$_3$S.12H$_2$O crystallizes in the trigonal space group $R\bar{3}c$ with a = 9·061 (2), c = 34·34 (2) Å (hexagonal axes), Z = 6, V = 2441·6 Å^3, D_c = 1·612 Mg m^{-3}, μ(Mo $K\alpha$) = 0·45 mm^{-1}, F(000) = 1248. Final R = 0·051 for 326 independent observed reflections. The structure consists of discrete (PO$_3$S)$^{3-}$ anions and (Na$_3$)$^{3+}$(H$_2$O)$_{12}$ groups. All Na, P and S atoms lie on the unique axis. Hydrogen bonds involving all water molecules link the cation complexes both directly and through water–anion interactions. The (PO$_3$S)$^{3-}$ anions are disordered with equal occupancy over two orientations related by the point symmetry 32. Evaluation of anion thermal parameters as well as low-temperature photographic diffraction data suggests that the disorder is static.

Introduction

The phosphorothioate anion has been the subject of a number of diverse studies. These have included the anion's role as a reducing agent (Neumann, Steinberg & Katchalski, 1965), a proposed phosphorylating agent of primordial nucleotides (Slabaugh, Harvey & Nagyvary, 1974) and its use in the preparation and study of nucleoside phosphorothioates (Burgers & Eckstein, 1979; Markham & Reed, 1978). Despite this,

crystallographic information on the anion and its salts has been limited to space group and unit-cell data (Palazzi, 1973; Elias, 1957). Thus a study was undertaken to determine the complete structure of the title compound.

Experimental

Small colorless crystals were grown at room temperature by evaporation from an aqueous solution of the title compound, obtained from Alfa Products. Crystals decomposed in air, presumably due to the loss of H$_2$S (Yasuda & Lambert, 1957). Each crystal studied was thus sealed in a 1·0 mm diameter quartz capillary tube containing a wick saturated with mother liquor. Precession photographs showed a rhombohedral lattice with Laue symmetry $\bar{3}m$1. Indexing of the corresponding hexagonal lattice showed reflection conditions hkl; $-h + k + l = 3n$ and $h\bar{h}l$; $l = 2n$, indicating space group $R\bar{3}c$ (No. 167) or $R3c$ (No. 161). These were not in agreement with Elias (1957) whose choice of possible space groups as $R\bar{3}m$, $R32$ or $R3m$ suggests that the c glide was overlooked.

Cell dimensions and intensity data were collected from a crystal of approximate dimensions 0·23 × 0·18 × 0·11 mm with a Picker four-circle diffractometer using Zr-filtered Mo $K\alpha$ radiation. The crystal was mounted with the b^* (hexagonal) axis parallel to the φ axis of the instrument. Lattice constants were determined by least-squares refinement of 2θ angles from ten independent reflections in the range 2θ = 45–50° where the α_1–α_2 doublet is resolved (λ for Mo $K\alpha_1$ =