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The crystal structure of fresnoite, $Ba_2(TiO)Si_2O_7$

By **Paul B. Moore** and **S. John Louisnathan**

Department of the Geophysical Sciences, University of Chicago, Chicago, Illinois

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Auszug

Die Kristallstruktur von Fresnoit, $Ba_2(TiO)Si_2O_7$, wurde aus der Patterson-Projektion $P(uv)$ bestimmt und nach der Methode der kleinsten Quadrate aus *hkl*-Interferenzen verfeinert. Eigentümlich für die Struktur ist die tetragonal-pyramidale Umgebung des Titans. Schichten aus heterozyklischen fünfgliedrigen Ringen, die von tetragonalen Ti-O-Pyramiden und Si-O-Tetraedern gebildet sind, werden durch Ba–O-Bindungen zusammengehalten. Die Bindungen innerhalb der Schichten sind vorwiegend kovalent; zwischen den Schichten ist Ionenbindung vorherrschend.

Abstract

The structure of fresnoite, $Ba_2(TiO)Si_2O_7$, was determined from the Patterson projection $P(uv)$ and refined by the least-squares method using three-dimensional single-crystal data. Its unique feature is the tetragonal-pyramidal coordination of titanium. Sheets made up of heterocyclic five-membered rings of Ti-O tetragonal pyramids and Si-O tetrahedra are held together by Ba–O bonds. The bonds within the sheet are predominantly covalent, and the intersheet bonds are mainly ionic in character.

1. Introduction

Fresnoite, a mineral found in the sanbornite deposits of eastern Fresno County, California, was first described by Alfors *et al.* (1965). Based on a spectrographic analysis they report the composition

$$(Ba_{1.95}, Ca_{0.05})(Ti_{0.96}, Mn_{0.01}, Mg_{0.02}, Fe_{0.05})Si_{2.00}O_{8.00}.$$

There are two formula units in the cell, and the measured density is 4.43 ± 0.02 g/cm^3. A preliminary note on the structure of fresnoite was reported earlier (Moore and Louisnathan, 1967).

2. Experiments

The lattice parameters of fresnoite, reported by Alfors *et al.* (1965), are $a = 8.52 \pm 0.01$ Å and $c = 5.210 \pm 0.001$ Å. We prepared a powder-diffractometer pattern of fresnoite which contained a small amount of spectrographically pure silicon as internal standard. Ni-filtered Cu$K\alpha$ radiation was used. A least-squares fit of the corrected line positions yielded $a = 8.518 \pm 0.002$ Å and $c = 5.211 \pm 0.001$ Å. Intensities of the $hk0$ to $hk5$ layers were measured on a manual scintillation-counter goniometer of Weissenberg geometry, from a single, anhedral, wedge-shaped crystal of $\sim 0.007 \text{mm}^3$ volume, using Zr-filtered Mo$K\alpha$ radiation. The size and shape of the crystal were carefully measured, and the observed intensities were corrected for Lorentz, polarization and absorption factors.

3. Determination of the structure and refinement

As the only systematic extinction conditions were $0kl$, $k \neq 2n$, the space group is $P4/mbm$, $P4bm$, or $P\bar{4}b2$. The location of Ba—Ba and Si—Si peaks on the z-axis Patterson projection ruled out $P\bar{4}b2$ as a possible space group. After assigning Ti to the origin in the xy plane, the positions of Ba and Si were obtained by identifying the Ba—Ti, Ba—Si and Ti—Si peaks. The expected tetrahedral geometry of the silicate groups allowed approximate location of the oxygen atoms and the space group was identified as $P4bm$. The z coordinates of Ti, Si, and three oxygen atoms were calculated from packing considerations, with Ba arbitrarily placed at $z = 0$. The fourth oxygen atom was placed 2 Å immediately below the Ti atom, and a structure-factor calculation showed that the model was satisfactory.

Using the least-squares SORFLS program (a local modified version of the ORFLS program of Busing *et al.* (1962) the structural parameters were refined. With unit weights and one scale factor for all reflections, and isotropic temperature factors for all atoms, six cycles gave $R = 0.11$. At this stage, different scale factors for each of the l layers were introduced and anomalous-dispersion correction terms for the scattering factors were applied as follows:

Atom	$f'_{\theta=0°}$	$f''_{\theta=0°}$
Ba	-0.60	2.65
Ti	0.20	0.55
Si	0.10	0.10

It was assumed that f' and f'' do not depend on θ. Four cycles brought R to 0.095. Next, a weighting scheme with $w = 1/(4.4 + |F_o| + |F_o|^2/260)$ was introduced. In order to determine the absolute configuration, two parallel refinements, one on hkl and the other on $\bar{h}\bar{k}\bar{l}$, were performed. After four cycles the results were

	R	R'
Refinement on hkl:	0.0838	0.0805
Refinement on $\bar{h}\bar{k}\bar{l}$:	0.0840	0.0806.

Further refinements were discontinued since subsequent iterations neither lowered R nor reduced the errors in the structural parameters. The differences in the z coordinates of the atoms between the two polarities, relative to the Ba atom, were within the errors. The preference of positive over negative polarity cannot be made with confidence. A possible reason for the insignificant differences between the two polarities is discussed later. Table 1 gives the values of $F_o(hkl)$ and $F_c(hkl)$ as calculated in the final refinement of the positive

Table 1. *Observed and calculated structure amplitudes in fresnoite*
The overall scale factor is 0.6 × 10^{-2}

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
2 0 0	2575	2702	6 1 1	418	330	5 2 2	3197	3253	5 2 3	4584	4741	5 3 4	3609	3181
4	3136	3018	7	495	619	6	2749	2878	6	3354	3403	6	602	432
6	6248	7055	8	2802	2962	7	4352	4598	7	2770	2869	7	2168	2250
8	1383	1293	9	1146	1525	8	2352	2544	8	1400	1590	8	135	212
10	509	509	10	2656	2878	9	1736	1809	9	525	444	9	2382	2334
1 1 0	1991	1526	2 2 1	2489	1695	10	877	966	10	440	705	10	149	166
2	3814	3511	3	1604	1414	3 3 2	7194	6533	3 3 3	7220	6183	4 4 4	2502	2615
3	5788	6033	4	712	685	4	782	841	4	493	515	5	3797	3393
4	6693	7032	5	4853	5035	5	4379	4062	5	3730	3687	6	1260	1253
5	615	686	6	4324	4551	6	1020	886	6	874	910	7	3846	3597
6	2573	2867	7	3411	3594	7	2000	2400	7	1017	1015	8	559	702
7	1131	1138	8	1339	1084	8	541	511	8	788	605	9	926	900
8	2722	2902	9	131	430	9	2808	3080	9	4550	4552	5 5 4	1615	1600
9	2205	2313	10	494	562	10	209	286	10	1158	1063	6	2096	1637
10	3849	3955	3 3 1	7999	6884	4 4 2	2752	2807	4 4 3	2920	2492	7	679	786
2 2 0	5557	4289	4	725	718	5	4333	4079	5	3761	3378	8	1554	1583
3	1627	1671	5	3792	3668	6	1308	1385	6	2268	2487	9	2831	2939
4	4493	4196	6	1356	1259	7	4393	4326	7	3948	3880	6 6 4	4347	3992
5	2384	2508	7	125	233	8	1132	1057	8	1894	1585	7	178	251
6	1356	1361	8	149	404	9	1293	1205	9	1163	1390	8	2370	1994
7	4882	5308	9	4678	4778	10	173	975	10	946	839	7 7 4	181	496
8	3103	3354	10	1501	957	5 5 2	1831	1834	5 5 3	2797	2759	2 0 5	2581	2885
9	1920	2295	4 4 1	2388	1656	6	2332	1579	6	305	564	4	1105	1093
10	1326	1367	5	4734	4388	7	491	531	7	2576	2206	6	3752	3919
3 3 0	7564	7239	6	2642	2629	8	1875	1886	8	1978	2097	8	3329	3203
4	757	747	7	4487	4261	9	3113	3005	9	1403	1122	1 1 5	1143	1190
5	4756	4645	8	941	1340	10	2868	2806	6 6 3	3578	3476	2	4078	4111
6	2049	1741	9	1043	1049	6 6 2	5238	4850	7	1601	1555	3	2013	2051
7	3367	3417	10	787	694	7	761	680	8	3044	3111	4	3731	3827
8	941	923	5 5 1	2479	2369	8	2472	2226	9	846	1167	5	1945	1956
9	2478	2359	6	161	366	9	544	308	7 7 3	703	385	6	596	511
10	567	426	7	2418	1890	10	989	320	8	2159	2107	7	809	776
4 4 0	4904	4528	8	2023	2124	7 7 2	1177	635	2 0 4	2469	2972	8	2085	2112
5	3760	3697	9	1640	1523	8	2541	2334	4	2703	3038	9	1315	1314
6	948	892	6 6 1	3810	3415	9	987	1022	6	5281	5497	2 2 5	1781	1897
7	4295	4495	7	1489	1524	10	2423	2500	8	1667	1552	3	759	684
8	603	772	8	3642	3641	8 8 2	2670	2822	10	943	462	4	1157	974
9	1385	1680	9	175	853	9	1476	798	1 1 4	1345	1379	5	2985	3106
5 5 0	2964	2839	7 7 1	1072	701	10	833	682	2	3356	3523	6	2324	2261
6	2407	1919	8	2217	2166	9 9 2	1962	1941	3	4548	4638	7	2780	2689
7	752	797	2 0 2	3638	3919	2 0 3	4240	5213	4	3901	4067	8	1181	1443
8	1942	2130	4	2691	2826	4	1131	1201	5	457	570	4 3 5	127	428
9	3511	3329	6	6334	6648	6	4087	4085	6	1767	1810	5	2750	2689
6 6 0	5855	5591	8	2094	2178	8	5335	5536	7	666	704	6	402	440
7	173	79	10	752	708	10	956	947	8	2086	2226	7	794	829
8	1622	1618	1 1 2	1456	1732	1 1 3	1563	1630	9	1642	1697	8	159	269
9	738	466	2	5681	5483	2	6007	6140	10	3451	3564	4 4 5	1266	1146
7 7 0	1698	262	3	4738	4900	3	1079	1363	2 2 4	3093	3011	5	3202	2843
8	2472	2474	4	5445	5401	4	5713	5832	3	2137	1926	6	1444	1377
2 0 1	6037	6145	5	1437	1557	5	3477	3452	4	1585	1580	7	3072	3028
4	3120	3089	6	1925	1892	6	524	542	5	2144	2165	8	1275	1196
6	4633	4829	7	308	488	7	1049	1004	6	2282	2355	5 5 5	1776	1844
8	4557	5279	8	2615	2672	8	2945	2749	7	4013	4124	6	158	489
10	642	1224	9	2051	2106	9	1583	1711	8	1725	1983	7	1352	1253
2 1 1	7974	7100	10	3505	3826	10	2045	2089	9	1730	1739	6 6 5	3317	3065
3	2901	2693	2 2 2	4121	3732	2 2 3	1803	1398	10	656	732			
4	5175	5557	3	1773	1627	3	1320	1385	3 3 4	5967	5201			
5	3512	3734	4	2735	2544	4	1497	1462	4	568	664			

Table 2. *Atomic coordinates and isotropic temperature factors of atoms in fresnoite*

The estimated standard deviation in these quantities are given in the parentheses (The first value is for the positive polarity and the second is for the negative polarity)

Atom	Coordinates			β
	x	y	z	
Ba	0.3272 (01)	$\frac{1}{2}+x$	0	0.89 (06)
	0.3272 (01)	$\frac{1}{2}+x$	0	0.89 (06)
Si	0.1282 (06)	$\frac{1}{2}+x$	0.5207 (30)	0.37 (13)
	0.1281 (06)	$\frac{1}{2}+x$	0.5136 (30)	0.39 (13)
Ti	0	0	0.5414 (18)	0.17 (12)
	0	0	0.5385 (18)	0.17 (13)
O(1)	0	0.5	0.6183 (91)	1.80 (72)
	0	0.5	0.6091 (96)	1.66 (69)
O(2)	0.1236 (19)	$\frac{1}{2}+x$	0.2125 (64)	0.51 (37)
	0.1241 (20)	$\frac{1}{2}+x$	0.2019 (62)	0.47 (37)
O(3)	0.2896 (23)	0.5762 (23)	0.6584 (45)	1.29 (33)
	0.2897 (23)	0.5758 (23)	0.6496 (45)	1.23 (33)
O(4)	0	0	0.2278 (91)	0.94 (57)
	0	0	0.2178 (95)	0.96 (57)

Table 3. *Interatomic distances and bond angles in fresnoite*

The estimated standard deviations in these quantities are given in parentheses

Ti polyhedron

Ti—O(3) = 2.001 (21) Å
Ti—O(4) = 1.634 (45)
O(3)—O(4) = 2.944 (43)
O(3)—O(3′) = 2.696 (28)
O(4)—Ti—O(3) = 107.74° (34)
O(3)—Ti—O(3′) = 144.54 (61)
Si—O(3)—Ti = 135.82 (47)

Ba polyhedron

Ba—O(3) [2 ×] = 2.801 (21)
Ba—O(2) = 2.690 (41)
Ba—O(3‴) [2 ×] = 3.157 (34)
Ba—O(2′) [2 ×] = 2.788 (30)
Ba—O(1) = 2.880 (36)
Ba—O(4) [2 ×] = 3.368 (31)

Si_2O_7 group

Si—O(1) = 1.626 (37)
Si—O(2) = 1.607 (39)
Si—O(3) [2 ×] = 1.613 (25)
O(3)—O(3″) = 2.569 (40)
O(3)—O(2) [2 ×] = 2.750 (33)
O(3)—O(1) [2 ×] = 2.559 (20)
O(2)—O(1) = 2.587 (26)
Si—O(1)—Si′ = 143.51° (60)

polarity. The final atomic coordinates, site-occupancy factors and the isotropic thermal-vibration parameters for both polarities are presented in Table 2.

Interatomic distances and bond angles together with the estimated standard errors in these quantities were calculated using the SORFFE program (a local modified version of the ORFFE program of Busing *et al.*, 1964). Calculations of errors in bond distances and angles took into account the errors in the cell dimensions and in the atomic coordinates. The bond distances and angles presented in Table 3 do not include any corrections for the thermal vibrations of the atoms.

4. Discussion

Figure 1 is a projection of the fresnoite structure along the x axis. The titanium atom is five-coordinated with tetragonal pyramidal geometry. These tetragonal pyramids occupy the corners and the base center of the primitive tetragonal cell. All the basal oxygen atoms of the Ti-O pyramid are shared by the adjacent Si tetrahedra, and the Si-O tetrahedra are joined in pairs forming Si_2O_7 groups. The Ti-O pyramid and these groups are linked into heterocyclic five-membered rings parallel to (001) forming sheets. Adjacent sheets are held together by Ba—O bonds. Thus, the crystal structure of fresnoite is markedly similar to that of melilite.

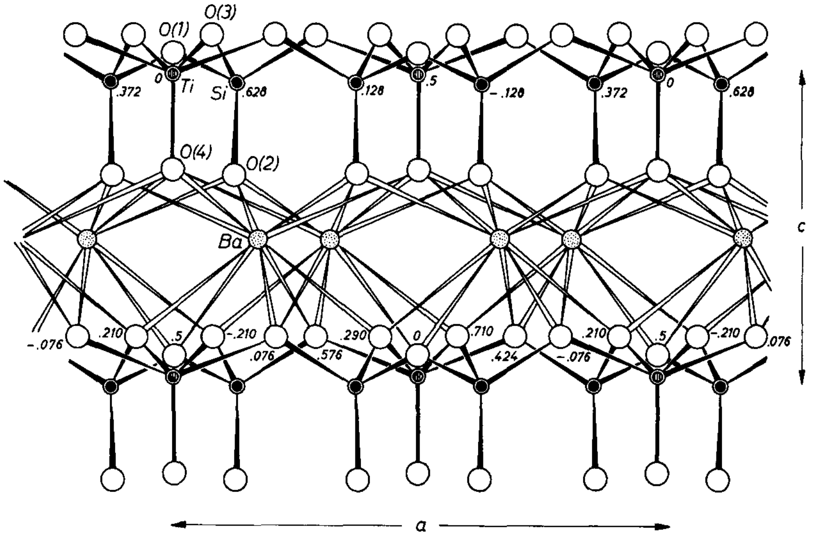

Fig. 1. Crystal structure of fresnoite; x-axis projection

a) The Ti-O tetragonal pyramid

The crystal chemistry of most transition metals is dominated by tetrahedral and octahedral coordination, and five-coordination is relatively unusual, especially in naturally occurring minerals. The trigonal-bipyramidal configuration of oxygen atoms around Al in andalusite and Al and Mg in grandidierite are two of the rare examples of five-coordination in minerals. KIMBALL (1940) proposed the valence-bond theory of directed hybrid orbitals and showed that dsp^3 or d^3sp hybrids which use the d_{z^2} atomic orbital would give rise to trigonal-bipyramidal configuration and that the d^2sp^2, d^4s, d^2p^3 or d^4p hybrids which use the $d_{x^2-y^2}$ atomic orbital would give rise to a tetragonal-pyramidal configuration. Very few instances of five-coordination were known before the early 1960's. In the past decade approximately forty complex organometallic compounds have been discovered whose metal atom is five-coordinated in tetragonal-pyramidal configuration. With the increasing knowledge of the geometry of these compounds it became clear that the valence-bond theory of directed orbitals alone could not satisfactorily explain the observed variations in the dimensions of the tetragonal pyramid. Moreover, the theory offered no reasonable means of predicting whether a central atom would employ its d_{z^2} orbital or the $d_{x^2-y^2}$ orbital. ZEMANN (1963) and GILLESPIE (1963), working individually, published satisfactory theories based on a point-charge model, considering the steric effect resulting from the electrostatic repulsive forces. Their theories, aside from mutually agreeing, provide a better explanation for the observed bond lengths and bond angles. They found that the trigonal bipyramid is energetically the most favorable configuration, very closely followed by a tetragonal pyramid with the apex—central atom—basal atom angle (called the apical angle at the central atom) of $104°04'$. ZEMANN (1963) found that the energy difference between the trigonal bipyramid and the tetragonal pyramid for an AB_5^{2-} complex is only 0.258 eV/complex and suggests that transitions between the two states are very likely.

The dimensions of the Ti tetragonal pyramid are given in Table 3. The Ti—O ionic-bond distance, calculated using the ionic radii of ZACHARIASEN (unpublished), is 2.06 Å. An approximate estimate of the Ti—O single-bond covalent distance, as calculated using PAULING's (1960) single-bond distances, is 1.98 Å. The four basal oxygen atoms are at a distance of 2.00 Å and the apical oxygen is at a distance of 1.63 Å from the Ti atom, indicating a high degree of covalency in the tetragonal pyramid. Indeed, the electrostatic-valence bond-strength calculation, ζ, is $\frac{4}{5} + \frac{2}{10} + \frac{2}{10} + \frac{2}{10} + \frac{2}{10} = 1.60$, indicating extreme cation undersaturation in the apical oxygen. The apical angle at Ti, namely, the O(4)—Ti—O(3) angle, is 107°42′, considerably larger than the predicted angle of 104°04′ (Zemann, 1963). The basal oxygen atoms, O(3), have a nearest cation-neighbor coordination number of four, suggesting a state of partial *nonequivalent-sp^3* hybridization. One of the four hybrids is used in σ bonding to Si, another in σ bonding to Ti and the remaining two enhance the π overlap both to Ti and Si. Thus, the Ti—O(3) bonds could be expected to have bond orders between 1 and $1^1/_2$. The apical oxygen, O(4), has one nearest neighbor of Ti, and four second-nearest neighbors of Ba at such large distances that the latter bonds are almost purely ionic in character. Thus the apical oxygen is not in any hybrid state, and it can donate an electron to the Ti atom enabling the latter to form a set of five hybrid orbitals which in turn take part in double to triple bonds to the apical oxygen, giving a very short Ti—O(4) distance. If repulsions between the bonding electrons are considered, the apical angle at Ti would be expected to increase to a larger value than the expected value of 104°04′, as observed in fresnoite. Lamprophyllite is the only other titanosilicate where Ti has oxygen ligands in tetragonal-pyramidal geometry (Woodrow, 1964). Unfortunately, the dimensions of the tetragonal pyramid in this crystal are not accurately known. In oxo-bis-acetyl-acetone-vanadium (IV), vanadium is in a tetragonal pyramid of five oxygen atoms. This vanadium complex crystallizes in space group $P\bar{1}$, the V—O distances to the basal oxygen atoms being 1.96, 1.96, 1.97 and 1.98 Å, with an apical oxygen distance of 1.56 Å, and the apical angle at V is 106° (Dodge, Templeton and Zalkin, 1961). The crystal structure of the mineral haradaite, $Sr(VO)[Si_2O_6]$ (Takeuchi and Joswig, 1967) has similar values: four V—O 1.99, one V—O 1.57 Å.

Masse, Grenier and Durif (1967) have published a description of the crystal structure of fresnoite when our preliminary report was in the press. Although there is no discrepancy in the gross features of the structure, some of their interatomic distances are questionable, especially their Ti—O(4) bond length of 1.98 Å and some of the dimensions of the Si_2O_7 group. The equalization of all the Ti—O distances is certainly invalid. The discrepancies in the Si_2O_7 group will be considered shortly.

b) The Si_2O_7 group

The general theme of chemical bonding within the Si_2O_7 group in fresnoite is identical to that observed in melilites; quantitatively, as inferred from the bond lengths and bond angles, there are significant differences. In discussing the nature of bonding within the Si_2O_7 group in Zn melilite (LOUISNATHAN, 1969) it was predicted that the dimensions of the pyrosilicate group would vary with different substitutions in the Zn or Ca sites. With the increase in the covalency of the bonding between oxygen atoms and the cations other than silicon, there also will be an increasing degree of equalization of bond lengths between the bridge-bonds and the terminal-bonds. The Ti, Si bridging oxygen, O(3), shares two of its four *nonequivalent-sp*^{3} hybrid orbitals in the bonding between Ti and Si. The unshared oxygen, O(2), is again more covalently bonded to Ba in fresnoite, than it is to Ca in hardystonite. The effect of this is to slightly lengthen the Si—O(2) bond relative to that oberved in hardystonite. The increase in the Si—O—Si angle in fresnoite relative to that observed in hardystonite is again due to an increased participation of the bridging oxygen in covalent bonding to a cation other than Si. The dimensions of the Si_2O_7 group observed in fresnoite and in hardystonite are compared in Table 4; the variations closely follow the above arguments. Table 4 also presents the dimensions of the Si_2O_7 group obtained by MASSE *et al.* (1967); their dimensions nearly correspond to those which would be found in an isolated pyrosilicate group, which is not true in this structure. Probably, the discrepancies observed in the various bond parameters between this work and that of MASSE *et al.* (1967) are largely due to insufficient data (50 reflections of *hk*0 and 0*kl* type) in the latter work, and lack of full three-dimensional refinement.

Table 4. *Comparison of the dimensions of* [Si_2O_7] *group in fresnoite and hardystonite*

	Fresnoite	Hardystonite	Fresnoite (MASSE *et al.*, 1967)
Si—O(1)	1.626 (37) Å	1.649 (03) Å	1.65 Å
Si—O(2)	1.607 (39)	1.583 (01)	1.62
Si—O(3)	1.613 (25) [2×]	1.619 (04) [2×]	1.60
Si—O(1)—Si′ angle	143.51° (60)	138.52° (33)	143°

c) Ba polyhedron

Barium in fresnoite is 10-coordinated. The expected coordination number when Ba cation is surrounded by oxygen anions is 12, and the Ba—O ionic-bond distance, as calculated using Zachariasen's (unpublished) ionic radii, is 2.94 Å. In the different Ba perovskites, where Ba is in 12-coordination, the Ba—O distance varies from 2.95 to 3.11 Å. The Ba—O distances in fresnoite are given in Table 3. There are six distances between 2.69 to 2.88 Å that are significantly shorter than the ionic-bond length, indicating the presence of considerable covalent character in these bonds. The Ba polyhedron is

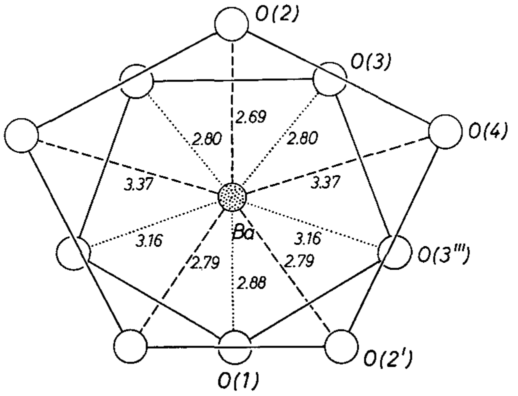

Fig. 2. The BaO_{10} polyhedron at point symmetry *m*. The dashed lines are bonds that reach upward from Ba atom and the dotted lines are bonds that reach downward

a slightly distorted pentagonal antiprism, the distortion being mainly in the areas of the top and bottom faces of the antiprism. Though the true symmetry of the Ba polyhedron is C_s, an approximate S_{10} symmetry results since there exist a nearly one-to-one correspondence between the bonds that reach up and down as shown in Fig. 2. The effect of this on the outer electrons of barium atom would be to somewhat make them spherically symmetrical, and, in turn, the effect of this on the anomalous scattering of x-rays by barium is to nearly equalize $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$. This is a possible reason for the non-resolution of the two polarities during the refinement of the structure.

d) Thermal-vibration parameters

The nature of chemical bonding discussed above leads to the following predictions regarding the thermal motion of the atoms in fresnoite. With 1 to $1\frac{1}{2}$ bond orders reaching Ti from basal oxygen atoms, and 2 to 3 bonds from the apical oxygen atom, the titanium is the most rigidly bonded atom in the structure, followed by Si and then by Ba. $\beta_{\mathrm{Ba}} = 0.89 > \beta_{\mathrm{Si}} = 0.37 > \beta_{\mathrm{Ti}} = 0.17$ is thus in conformity with the arguments given. Similarly, for the anions, the predicted order of increasing β is O(2), O(4), O(3) and O(1), as observed.

5. Relationship of crystal structure to paragenesis

Fresnoite is associated with sanbornite, gillespite and a number of other new minerals described by ALFORS *et al.* (1965). The assemblage is typically a high-temperature type as inferred from the melting points of the minerals, and fresnoite has a high melting point relative to a number of other minerals with which it is associated. Geologically the occurrence of fresnoite is in the migmatite zone. The petrology of this area is described by MACDONALD (1941). The observed average grain size of about 0.3 mm, contrasted with the late-stage giant crystals of sanbornite, and the high melting point suggest that fresnoite was one of the early products to crystallize out of the migmatic fluid, crystallizing almost immediately after coming into contact with the walls of the host rocks. BOBOVICH (1963), and BOBOVICH and PETROVSKII (1963) have made a spectroscopic study of the coordination state of titanium in glassy and recrystallized silicate melts, and have found that titanium has 4 and 5 coordination in glasses which, on recrystallization, passes on to 6 coordination. Thus it is possible that the five coordination in fresnoite reflects the genesis of the mineral.

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