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## Key indicators

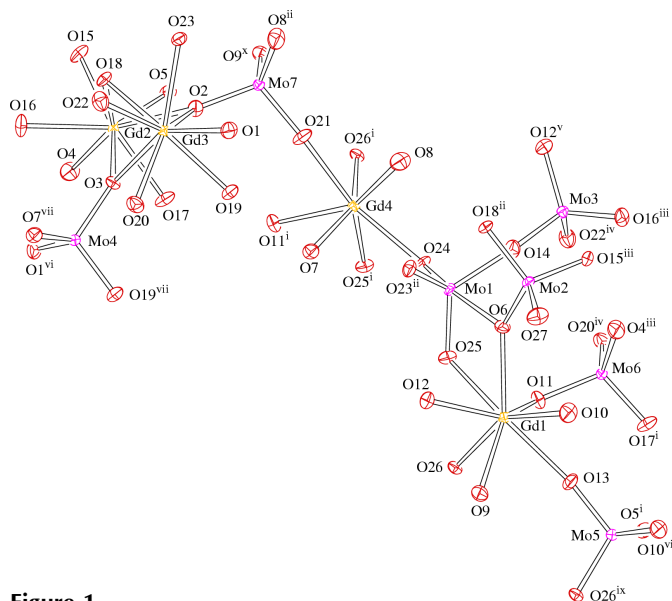
Single-crystal X-ray study  
 $T = 296$  K  
Mean  $\sigma(\text{Mo}-\text{O}) = 0.005$  Å  
 $R$  factor = 0.039  
 $wR$  factor = 0.108  
Data-to-parameter ratio = 19.7For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.**Gd<sub>4</sub>Mo<sub>7</sub>O<sub>27</sub>, a novel phase in the  
Gd<sub>2</sub>O<sub>3</sub>–MoO<sub>3</sub> system**

The title compound, heptamolybdenum(VI) tetragadolinate(III), a novel phase in the the Gd<sub>2</sub>O<sub>3</sub>–MoO<sub>3</sub> system, has been prepared by pyrolysis of [Gd<sub>2</sub>(H<sub>2</sub>O)<sub>12</sub>Mo<sub>8</sub>O<sub>27</sub>]·8H<sub>2</sub>O at 1023 K for 2 h in air. The compound can be described as a layer structure consisting of {MoO<sub>4</sub>}-, {Mo<sub>3</sub>O<sub>11</sub>}- and {Gd}-containing layers, which are stacked along the *a* direction. The {Mo<sub>3</sub>O<sub>11</sub>} group is composed of trigonal bipyramidal MoO<sub>5</sub> connected to two MoO<sub>4</sub> tetrahedra, with corner-sharing. The coordination polyhedra of square-antiprismatic GdO<sub>8</sub> and monocapped trigonal prismatic GdO<sub>7</sub> are dimerized to give {Gd<sub>2</sub>O<sub>*n*</sub>} (*n* = 12 and 13) groups which possess short Gd···Gd separations [3.6345 (4)–3.6404 (4) Å].

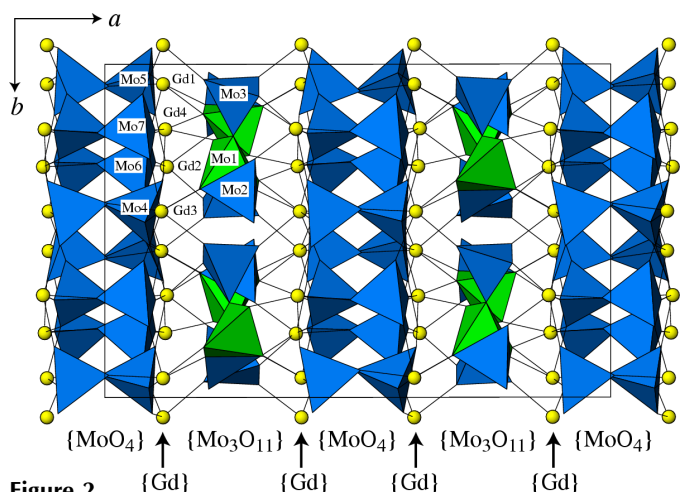
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## Comment

Solid-state materials based on  $R_2(\text{MoO}_4)_3$ , where *R* is a rare earth element, have attracted much attention because of their ferroelectric/ferroelastic (Borchardt & Bierstedt, 1966; Aizu *et al.*, 1969), magnetoelectric (Ponomarev *et al.*, 1994, 1995; Wiegelmann *et al.*, 1996), and other unusual physical properties (Evans *et al.*, 1997). Although many *m:n* phases in the  $mR_2O_3.nMoO_3$  system have been found through phase-equilibrium studies (Brixner *et al.*, 1979), interest is mainly focused on the compounds  $R_2(\text{MoO}_4)_3$  (*m:n* = 1:3). However, recent discoveries of potent oxide-ion conduction in La<sub>2</sub>Mo<sub>2</sub>O<sub>9</sub> (*m:n* = 1:2) (Lacorre *et al.*, 2000; Goutenoire *et al.*, 2000) and polymorphism of  $R_2\text{MoO}_6$  (*m:n* = 1:1) (Xue *et al.*, 1995)



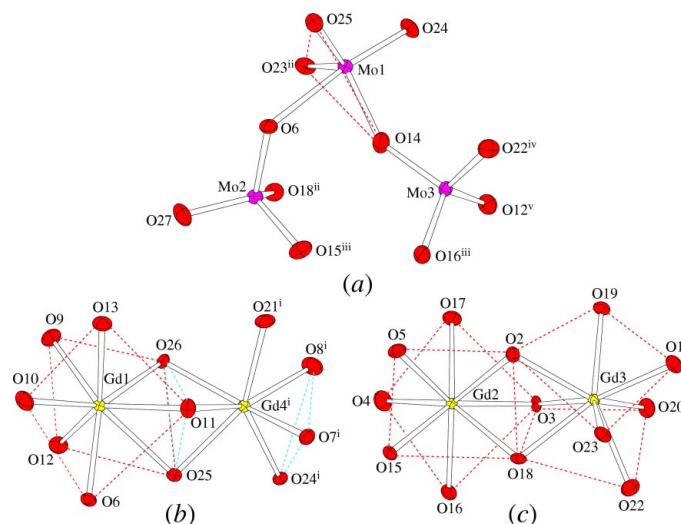
**Figure 1**  
ORTEP (Johnson, 1976) plot, showing the asymmetric unit of Gd<sub>4</sub>Mo<sub>7</sub>O<sub>27</sub> and extra O atoms generated by symmetry operations. The displacement ellipsoids are drawn at the 50% probability level. Symmetry codes are described in the footnote of Table 1.



**Figure 2** Packing view of  $\text{Gd}_4\text{Mo}_7\text{O}_{27}$ , projected on to the (110) plane, drawn using a combination of polyhedral (for Mo) and ball-and-stick (for Gd) models. Only Gd and Mo atoms are labelled. The blue and green polyhedra denote the  $\text{MoO}_4$  and  $\text{MoO}_5$  groups. The yellow spheres are the Gd atoms.

stimulated our interest in the syntheses and structures of various other  $m:n$  compositions. The  $m\text{Gd}_2\text{O}_3 \cdot n\text{MoO}_3$  system has been well explored (Megumi *et al.*, 1974), and  $m:n = 1:1$ ,  $1:3$ ,  $1:4$  and  $1:6$  phases are known in the phase diagram. We report here the synthesis and crystal structure of  $\text{Gd}_4\text{Mo}_7\text{O}_{27}$  ( $m:n = 2:7 = 1:3.5$ ), the first observation of a phase intermediate between  $m:n = 1:3$  and  $1:4$ . The compound is isomorphous with  $\text{Eu}_4\text{Mo}_7\text{O}_{27}$ , which we reported recently (Naruke & Yamase, 2001).

Fig. 1 shows the asymmetric unit of  $\text{Gd}_4\text{Mo}_7\text{O}_{27}$  and several extra O atoms. All the metal atoms are coordinated and linked by O atoms; Gd atoms are hepta- and octacoordinate ( $\text{Gd}-\text{O} < 2.7 \text{ \AA}$ ), while Mo atoms are tetra- and pentacoordinate ( $\text{Mo}-\text{O} < 2.8 \text{ \AA}$ ). All atoms occupy general positions (*i.e.*  $f$  in the Wyckoff notation). Fig. 2 shows the crystal structure viewed down the  $c$  axis. The structure consists of  $\{\text{MoO}_4\}$ -,  $\{\text{Mo}_3\text{O}_{11}\}$ - and  $\{\text{Gd}\}$ -containing layers which are stacked along the  $a$  direction. The distance between two  $\{\text{Mo}_3\text{O}_{11}\}$  layers (equal to the distance between two  $\{\text{MoO}_4\}$  layers) is  $11.134 \text{ \AA}$  [=  $(a/2)\sin\beta$ ]. The  $\{\text{Mo}_3\text{O}_{11}\}$  group (Fig. 3a) comprises a trigonal bipyramidal  $\text{Mo}_1\text{O}_5$  unit (trigonal plane of O14/O23<sup>ii</sup>/O25, with apical O6 and O24) connected to  $\text{Mo}_2\text{O}_4$  and  $\text{Mo}_3\text{O}_4$  tetrahedra *via* the atoms O6 and O14, respectively. Bond distances are listed in Table 1. The length [ $2.362(4) \text{ \AA}$ ] of the axial  $\text{Mo}_1-\text{O}_6$  bond is much larger than that [ $1.729(4) \text{ \AA}$ ] of the opposite  $\text{Mo}_1-\text{O}_{24}$  bond (Table 1). The  $\text{Mo}_1$  atom is displaced from the trigonal plane by  $0.3492(5) \text{ \AA}$  towards O24. Thus, the  $\text{Mo}_1\text{O}_5$  polyhedron can also be viewed as an  $\text{Mo}_1\text{O}_4$  tetrahedron capped by the atom O6. O27 is a terminal oxygen bonded only to Mo2; the second nearest metal from O27 is Mo5, positioned at a distance of  $3.078(5) \text{ \AA}$ . Atom O14 links Mo1 and Mo3. All the O atoms in the  $\{\text{Mo}_3\text{O}_{11}\}$  group (except for O27 and O14) also coordinate to Gd atoms. Each of the atoms Mo4, Mo5, Mo6 and Mo7 forms an  $\text{MoO}_4$  tetrahedron which is separated from other molybdate groups. As shown in Fig. 2, these discrete tetrahedra form double layers in the lattice. Each of the atoms Gd1,



**Figure 3** ORTEPII (Johnson, 1976) drawing of (a)  $\{\text{Mo}_3\text{O}_{11}\}$ , (b)  $\{\text{Gd}_2\text{O}_{12}\}$ , and (c)  $\{\text{Gd}_2\text{O}_{13}\}$  groups. The ellipsoids are drawn at the 50% probability level. The dashed lines in (a) denote the basal plane of the  $\text{Mo}_1\text{O}_5$  trigonal bipyramid. In (b) and (c), the squares in the  $\text{GdO}_8$  square antiprisms and triangles in the  $\text{GdO}_7$  monocapped trigonal prism are drawn with red and blue dashed lines, respectively. Symmetry codes are described in the footnote of Table 1.

Gd2 and Gd3 is octacoordinated by O atoms, with approximate square antiprisms (Figs. 3b and c). On the other hand, atom Gd4 achieves sevenfold coordination by O atoms, with a distorted monocapped trigonal prism (Fig. 3b). The  $\text{Gd}_1\text{O}_8$  and  $\text{Gd}_4\text{O}_7$  polyhedra share the plane defined by atoms O11, O25 and O26, to form a  $\{\text{Gd}_2\text{O}_{12}\}$  group. Similarly, two square antiprisms of  $\text{Gd}_2\text{O}_8$  and  $\text{Gd}_3\text{O}_8$  share the plane defined by atoms O2, O3 and O18, giving rise to a  $\{\text{Gd}_2\text{O}_{13}\}$  group. This face-sharing dimerization of the  $\text{GdO}_n$  polyhedra induces short  $\text{Gd}_1 \cdots \text{Gd}_4$  separations [ $\text{Gd}_1 \cdots \text{Gd}_4$   $3.6404(4) \text{ \AA}$  and  $\text{Gd}_2 \cdots \text{Gd}_3$   $3.6345(4) \text{ \AA}$ ], which are comparable to the  $\text{Gd} \cdots \text{Gd}$  distances ( $3.853\text{--}3.599 \text{ \AA}$ ) in  $\text{Gd}_2\text{O}_3$  (Bartos *et al.*, 1993). Similar  $\{\text{R}_2\text{O}_{n'}\}$  ( $n' = 12$  or  $13$ ) dimers have been observed for other rare-earth molybdates:  $\text{R}_6\text{Mo}_{10}\text{O}_{39}$ , where  $\text{R} = \text{Ce}$  (Gatehouse & Same, 1978) and  $\text{Eu}$  (Naruke & Yamase, 2001), and  $\text{R}_2\text{Mo}_4\text{O}_{15}$ , where  $\text{R} = \text{La}$  (Dubois *et al.*, 2001) and  $\text{Ce}$  (Fallon & Gatehouse, 1982).

In conclusion,  $\text{Gd}_4\text{Mo}_7\text{O}_{27}$  can be described as a layer compound, being isostructural with  $\text{Eu}_4\text{Mo}_7\text{O}_{27}$  (Naruke & Yamase, 2001). Comparison of geometrical parameters between  $\text{Gd}_4\text{Mo}_7\text{O}_{27}$  and  $\text{Eu}_4\text{Mo}_7\text{O}_{27}$  exhibited no remarkable difference, because of the similar ionic radii, *viz.*  $\text{Eu}^{3+}$  ( $1.066 \text{ \AA}$ ) and  $\text{Gd}^{3+}$  ( $1.053 \text{ \AA}$ ) (Shannon, 1976). We should note another layer compound,  $\text{La}_2\text{MoO}_6$  (Xue *et al.*, 1995), where  $\text{LaO}_8$  polyhedra are connected to form a  $\{\text{La}_2\text{O}_2\}_\infty$  sheet sandwiched between  $\{\text{MoO}_4\}$ -containing layers.

## Experimental

A precursor  $[\text{Gd}_2(\text{H}_2\text{O})_{12}\text{Mo}_8\text{O}_{27}] \cdot 8\text{H}_2\text{O}$  was synthesized using the same preparation procedure as for  $[\text{Eu}_2(\text{H}_2\text{O})_{12}\text{Mo}_8\text{O}_{27}] \cdot 6\text{H}_2\text{O}$  (Yamase & Naruke, 1991) by replacement of  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  with  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . Thermal decomposition of the precursor was carried out in a furnace at  $1023 \text{ K}$  for 2 h. Details of the decomposition condition are described in our earlier paper (Naruke &

Yamase, 2001). Crystals of Gd<sub>4</sub>Mo<sub>7</sub>O<sub>27</sub>, occurring in a colored glassy Gd<sub>2</sub>O<sub>3</sub>–MoO<sub>3</sub> phase, were carefully collected with a needle.

Crystal data

Gd<sub>4</sub>Mo<sub>7</sub>O<sub>27</sub>  $D_x = 4.908 \text{ Mg m}^{-3}$   
 $M_r = 1732.56$  Mo  $K\alpha$  radiation  
 Monoclinic,  $C2/c$  Cell parameters from 15047 reflections  
 $a = 23.034 (2) \text{ \AA}$   $\theta = 2.8\text{--}30.0^\circ$   
 $b = 14.677 (2) \text{ \AA}$   $\mu = 14.88 \text{ mm}^{-1}$   
 $c = 14.348 (1) \text{ \AA}$   $T = 296.2 \text{ K}$   
 $\beta = 104.816 (3)^\circ$  Block, colorless  
 $V = 4689.4 (8) \text{ \AA}^3$   $0.15 \times 0.11 \times 0.11 \text{ mm}$   
 $Z = 8$

Data collection

Rigaku RAXIS-RAPID Imaging 6779 independent reflections  
 Plate diffractometer 5944 reflections with  $F^2 > 2\sigma(F^2)$   
 $\omega$  scans  $R_{\text{int}} = 0.048$   
 Absorption correction: numerical (Higashi, 1999)  $\theta_{\text{max}} = 30.0^\circ$   
 $T_{\text{min}} = 0.101, T_{\text{max}} = 0.197$   $h = 0 \rightarrow 32$   
 24606 measured reflections  $k = 0 \rightarrow 20$   
 $l = -20 \rightarrow 19$

Refinement

Refinement on  $F^2$   $(\Delta/\sigma)_{\text{max}} = 0.002$   
 $R[F^2 > 2\sigma(F^2)] = 0.039$   $\Delta\rho_{\text{max}} = 4.62 \text{ e \AA}^{-3}$   
 $wR(F^2) = 0.108$   $\Delta\rho_{\text{min}} = -3.57 \text{ e \AA}^{-3}$   
 $S = 1.38$  Extinction correction: Zachariasen  
 6778 reflections (1967) type 2 Gaussian isotropic  
 344 parameters Extinction coefficient: 0.00217 (4)  
 $w = 1/[\sigma^2(F_o^2) + 0.05P^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

Table 1 Selected interatomic distances (Å).

Gd(1)—O(9)	2.346 (4)	Gd(4)—O(11 <sup>i</sup> )	2.428 (5)
Gd(1)—O(26)	2.355 (4)	Mo(1)—O(24)	1.729 (4)
Gd(1)—O(6)	2.368 (4)	Mo(1)—O(23 <sup>ii</sup> )	1.732 (4)
Gd(1)—O(10)	2.371 (5)	Mo(1)—O(25)	1.777 (4)
Gd(1)—O(12)	2.379 (4)	Mo(1)—O(14)	1.913 (5)
Gd(1)—O(13)	2.396 (5)	Mo(1)—O(6)	2.362 (4)
Gd(1)—O(11)	2.452 (4)	Mo(2)—O(27)	1.697 (4)
Gd(1)—O(25)	2.659 (4)	Mo(2)—O(15 <sup>iii</sup> )	1.738 (4)
Gd(2)—O(5)	2.309 (4)	Mo(2)—O(18 <sup>iii</sup> )	1.811 (4)
Gd(2)—O(15)	2.310 (4)	Mo(2)—O(6)	1.823 (4)
Gd(2)—O(17)	2.383 (5)	Mo(3)—O(16 <sup>iii</sup> )	1.732 (4)
Gd(2)—O(4)	2.386 (5)	Mo(3)—O(22 <sup>iv</sup> )	1.743 (5)
Gd(2)—O(3)	2.388 (4)	Mo(3)—O(12 <sup>v</sup> )	1.745 (4)
Gd(2)—O(16)	2.441 (4)	Mo(3)—O(14)	1.845 (5)
Gd(2)—O(18)	2.444 (4)	Mo(4)—O(1 <sup>vi</sup> )	1.742 (5)
Gd(2)—O(2)	2.464 (5)	Mo(4)—O(19 <sup>vii</sup> )	1.743 (4)
Gd(3)—O(20)	2.342 (4)	Mo(4)—O(7 <sup>viii</sup> )	1.769 (4)
Gd(3)—O(22)	2.377 (5)	Mo(4)—O(3)	1.808 (4)
Gd(3)—O(1)	2.378 (5)	Mo(5)—O(5 <sup>i</sup> )	1.734 (4)
Gd(3)—O(3)	2.382 (4)	Mo(5)—O(13)	1.734 (5)
Gd(3)—O(19)	2.385 (4)	Mo(5)—O(10 <sup>ix</sup> )	1.745 (5)
Gd(3)—O(18)	2.417 (4)	Mo(5)—O(26 <sup>x</sup> )	1.832 (4)
Gd(3)—O(2)	2.431 (4)	Mo(6)—O(17 <sup>i</sup> )	1.743 (5)
Gd(3)—O(23)	2.481 (4)	Mo(6)—O(4 <sup>iii</sup> )	1.743 (5)
Gd(4)—O(7)	2.268 (4)	Mo(6)—O(20 <sup>iv</sup> )	1.755 (5)
Gd(4)—O(8)	2.320 (6)	Mo(6)—O(11)	1.810 (4)
Gd(4)—O(26 <sup>i</sup> )	2.329 (4)	Mo(7)—O(9 <sup>ii</sup> )	1.741 (5)
Gd(4)—O(21)	2.343 (5)	Mo(7)—O(8 <sup>iii</sup> )	1.747 (6)
Gd(4)—O(24)	2.384 (4)	Mo(7)—O(21)	1.750 (5)
Gd(4)—O(25 <sup>i</sup> )	2.409 (4)	Mo(7)—O(2)	1.792 (5)

Symmetry codes: (i)  $\frac{1}{2} - x, \frac{3}{2} - y, -z$ ; (ii)  $1 - x, y, \frac{1}{2} - z$ ; (iii)  $x - \frac{1}{2}, \frac{3}{2} - y, \frac{1}{2} + z$ ; (iv)  $x - \frac{1}{2}, y - \frac{1}{2}, z$ ; (v)  $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (vi)  $x, 2 - y, z - \frac{1}{2}$ ; (vii)  $1 - x, 2 - y, -z$ ; (viii)  $-x, y, \frac{1}{2} - z$ ; (ix)  $-x, 2 - y, -z$ ; (x)  $\frac{1}{2} + x, y - \frac{1}{2}, z$ .

Difference Fourier peaks with  $\Delta\rho_{\text{max}} = 4.62$  and  $\Delta\rho_{\text{min}} = -3.57 \text{ e \AA}^{-3}$  are observed  $0.743$  and  $0.058 \text{ \AA}$ , respectively, from atom Gd3.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2000); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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References

Aizu, K., Kumada, A., Yumoto, H. & Ashida, S. (1969). *J. Phys. Soc. Jpn.* **27**, 511.  
 Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.  
 Bartos, A., Lieb, K. P., Uhrmacher, M. & Wiarda, D. (1993). *Acta Cryst.* **B49**, 165–169.  
 Borchardt, H. J. & Bierstedt, P. E. (1966). *Appl. Phys. Lett.* **8**, 50–52.  
 Brixner, L. H., Barkley, J. R. & Jeitschko, W. (1979). *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 3, edited by K. A. Gschneidner Jr and L. Eyring, pp. 609–654. Amsterdam: North-Holland Publishing.  
 Evans, J. S. O., Marry, T. A. & Sleight, A. W. (1997). *J. Solid State Chem.* **133**, 580–583.  
 Dubois, F., Goutenoire, F., Lalignat, Y., Suard, E. & Lacorre, P. (2001). *J. Solid State Chem.* **159**, 228–233.  
 Fallon, G. D. & Gatehouse, B. M. (1982). *J. Solid State Chem.* **44**, 156–161.  
 Gatehouse, B. M. & Same, R. (1978). *J. Solid State Chem.* **25**, 115–120.  
 Goutenoire, F., Isnard, O., Retoux, R. & Lacorre, P. (2000). *Chem. Mater.* **12**, 2575–2580.  
 Higashi, T. (1999). *SHAPE and NUMABS*. Rigaku Corporation, Tokyo, Japan.  
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
 Lacorre, P., Goutenoire, F., Bohnke, O., Retoux, R. & Lalignat, Y. (2000). *Nature (London)*, **404**, 856–858.  
 Megumi, K., Yumoto, H., Ashida, S., Akiyama, S. & Furuhashi, Y. (1974). *Mater. Res. Bull.* **9**, 391–400.  
 Molecular Structure Corporation (2000). *TEXSAN*. Version 1.11. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.  
 Naruke, H. & Yamase, T. (2001). *J. Solid State Chem.* **161**, 85–92.  
 Ponomarev, B. K., Ivanov, S. A., Popov, Yu. F., Negrii, V. D. & Red'kin, B. S. (1994). *Ferroelectrics*, **161**, 43–48.  
 Ponomarev, B. K., Popov, Yu. F., Shmyt'ko, I. M., Bagautdinov, B. Sh. & Red'kin, B. S. (1995). *Ferroelectrics*, **169**, 97–103.  
 Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.  
 Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.  
 Wiegelmann, H., Ponomarev, B. K., Van Tol, J., Jansen, A. G. M., Wyder, P. & Red'kin, B. S. (1996). *Ferroelectrics*, **183**, 195–204.  
 Xue, J. S., Antonio, R. & Soderholm, L. (1995). *Chem. Mater.* **7**, 333–340.  
 Yamase, T. & Naruke, H. (1991). *J. Chem. Soc. Dalton Trans.* pp. 285–292.  
 Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.