THE CRYSTAL STRUCTURE OF BARIUM TETRAGERMANATE

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Abstract

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Yu. I. Smolin

THE CRYSTAL STRUCTURE OF BARIUM TETRAGERMANATE

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Compounds of the type $MeGe_4O_9$ (where Me = Sr, Pb, Ba) were first described by Robbins and Levin ([1]), who, in particular, having determined from Debyegrams the parameters of the hexagonal cells of these compounds and taking into account the multiple relations of the parameters found to the parameters of benitoite $BaTiSi_3O_9$ ([2]), proposed the existence in the structures under consideration of Ge_3O_9 rings constructed from germanium–oxygen tetrahedra and germanium atoms in sixfold coordination.

The present work was undertaken in order to test these assumptions by means of a direct structure determination.

A crystal of $BaGe_4O_9$, grown by slow cooling of a melt of the same composition, was investigated. From X-ray goniometric scans the crystal was found to belong to the trigonal system (diffraction symmetry $P\bar{3}m1$). The unit-cell parameters, determined from the scans, were refined from Debyegrams and proved to coincide with those given in ([1]): $a = 11.61 \pm 0.01$ Å; $c = 4.74 \pm 0.01$ Å; $z = 3$. Intensity measurements were carried out on a diffractometer with a scintillation counter using monochromatic CuK_α radiation ($hk0$ reflections) and monochromatic MoK_α radiation for $I(hkl)$ with l from 0 to 5 and up to $\sin\theta/\lambda = 1.1$ Å^{-1} in each layer. In all, 848 nonzero, nonequivalent reflections were measured with MoK_α. By mechanical treatment the investigated $BaGe_4O_9$ crystal was given the form of a true sphere 0.3 mm in diameter. Corrections for polarization, the kinematic factor, and absorption were taken into account ([3]).

In measuring the crystal with CuK_α radiation, which is close to the absorption edge of the Ba L-series ($\Delta f'' \approx 8.6$) ([4]), a sufficiently strong anomalous-scattering effect was observed: $F(hk0) \neq F(\bar{h}\bar{k}0)$. The presence of anomalous scattering excludes centrosymmetric groups, and therefore within the observed symmetry only two space groups are possible, $P321$ and $P\bar{3}m1$. The choice between these groups can readily be made using the anomalous-scattering effect ([5,6]). Thus, for the group $P321$ the symmetry of the 001 projection is $p31m$, whereas for the group $P\bar{3}m1$ it is $p\bar{3}m1$. However, these two plane groups differ in the anomalous-scattering region simply as follows: when $F(hk0) \neq F(\bar{h}\bar{k}0)$,

Fig. 1. Projection of the structure of $BaGe_4O_9$ onto the plane 001. The circles indicate the z-coordinates of the atoms in hundredths of the period

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for $p31m$ one must have $F(hk) = F(kh) \neq F(\bar{k}\bar{h})$, whereas for $P\bar{3}m1$, $F(hk) = F(\bar{k}\bar{h}) \neq F(kh)$. Intensity measurements carried out with CuK_α showed that in our case $F(hk) = F(\bar{k}\bar{h})$, i.e., the symmetry of the projection is $p\bar{3}1m$, and thus the space group of symmetry is $P321$.

The anomalous-scattering effect was then used to determine the positions of the atoms in the 001 projection. Since among the $hk0$ reflections there are no reflections with $h-k \neq 3n$, a cell three times smaller, with one anomalously scattering atom, could be adopted for the projection. In this case the P_s-function, constructed from $\Delta|F(hk0)|^2 = |F(hk0)|^2 - \cdot F(\bar{h}\bar{k}0)|^2$, should by its positive maxima give the positions of all atoms relative to the anomalously scattering one ([5,7,8]). In our case it was possible by this method to establish the position of the germanium atoms rela-

with respect to barium. The oxygens were not clearly fixed in the P_s-function, apparently because of the effect of series termination caused by the need to use CuK_α radiation. After the coordinates of the germanium atoms had been determined, there still remained an ambiguity associated with the choice of the origin. In the P_s-function the anomalously scattering atom is always at the origin, but in the reduced cell $p3m1$ considered by us barium can occupy a position on any of the threefold axes, which, on transformation to the full cell, leads to nonalternative positions for the barium atom—at the origin and at the point $1/3, 1/3$.

Fig. 1. Projection of the structure of $BaGe_4O_9$ onto the plane 001. The circles indicate the z-coordinates of the atoms in hundredths of the period.

The first variant was considered improbable for a number of reasons, including the excessively high local symmetry for the barium atom. The z-coordinates of the Ge atoms and the oxygen positions were determined from three-dimensional syntheses of the electron density, the initial values of the z-coordinates being assigned from geometrical analysis. The structure found in this way was refined against all $F(hkl)$ measurements by the least-squares method, using the Hughes weighting scheme ([9]), to a value $R = 0.058$. In the refinement, atomic factors for neutral atoms were used, with a dispersion correction for barium and germanium. The results of the refinement are given in Table 1.

The projection of the structure onto the plane 001 is shown in Fig. 1, where the z-coordinates of the atoms in hundredths of the period are also indicated. As is seen from the figure, the structure of barium tetragermanate is built of layers of Ge_3O_9 rings, consisting of germanium-oxygen tetrahedra, the oxygens of which form coordination polyhedra of barium and of germanium lying between the

layers of rings and linking these rings to one another. Part of the germanium atoms in the structure, in accordance with the supposition expressed in ([1]), are located in octahedra formed by the terminal oxygens of the Ge_3O_9 rings. The Ge–O distances in the octahedron Ge_1, lying at the origin, are 1.880 ± 0.0087 Å. The octahedron Ge_2 is shown in Fig. 1. The interatomic Ge–O distances in it are: 1.860 ± 0.0098 and 1.886 ± 0.0092 Å. As is seen from the figure, the coordination polyhedron of Ba includes both terminal and

bridging oxygens of the Ge_3O_9 rings. The coordination number of barium in the structure is 10. The Ba–O distances in this polyhedron are:

$Ba - O_3$	2.771 ± 0.0033 Å	$Ba - O_1'$	3.252 ± 0.0028 Å
$Ba - O_5'$	3.038 ± 0.0032 Å	O_2	2.713 ± 0.0075 Å
O_4	2.918 ± 0.0081 Å		

The triple Ge_3O_9 rings have intrinsic symmetry 2. All distances and angles in the ring are given in Table 2.

Table 1

Atomic coordinates, root-mean-square errors, and temperature factors

	x/a	$\sigma x/a$	y/b	$\sigma y/b$	z/c	$\sigma z/c$	B, Å^2
Ba	0.66895	0.00006	0	–	0	–	0.641
Ge_1	0	–	0	–	0	–	0.375
Ge_2	1/3	–	2/3	–	−0.1067	0.0011	0.433
Ge_3	0	–	0.17881	0.00008	1/2	–	0.369
Ge_4	0.14966	0.00007	0.48733	0.00006	0.4075	0.0010	0.414
O_1	0	–	0.47711	0.00070	1/2	–	0.961
O_2	0.18239	0.00055	0.59497	0.00061	0.1199	0.0029	0.756
O_3	0.08665	0.00052	0.15153	0.00052	0.7690	0.0027	0.641
O_4	0.14156	0.00044	0.32376	0.00049	0.3150	0.0025	0.493
O_5	0.26204	0.00056	0.51218	0.00051	0.6679	0.0027	0.608

When the determination of the structure had been completed, we learned of the work of K. Robbins, A. Perloff, and S. Block, reporting the determination of the structure of $BaGe_4O_9$ ([10]). These authors, noting that the diffraction symmetry of the crystal is $P\bar{3}m1$, overlooked the possibility that in this case the space group $P321$ might occur and, having convinced themselves that it was impossible to describe the structure in the symmetries $p\bar{3}m1$ and $P3m1$, adopted the group $P3$. Refinement of the correctly found structural motif in a group with lowered

Table 2

Interatomic distances and angles in the Ge_3O_9 ring

Ge_3–O_3 1.749 ± 0.011 Å	O_1–O_2 2.589 ± 0.010 Å
Ge_3–O_4 1.760 ± 0.0069 Å	O_1–O_4 2.815 ± 0.010 Å
O_3–O_3' 3.089 ± 0.021 Å	O_1–O_5 2.969 ± 0.0081 Å
O_3–O_4 2.852 ± 0.0144 Å	O_2–O_4 2.976 ± 0.011 Å
O_3–O_4' 2.752 ± 0.0098 Å	O_2–O_5 3.068 ± 0.018 Å
O_4–O_4' 2.847 ± 0.017 Å	O_4–O_5 2.610 ± 0.012 Å
O_3–Ge_3–O_4' $103°17'$	O_1–Ge_4–O_2 $95°35'$
O_3–Ge_3–O_3' $124°05'$	O_1–Ge_4–O_4 $106°27'$
O_3–Ge_3–O_4 $108°45'$	O_1–Ge_4–O_5 $118°46'$
O_4–Ge_3–O_4' $107°57'$	O_2–Ge_4–O_4 $114°44'$
Ge_4–O_1 1.738 ± 0.0037 Å	O_2–Ge_4–O_5 $124°17'$
Ge_4–O_2 1.758 ± 0.012 Å	O_4–Ge_4–O_5 $96°52'$
Ge_4–O_4 1.776 ± 0.0064 Å	Ge_3–O_4–Ge_4 $124°45'$
Ge_4–O_5 1.712 ± 0.010 Å	Ge_4–O_1–Ge_4' $128°50'$

symmetry, although it allowed these authors to obtain an R-factor value of 0.068 for 327 reflections, nevertheless led to noticeable inaccuracies in the determination of the atomic coordinates, which in particular caused a large scatter in the values of interatomic distances (1.617-1.895 Å for Ge–O in the tetrahedron). The appearance of negative values of individual temperature factors for some atoms, which the authors explained by failure to take absorption into account, was apparently caused by the same reason.

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Institute of Silicate Chemistry
named after I. V. Grebenshchikov
Academy of Sciences of the USSR

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