

Single Crystal Structure Determinations of BaTiAl₆O₁₂ and Ba₃TiAl₁₀O₂₀

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BaTiAl₆O₁₂ crystallizes in the orthorhombic system with unit-cell dimensions $a = 4.862(1)$, $b = 7.136(2)$, $c = 13.598(3)$ Å and space group $Pnmm$ with $z = 2$. The structure was solved by Patterson and Fourier methods. Of the 714 unique reflections measured by counter techniques, 253 with $I > 3\sigma(I)$ were used in the least-squares refinement of the model to a conventional R of 0.042 ($R_w = 0.037$). The structure of BaTiAl₆O₁₂ consists of octahedra (mixed Ti and Al occupancy) and tetrahedra (all Al) in a three-dimensional array forming tunnels in which barium ions are located. The octahedra form ribbons or strings by edge-sharing to one another, and are corner-shared to tetrahedra. The corner-shared array of tetrahedra links the ribbons of octahedra. Ba₃TiAl₁₀O₂₀ crystallizes in the monoclinic system with unit-cell dimensions $a = 15.631(4)$, $b = 11.373(2)$, and $c = 4.981(1)$ Å, $\beta = 107.77(2)^\circ$, and space group $C2/m$ with $z = 2$. The structure was solved by Patterson and Fourier methods and of the 2909 unique reflections measured by counter techniques, 1561 with $I > 3\sigma(I)$ were used in the least-squares refinement of the model to a conventional R of 0.046 ($R_w = 0.042$). The structure consists of sheets of corner-shared tetrahedra linked by parallel ribbons of edge-shared octahedra. (The octahedra are of mixed Ti and Al occupancy.) The barium ions are located in tunnels of two different types. © 1985 Academic Press, Inc.

Introduction

An interest in mixed metal oxide compounds, especially those formed by alkali and alkaline earth oxides and the oxides of Groups IVB, VB, and VIB of the periodic table, that might contain large cations in tunnels or cavities, led to the recent determination of the structure of Ba₂Ti₉O₂₀ (1). The relationship of this structure to that of hollandite, and the recent determination of the structure of zirconolite (2), and their possible interest to the SYNROC process caused our attention to be drawn to com-

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pounds in the BaO-TiO₂-Al₂O₃ system other than BaAl₂Ti₆O₁₆ (hollandite structure) whose structures, it was thought, were not known. Three phases were reported for this system by Guha, Kolar, and Volavšek (3) and subsequently confirmed in a further study (4). These were BaTi₅Al₂O₁₄ (tetragonal), BaTiAl₆O₁₂ (tetragonal), and Ba₃TiAl₁₀O₂₀ (orthorhombic) for which the unit-cell dimensions, crystal systems, and compositions were determined by X-ray powder diffraction methods and petrographic examination (3). More recent data for BaTiAl₆O₁₂, also from an X-ray powder study, have suggested that it is orthorhombic (5).

The structure of $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$ was reported recently (6) as the result of a neutron powder profile analysis starting with the parameters of $\text{Pb}_3\text{GeGa}_{10}\text{O}_{20}$ (7).

As part of a single crystal X-ray diffraction study of compounds formed in the $\text{BaO-TiO}_2\text{-Al}_2\text{O}_3$ system we report here the single crystal structure determinations of $\text{BaTiAl}_6\text{O}_{12}$ and $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$.

Experimental

$\text{BaTiAl}_6\text{O}_{12}$. A suitable crystal fragment ($0.05 \times 0.025 \times 0.025$ mm) was selected from the crystalline mass obtained by heating BaCO_3 , TiO_2 , and Al_2O_3 in the mole ratio 1:1:3 in a platinum crucible at 1350°C for 3 days followed by slow cooling to room temperature. The crystal was mounted on a silica capillary using clear epoxy resin and crystal data were obtained using a Philips PW1100 single crystal diffractometer in a manner described earlier (8). Using appropriate standard materials the electron microprobe analysis results for $\text{BaTiAl}_6\text{O}_{12}$ were: found—28.18% BaO , 14.59% TiO_2 , and 55.25% Al_2O_3 ; calc.—28.44, 14.82, and 56.74%, respectively.

Crystal data. $\text{BaTiAl}_6\text{O}_{12}$, $M = 539.13$, orthorhombic, $a = 4.862(1)$, $b = 7.136(2)$, $c = 13.598(3)$ Å; $U = 471.8$ Å³, $D_c = 3.79$, $D_m = 3.74(2)$ g cm⁻³ (by flotation), $z = 2$. $F(000) = 504$, $\mu = 57.8$ cm⁻¹ (MoK_α $\lambda = 0.7107$ Å). Systematic absences observed were for $h0l$, $h + l = 2n + 1$ and for $0kl$, $k + l = 2n + 1$ indicating space groups $Pn\bar{m}$ or $Pnn2$. Successful refinement in $Pn\bar{m}$ was taken as confirmation of the centrosymmetric space group.

Intensity measurements. Intensity data were collected using the diffractometer with MoK_α radiation (graphite monochromator) out to $2\theta = 60^\circ$ and the ω scan technique with a symmetric scan range of $\pm (1.00 + 0.3 \tan \theta)$ in 2θ from the calculated Bragg angle, at a scan rate of $0.045^\circ \text{ sec}^{-1}$. No reflection was sufficiently intense to re-

quire the insertion of an attenuation filter. Of the 714 independent reflections measured, 253 were considered to be significantly above the background [$I > 3\sigma(I)$] and only these were used in subsequent calculations. Three standard reflections, measured at 2 hr intervals, showed no significant variation in intensity. An absorption correction, on the basis of indexed crystal faces, was applied.

$\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$. A suitable crystal fragment ($\sim 0.015 \times 0.02 \times 0.02$ mm) was selected from the crystalline mass obtained by heating BaCO_3 , TiO_2 , and Al_2O_3 in the mole ratio 3:1:5 in a platinum crucible at 1350°C for 2 days followed by slow cooling to room temperature. The crystal was mounted on a silica capillary using clear epoxy resin and crystal data were obtained using the diffractometer as above. Using appropriate standard materials the electron microprobe analysis results for $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$ were: found—42.99% BaO , 7.68% TiO_2 , and 48.34% Al_2O_3 ; calc.—43.82, 7.61, and 48.57%, respectively.

Crystal data. $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$, $M = 1049.73$, monoclinic, $a = 15.631(4)$, $b = 11.373(2)$, $c = 4.981(1)$ Å, $\beta = 107.77(2)^\circ$. $U = 843.2$ Å³, $D_c = 4.13$ g cm⁻³ for $z = 2$. Insufficient material was available for a density measurement. $F(000) = 959.8$, $\mu = 82.4$ cm⁻¹ for MoK_α ($\lambda = 0.7107$ Å). Systematic absences observed were hkl , $h + k = 2n + 1$ indicating space groups $C2/m$, $C2$, or Cm . Successful refinement confirmed the centrosymmetric space group. Earlier reports of the unit-cell dimensions for this compound were given in the nonstandard space group $I2/m$. The coordinates given here may be transformed to $I2/m$ by applying to them the transformation

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 1 & 0 & -1 \end{bmatrix}.$$

Intensity measurements. These were made as for $\text{BaTiAl}_6\text{O}_{12}$ with the following

TABLE I
FINAL ATOMIC PARAMETERS WITH THEIR
ESTIMATED STANDARD DEVIATIONS IN
PARENTHESES ($\times 10^4$)

Atom	x/a	y/b	z/c	U_{11}
BaTiAl ₆ O ₁₂				
Ba	0	0	0	<i>a</i>
<i>M</i> (1) ^b	$\frac{1}{2}$	$\frac{1}{2}$	0	99(15)
<i>M</i> (2)	$\frac{1}{2}$	0	6076(3)	78(10)
Al(1)	48(21)	2842(5)	3188(2)	54(8)
O(1)	0	$\frac{1}{2}$	3772(9)	97(28)
O(2)	-3249(31)	8619(20)	$\frac{1}{2}$	77(31)
O(3)	1780(21)	-1398(12)	3977(6)	24(19)
O(4)	1602(21)	6875(13)	2023(7)	68(20)
Ba ₃ TiAl ₁₀ O ₂₀				
Ba(1)	0	0	0	<i>c</i>
Ba(2) ^d	27934(3)	0	25149(12)	<i>c</i>
<i>M</i> (1) ^b	0	$\frac{1}{2}$	0	65(5)
<i>M</i> (2)	0	3677(2)	$\frac{1}{2}$	53(3)
Al(1)	1356(1)	2887(1)	1615(3)	35(3)
Al(2)	1476(1)	1394(2)	-3394(4)	40(3)
O(1)	5636(4)	0	3868(12)	51(9)
O(2)	865(3)	2451(4)	4366(9)	62(7)
O(3)	4306(3)	1203(4)	1086(8)	49(6)
O(4)	8941(4)	0	4670(13)	90(11)
O(5)	7388(3)	1429(4)	3064(9)	99(8)
O(6)	1379(3)	1512(4)	25(9)	74(7)

^a U_{11} U_{22} U_{33} U_{23} U_{13} U_{12}
185(11) 151(10) 128(9) 0 0 122(31)

^b *M*(1) occupancy 0.70 Al + 0.30 Ti; *M*(2) occupancy 0.65 Al + 0.35 Ti.

^c U_{11} U_{22} U_{33} U_{23} U_{13} U_{12}
Ba(1) 51(3) 129(4) 83(3) 0 4(2) 0
Ba(2) 59(2) 88(2) 78(2) 0 -1(2) 0

The anisotropic thermal parameters are of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$.

^d Ba(2) position parameters $\times 10^5$.

exceptions. The symmetric scan range was $\pm (1.2 + 0.3 \tan \theta)^\circ$ and of the 2909 independent reflections measured, 1561 were used in the refinement [$I > 3\sigma(I)$]. The data crystal was inadvertently lost before attempts were made to index its irregular bounding surfaces. Its small size and approximately equal dimensions indicate that absorption effects will be minimal.

Both data sets were processed in a manner described previously (8). The atomic

scattering factors were for neutral atoms and were corrected for anomalous dispersion effects (9). All calculations were carried out on the Monash University Burrough B6700 and VAX 11/780 computers; the major program used was SHELX (10).

Structure Solution and Refinement

Both structures were solved for a general metal atom position (Ti) using conventional Patterson methods. Subsequent structure factor and difference Fourier synthesis calculations enabled the location of all atomic positions. The conventional $R = \sum |F_o| - |F_c| / \sum |F_o|$ at this stage for BaTiAl₆O₁₂ was 0.11 and for Ba₃TiAl₁₀O₂₀ was 0.19.

Refinement of all parameters, with anisotropic thermal parameters for the Ba atoms and adjustment of the Ti/Al ratio in each of the sites *M*(1) and *M*(2) with due consideration of the compositions of the compound and the residual electron density shown by a Fourier difference synthesis at each step, resulted in $R = 0.042$, and $R_w = 0.037$, where $R_w = \sum (\omega^{1/2} |F_o| - |F_c|) / \sum (\omega^{1/2} |F_o|)$ and $\omega = (\sigma^2(F_o))^{-1}$, for BaTiAl₆O₁₂ and $R = 0.046$, $R_w = 0.042$ for Ba₃TiAl₁₀O₂₀. Maxima and minima in the final Fourier syntheses were, for BaTiAl₆O₁₂ 0.8 and 2 (in the vicinity of Ba²⁺) $e \text{ \AA}^{-3}$, and for Ba₃TiAl₁₀O₂₀ 0.5 and 2 (in the vicinity of Ba²⁺) $e \text{ \AA}^{-3}$. Final parameters and their estimated standard deviations are presented in Table I¹ and selected interatomic distances in Table II.

¹ For a table of observed and calculated structure factors see NAPS Document No. 04314 for 20 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75 for up to 20 pages plus \$0.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of \$15. Foreign orders add \$4.50 for postage and handling for the first 20 pages, and \$1.00 for additional 10 pages of material. Remit \$1.50 for postage of any microfiche orders.

TABLE II
SELECTED BOND LENGTHS (Å) WITH THEIR
ESTIMATED STANDARD DEVIATIONS IN
PARENTHESES

BaTiAl ₆ O ₁₂			
<i>M</i> (1)–O(1)	1.879(6) × 2	Al(1)–O(5)	1.737(5)
–O(3)	1.924(4) × 4	–O(6)	1.759(5)
		–O(3)	1.761(4)
<i>M</i> (2)–O(3)	1.925(4) × 2	–O(2)	1.807(5)
–O(2)	1.964(5) × 2		
–O(1)	1.979(5) × 2	Al(2)–O(5)	1.735(5)
		–O(4)	1.758(3)
Ba –O(2)	2.719(15) × 2	–O(6)	1.760(5)
–O(1)	2.950(7) × 2	–O(2)	1.791(4)
–O(3)	3.316(9) × 4		
Ba ₃ TiAl ₁₀ O ₂₀			
<i>M</i> (1)–O(2)	1.86 (1) × 2	Al(1)–O(1)	1.733(6)
–O(3)	1.919(8) × 4	–O(3)	1.731(10)
		–O(4)	1.787(10)
<i>M</i> (2)–O(3)	1.857(9) × 2	–O(4)	1.795(13)
–O(2)	1.960(9) × 2		
–O(4)	2.013(9) × 2		
Ba(1)–O(4)	2.665(6) × 2		
–O(6)	2.755(4) × 4		
–O(4)	3.241(8) × 2		
Ba(2)–O(1)	2.564(5)		
–O(6)	2.777(4) × 2		
–O(5)	2.820(5) × 2		
–O(3)	2.999(4) × 2		
–O(5)	3.157(5) × 2		

Description and Discussion of the Structures

BaTiAl₆O₁₂. This structure can be described in terms of its two types of octahedra (*M*(1) is 0.30 Ti + 0.70 Al and *M*(2) is 0.35 Ti + 0.65 Al) and tetrahedra (AlO₄) forming a three-dimensional framework in which there are tunnels containing barium ions (Fig. 1). The *M*(1) octahedra are edge-shared to four octahedra and corner-shared to four tetrahedra; the *M*(2) octahedra are edge-shared to three octahedra and corner-shared to six tetrahedra and the single AlO₄ tetrahedral unit is corner-shared to four octahedra and three other tetrahedra. The ribbons of octahedra are stacked one above

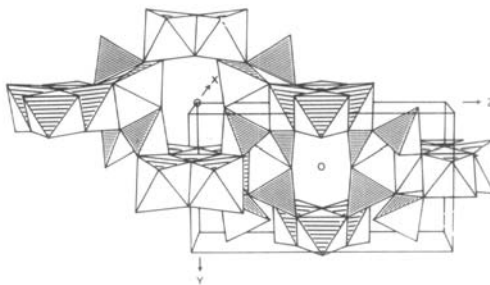


FIG. 1. View approximately along [100] of the BaTiAl₆O₁₂ structure showing the "six-sided" tunnels.

the other in the 002 planes and are inverted with respect to one another alternately along the [001] direction (Fig. 2). There is only one tunnel type in this structure and in projection along [100] it appears to be "six-sided."

The *M*(1)–O distances range from 1.86(1) to 1.919(8) Å [mean 1.899 Å], *M*(2)–O range from 1.857(9) to 2.013(9) Å [mean 1.943 Å], and the Al–O distances are 1.732(6) to 1.792(14) Å [mean 1.760 Å]. There is only one barium site in the tunnels; it is a 10-coordinate site and the Ba–O distances are from 2.719(15) to 3.316(9) Å [mean 3.050 Å].

Ba₃TiAl₁₀O₂₀. This structure can also be described as consisting of sheets of corner-shared tetrahedra, two deep, linked by corner-sharing to parallel ribbons of edge-shared octahedra (Figs. 3 and 4). There are

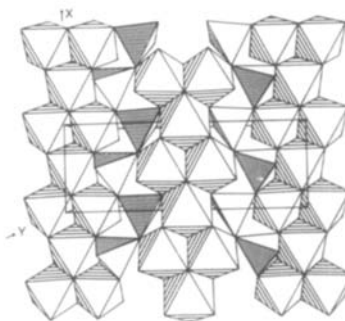


FIG. 2. Diagram showing the linking of the ribbons of octahedra by corner-sharing tetrahedra in BaTiAl₆O₁₂.

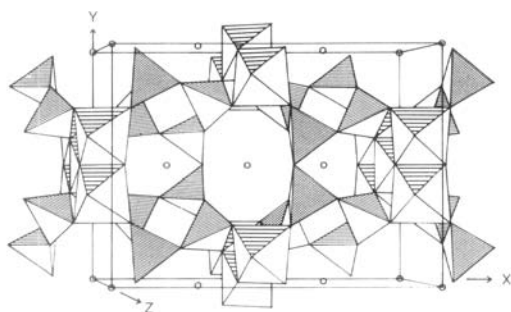


FIG. 3. View approximately along [001] showing the two tunnel types in $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$.

two types of each polyhedron; of the octahedra $M(1)$ [0.30 Ti + 0.70 Al] is edge-shared to four other octahedra and corner-shared to four tetrahedra, and the second, $M(2)$ [0.35 Ti + 0.65 Al] is edge-shared to three other octahedra and corner-shared to six tetrahedra. Thus, in general terms the ribbons of octahedra and their immediate surroundings are the same in both structures. There are two types of tetrahedral site in $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$. The first, Al(1), is corner-shared to three other tetrahedra and three octahedra, whereas the second, Al(2), is corner-shared to four other tetrahedra and one octahedron.

In this structure the framework of octahedra and tetrahedra encompass two distinct tunnel types (Fig. 3), that may be described as "five-sided" and "six-sided," in projection. The five-sided tunnels have only one ribbon of octahedra forming a side

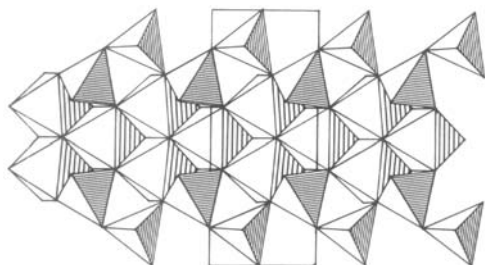


FIG. 4. The ribbon of octahedra in $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$ with the linking tetrahedra.

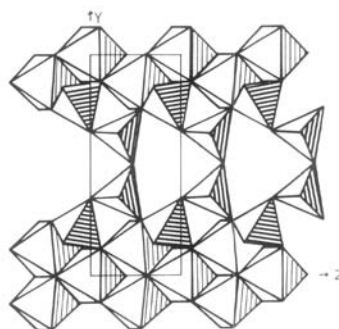


FIG. 5. The triangular shaped holes that link the "five-sided" and "six-sided" tunnels in $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$ are illustrated here.

of the tunnel, whereas the six-sided tunnels have ribbons of octahedra opposite one another and "edge" on to the tunnel compared with the tunnels in $\text{BaTiAl}_6\text{O}_{12}$ in which "flat" faces of the ribbons involved are presented to the interior of the tunnels. Each ribbon forms part of two tunnels of each type. The two tunnel types here are interconnected by approximately triangular shaped holes (Fig. 5).

The $M(1)$ sites have M -O distances ranging from 1.882(6) to 1.925(5) Å [mean 1.911 Å], and $M(2)$ has M -O distances of 1.924(4) to 1.980(5) Å [mean 1.955 Å]; the Al-O distances within the tetrahedra range from 1.735(5) to 1.806(5) Å [mean 1.764 Å]. The barium ions are considered to be 8-coordinate in the five-sided tunnels and 10-coordinate in the six-sided tunnels. The Ba-O distances range from 2.564(5) to 3.241(8) Å [mean 3.260 Å].

The general structure for $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$ does not differ from the original single crystal determination of a structure of this type (7); however, more precise parameters and bond lengths are now available than was the case before this report. Determination of the single crystal structures of $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$ and $\text{BaTiAl}_6\text{O}_{12}$ means that all three known compounds in the $\text{BaO} : \text{TiO}_2 : \text{Al}_2\text{O}_3$ system have now been characterized in this manner.

The structures reported here have three distinctive characteristics in common; (i), the aluminum ions occupy both tetrahedral and octahedral sites; (ii), the octahedra are occupied by aluminium and titanium ions—the two types of octahedra have the same occupancy in both structures as determined within the limits of the X-ray method; and (iii), both frameworks contain tunnels that are occupied by barium ions.

Aluminium exhibits both tetrahedral and octahedral coordination in other compounds, e.g., α - Al_2O_3 , $\text{Al}(\text{NiAl})\text{O}_4$ (inverse spinel structure), $(\text{Mg}_2\text{Al})(\text{OH})_4\text{SiAlO}_5$, $\text{KAl}_2(\text{OH})_2\text{Si}_3\text{AlO}_{10}$, and $\text{YAl}_5\text{O}_{12}$ (11). The third and last examples also exhibit mixed occupancy of the octahedral sites. Al_2TiO_5 (12) and $\text{Ca}_{0.6}(\text{AlTi})_2\text{O}_3$ (13) have Al and Ti in mixed octahedral sites; in Al_2TiO_5 the Al and Ti are present in the same proportions as in the octahedra ribbons in the compounds described here; however, the Al and Ti in Al_2TiO_5 are completely disordered, whereas in $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$ and $\text{BaTiAl}_6\text{O}_{12}$ Al shows a small preference for the twofold ($M(1)$) site over the fourfold ($M(2)$) site. It has been suggested that a metal ion of lower valence may favor a more restricted site in order to minimize ionic repulsion between metal ions (14).

Compounds whose structures consist of a framework of octahedra and tetrahedra that also enclose tunnels are not common. However, a recent report (15) of a mixed-valence tungsten oxide with a framework of WO_6 octahedra and P_2O_7 groups, $\text{P}_8\text{W}_{12}\text{O}_{52}$, has two types of tunnels—"distorted pentagonal and distorted hexagonal tunnels." The distorted hexagonal tunnels are similar to the six-sided tunnels observed here, although it should be noted that the tunnels in $\text{P}_8\text{W}_{12}\text{O}_{52}$ do not contain any cations. It was reported that the insertion of ions such as Li^+ and Na^+ would be considered (15).

Finally, the significance of $\text{Ba}_3\text{TiAl}_{10}\text{O}_{20}$ and $\text{BaTiAl}_6\text{O}_{12}$ to the SYNROC process has yet to be assessed; however, a recent report on the latter compound indicated that it was unstable under hydrothermal conditions (5).

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