

Hydrothermal Synthesis and Crystal Structure of BaV_3O_8

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A single crystal of a barium vanadium oxide BaV_3O_8 in a mixed valence state of V(V) and V(IV) has been grown hydrothermally from $\text{VO}(\text{OH})_2$ and BaCl_2 . The black crystal with a rod-like shape exhibits the monoclinic system $P2_1$ with $a = 7.4347(11)$ Å, $b = 5.5512(7)$ Å, $c = 8.2012(7)$ Å, $\beta = 107.179(8)^\circ$, and $Z = 2$. The structural analysis led to $R = 0.058$ and $R_w = 0.021$ for 1579 unique reflections. BaV_3O_8 was revealed to adopt a layered structure made up of V_3O_8 layers stacking along the c -axis with interstitial Ba^{2+} ions. The V–O framework of the V_3O_8 layer consists of VO_4 tetrahedra and VO_6 octahedra connected by sharing vertices. The valence states of the V sites are differentiated as V(V) in the tetrahedral sites and as V(IV) in the octahedral sites. © 1995 Academic Press, Inc.

INTRODUCTION

The structures of the Ba–V–O compounds of V(V) generally consist of $\text{V}(\text{VO})_4$ tetrahedra which form vertex-shared units in BaV_2O_6 (1), $\text{Ba}_2\text{V}_2\text{O}_7$ (2), $\text{Ba}_3\text{V}_4\text{O}_{13}$ (3), and $\text{Ba}(\text{VO}_3)_2 \cdot \text{H}_2\text{O}$ (4) or isolated VO_3^{3+} ions in $\text{Ba}_3\text{V}_2\text{O}_8$ (5). Only a few Ba–V–O compounds of V(IV) are known, for example, BaVO_3 and Ba_2VO_4 . BaVO_3 , actually regarded as nonstoichiometric BaVO_{3-x} , exhibits complex polytypism based on the structure of $\text{Ba}_3\text{V}_2\text{O}_8$. Ba_2VO_4 has an isolated VO_4^{4+} tetrahedral unit that is unusual for V(IV)–O coordination (6). As for mixed valence compounds of V(V) and V(IV), the structures of $\text{Ba}_8\text{V}_7\text{O}_{22}$ (7) and $\text{BaV}_3\text{O}_8(\text{VO})_{0.4} \cdot n\text{H}_2\text{O}$ (8) have been determined very recently. The structure of $\text{Ba}_8\text{V}_7\text{O}_{22}$ is related to that of BaVO_3 and is claimed to contain three valence states: V(III), V(IV), and V(V) (7). $\text{BaV}_3\text{O}_8(\text{VO})_{0.4} \cdot n\text{H}_2\text{O}$ consist of a V–O framework with a structural type intermediate between layered and tunnel types; the V_3O_8 framework is similar to that of the β -vanadium bronze where V^{4+} and V^{5+} ions are distributed over the octahedral and trigonal bipyramidal sites (8). Bouloux *et al.* studied the $\text{BaO}-\text{V}_2\text{O}_4-\text{V}_2\text{O}_5$ system where mixed valence phases of $\text{Ba}_{1+y}(\text{V}_3\text{O}_8)_2$ ($0.84 \leq y \leq 1$), $\text{Ba}_x\text{V}_7\text{O}_{16}$ ($x = 0.40$), and $\text{Ba}_2\text{V}_3\text{O}_9$ were reported to exist (9); the crystal systems of these phases were given but the structures remain unknown. The structures of the mixed valence Ba–V–O compounds are of interest in terms of V–O framework

structures and V–O coordinations. In the present work, a single crystal of mixed valence BaV_3O_8 , which corresponds to the above-mentioned $\text{Ba}_{1+y}(\text{V}_3\text{O}_8)_2$ with $y = 1$, has been grown by the hydrothermal method and structurally characterized.

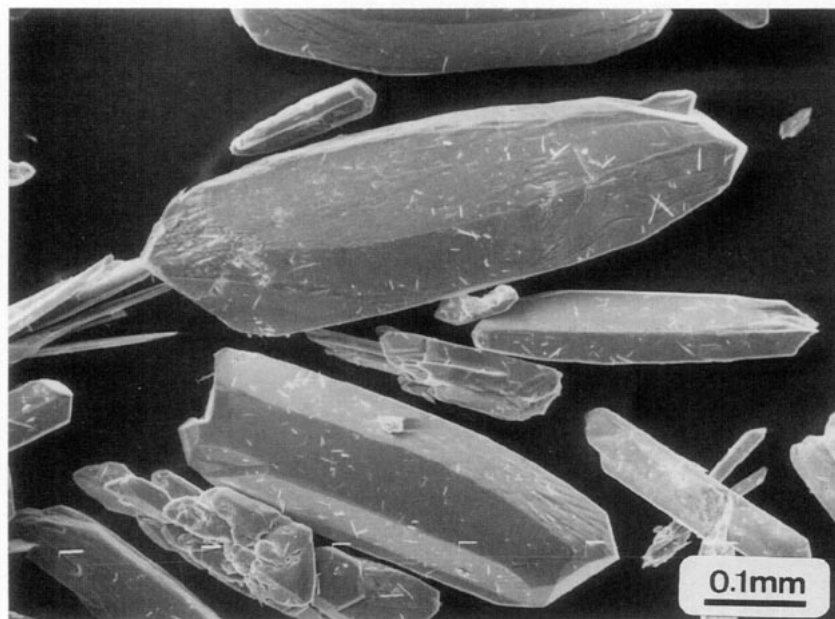
EXPERIMENTAL

Sample Preparation

$\text{VO}(\text{OH})_2$ crystalline powders with duttonite phase (10) were prepared by the hydrothermal treatment of a mixture of VOSO_4 and NaOH solutions at 150°C . The $\text{VO}(\text{OH})_2$ powders dispersed in a 0.1 M BaCl_2 solution were sealed in a Pyrex ampoule and treated hydrothermally at 270°C for 40 hr. The precipitate was filtered out and washed thoroughly with distilled water. The products were found to be biphasic with a minor amount of $\text{VO}_2(\text{A})$ (11, 12). The X-ray diffraction pattern of the main phase was essentially the same as that of BaV_3O_8 ($\text{Ba}_{1+y}(\text{V}_3\text{O}_8)_2$, with $y = 1$) given by Bouloux *et al.* (9). An atomic ratio of Ba : V was confirmed to be 1 : 3 for the main phase by using a Phillips PV9900 EDAX system, yielding the formula BaV_3O_8 . Unfortunately an attempt to obtain a monophasic product of BaV_3O_8 was unsuccessful. The products contained single crystals of BaV_3O_8 which exhibit a black rod-like shape as shown in Fig. 1.

Single-Crystal Structure Determination

The structure determination was performed on a crystal $0.3 \times 0.05 \times 0.03$ mm in size by using a Rigaku AFC7R four-circle diffractometer with monochromatized $\text{MoK}\alpha$ radiation. The crystal system is monoclinic and the lattice parameters were determined from 25 reflections with $36^\circ \leq 2\theta \leq 39^\circ$ and found to be $a = 7.4347(11)$ Å, $b = 5.5512(7)$ Å, $c = 8.2012(7)$ Å, and $\beta = 107.179(8)^\circ$; the b -axis is parallel to the elongated direction of the crystal shape, shown in Fig. 1. The unit cell volume of $323.38(6)$ Å³ corresponds to $Z = 2$. The systematic extinction of $0k0$ for $k = 2n + 1$ yielded possible space groups of $P2_1/m$ and $P2_1$. The data collection was made by the $2\theta - \omega$ scan technique for a 2θ range of 3 to 80° ; no

FIG. 1. Scanning electron micrograph of BaV_3O_8 crystals.

significant intensity fluctuation was observed for standard reflections of $(0, -2, 0)$, $(1, -1, 2)$, and $(0, -1, -2)$, which were monitored every 150 reflections. The data processing and structure determination were performed using the TEXSAN crystallographic software package (13). It gave 2066 reflections with $I > 0$, of which 1579 unique reflections with $I > 3\sigma(I)$ were used in the structural analysis. The correction of absorption effect was made by the

ψ -scan method around the elongated axis with a transmission factor of 0.776–1.000 (14). The statistical treatment of the intensity data favored the noncentrosymmetric space group of $P2_1$. The structure was solved as follows. The direct method using the program R-SAPI88 (15) was successfully applied to locate Ba and V atoms. Five O atoms were also located simultaneously. The three remaining O atoms were found by the differential Fourier method. The absorption correction was made based on this structure model using the program DIFABS (16) and then the anisotropic thermal parameters were applied. The refinements made by the full-matrix least-squares method led to the final R values of $R = 0.021$ and $R_w = 0.028$.

TABLE 1
Crystal Data and Experimental Parameters

Chemical formula	BaV_3O_8
Crystal system	Monoclinic
Space group	$P2_1$
a (Å)	7.4347(11)
b (Å)	5.5512(7)
c (Å)	8.2012(7)
β (°)	107.179(8)
z	2
D_c (g cm $^{-3}$)	4.29
Crystal size (mm)	$0.3 \times 0.05 \times 0.03$
Radiation	$\text{MoK}\alpha$
Linear absorption coefficient (cm $^{-1}$)	92.64
Scan technique	$2\theta - \omega$
Scan width (°)	$\Delta\omega = 1.78 + 0.38 \tan \theta$
Scan speed (°min $^{-1}$)	4.0
Maximum 2θ (°)	80
No. of reflections ($I > 0$)	2066
No. of unique reflections ($I > 3\sigma(I)$)	1579
R_{int}	0.025
No. of parameters	109
R	0.028
R_w	0.021

TABLE 2
Atomic Parameters and Isotropic Temperature Factors for BaV_3O_8

Atom	x	y	z	$B_{\text{eq}}(\text{\AA}^2)^a$
Ba	0.21996(4)	0	-0.09856(4)	1.077(8)
V(1)	0.07235(9)	-0.0002(8)	0.36100(9)	0.64(2)
V(2)	0.29418(9)	0.5022(9)	0.21642(9)	0.60(2)
V(3)	0.58540(9)	-0.0010(8)	0.31646(8)	0.57(2)
O(1)	0.4688(20)	0.2441(28)	0.1900(16)	0.7(2)
O(2)	0.4335(5)	0.5062(33)	0.4907(4)	1.0(1)
O(3)	0.4862(19)	0.7511(26)	0.2067(16)	0.7(2)
O(4)	0.1334(24)	0.2459(31)	0.2621(24)	1.1(3)
O(5)	0.1307(24)	-0.2577(31)	0.2765(25)	1.3(3)
O(6)	0.1757(5)	0.4787(20)	0.0144(43)	0.9(2)
O(7)	-0.1804(4)	0.0036(39)	0.3122(4)	1.2(1)
O(8)	0.1723(5)	-0.0033(44)	0.5652(5)	1.8(2)

^a $B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

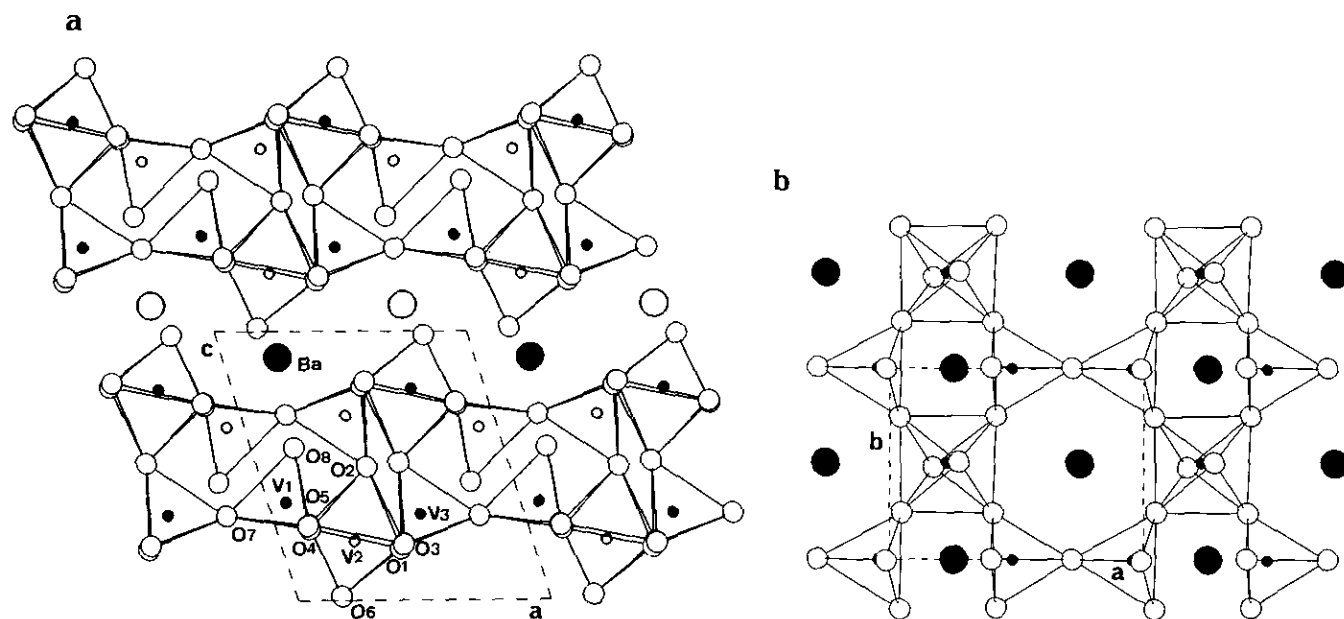


FIG. 2. Crystal structure of BaV₃O₈ viewed along (a) the *b*-axis and (b) the *c**-axis. Large, medium, and small circles denote Ba, O, and V atoms, respectively, in (a) and (b). Ba and V atoms at $y \approx 0$ are represented by closed circles and at $y \approx \frac{1}{2}$ by open circles in (a).

Full occupancies were confirmed for the Ba and V sites. The crystal data and the experimental parameters are listed in Table 1. The atomic parameters and the isotropic temperature factors are listed in Table 2.

TABLE 3
Bond Distances (Å) and Angles (°) for V–O Polyhedra
in BaV₃O₈

V(1)O ₄ tetrahedron			
V(1)–O(4) 1.72(2)	V(1)–O(5) 1.70(2)	V(1)–O(7) 1.802(3)	
V(1)–O(8) 1.619(4)			
O(4)–V(1)–O(5) 107.3(8)	O(4)–V(1)–O(7) 106.8(8)		
O(4)–V(1)–O(8) 113(1)	O(5)–V(1)–O(7) 107.1(8)		
O(5)–V(1)–O(8) 109(1)	O(7)–V(1)–O(8) 111.1(6)		
V(2)O ₆ octahedron			
V(2)–O(1) 1.99(2)	V(2)–O(2) 2.181(3)	V(2)–O(3) 2.01(2)	
V(2)–O(4) 1.96(2)	V(2)–O(5) ⁱ 1.96(2)	V(2)–O(6) 1.636(4)	
O(1)–V(2)–O(2) 89.6(5)	O(1)–V(2)–O(3) 89.8(2)		
O(1)–V(2)–O(4) 87.3(7)	O(1)–V(2)–O(5) ⁱ 171.8(7)		
O(1)–V(2)–O(6) 90.3(5)	O(2)–V(2)–O(3) 84.7(5)		
O(2)–V(2)–O(4) 86.6(6)	O(2)–V(2)–O(5) ⁱ 82.8(6)		
O(2)–V(2)–O(6) 174.3(4)	O(3)–V(2)–O(4) 170.8(7)		
O(3)–V(2)–O(5) ⁱ 92.5(7)	O(3)–V(2)–O(6) 101.0(4)		
O(4)–V(2)–O(5) ⁱ 89.3(2)	O(4)–V(2)–O(6) 87.7(6)		
O(5)–V(2)–O(6) 96.9(6)			
V(3)O ₄ tetrahedron			
V(3)–O(1) 1.77(2)	V(3)–O(2) ⁱⁱ 1.629(3)	V(3)–O(3) ⁱⁱⁱ 1.69(1)	
V(3)–O(7) ^{iv} 1.752(3)			
O(1)–V(3)–O(2) ⁱⁱ 112.4(7)	O(1)–V(3)–O(3) ⁱⁱⁱ 104.6(2)		
O(1)–V(3)–O(6) ^{iv} 107.1(8)	O(2) ⁱⁱ –V(3)–O(3) ⁱⁱⁱ 137.0(5)		
O(2) ⁱⁱ –V(3)–O(7) ^{iv} 118.1(7)	O(3) ⁱⁱⁱ –V(3)–O(7) ^{iv} 106.3(8)		

Note. Symmetry codes: (i) $x, 1 + y, z$; (ii) $1 - x, y - \frac{1}{2}, 1 - z$; (iii) $x, y - 1, z$; (iv) $1 + x, y, z$.

RESULTS

Description of the Structure

As depicted in Fig. 2, the structure of BaV₃O₈ is a layered type consisting of V₃O₈ layers and interstitial Ba²⁺ ions. The V₃O₈ layer is parallel to the *ab* plane. The V–O framework structure of the V₃O₈ layer comprises two types of V–O polyhedra: VO₄ tetrahedra for V(1) and V(3) and VO₆ octahedra for V(2). The V–O distances and O–V–O angles for the V–O polyhedra are listed in Table 3. As seen in Fig. 2, the V₃O₈ layer may be described as follows. The V(1)O₄ and V(3)O₄ tetrahedra share the O(7) atom to form a V₂O₇ unit. The V₂O₇ units and the V(2)O₆ octahedra are linked alternately along the *b*-axis by sharing vertices to form a V₃O₈ sheet. Two V₃O₈ sheets are connected between the V(2)O₆ and V(3)O₄ units by sharing the O(2) atom making up the V₃O₈ layer. Since the V–O polyhedra are joined by sharing vertices, the V–V distances show rather large values of 3.5 to 3.6 Å. Assuming the coordination sphere of Ba²⁺ ion is less than 3.3 Å, the Ba atom is surrounded by 12 oxygens at the Ba–O distances listed in Table 4, as depicted in Fig. 3. The Ba–O(8) distance of 2.675 Å is shorter than other Ba–O distances and hence the interaction between Ba and the apical oxygen of the V(1)O₄ tetrahedron may play a dominant role in setting the Ba position.

Bond Strength Analysis

The bond strength calculations were made by using the empirical parameters given by Brown and Wu (17) and

TABLE 4
Bond Distances (Å) for Ba-O Polyhedron
in BaV_3O_8

Ba-O(1)	2.88(1)	Ba-O(1) ⁱ	2.99(2)
Ba-O(3) ⁱⁱ	3.03(1)	Ba-O(3) ⁱ	2.94(1)
Ba-O(4) ⁱⁱⁱ	2.93(2)	Ba-O(5) ^{iv}	2.91(2)
Ba-O(6)	2.87(1)	Ba-O(6) ⁱⁱ	3.09(1)
Ba-O(6) ⁱⁱⁱ	3.216(4)	Ba-O(7) ^{iv}	3.27(2)
Ba-O(7) ⁱⁱⁱ	3.23(2)	Ba-O(8) ^v	2.675(4)

Note. Symmetry codes: (i) $1-x, y-\frac{1}{2}, -z$; (ii) $x, y-1, z$; (iii) $-x, y-\frac{1}{2}, -z$; (iv) $-x, y+\frac{1}{2}, -z$; (v) $x, y, z-1$.

TABLE 5
Bond Strength Calculations for BaV_3O_8

	Ba	V(1)	V(2)	V(3)	Total
O(1)	0.36		0.54	1.06	1.97
O(2)			0.34	1.62	1.96
O(3)	0.32		0.52	1.35	2.19
O(4)	0.18	1.23	0.59		2.00
O(5)	0.19	1.31	0.59		2.09
O(6)	0.43		1.51		1.94
O(7)	0.18	0.97		1.12	2.27
O(8)	0.34	1.67			2.01
Total	2.00	5.18	4.09	5.15	

the results are listed in Table 5. The values obtained for Ba and O lie in an allowable range for divalent ions. V(1), V(2), and V(3) show the values of 5.18, 4.09, and 5.15, respectively, which clearly indicate that V^{5+} ions occupy the tetrahedral sites of V(1) and V(3) and that V^{4+} ions occupy the octahedral site of V(2).

DISCUSSION

The structure of BaV_3O_8 has been determined to be a layered type consisting of V_3O_8 layers stacking along the c -axis with interstitial Ba^{2+} ions. The compound was first reported by Bouloux *et al.* (9) in their extensive study on the phase relation of the $\text{BaO}-\text{V}_2\text{O}_5-\text{VO}_2$ system. They expressed the formula as $\text{Ba}_{1+y}(\text{V}_3\text{O}_8)_2$ after the $M_{1+y}(\text{V}_3\text{O}_8)_2$ phase ($M = \text{Mg, Zn, Co, and Ni}$) (18) with

the nonstoichiometric range of $0.84 \leq y \leq 1$ and hence $y = 1$ gives BaV_3O_8 . The lattice parameters for BaV_3O_8 were reported as $a = 8.191(5) \text{ Å}$, $b = 5.554(4) \text{ Å}$, $c = 14.877(8) \text{ Å}$, and $\beta = 107.24(10)^\circ$; note that the a - and c -parameters correspond to our c - and a -parameters, respectively. A difference is seen between their c -parameter (14.877 Å) and our a -parameter (7.4347 Å): the former is twice the latter. It suggests that the phase of Bouloux *et al.* exhibits a double-period structure along the present a -axis but the structural details are unknown.

BaV_3O_8 presents a structural type of a mixed valence V_3O_8 layer featured by the coexistence of VO_4 tetrahedra and VO_6 octahedra. The V-O polyhedral framework having both tetrahedra and octahedra is little known; an example is found in recently characterized $\text{Ba}_8\text{V}_7\text{O}_{22}$ (7). As revealed by the bond strength calculations in Table 5, the valence states of the V sites are clearly differentiated, that is, two tetrahedral sites (V(1) and V(3)) for V(V) and one octahedral site (V(2)) for V(IV) . It is interesting to note that, although the large size of the Ba^{2+} ion is claimed to favor the formation of V(IV)O_4 tetrahedra (9, 10), V^{4+} ions adopt the usual VO_6 octahedral formation in BaV_3O_8 . Taking into account the well-differentiated valence states of the V sites and the full occupancy of the Ba site, the formula BaV_3O_8 is regarded as stoichiometric rather than nonstoichiometric as $\text{Ba}_{1+y}(\text{V}_3\text{O}_8)_2$ with $y = 1$. A similar mixed valence M-V-O compound is found in the $M_2\text{V}_3\text{O}_8$ phase ($M = \text{K}$ (19), NH_4 (20), Rb (21)) consisting of V_3O_8 layers and interstitial M^+ ions. The V_3O_8 layer is made up of VO_5 tetragonal pyramids and VO_4 tetrahedra which are connected alternately by sharing vertices forming single sheet in contrast to the double sheet of the present V_3O_8 layer. V^{4+} and V^{5+} ions occupy separately the former and the latter sites, respectively, resulting in the stoichiometric $M_2\text{V}_3\text{O}_8$ phase. Consequently, BaV_3O_8 , as well as $M_2\text{V}_3\text{O}_8$, is classified with class I mixed valence compounds, which are defined as those metal ions of differing valences in sites of different symmetry and ligand field strength (22).

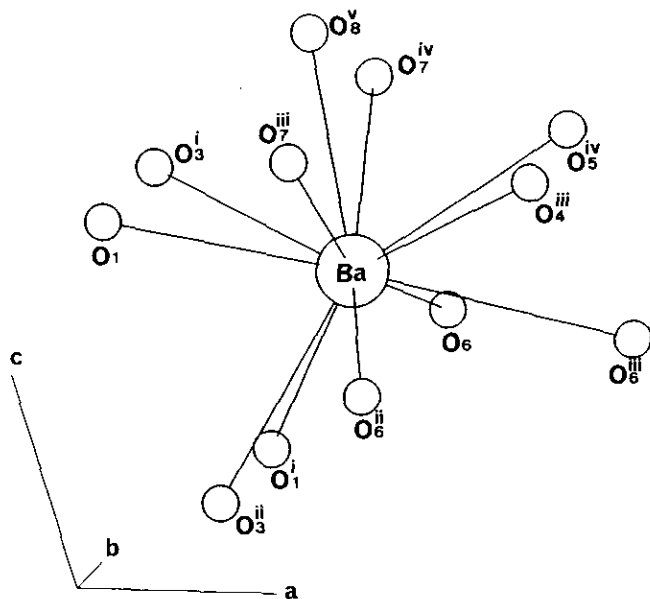


FIG. 3. Coordination of Ba atoms with oxygens. The Roman numerals superscripts of the oxygens refer to the symmetry codes given in Table 4.

REFERENCES

1. S. Launay and J. Thoret, *C.R. Acad. Sci. Paris Ser. D* **277**, 541, (1973).
2. F. C. Hawthorne and C. Calvo, *J. Solid State Chem.* **26**, 345 (1978).
3. B. M. Gatehouse, L. W. Guddat, and R. S. Roth, *J. Solid State Chem.* **71**, 390 (1987).
4. L. Ulicka, F. Pavelcik, and K. Huml, *Acta Crystallogr. Sect. C* **43**, 2266 (1987).
5. P. Süssse and M. J. Buerger, *Z. Kristallogr.* **131**, 161 (1970).
6. G. Liu and J. E. Greedan, *J. Solid State Chem.* **103**, 228 (1993).
7. G. Liu and J. E. Greedan, *J. Solid State Chem.* **108**, 371 (1994).
8. Y. Oka, O. Tamada, T. Yao, and N. Yamamoto, *J. Solid State Chem.*, **114**, 359 (1995).
9. J. C. Bouloux, J. Galy, and P. Hagenmüller, *Rev. Chim. Miner.* **11**, 45 (1974).
10. H. T. Evans, Jr. and M. E. Mrose, *Acta Crystallogr.* **11**, 56 (1958).
11. F. Théobald, *J. Less-Common Met.* **53**, 55 (1977).
12. Y. Oka, T. Yao, and N. Yamamoto, *J. Solid State Chem.* **86**, 116 (1990).
13. "TEXSAN: Single Crystal Structure Analysis, ver. 5.0." Molecular Structure Corp., The Woodlands, TX, 1989.
14. A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr. Sect. A* **24**, 351 (1968).
15. F. Hai-Fu, "Structure Analysis Programs with Intelligent Control." Rigaku Corp., Tokyo, Japan, 1988.
16. N. Walker and D. Stuart, *Acta Crystallogr. Sect. A* **39**, 158 (1983).
17. I. D. Brown and K. K. Wu, *Acta Crystallogr. Sect. B* **32**, 1957 (1976).
18. P. Hagenmüller, J. Galy, M. Pouchard, and A. Casalot, *Mater. Res. Bull.* **1**, 95 (1966).
19. J. Galy and A. Carpy, *Acta Crystallogr. Sect. B* **31**, 1794 (1975).
20. F. R. Théobald, J. G. Théobald, J. C. Védérine, R. Clad, and J. Renard, *J. Phys. Chem. Solids* **45**, 581 (1984).
21. M. Ha-Eierdanz and U. Müller, *Z. Anorg. Allg. Chem.* **613**, 63 (1992).
22. M. B. Robin and P. Day, in "Advances in Inorganic and Radio Chemistry." (H. J. Emeléus and A. G. Sharpe, Eds.), Vol. 10, p. 247. Academic Press, New York/London, 1967.