The Room-Temperature Structure of BaZnGeO₄

BY K. IJIMA AND F. MARUMO

The Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta 4259, Midori-ku, Yokohama 227, Japan

AND H. TAKEI

Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai 980, Japan

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Abstract

The room-temperature phase of BaZnGeO₄ shows two types of superlattice reflexions. The first appear on the (001)* reciprocal-lattice plane, giving relationships \( a = a_{sub} - b_{sub} \) and \( b = a_{sub} + 2b_{sub} \). The second type appear along the \( c^* \) direction, and are very weak and incommensurate with a relationship \( c \approx 4c_{sub} \). The superstructure has been determined neglecting the incommensurate reflexions. The space group is \( P6_3 \) with unit-cell dimensions \( a = 9.2905(3) \) Å, \( c = 8.728(1) \) 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

BaZnGeO₄ 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 BaAl₂O₄ (Do Dinh & Durif, 1964). However, Takei, Tsunekawa & Maeda (1980) discovered the existence of a superstructure of BaZnGeO₄ which is different from that of BaAl₂O₄ reported by Von Hörkner & Müller-Buschbaum (1979). Takei & Tsunekawa (1980) studied the thermal phase transition of BaZnGeO₄ 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 BaAl₂O₄, 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 \( \beta \)-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 BaZnGeO₄ is caused by ordering of Zn and Ge atoms as in \( \beta \)-eucryptite and nepheline. Structure determination of phase III at room temperature was undertaken...
Experimental

Single crystals of BaZnGeO₄ 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 \( c \approx 4c_{sub} \) (Fig. 1). The main diffraction spots corresponding to the subcell indicated that the structure is of the BaAl₂O₄ 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 P6₃ or P6₃/m from the restriction \( l = 2n \) for the reflexion 00l. Since piezoelectricity had been detected, P6₃ was selected for the true space group. The space group of the subcell was determined to be P6₃2₂. This is the same as that of the average structure of BaAl₂O₄, showing the symmetry 6/mmm.

Polynomial 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 BaZnGeO₄ is essentially identical to the substructure of BaAl₂O₄ obtained by disregarding the doubling of the a axis (Perrotta & Smith, 1968). Therefore, two Ba atoms are allocated to the 2(a) sites of P6₃2₂ 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:

\[
\begin{align*}
\text{Ba} & \rightarrow \text{Ba} (1) \quad \text{O} (1) \\
\text{Ba} (2) & \rightarrow \text{O} (2) \\
\text{Ba} (3) & \rightarrow \text{O} (3) \\
T & \rightarrow T (1) \quad O (2) \quad O (4).
\end{align*}
\]

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
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 Δx = 0.005, Δy = −0.005 and Δz = −0.001 for T(1) and Δx = −0.001, Δy = 0.006 and Δz = 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 at random.

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

#### (i) Environment of Ba atoms

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba(1)–O(1')</td>
<td>2.73 (9)</td>
</tr>
<tr>
<td>Ba(1)–O(2')</td>
<td>2.92 (4)</td>
</tr>
<tr>
<td>Ba(2)–O(1')</td>
<td>2.76 (4)</td>
</tr>
<tr>
<td>Ba(2)–O(2')</td>
<td>2.76 (4)</td>
</tr>
<tr>
<td>O(1')–O(2')</td>
<td>1.79 (2)</td>
</tr>
</tbody>
</table>

#### (ii) T(1)O₄ tetrahedron

<table>
<thead>
<tr>
<th>Bond Angles</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1')–T(1)–O(2')</td>
<td>112 (2)</td>
</tr>
<tr>
<td>O(2')–T(1)–O(3')</td>
<td>110 (2)</td>
</tr>
<tr>
<td>O(3')–T(1)–O(4')</td>
<td>104 (2)</td>
</tr>
</tbody>
</table>

#### (iii) T(2)O₄ tetrahedron

<table>
<thead>
<tr>
<th>Bond Angles</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1')–T(2)–O(2')</td>
<td>113 (3)</td>
</tr>
</tbody>
</table>

### Symmetry codes

<table>
<thead>
<tr>
<th>Symmetry Code</th>
<th>Translation</th>
</tr>
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<tbody>
<tr>
<td>(0) x, y, z</td>
<td>(vii) 1 − x + y, 1 − x, z</td>
</tr>
<tr>
<td>(i) y − x, 1 − x, z</td>
<td>(viii) x − 1, y − 1, z</td>
</tr>
<tr>
<td>(ii) x, y − 1, z</td>
<td>(ix) y − 1, 1 − x, z</td>
</tr>
<tr>
<td>(iii) 1 − y, x − y, z</td>
<td>(x) 1 + x − y, 1 − x, z</td>
</tr>
<tr>
<td>(iv) y, y − x, z</td>
<td>(xi) x − y, x − 1, z</td>
</tr>
<tr>
<td>(v) x − y, x − z</td>
<td>(xii) y − y, y − 1, z</td>
</tr>
<tr>
<td>(vi) 1 − y, 1 + x − y, z</td>
<td>(xiii) 1 − x, 1 − y, z</td>
</tr>
</tbody>
</table>

† These oxygen atoms each have a population of 1/3.
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 (Rw = 0.0593), 0.0482 (Rw = 
0.0619) and 0.0503 (Rw = 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 

Description of the structure and discussion

The structure of BaZnGeO₄ viewed along the c axis is 
shown in Fig. 3. Fundamentally the structure is 
isomorphous with BaAl₂O₄. The TO₄ 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 crystallo-
graphically 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 
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 
BaAl₂O₄, 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 BaAl₂O₄ (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 
decrease 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)O₄ and T(2)O₄ 
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 
deprivation from the average structure is primarily due to 
the ordering of the tetrahedral metals with concomitant 
movements of the coordinating oxygen atoms.

Professor Y. Iitaka of the University of Tokyo is 
gratefully thanked for affording the authors 
facilities to collect intensity data. The calculations were 
carried out on the FACOM M-160 and HITAC M-170 
systems at the computer center of Tokyo Institute of 
Technology.

References

129–147.


417–425.


Disorder in the Structure of Trisodium Phosphorothioate Dodecahydrate*

BY BARRY M. GOLDSTEIN†

Department of Radiation Biology and Biophysics, School of Medicine and Dentistry, The University of Rochester, Rochester, New York 14642, USA

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Abstract

\( \text{Na}_3\text{PO}_3\text{S} \cdot 12\text{H}_2\text{O} \) crystallizes in the trigonal space group \( R3c \) with \( a = 9.061(2), c = 34.34(2) \AA \) (hexagonal axes), \( Z = 6, V = 2441.6 \text{Å}^3, D_c = 1.612 \text{Mg m}^{-3}, \mu(\text{Mo } K\alpha) = 0.45 \text{mm}^{-1}, F(000) = 1248 \). Final \( R \) = 0.051 for 326 independent observed reflections. The structure consists of discrete \( (\text{PO}_3\text{S})^3^- \) anions and \( (\text{Na}_3)^{12+}(\text{H}_2\text{O})_{12} \) 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 \( (\text{PO}_3\text{S})^3^- \) 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 \( \text{H}_2\text{S} \) (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 \( 3\text{m}l \). Indexing of the corresponding hexagonal lattice showed reflection conditions \( hkl; -h + k + l = 3n \) and \( hhl; l = 2n \), indicating space group \( R3c \) (No. 167) or \( R3c \) (No. 161). These were not in agreement with Elias (1957) whose choice of possible space groups as \( R3m, R32 \) or \( R3m \) suggests that the \( c \) glide was overlooked.

Cell dimensions and intensity data were collected from a crystal of approximate dimensions \( 0.23 \times 0.18 \times 0.11 \text{mm} \) with a Picker four-circle diffractometer using \( \text{Zr} \)-filtered \( \text{Mo } K\alpha \) radiation. The crystal was mounted with the \( b^* \) (hexagonal) axis parallel to the \( \phi \) axis of the instrument. Lattice constants were determined by least-squares refinement of 2\( \theta \) angles from ten independent reflections in the range \( 2\theta = 45–50^\circ \) where the \( a_1-a_2 \) doublet is resolved (\( \lambda \) for \( \text{Mo } K\alpha_1 = \)