

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j.$$

	x	y	z	U_{eq}
Cu1	0	0	0	0.026 (1)
Fe1	0.3348 (1)	0.2430 (1)	0.1195 (1)	0.021 (1)
P2	0.3565 (1)	0.2781 (2)	-0.0947 (1)	0.021 (1)
P1	-0.0515 (1)	0.2541 (2)	-0.1686 (1)	0.021 (1)
O21	0.2440 (4)	0.2024 (6)	-0.0130 (3)	0.025 (1)
O11	0.1895 (4)	0.2815 (6)	-0.1708 (2)	0.026 (1)
O12	-0.0814 (4)	-0.0036 (5)	-0.1191 (2)	0.024 (1)
O13	-0.1324 (4)	0.4751 (5)	-0.1180 (2)	0.026 (1)
O14	-0.1287 (4)	0.2281 (6)	-0.2587 (2)	0.027 (1)
O22	0.5118 (4)	0.0828 (6)	-0.1171 (2)	0.028 (1)
O23	0.4357 (4)	0.5519 (6)	-0.0876 (2)	0.026 (1)

Table 2. Selected geometric parameters (\AA)

Cu1—O21	1.934 (3)	Fe1—O23 ^a	1.926 (3)
Cu1—O21 ⁱ	1.934 (3)	P2—O21	1.550 (3)
Cu1—O12	1.920 (3)	P2—O22	1.487 (3)
Cu1—O12 ⁱ	1.920 (3)	P1—O11	1.596 (3)
Fe1—O21	2.146 (3)	P1—O13	1.498 (3)
Fe1—O13 ⁱⁱ	1.973 (3)	P2—O11	1.592 (3)
Fe1—O22 ⁱⁱⁱ	1.964 (3)	P2—O23	1.510 (3)
Fe1—O12 ⁱ	2.077 (3)	P1—O12	1.555 (3)
Fe1—O14 ^{iv}	1.916 (3)	P1—O14	1.487 (3)

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

A variable scan rate was used, with a scan width of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$. Refinement was completed using full-matrix least-squares methods.

Data collection: XSCANS (Siemens, 1991a). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXS86. Molecular graphics: XP (Siemens, 1990).

The authors express their thanks to the National Science Foundation for assistance in the form of a grant to permit collaborative investigation and to the Moroccan–American Commission for a Fulbright grant to EMH.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1137). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Benhamada, L., Grandin, A., Borel, M., Leclaire, A. & Raveau, B. (1991). *Acta Cryst.* **C47**, 2437–2438.
- Boutfessi, A., Boukhari, A. & Holt, E. M. (1995). *Acta Cryst.* **C51**, 346–348.
- Ijjaali, M., Venturini, G., Gerardin, R., Malaman, B. & Gleitzer, C. (1991). *Eur. J. Solid State Inorg. Chem.* **28**, 983–998.
- Ijjaali, M., Venturini, G., Malaman, B. & Gleitzer, C. (1990). *C. R. Acad. Sci. Paris Sér. II*, **310**, 1419–1423.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Siemens (1990). *XP. Interactive Molecular Graphics Program*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1991a). *XSCANS User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1991b). *XEMP. Empirical Absorption Correction Program*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Ust'yanitsev, V. M. & Tretnikova, M. G. (1974). *Izv. Akad. Nauk SSSR Neorg. Mater.* **10**, 676–678.

Wang, S. & Hwu, S.-J. (1991). *J. Solid State Chem.* **90**, 31–41.

Wanklyn, B. M., Wondre, F. R., Davison, W. & Salmon, R. (1983). *J. Mater. Sci. Lett.* **2**, 511–515.

Acta Cryst. (1996). **C52**, 1599–1601

Refinement of $\text{La}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_{7-x}$ from a Twinned Crystal

MICHAEL HJORTH

Department of Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark. E-mail: michael@skemi.klb.dtu.dk

(Received 23 October 1995; accepted 6 February 1995)

Abstract

The structure of the title compound (barium copper lanthanum oxide, $\text{Ba}_{1.50}\text{Cu}_3\text{La}_{1.50}\text{O}_{6.66}$) has been refined from a twinned crystal using single-crystal methods. The results of the present investigation show lower standard deviations than the results of earlier powder diffraction refinements, but the studies are otherwise in agreement.

Comment

A common problem in the study of metal oxide structures is the frequent occurrence of twinning. Thus, many recent metal oxide structure determinations are based on powder diffraction data. The present study was undertaken in order to compare the results of the earlier investigations (Izumi, Asano, Ishigaki, Takayama-Muromachi, Matsui & Uchida, 1987; Torardi, McCarron, Subramanian, Sleight & Cox, 1987) with the result from a refinement based on single-crystal methods using a twinned crystal.

The present investigation shows generally lower standard deviations for all parameters, especially for displacement parameters, than the earlier studies. Initially, the refinement was performed with all atoms anisotropic. However, the ellipsoid of O3 became unreasonably large, so it was decided to refine O3 as disordered over two (isotropic) positions. The anisotropic displacements of Cu1 and O1 (Fig. 1) show the same tendency, but these values are more reasonable. In contrast, the atomic displacements in the $\text{La}_2\text{—Cu}_2\text{—O}_2$ system are small. The results are in agreement with the powder diffraction

refinements, but show that the displacement is highly anisotropic. O3 is partially occupied [33 (3)%].

Refining the site occupancy for O1 and Cu1 led to a decrease in the occupancy for both sites. However, the difference from full occupancy was barely significant, so it was decided to allow the O1 and Cu1 sites to have full occupancy in the final refinements. Thus, the occupancy of Cu1 and O1 might be slightly less than one, as also observed by Izumi *et al.* (1987). The La:Ba ratio was not refined, but energy-dispersive X-ray (EDX) analysis indicated a ratio close to or slightly less than 1:1. The ratio was, therefore, fixed to 1:1. The relative proportions of the three twin components were refined, giving 32, 40 (2) and 28 (1)% for the three perpendicular orientations, respectively.

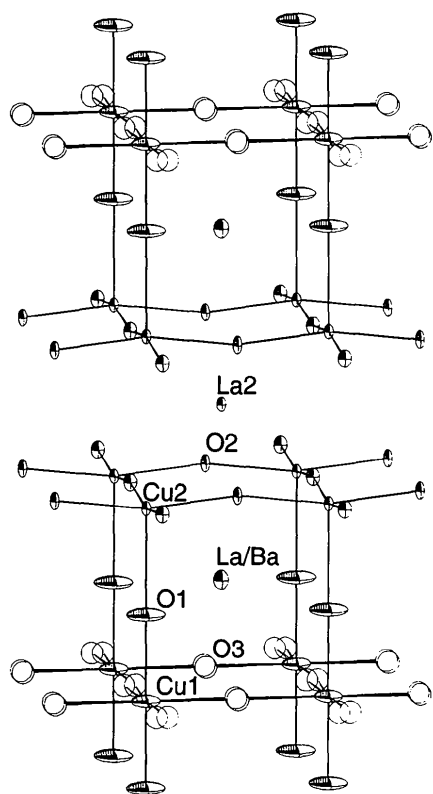


Fig. 1. View of the crystal packing. Displacement ellipsoids are scaled to the 50% probability level.

Experimental

Crystals of the title compound were prepared from stoichiometric amounts of La₂O₃, BaCO₃ and CuO, which were mixed thoroughly then heated at 1223 K for 24 h. The sample was then cooled slowly (over 12 h). The crystal size can be increased by repeating the procedure.

Crystal data

Ba_{1.50}Cu₃La_{1.50}O_{6.66}
M_r = 711.55

Mo *K*α radiation
 λ = 0.71073 Å

Tetragonal

P4/mmm

a = 3.911 (2) Å

c = 11.734 (1) Å

V = 179.48 (13) Å³

Z = 1

D_x = 6.583 Mg m⁻³

Data collection

CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

by integration from crystal shape

T_{min} = 0.42, *T_{max}* = 0.57

2116 measured reflections

1336 independent reflections

R_{int} = 0.0535

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.0327

wR(*F*²) = 0.1135

S = 1.067

1333 reflections

23 parameters

w = 1/[σ²(*F_o*²) + (0.0410*P*)² + 0.3168*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

Cell parameters from 25 reflections

θ = 8.7–22.6°

μ = 25.50 mm⁻¹

T = 293 (2) K

Prismatic

0.05 × 0.02 × 0.01 mm

Black

θ_{\max} = 45.21°

h = 0 → 7

k = 0 → 7

l = 0 → 23

3 standard reflections

frequency: 60 min

intensity decay:

insignificant

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

U_{iso} for O3, *U_{eq}* = (1/3)Σ_{*i*}Σ_{*j*}*U_{ij}a_i^{*}a_j^{*}* for all others.

Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{iso}/U_{eq}</i>	
Ba1	0.75	1/2	1/2	0.18479 (5)	0.01299 (12)
La1	0.25	1/2	1/2	0.18479 (5)	0.01299 (12)
La2	1.00	1/2	1/2		0.00571 (11)
Cu1	1.00	0	0	0	0.0272 (4)
Cu2	1.00	0	0	0.34636 (10)	0.00560 (10)
O1	1.00	0	0	0.1559 (6)	0.049 (4)
O2	1.00	0	1/2	0.3650 (3)	0.0087 (6)
O3	0.16 (2)	0.030 (16)	1/2	0	0.022 (7)

Table 2. Selected geometric parameters (Å)

Ba1—O1	2.786 (2)	Cu1—O1	1.829 (7)
Ba1—O3	2.84 (4)	Cu1—O3	1.959 (4)
Ba1—O2	2.880 (3)	Cu2—O2	1.9676 (11)
La2—O2	2.517 (3)	Cu2—O1	2.235 (7)

The crystal is an intergrowth of three perpendicular orientations. Data were collected in the apparent $3a \times 3b \times c$ supercell. Of the measured reflections, 596 were non-overlapping, each measured three times, and 328 were overlaps of three reflections, giving a total of 2116 measured reflections. Merging of equivalent reflections in the set of non-overlapping reflections then gave 1336 independent reflections. The absorption correction was optimized by checking the azimuthal scans of ten reflections. The starting model for the refinement was taken from the study by Torardi, McCarron, Subramanian, Sleight & Cox (1987).

Data reduction: CADABS (Norrestam, 1976). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976).

The crystals were kindly supplied by John J. Neumeier, Physics Department, Ludwig-Maximilian University, Munich.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1132). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Izumi, F., Asano, H., Ishigaki, T., Takayama-Muromachi, E., Matsui, Y. & Uchida, Y. (1987). *Jpn J. Appl. Phys.* **26**, L1153–L1155.
 Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Norrestam, R. (1976). *CADABS. Program for CAD-4 Absorption Correction*. Technical University of Denmark, Denmark.
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
 Torardi, C. C., McCarron, E. M., Subramanian, M. A., Sleight, A. W. & Cox, D. E. (1987). *Mater. Res. Bull.* **22**, 1563–1571.

Acta Cryst. (1996). **C52**, 1601–1603

A New Form of Lithium Zinc Phosphate with an Ordered Phenakite Structure, LiZnPO_4

XIANHUI BU, THURMAN E. GIER AND GALEN D. STUCKY

Chemistry Department, University of California, Santa Barbara, CA 93106, USA. E-mail: xianhui@sbxray.ucsb.edu

(Received 19 September 1995; accepted 27 November 1995)

Abstract

A new form of LiZnPO_4 with an ordered non-centrosymmetric phenakite-type structure is reported.

Comment

A variety of framework topologies have been found for open-framework zincophosphates based on tetrahedral ZnO_2^{2-} and PO_4^{3-} units. In addition to about a dozen novel zincophosphate open-framework structures (Feng, Bu & Stucky, 1995), structural analogs of some natural zeolites such as sodalite and zeolite X have been reported in the zincophosphate system (Gier & Stucky, 1991). Since there are many structure types based on tetrahedral T^{3+}/T^{4+} atoms, such as for the aluminosilicates, it is of interest to investigate to what extent these structure types exist in T^{2+}/T^{5+} systems such as the zin-

cophosphates. The difficulties in working with T^{2+}/T^{5+} systems include the large difference in the ionic radii of T^{2+} and T^{5+} , especially in the zincophosphate system, and the increased tendency for divalent metals such as Zn^{2+} and Co^{2+} to assume non-tetrahedral coordination geometry. Here we report the discovery of a new zincophosphate in another structural family, phenakite. This is the first report of a phenakite-type structure in the T^{2+}/T^{5+} system.

The mineral phenakite, Be_2SiO_4 , is rhombohedral and contains continuous six-ring channels parallel to the c axis. Derivatives of the phenakite structure include Zn_2SiO_4 , Li_2BeF_4 , Li_2SeO_4 , Li_2WO_4 and $\alpha\text{-LiABO}_4$ (where $A = \text{Al, Ga}$ and $B = \text{Si, Ge}$) (Fleet, 1987). All have the space group $R\bar{3}$ except for $\alpha\text{-LiGaSiO}_4$.

The centrosymmetric $R\bar{3}$ phenakite structure has seven atom positions, three of which are different tetrahedral sites and four of which are O-atom sites. The site which contains Si in phenakite may be labeled $T1$ and the other tetrahedral sites, which contain Be in phenakite, may be labeled $T2$ and $T3$. The key structural feature of the phenakite structure is that all the O atoms are bonded to three tetrahedrally coordinated atoms and there are no edge-sharing tetrahedra.

In the non-centrosymmetric title compound, LiZnPO_4 , there are fourteen unique atom positions, six of which are tetrahedral sites. Each O atom is bonded to one Li, one Zn and one P cation. The two divalent Zn cations occupy the two Si positions ($T1$) which are related by an inversion center in the $R\bar{3}$ structure. One Li cation and one P cation occupy the $T2$ positions that in $R\bar{3}$ would be related by a center of symmetry, and the other Li and P cations occupy the corresponding $T3$ positions. This reduces the lattice symmetry from $R\bar{3}$ to $R3$.

As expected for tetrahedral zincophosphates, there is a strict alternation of the ZnO_2^{2-} and PO_4^{3-} units. The

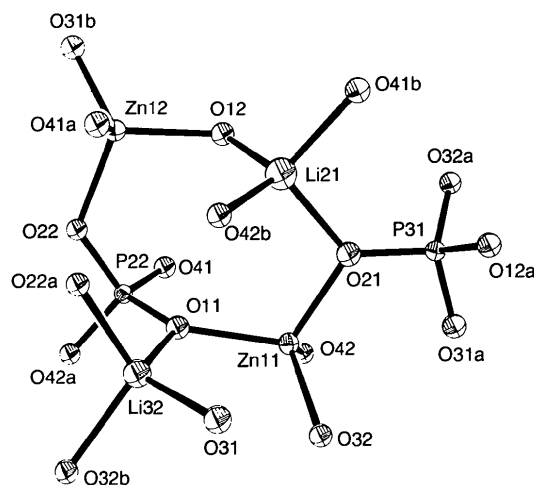


Fig. 1. A view of the Zn, P and Li tetrahedra showing the atomic labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.