

## LETTER TO THE EDITOR

# Phase Transition and Negative Thermal Expansion in Tetragonal NbOPO<sub>4</sub>

T. G. Amos, A. Yokochi, and A. W. Sleight<sup>1</sup>

*Department of Chemistry, Oregon State University, Corvallis, Oregon 97331-4003*

Communicated by J. M. Honig, June 22, 1998; accepted September 2, 1998

---

The structure of tetragonal NbOPO<sub>4</sub> has been studied from room temperature to 500°C by X-ray powder diffraction and to 327°C by neutron powder diffraction. Rietveld refinements were conducted on neutron data collected at 25, 100, 175, 200, 225, 275, and 327°C. A phase transition was found at about 200°C. The space group is *P4/n* below this transition and *P4/nmm* above this transition. The *c* cell edge shows positive thermal expansion over the entire temperature range. The *a* and *b* cell edges show positive thermal expansion below the transition and negative thermal expansion above the transition. The negative thermal expansion is attributed to rocking motions of the corner-shared NbO<sub>6</sub> octahedra and PO<sub>4</sub> tetrahedra. © 1998 Academic Press

---

### INTRODUCTION

Three different polymorphs of NbOPO<sub>4</sub> have been reported (1–4). The structures of monoclinic and orthorhombic NbOPO<sub>4</sub> are based on the same connectivity of NbO<sub>6</sub> octahedra and PO<sub>4</sub> tetrahedra. A different connectivity of NbO<sub>6</sub> octahedra and PO<sub>4</sub> tetrahedra is found for tetragonal NbOPO<sub>4</sub>. Two structure refinements of tetragonal NbOPO<sub>4</sub> have appeared. Both are based on room temperature single crystal X-ray diffraction data using group *P4/n* (1, 4).

We have been searching for negative thermal expansion in network structures where polyhedra share corners only. If the polyhedra are exclusively tetrahedra or octahedra, the network formula must be MO<sub>2</sub> and AO<sub>3</sub>, respectively. Negative thermal expansion has now been established for two MO<sub>2</sub> networks based on corner-sharing tetrahedra (5, 6). Mixing tetrahedra and octahedra which share corners leads to formulae such as AM<sub>2</sub>O<sub>7</sub>, A<sub>2</sub>M<sub>3</sub>O<sub>12</sub>, and AMO<sub>5</sub>, where *A* and *M* are the octahedral and tetrahedral cations, respectively. We have reported previously on negative

thermal expansion in the AM<sub>2</sub>O<sub>7</sub> and A<sub>2</sub>M<sub>3</sub>O<sub>12</sub> networks (7–9). We now report on the first example of negative thermal expansion behavior in a AMO<sub>5</sub> or AOMO<sub>4</sub> network.

### EXPERIMENTAL

A fivefold excess of H<sub>3</sub>PO<sub>4</sub> (83%) was placed with Nb<sub>2</sub>O<sub>5</sub> in a platinum crucible. This was heated at 900°C for 12 h. After cooling to room temperature, the product was washed with boiling water and then heated at 1090°C for 8 h.

X-ray powder diffraction data were obtained with an Inel diffractometer using CuKα<sub>1</sub> radiation. The sample was mounted in a capillary, and diffraction patterns were obtained over the temperature range from 25 to 500°C.

Neutron powder diffraction data were obtained over the temperature range from 25 to 327°C at the NIST reactor using the BT-1 high-resolution diffractometer at a wavelength of 1.5401 Å. Refinements of the neutron powder diffraction data were performed using GSAS software (10).

### RESULTS

The X-ray powder diffraction data showed positive thermal expansion for both the *a* and *c* unit-cell edges of tetragonal NbOPO<sub>4</sub> from room temperature to about 200°C. At higher temperatures, the *c* cell edge continued to increase but the *a* cell edge decreased (Fig. 1). This suggested a phase transition close to 200°C. The best candidate for the high temperature structure of tetragonal NbOPO<sub>4</sub> appeared to be space group *P4/nmm*. The relationship between the structures of NbOPO<sub>4</sub> in space groups *P4/n* and *P4/nmm* is shown in Fig. 2. The systematic absences for the two space groups are the same. Both space groups have P in a 1/4, 3/4, 1/2 position, and both Nb and one O in a 1/4, 1/4, *z* position. However, the oxygen atoms of the PO<sub>4</sub> group are in an

<sup>1</sup>To whom correspondence should be addressed.

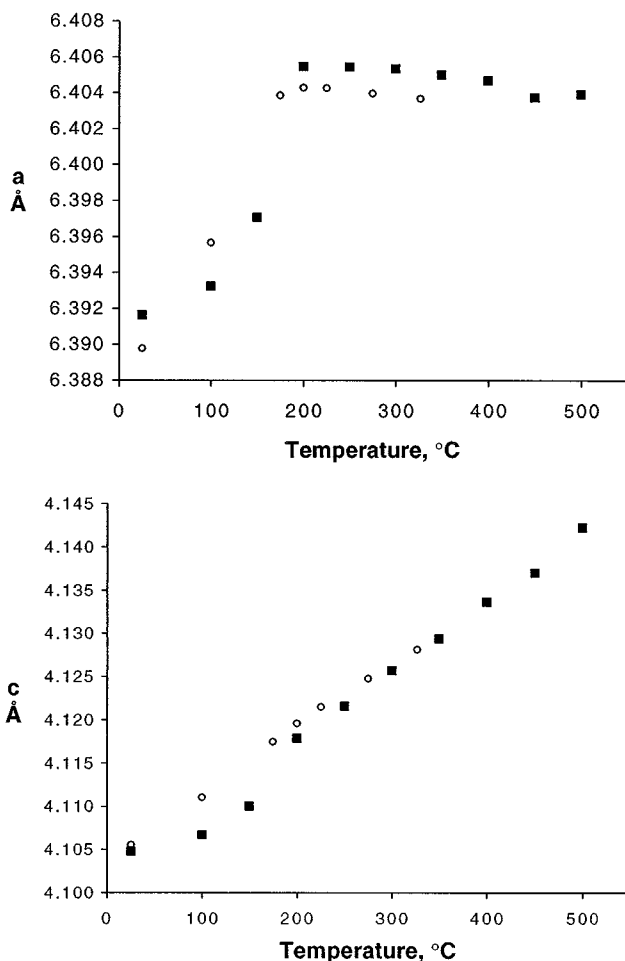


FIG. 1. Cell edges of tetragonal NbOPO<sub>4</sub> vs temperature. Closed squares are X-ray data, and open circles are neutron data.

xyz position in *P4/n*, but in a 3/4, y, z position in *P4/nmmm*. Because X-ray diffraction data lack sensitivity to a small departure of the x parameter from 0.75, neutron diffraction data were used to distinguish between space groups *P4/n* and *P4/nmmm*.

Refinements of the room-temperature neutron diffraction data in space group *P4/n* gave final parameters in good

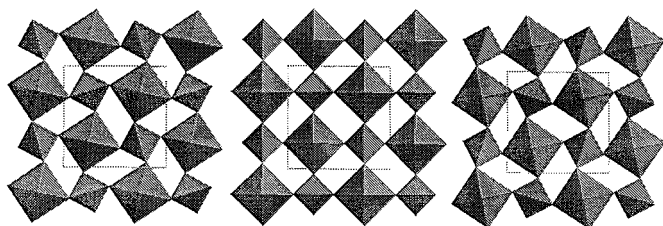


FIG. 2. Structure of tetragonal NbOPO<sub>4</sub> as NbO<sub>6</sub> octahedra and PO<sub>4</sub> tetrahedra viewed down the c axis. Central structure is in space group *P4/nmmm*. The tilted versions on either side are in space group *P4/n*.

TABLE 1  
Agreement Factors

Temperature (°C)	$\chi^2$	$R_p$	$wR_p$
25	1.514	0.0665	0.0885
100	1.452	0.0658	0.0859
175	1.428	0.0681	0.0880
200	1.344	0.0646	0.0844
225	1.378	0.0652	0.0855
275	1.203	0.0725	0.0917
327	1.384	0.0657	0.0845

agreement with results in previous studies (1, 4). Attempts to refine these data in space group *P4/nmm* were not successful. Likewise, at 100 and 175°C, space group *P4/n* gave significantly better refinements than *P4/nmm*. However, for data collected at 200, 225, 275, and 327°C, refinement of the additional parameter in space group *P4/n* did not give any improvement in fit to the observed data. Therefore, only refinements in space group *P4/nmm* are presented for data taken at 200°C and higher. Figure 3 shows the agreement between observed and calculated intensities for the neutron diffraction data obtained at room temperature and 327°C. Table 1 gives the agreement factors for each of the refinements. Table 2 gives the refined positional parameters at each temperature, and some bond lengths and angles are given in Tables 3 and 4. It is the x parameter of O2 going to 0.75 that causes the space group to change from *P4/n* to *P4/nmm*. A plot of this parameter vs temperature is shown in Fig. 4. Note also that the P–O<sub>2</sub>–Nb angle (Table 4) increases significantly from 25 to 200°C and remains essentially constant at higher temperatures. Thermal ellipsoids are shown in Fig. 5 for a fragment of the NbOPO<sub>4</sub> structure refined at 327°C. The magnitudes of the thermal motions are plotted against temperature in Fig. 6. As can be seen in Fig. 5, Nb is displaced out of the plane of the four O2 atoms by about 0.28 Å toward the O1 atom to which it forms the shorter bond.

TABLE 2  
Atomic Positions

Temperature (°C)	z (O1)	x (O2)	y (O2)	z (O2)	z (Nb)
25	0.2077(4)	0.7731(2)	0.4446(1)	0.2861(2)	0.7824(3)
100	0.2058(4)	0.7694(2)	0.4443(1)	0.2866(2)	0.7818(3)
175	0.2058(4)	0.7582(5)	0.4445(1)	0.2866(2)	0.7816(3)
200	0.2048(4)	0.75	0.4445(1)	0.2869(2)	0.7815(3)
225	0.2049(4)	0.75	0.4444(1)	0.2875(2)	0.7813(3)
275	0.2036(5)	0.75	0.4446(1)	0.2877(3)	0.7819(4)
327	0.2046(5)	0.75	0.4443(1)	0.2876(2)	0.7815(4)

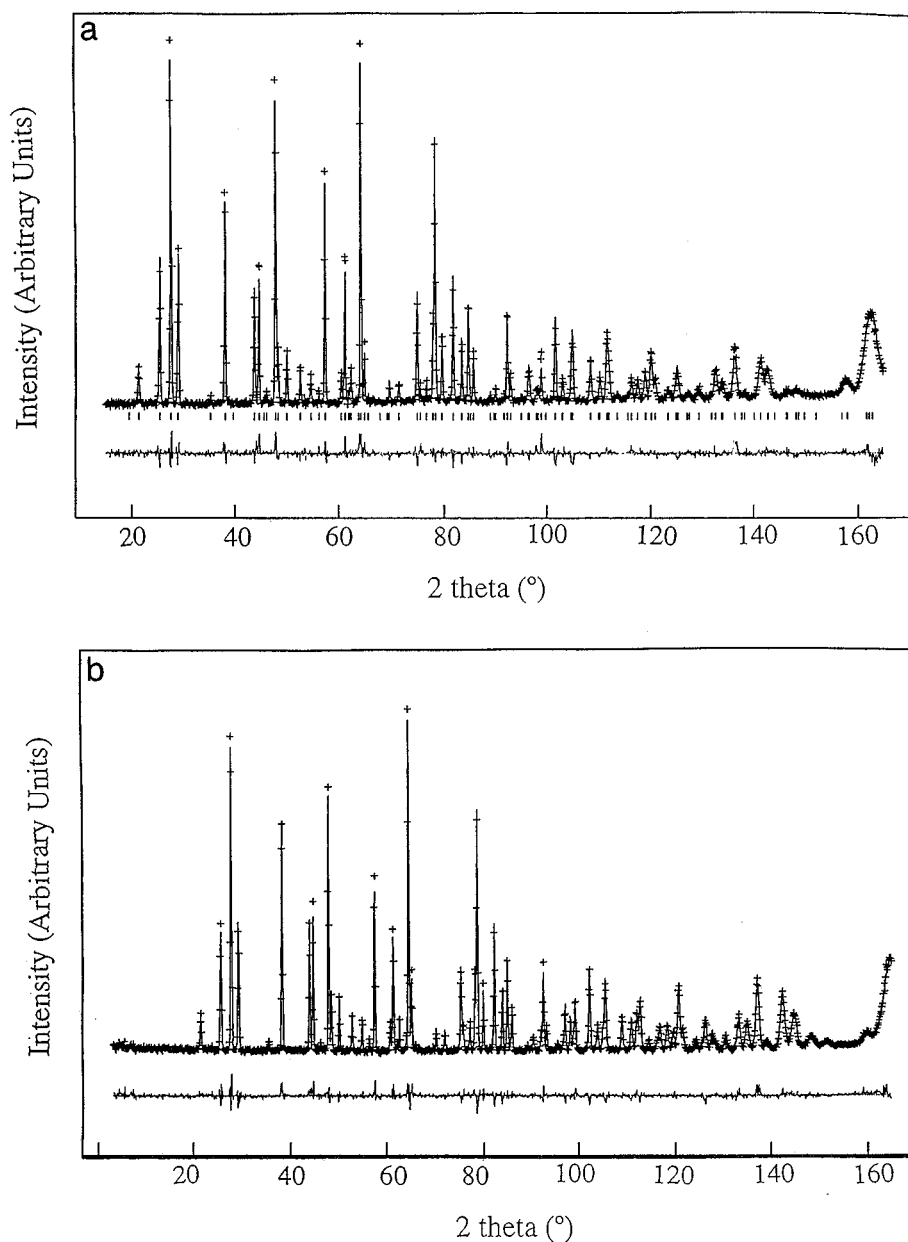


FIG. 3. Observed, calculated, and difference plots for Rietveld refinements at 25°C (a) and 327°C (b).

TABLE 3  
Bond Lengths (Å)

Temperature (°C)	P-O2	Nb-O2	Nb-O1'	Nb-O1
25	1.5275(8)	1.9788(8)	1.746(2)	2.360(2)
100	1.5263(8)	1.9789(8)	1.743(2)	2.368(2)
175	1.5252(9)	1.9772(9)	1.747(2)	2.371(2)
200	1.524(1)	1.977(1)	1.744(2)	2.376(2)
225	1.522(1)	1.977(1)	1.746(2)	2.376(2)
275	1.523(1)	1.976(1)	1.740(2)	2.385(2)
327	1.522(1)	1.978(1)	1.747(2)	2.382(2)

TABLE 4  
Bond Angles (Å)

Temperature (°C)	O2-P-O2'	O2-P-O2	O2-Nb-O2	P-O2-Nb
25	109.24(3)	109.93(8)	163.58(9)	151.30(7)
100	109.28(3)	109.85(6)	163.64(9)	151.78(7)
175	109.39(3)	109.64(7)	163.68(10)	152.74(8)
200	109.38(3)	109.65(6)	163.60(9)	153.03(7)
225	109.33(3)	109.75(6)	163.52(9)	153.11(7)
275	109.30(3)	109.82(6)	163.31(9)	153.26(7)
327	109.39(3)	109.64(6)	163.43(9)	153.11(7)

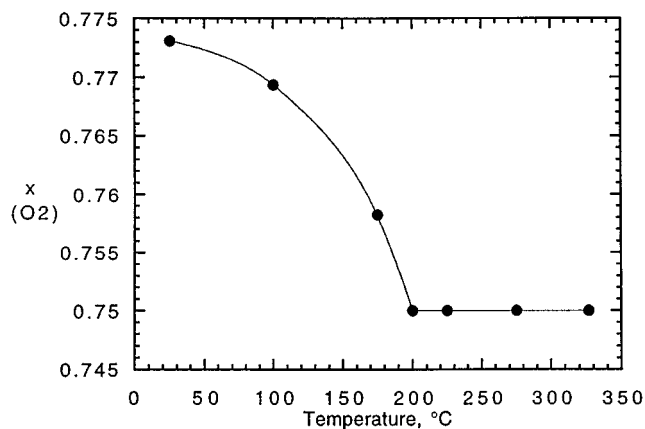


FIG. 4. The  $x$  parameter for O2 vs temperature.

### DISCUSSION

Rocking corner-sharing polyhedra back and forth can lead to negative thermal expansion. This is shown for tetragonal  $\text{NbOPO}_4$  in Fig. 2. The central structure in Fig. 2 is  $\text{NbOPO}_4$  in space group  $P4/nmm$ . Rocking the polyhedra in either direction destroys mirror planes reducing the space group symmetry to  $P4/n$  and causes a contraction of the structure without any change in Nb–O or P–O distances. This rocking motion causes a decrease in the  $a$  and  $b$  cell edges, but has no impact on the  $c$  cell edge. As temperature increases above  $200^\circ\text{C}$ , the rocking motion increases. Thus, the structure contracts in two dimensions. Below  $200^\circ\text{C}$ , the structure becomes locked into space group  $P4/n$  and normal positive thermal expansion occurs. The length of the  $c$  cell edge is exactly the sum of the two Nb–O bonds along this axis. The  $c$  cell edge increases by just over  $0.02 \text{ \AA}$  as the temperature increases from  $25$  to  $327^\circ\text{C}$ . The refined  $z$  parameters of Nb and O(1) indicate that the

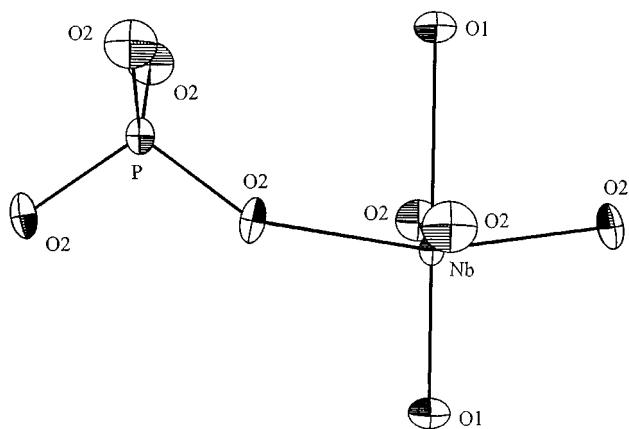


FIG. 5. The asymmetric unit of the tetragonal  $\text{NbOPO}_4$  structure at  $327^\circ\text{C}$  viewed down the  $a$  axis.

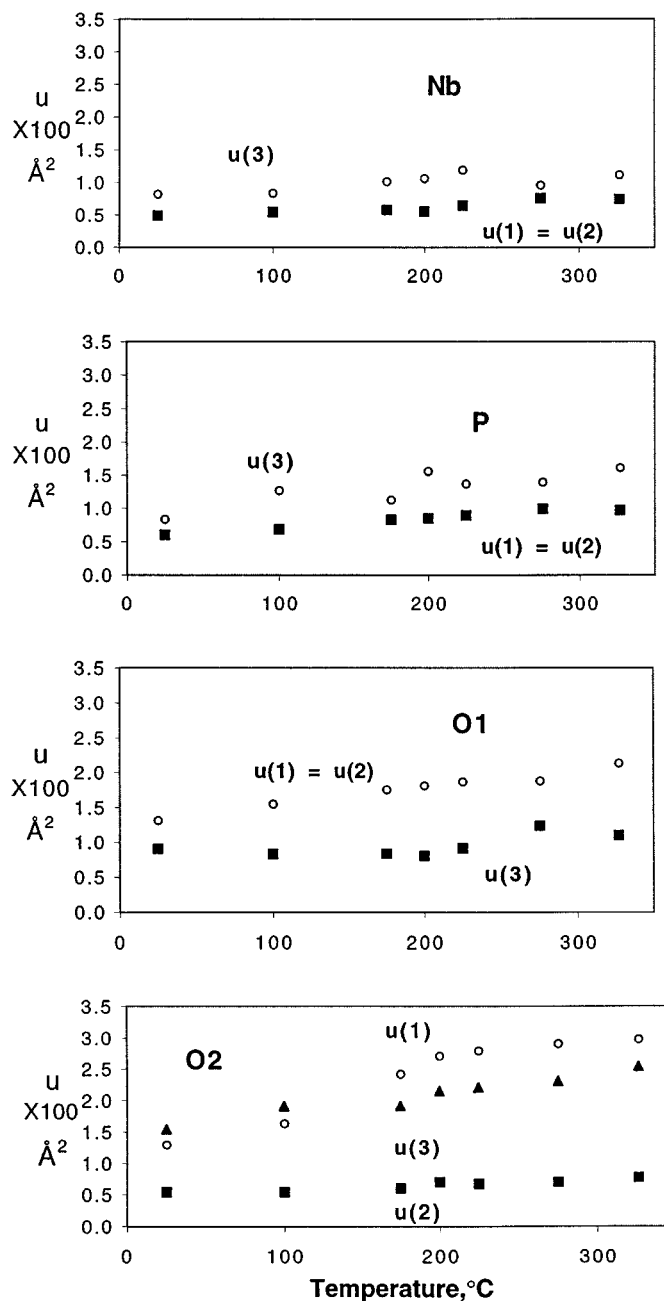


FIG. 6. The  $u$  values ( $\times 100$ ) for the major axes of the thermal ellipsoids.

short Nb–O distance does not change significantly as temperature changes over this temperature range. It is the long Nb–O distance that becomes even longer with increasing temperature. This is consistent with the fact that weaker bonds show stronger thermal expansion than strong bonds.

The alternating short and long Nb–O bonds along the  $c$  axis can be viewed as a ferroelectric type distortion. However, adjacent Nb–O chains have opposite polarities,

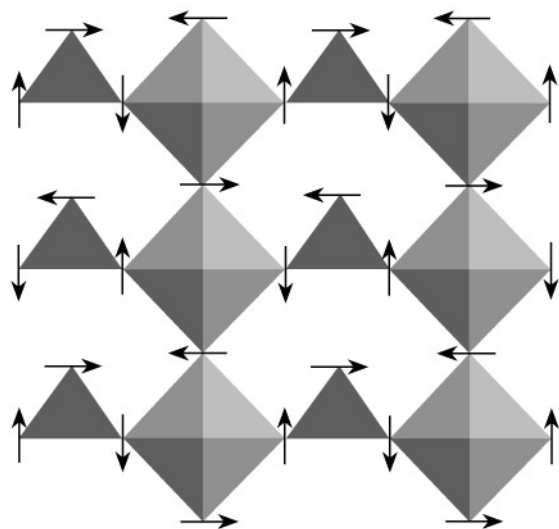


FIG. 7. The NbOPO<sub>4</sub> structure viewed down the *a* axis. Arrows indicated cooperative tilting which could also occur in the opposite direction.

so there is no net moment. The tetragonal NbOPO<sub>4</sub> structure can be formed with perfectly regular tetrahedra and octahedra, but that does not increase lattice symmetry above *P4/nmm*. For all Nb–O distances equal to 1.939 Å and P–O distances of 1.5223 Å, the unit cell edges are 6.364 Å and 3.878 Å in space group *P4/nmm*. These perfectly regular polyhedra can be rocked with no change in shape. Tilting these regular polyhedra in space group *P4/n* by increasing *x* of O2 from 0.75 to 0.85 results in a decrease of *a* to 5.885 Å with no change in the *c* cell edge.

The thermal expansion of the *c* cell edge over the entire temperature range studied does not mean that there are no polyhedra rocking motions which tend to cause contraction of this cell edge. The thermal ellipsoids (Fig. 4) indicate rocking of polyhedra as shown in Fig. 7 in addition to that depicted in Fig. 2. Such rocking motion will tend to cause thermal contraction of all cell edges. However, the

lengthening of the long Nb–O bond with increasing temperature dominates behavior along the *c* axis.

Thermal expansion coefficients ( $\Delta l/l$  per degree or  $\alpha$ ) calculated from the data in Fig. 1 are  $2.0 \times 10^{-5}/^\circ\text{C}$  for *c*,  $1.2 \times 10^{-5}/^\circ\text{C}$  for *a* up to 200°C, and  $-1.0 \times 10^{-6}/^\circ\text{C}$  for *a* above 200°C. This gives a bulk linear coefficient of  $6 \times 10^{-6}/^\circ\text{C}$  above 200°C. Thus, although two-dimensional negative thermal expansion behavior has been demonstrated for tetragonal NbOPO<sub>4</sub>, it is a small effect relative to the values found for ZrW<sub>2</sub>O<sub>8</sub> ( $\alpha = -8.7 \times 10^{-6}/^\circ\text{C}$ ), faujasite SiO<sub>2</sub> ( $\alpha = -4.2 \times 10^{-6}/^\circ\text{C}$ ), AlPO<sub>4</sub>-17 ( $\alpha = -11.7 \times 10^{-6}/^\circ\text{C}$ ), and several members of the Sc<sub>2</sub>W<sub>3</sub>O<sub>12</sub> family (5, 6, 8, 9, 11). Furthermore, the substantial thermal expansion in one dimension gives an overall bulk thermal expansion for NbOPO<sub>4</sub> which is normal for an oxide.

#### ACKNOWLEDGMENTS

This work was supported through NSF Grant DMA-9308530. Neutron diffraction data were obtained at the NIST Center for Neutron Research.

#### REFERENCES

1. J. M. Longo and P. Kierkegaard, *Acta Chem. Scand.* **20**, 72 (1966).
2. H. Chahboun, D. Groult, M. Hervieu, and B. Raveau, *J. Solid State Chem.* **65**, 331 (1986).
3. D. L. Serra and S.-J. Hwu, *Acta Crystallogr. Sect. C* **48**, 733 (1992).
4. U. Kaiser, G. Schmidt, R. Glaum, and R. Gruehn, *Z. Anorg. Allg. Chem.* **607**, 113 (1992).
5. M. P. Attfield and A. W. Sleight, *Chem. Comm.*, 601 (1998).
6. M. P. Attfield and A. W. Sleight, *Chem. Matter.* **10**, 2013 (1998).
7. V. Korthuis, N. Khosrovani, A. W. Sleight, N. Roberts, R. Dupree, and W. W. Wareen, Jr., *Chem. Mater.* **7**, 412 (1995).
8. J. S. O. Evans, T. A. Mary, and A. W. Sleight, *J. Solid State Chem.* **133**, 580 (1997).
9. J. S. O. Evans, T. A. Mary, and A. W. Sleight, *J. Solid State Chem.* **137**, 148 (1998).
10. A. C. Larson and R. B. Von Dreele, LANSCE, Los Alamos National Lab, Los Alamos, NM, 1994.
11. T. A. Mary, J. S. O. Evans, A. W. Sleight, and T. Vogt, *Science* **272**, 90 (1996).