JOURNAL OF SOLID STATE CHEMISTRY 49, 59–64 (1983)

The Crystal Structure of $Ba_2Ti_9O_{20}$: A Hollandite Related Compound

G. D. FALLON AND B. M. GATEHOUSE

Chemistry Department, Monash University, Clayton, Victoria 3168, Australia

Received December 1, 1982

$Ba_2Ti_9O_{20}$ crystallizes in the triclinic system with unit cell dimensions (from single crystal data) a = 14.358(4), b = 14.095(4), c = 7.477(1) Å, α = 95.53(3), β = 100.55(3), γ = 89.95(2)°, and space group $P\bar{1}$, z = 4. The structure was solved using Patterson ("P1" method) and Fourier techniques. Of the 8625 unique reflections measured by counter techniques 3767 with $I \geqq 3\sigma(I)$ were used in the least-squares refinement of the model to a conventional R of 0.057 ($R\omega$ = 0.054). The structure of $Ba_2Ti_9O_{20}$ is very similar to that of hollandite except that additional barium ions replace oxygen ions and disrupt the tunnel walls resulting in the formation of cavities, rather than tunnels, that contain two barium ions per cavity.

Introduction

The composition $Ba_2Ti_9O_{20}$, claimed (*1*) to be stabilized by minute additions of SnO_2 or ZrO_2, was shown subsequently (*2*) to be obtainable as a single phase either from $BaTiO_3$ + TiO_2 or from $BaCO_3$ + TiO_2. In spite of considerable interest in this material, in view of its behavior as a microwave dielectric resonator (*3, 4*), the unit-cell parameters and space group for single crystals were only reported recently (*5*).

The structures of a number of compounds in the BaO : TiO_2 system have been reported and include the following: 1 : 1 (BaO : TiO_2) (*6*), 1 : 2 (*7*), 1 : 4 (*8*), 1 : 5 (*9*), 1 : 6 (*10*), 4 : 13 (*11*), and 6 : 17 (*12*).

The preparation and study of single crystals of $Ba_2Ti_9O_{20}$ was carried out as part of a general examination of the BaO–Ta_2O_5–TiO_2 system being made here, and is of interest in view of difficulties being experienced in interpreting the lattice image data of this composition in several laboratories (*13*).

The unit-cell parameters reported earlier for $Ba_2Ti_9O_{20}$ were for a monoclinic cell (*5*); however, recent diffractometer data show good agreement with the triclinic cell reported here (*22*).

Experimental

A clear tabular crystal (0.07 × 0.03 × 0.08 mm) was selected from a homogeneous mass of single crystals of $Ba_2Ti_9O_{20}$ prepared by heating $BaCO_3$ + TiO_2 in the mole ratio 1 : 4.5 at 1350°C in a platinum crucible for 4 days followed by slow cooling to 700°C over 36 hr. The crystal was mounted on a silica capillary with clear epoxy resin ("Resiweld") and the crystal data were obtained using a Philips PW 1100 computer-controlled diffractometer. Lattice parameters were obtained from the average of 28 orientation matrices automatically determined at various stages of the

0022-4596/83 $3.00

data collection using 22 reflections in the range $2\Theta = 20$ to $34°$.

Crystal Data

$Ba_2Ti_9O_{20}$, $M = 1025.77$, tricilinic, $a = 14.358(4)$, $b = 14.095(4)$, $c = 7.477(1)$ Å, $\alpha = 95.53(3)$, $\beta = 100.55(3)$, $\gamma = 89.95(2)°$; $U = 1480.4$ Å^3, $D_m(5) = 4.60$, $D_c = 4.60$ g cm^{-3}, $z = 4$, $F(000) = 1880$. $\mu = 93.9$ cm^{-1} for Mo$K\alpha$ (0.7107 Å) radiation. Space group $P\bar{1}$ confirmed by successful refinement.

Intensity Measurements

Intensity measurements were made with the crystal described above using the diffractometer and Mo$K\alpha$ radiation monochromated with a flat graphite monochromator crystal. A unique data set was collected out to 2Θ (Mo$K\alpha$) $= 60°$ using the ω-2Θ scan technique with a symmetric scan range of $\pm(1.3 + 0.30 \tan \Theta)°$ in 2Θ from the calculated Bragg angle, at a scan rate of $0.03°$ sec^{-1}. No reflection was sufficiently intense to require the insertion of an attenuation filter. Of the 8625 unique reflections measured 3767 were considered to be significantly above the background ($I \geqq 3\sigma(I)$) and only these were used in the refinement. Three standard reflections, measured at 2-hr intervals, showed no significant variation in intensity.

The data were processed in a manner described previously (*14*). An absorption correction was applied to the data based on the indexed crystal faces 010, $0\bar{1}0$, $00\bar{1}$, $\bar{1}00$, $\bar{6}22$, $5\bar{1}2$, and $62\bar{2}$. No extinction correction was applied. The atomic scattering factors used were for neutral atoms and were corrected for anomalous dispersion (*15*). All calculations were carried out on the Monash University Burroughs B6700 computer; the major program used was SHELX (*16*).

Structure Solution and Refinement

The structure was solved using a method described by Abrahams (*17*) and referred to by this laboratory as the "P1" method (*18*, *19*). Following the location of the heavy atoms in the unit cell and determination of the center of symmetry a structure factor calculation gave a conventional $R = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.235$; parameters for the 40 oxygen atoms were taken from the subsequent difference Fourier synthesis. Full-matrix least-squares refinement of all positional parameters and isotropic thermal parameters for Ba + Ti (oxygen thermal parameters fixed at $U = 0.03$ Å^2) gave $R = 0.092$. Further refinement as above but with anisotropic thermal parameters for the barium atoms and refinement of isotropic thermal parameters for oxygen resulted in $R = 0.057$ and $R\omega = [\Sigma\omega^{1/2}(||F_0| - |F_c||)/\Sigma\omega^{1/2}|F_0|] = 0.054$, $\omega = (\sigma^2(F))^{-1}$; 269 parameters were varied at this stage. In view of the irregularity of the oxygen thermal parameters, those of 11 oxygen atoms were negative (the most negative was O(1) at $U = -0.0127$), and the rest positive (the most positive was O(17) at $U = 0.0147$); the structure was refined, finally, with one thermal parameter for all of the 40 oxygen atoms. The final R was 0.057, $R\omega = 0.054$ for 230 variables. In other words, the refinement of individual isotropic thermal parameters for the oxygen atoms was not statistically significant.

Final parameters with their estimated standard deviations are presented in Table I.[1]

---

[1] See NAPS document No. 04099 for 21 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75 up to 20 pages plus \$.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 I

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

	x	y	z	U (Å^2)
Ba(1)	−1280(1)	2508(1)	71(2)	[a]
Ba(2)	2258(1)	2510(1)	−99(2)	[a]
Ba(3)	−4768(1)	−4374(1)	−2501(2)	[a]
Ba(4)	4239(1)	617(1)	−2590(2)	[a]
Ti(1)	684(3)	75(3)	1771(5)	35(8)
Ti(2)	−1450(2)	−26(3)	1920(5)	32(7)
Ti(3)	75(3)	1607(3)	−4558(6)	38(9)
Ti(4)	2851(2)	−4(2)	1753(5)	34(7)
Ti(5)	1975(3)	−1555(3)	−5437(6)	46(9)
Ti(6)	2125(3)	1567(3)	−4853(3)	18(8)
Ti(7)	−4055(2)	1647(5)	−4473(5)	33(7)
Ti(8)	−3363(2)	1679(2)	1675(5)	39(7)
Ti(9)	4517(2)	1731(3)	2004(5)	37(7)
Ti(10)	3088(3)	3380(3)	−5465(5)	31(8)
Ti(11)	1004(3)	3431(3)	−5418(6)	26(9)
Ti(12)	−1050(3)	3444(3)	−5326(6)	47(9)
Ti(13)	3121(3)	−3498(3)	−4649(5)	49(7)
Ti(14)	3639(2)	−3370(3)	1649(5)	56(7)
Ti(15)	4291(2)	3200(3)	−1965(5)	33(7)
Ti(16)	2531(2)	−5095(2)	−1814(5)	34(7)
Ti(17)	356(3)	−5041(3)	−1773(5)	36(8)
Ti(18)	1797(3)	−5011(3)	1826(5)	29(7)
O(1)	6771(12)	4289(11)	2727(24)	31(3)
O(2)	3220(10)	7458(11)	−82(21)	31
O(3)	2685(11)	4143(11)	2570(23)	31
O(4)	1131(11)	2413(11)	−3634(22)	31
O(5)	851(11)	−2385(11)	3539(22)	31
O(6)	2175(11)	−2618(11)	6433(21)	31
O(7)	2192(11)	846(10)	−2722(23)	31
O(8)	1864(11)	2587(11)	3494(21)	31
O(9)	4442(10)	−1070(9)	−870(20)	31
O(10)	1236(12)	5820(11)	−2662(23)	31
O(11)	1117(12)	−887(11)	5888(22)	31
O(12)	157(11)	−2650(11)	−3570(22)	31
O(13)	580(1)	5723(11)	622(21)	31
O(14)	4293(8)	2447(10)	−167(19)	31
O(15)	2484(10)	−777(10)	−766(21)	31
O(16)	3572(10)	849(9)	860(19)	31
O(17)	3179(10)	2479(11)	−3605(20)	31
O(18)	8098(11)	4084(10)	6068(22)	31
O(19)	739(11)	4219(11)	−7349(23)	31
O(20)	1469(11)	4299(11)	−666(21)	31
O(21)	3427(10)	4088(9)	−860(20)	31
O(22)	105(12)	4067(11)	−3947(22)	31
O(23)	2820(10)	782(10)	4003(20)	31
O(24)	4925(11)	1013(11)	−5838(20)	31
O(25)	903(12)	906(11)	3999(23)	31
O(26)	2097(11)	4076(11)	6000(22)	31
O(27)	2601(10)	5772(10)	575(20)	31
O(28)	3099(11)	−1013(11)	−4146(21)	31
O(29)	1779(11)	−811(11)	2544(23)	31
O(30)	3788(11)	−769(11)	2710(23)	31
O(31)	444(10)	−685(11)	−746(21)	31
O(32)	4113(12)	3997(11)	6000(21)	31
O(33)	6136(10)	4071(10)	6140(20)	31
O(34)	4600(10)	6031(9)	740(20)	31
O(35)	3790(9)	2651(9)	3006(18)	31
O(36)	1612(10)	643(10)	637(21)	31
O(37)	4702(9)	7511(10)	3012(18)	31
O(38)	5878(9)	2542(10)	3317(18)	31
O(39)	226(12)	709(11)	−2691(23)	31
O(40)	2878(10)	−2506(10)	3412(19)	31

[a] Anisotropic thermal parameters for barium atoms are:

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba(1)	76(6)	68(6)	78(6)	−20(5)	15(5)	2(5)
Ba(2)	92(6)	47(6)	62(6)	−23(5)	7(5)	12(5)
Ba(3)	84(6)	57(7)	88(7)	−8(5)	28(5)	6(5)
Ba(4)	56(6)	24(6)	76(6)	−15(5)	23(5)	7(5)

and are of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots 2U_{12}hka^*b^* + \cdots)](\times 10^4)$.

Description and Discussion of the Structure

The $Ba_2Ti_9O_{20}$ structure is best described as being derived from that of hollandite (*20, 21*). Figure 1 shows an idealized view looking approximately along [010]; the boldly lined octahedra, in edge-shared strings two wide by three long, form the side walls, and the strings two wide by four long form the top and bottom (not seen) walls of a hollandite-like tunnel. At the center of the figure four octahedra (edge-shared pairs corner-shared to one another) are placed diagonally across the tunnels blocking them and forming cavities. The edge-shared pairs of blocking octahedra can be seen more clearly in the [100] projec-

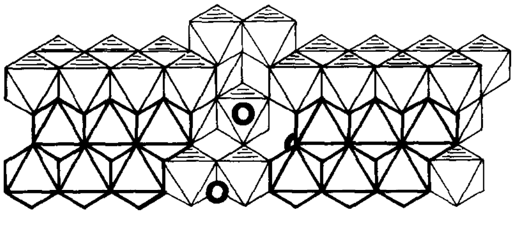

FIG. 1. An idealized view of the structure of $Ba_2Ti_9O_{20}$ looking approximately along [010]. Bold circles represent Ba^{2+} ions.

tion (Fig. 2) that shows the cavities in cross section. The disruption of the hollandite tunnel walls and concomitant formation of cavities are suggested to occur as the result of two barium ions per unit cell (full bold circles in Fig. 1) substituting for oxygen ions in the anion layers. The anion sites along the axes of the cavities are occupied thus: Ba^{2+}–vacancy–Ba^{2+}. An anion vacancy of this type, i.e., between two Ba^{2+} ions, occurs also in $Ba_6Ti_{17}O_{40}$ (*12*).

Ba(1) and Ba(2), situated in the cavities, have slightly distorted cuboctahedral coordination polyhedra consisting of 11 oxygen ions and 1 vacancy. The Ba–O distances range from 2.79 to 3.14 Å (mean 2.94 Å). Ba(1) and Ba(2) are situated in cubic packed anion layers. Ba(3) and Ba(4) are both 12-coordinate with Ba–O distances ranging from 2.75 to 3.21 Å (mean 2.93 Å). The coordination polyhedra of Ba(3) and Ba(4) are best described as slightly distorted twinned cuboctahedra. These may be envisaged as the polyhedra obtained when one-half of a cuboctahedron, cut through the equatorial layer of six oxygen atoms, is reflected in this plane (*23*). The barium atoms Ba(3) and Ba(4) are located in hexagonal packed anion layers.

The titanium ions are all octahedrally coordinated to oxygen with Ti–O distances over the 18 different octahedra varying between 1.75 and 2.33 Å (mean 1.98 Å). The shortest and longest Ti–O distances are associated with Ti(8), and the shortest O–O distances are both associated with Ti(1) [O(31)–O(36) 2.53(2) Å and O(31)–O(39) 2.54(2) Å].

As the barium ions in most of the barium titanates whose structures are known occupy anion sites the structures can be described in terms of approximately close-packed layers of barium and oxygen ions, with titanium occupying octahedral sites between the layers. $Ba_2Ti_9O_{20}$ may also be described in this manner. The barium–oxygen layers are perpendicular to [010], and in terms of the conventional notation for close-packed layers the stacking sequence is ...ACBCBABAC... (...chh...) with six layers per unit cell.

The titanium minerals "hollandite," perovskite, and zirconolite make up the material known as "SYNROC" in the SYNROC process–a proposed means by which high-level nuclear waste can be immobilized (*24*). In terms of resistance to hydrothermal leaching SYNROC has been shown (*24*) to be superior to alternative ceramic waste forms and to borosilicate glasses. The structure of the "hollandite" phase is not known, but its formula is given as $BaAl_2Ti_6O_{16}$ (*24*) that contains 65.3% TiO_2. Analyses of both SYNROC A and SYNROC B show them to contain 73.0 and 73.2% TiO_2, respectively (*24*), both consid-

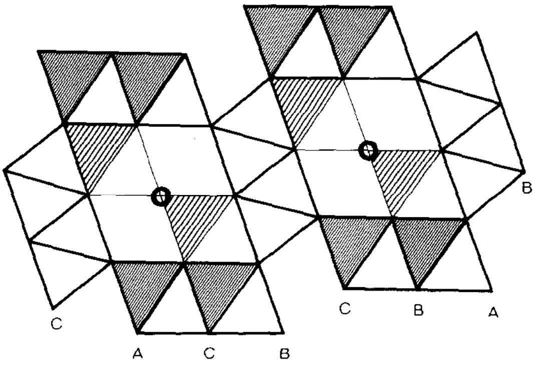

FIG. 2. An idealized [100] projection showing the octahedra blocking the hollandite-like tunnels and the unit-cell anion stacking sequence, ACBCBA.

TABLE II

SELECTED INTERATOMIC DISTANCES (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Ba(1)-O(2)	2.79(1)	Ba(2)-O(20)	2.80(2)
-O(12)	2.80(2)	-O(4)	2.83(2)
-O(13)	2.82(2)	-O(8)	2.84(2)
-O(5)	2.87(2)	-O(35)	2.88(1)
-O(31)	2.89(2)	-O(3)	2.89(2)
-O(10)	2.90(2)	-O(7)	2.90(2)
-O(29)	2.94(2)	-O(36)	2.93(2)
-O(27)	3.10(1)	-O(14)	2.93(1)
-O(6)	3.11(2)	-O(21)	2.95(2)
-O(15)	3.13(2)	-O(16)	3.06(1)
-O(40)	3.14(1)	-O(17)	3.14(2)
Ba(3)-O(34)	2.75(2)	Ba(4)-O(9)	2.80(1)
-O(33)	2.75(2)	-O(24)	2.84(2)
-O(34)	2.78(1)	-O(28)	2.85(2)
-O(32)	2.82(2)	-O(30)	2.86(2)
-O(1)	2.85(2)	-O(24)	2.89(2)
-O(21)	2.87(1)	-O(16)	2.90(2)
-O(35)	2.90(1)	-O(9)	2.93(1)
-O(3)	3.02(2)	-O(7)	2.94(2)
-O(32)	3.03(2)	-O(23)	2.98(1)
-O(38)	3.09(1)	-O(14)	3.00(1)
-O(33)	3.12(1)	-O(37)	3.12(1)
-O(14)	3.21(1)	-O(17)	3.12(2)
Ti(1)-O(31)	1.90(2)	Ti(2)-O(7)	1.79(2)
-O(25)	1.92(2)	-O(11)	1.97(2)
-O(36)	1.92(2)	-O(15)	1.99(2)
-O(39)	1.97(2)	-O(36)	2.00(2)
-O(29)	2.04(2)	-O(39)	2.02(2)
-O(31)	2.04(2)	-O(31)	2.12(2)
Ti(3)-O(4)	1.88(2)	Ti(4)-O(30)	1.81(2)
-O(5)	1.94(2)	-O(16)	1.84(2)
-O(25)	1.95(2)	-O(23)	1.93(2)
-O(39)	1.96(2)	-O(15)	2.06(2)
-O(11)	2.03(2)	-O(36)	2.07(2)
-O(12)	2.11(2)	-O(29)	2.12(2)
Ti(5)-O(28)	1.85(2)	Ti(6)-O(23)	1.76(2)
-O(29)	1.90(2)	-O(7)	1.96(2)
-O(11)	1.91(2)	-O(8)	1.98(2)
-O(5)	1.99(2)	-O(25)	2.00(2)
-O(40)	2.10(2)	-O(17)	2.02(1)
-O(6)	2.13(2)	-O(4)	2.13(2)
Ti(7)-O(24)	1.81(1)	Ti(8)-O(9)	1.75(1)
-O(30)	1.88(2)	-O(2)	1.82(2)
-O(37)	1.89(1)	-O(15)	1.95(2)
-O(28)	2.02(2)	-O(38)	2.09(1)
-O(40)	2.07(1)	-O(28)	2.13(2)
-O(38)	2.16(2)	-O(6)	2.33(1)

TABLE II—*Continued*

Ti(9)-O(35)	1.85(1)	Ti(10)-O(32)	1.83(2)
-O(16)	1.87(1)	-O(35)	1.89(1)
-O(14)	1.97(2)	-O(3)	1.91(2)
-O(24)	1.99(2)	-O(17)	1.96(2)
-O(9)	2.03(2)	-O(8)	2.07(2)
-O(38)	2.27(1)	-O(26)	2.13(2)
Ti(11)-O(19)	1.89(2)	Ti(12)-O(10)	1.89(2)
-O(26)	1.90(2)	-O(18)	1.92(2)
-O(8)	1.94(2)	-O(12)	1.95(2)
-O(12)	1.99(2)	-O(22)	1.95(2)
-O(22)	2.00(2)	-O(6)	2.00(2)
-O(4)	2.04(2)	-O(5)	2.08(2)
Ti(13)-O(33)	1.82(2)	Ti(14)-O(34)	1.82(2)
-O(1)	1.89(2)	-O(2)	1.84(2)
-O(18)	2.01(2)	-O(27)	1.93(1)
-O(38)	2.02(1)	-O(33)	1.98(2)
-O(6)	2.06(2)	-O(37)	2.02(1)
-O(40)	2.09(2)	-O(40)	2.15(2)
Ti(15)-O(14)	1.79(2)	Ti(16)-O(1)	1.78(2)
-O(34)	1.96(1)	-O(21)	1.82(1)
-O(32)	1.96(2)	-O(26)	1.92(2)
-O(21)	1.99(2)	-O(27)	2.05(1)
-O(27)	1.99(1)	-O(20)	2.10(2)
-O(17)	2.03(1)	-O(10)	2.29(2)
Ti(17)-O(22)	1.94(2)	Ti(18)-O(3)	1.80(2)
-O(20)	1.94(2)	-O(18)	1.93(2)
-O(13)	1.97(2)	-O(20)	1.99(2)
-O(10)	1.99(2)	-O(27)	2.00(2)
-O(19)	2.00(2)	-O(19)	2.09(2)
-O(13)	2.01(2)	-O(13)	2.13(2)

erably more TiO_2 than $BaAl_2Ti_6O_{16}$ and $Ba_2Ti_9O_{20}$ (70.1% TiO_2). The tunnels in the hollandite structure are continuous and, therefore, likely to be more susceptible to leaching than the blocked hollandite-like tunnels in $Ba_2Ti_9O_{20}$. If the $Ba_2Ti_9O_{20}$ structure can be shown to take up a small percentage of larger cations such as Rb^+ or Cs^+ then it should be worthy of examination in the SYNROC context. It is possible in fact that $Ba_2Ti_9O_{20}$ has the structure of the "hollandite" phase of SYNROC.

Acknowledgment

This work forms part of a project supported by the Australian Research Grants Scheme.

References

1. G. H. Jonker and W. Kwestroo, *J. Amer. Ceram. Soc.* **41,** 390 (1958).
2. T. Negas, R. S. Roth, H. S. Parker, and D. Minor, *J. Solid State Chem.* **9,** 297 (1974).
3. H. M. O'Bryan, Jr., J. Thomson, Jr., and J. K. Plourde, *J. Amer. Ceram. Soc.* **57,** 450 (1974).
4. J. K. Plourde, D. F. Linn, H. M. O'Bryan, Jr., and John Thomson, Jr., *J. Amer. Ceram. Soc.* **58,** 418 (1975).
5. H. M. O'Bryan, W. H. Grodkiewicz, and J. L. Bernstein, *J. Amer. Ceram. Soc.* **63,** 309 (1980).
6. R. D. Burbank and H. T. Evans, Jr., *Acta Crystallogr.* **1,** 330 (1948).
7. E. Tillmanns, *Acta Crystallogr. Sect. B* **30,** 2894 (1974).
8. K. Lukaszewicz, *Kiczniki Chem.* **31,** 1111 (1957).
9. E. Tillmanns, *Acta Crystallogr. Sect. B* **25,** 1444 (1969).
10. E. Tillmanns, *Cryst. Struct. Commun.* **1,** 1 (1972).
11. E. Tillmanns, *Inorg. Nucl. Chem. Lett.* **7,** 1169 (1971).
12. E. Tillmanns and W. H. Baur, *Acta Crystallogr. Sect. B* **26,** 1645 (1970).
13. Allan Pring, Department of Physical Chemistry, Cambridge University, private communication.
14. B. M. Gatehouse, T. Negas, and R. S. Roth, *J. Solid State Chem.* **18,** 1 (1976).
15. D. T. Cromer and J. T. Waber; D. T. Cromer and J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. IV, Kynoch Press, Birmingham (1974).
16. G. M. Sheldrick, "SHELX-76" (A Programme for Crystal Structure Determination), Cambridge University (1976).
17. S. C. Abrahams, *J. Chem. Phys.* **46,** 2052 (1967).
18. B. M. Gatehouse and P. Leverett, *J. Solid State Chem.* **1,** 484 (1970).
19. G. D. Fallon and B. M. Gatehouse, *J. Solid State Chem.* **44,** 156 (1982).
20. A. Byström and A. M. Byström, *Acta Crystallogr.* **3,** 146 (1950).
21. J. E. Post, R. B. Von Dreele, and P. R. Buseck, *Acta Crystallogr. Sect. B* **38,** 1056 (1982).
22. H. M. O'Bryan, private communication (1982).
23. A. F. Wells, "Structural Inorganic Chemistry," 4th ed., p. 125, Clarendon Press (1975).
24. A. E. Ringwood, S. E. Kesson, N. G. Ware, W. O. Hibberson, and A. Major, *Geochem. J.* **13,** 141 (1979).