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BRIEF COMMUNICATION

On the Space Group of BaV_3O_8

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The crystal structure of BaV_3O_8, recently described in space group $P2_1$, is better described in $P2_1/m$. Refinement in $P2_1/m$ leads to small but highly significant changes in bond lengths and angles; the general description of the structure is unchanged.

The crystal structure of the mixed-valent compound BaV_3O_8 has recently (1) been described in the noncentrosymmetric, polar space group $P2_1$ (monoclinic; $a = 7.4347(11)$, $b = 5.5512(7)$, $c = 8.2012(7)$ Å, $\beta = 1.07.179(8)°$, $Z = 2$). The reported structure conforms quite closely to the centrosymmetric space group $P2_1/m$, and further refinement in that space group seemed appropriate. This refinement was successful. It was based on the 1579 reflections included in the supplementary material (2), and converged quickly ($(\Delta/\sigma)_{max} < 0.01$) to an R of 0.029 for 67 parameters—adequately close, surely, to the 0.028 for 109 parameters obtained in the earlier $P2_1$ refinement (Table 1 of Ref. 1). Coordinates are given in Table 1.

TABLE 1
Coordinates, Space Group $P2_1/m$

Atom	Site	x	y	z	U_{eq}[a]
Ba	2(*e*)	0.21998(4)	0.25	−0.09854(4)	0.0133(1)
V(1)	2(*e*)	0.07233(10)	0.25	0.36101(9)	0.0080(1)
V(2)	2(*e*)	0.29416(10)	0.75	0.21642(9)	0.0076(1)
V(3)	2(*e*)	0.58535(9)	0.25	0.31653(9)	0.0071(1)
O(1)	4(*a*)	0.4777(3)	0.4970(4)	0.1980(3)	0.0114(3)
O(2)	2(*e*)	0.4339(5)	0.75	0.4901(4)	0.0126(6)
O(4)	4(*a*)	0.1319(4)	0.5016(5)	0.2689(4)	0.0182(4)
O(6)	2(*e*)	0.1759(6)	0.75	0.0147(5)	0.0188(7)
O(7)	2(*e*)	−0.1802(5)	0.25	0.3125(5)	0.0159(7)
O(8)	2(*e*)	0.1716(6)	0.25	0.5652(5)	0.0227(8)

[a] $U_{eq} = \frac{1}{3} \sum_i \sum_j [U_{ij}(a_i^* a_j^*)(\mathbf{a}_i \cdot \mathbf{a}_j)]$.

TABLE 2
V–O Bond Lengths and Angles

Distance(Å)		Angle(°)	
V(1)–O(4)	1.707(3)(× 2)	O(7)–V(1)–O(4)	106.9(2)(× 2)
V(1)–O(7)	1.801(4)	O(8)–V(1)–O(4)	111.1(2)(× 2)
V(1)–O(8)	1.619(4)	O(4)–V(1)–O(4)	109.8(1)
		O(8)–V(1)–O(7)	110.9(2)
V(2)–O(1)	1.995(2)(× 2)	O(2)–V(2)–O(1)	87.1(1)(× 2)
V(2)–O(2)	2.177(3)	O(4)–V(2)–O(1)	90.0(1)(× 2)
V(2)–O(4)	1.962(3)(× 2)	O(6)–V(2)–O(1)	95.7(2)(× 2)
V(2)–O(6)	1.628(4)	O(1)–V(2)–O(1)	89.5(1)
		O(4)–V(2)–O(1)	172.0(1)(× 2)
		O(4)–V(2)–O(2)	84.9(1)(× 2)
		O(6)–V(2)–O(2)	176.1(2)
		O(6)–V(2)–O(4)	92.3(2)(× 2)
		O(4)–V(2)–O(4)	89.3(1)
V(3)–O(1)	1.734(2)(× 2)	O(7)–V(3)–O(1)	106.7(1)(× 2)
V(3)–O(2)	1.634(3)	O(1)–V(3)–O(1)	104.5(1)
V(3)–O(7)	1.753(4)	O(2)–V(3)–O(1)	112.7(1)(× 2)
		O(2)–V(3)–O(7)	113.0(2)

The general features of the structure—which is based on two $V^{V}O_4$ tetrahedra and a $V^{IV}O_6$ octahedron—are unchanged; however, some changes in the bond lengths and angles are of great statistical significance. Revised V–O distances and O–V–O angles are given in Table 2. All four independent cations lie on mirror planes.

The earlier authors were led to choose space group $P2_1$ over $P2_1/m$ because "the statistical treatment of the intensity data favored the noncentrosymmetric space

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group.'' This misleading indication probably resulted from the fact that the unit cell contains only a small number of dominating scatterers—two Ba atoms. It has been shown that such a situation results in the intensity distribution being biased toward a noncentrosymmetric indication (3).

REFERENCES

1. Y. Oka, T. Yao, and N. Yamamoto, *J. Solid State Chem.* **117,** 407 (1995).
2. A listing of F_{obs} and F_{calc} was kindly furnished by the Editorial Office of *J. Solid State Chem.*
3. A. Hargreaves, *Acta Crystallogr.* **8,** 12 (1955).