

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for $\text{BaFe}_2^{\text{III}}(\text{P}_2\text{O}_7)_2$

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Ba1	1/4	3/4	0	0.024 (1)
Fe2	1/2	0.4521 (1)	1/4	0.014 (1)
Fe3	0	1/2	0	0.014 (1)
P1	0.5606 (2)	0.6910 (2)	0.0561 (2)	0.014 (1)
O11	0.4663 (5)	0.6003 (5)	0.1058 (5)	0.017 (1)
O12	0.5243 (5)	0.8273 (5)	0.0832 (6)	0.019 (1)
O13	0.5648 (5)	0.6677 (5)	-0.0946 (6)	0.020 (2)
O14	0.7009 (5)	0.6736 (5)	0.1565 (5)	0.016 (1)
P2	0.7810 (2)	0.5435 (2)	0.2015 (2)	0.014 (1)
O21	0.6822 (5)	0.4428 (5)	0.2153 (5)	0.018 (1)
O22	0.8472 (5)	0.5059 (5)	0.0861 (6)	0.020 (2)
O23	0.8736 (5)	0.5820 (5)	0.3395 (5)	0.019 (2)

Table 4. Selected geometric parameters (\AA) for $\text{BaFe}_2^{\text{III}}(\text{P}_2\text{O}_7)_2$

Ba1—O11	2.771 (5)	Fe3—O23 ^{viii}	1.999 (5)
Ba1—O12	2.944 (5)	P1—O11	1.531 (6)
Ba1—O11 ⁱ	2.771 (5)	P1—O12	1.516 (5)
Ba1—O12 ⁱ	2.944 (5)	P1—O13	1.491 (6)
Ba1—O22 ⁱⁱ	2.921 (6)	P1—O14	1.590 (5)
Ba1—O22 ⁱⁱⁱ	2.921 (6)	P2—O14	1.611 (5)
Ba1—O21 ⁱⁱ	3.101 (6)	P2—O22	1.501 (6)
Ba1—O21 ⁱⁱⁱ	3.101 (6)	P2—O21	1.511 (6)
Ba1—O23 ^{iv}	2.854 (6)	P2—O23	1.521 (5)
Ba1—O23 ^v	2.854 (6)	Fe2—O11 ^v	2.063 (5)
Fe3—O12 ^{vi}	1.971 (5)	Fe2—O11	2.063 (5)
Fe3—O12 ^{vii}	1.971 (5)	Fe2—O13 ⁱⁱⁱ	1.958 (5)
Fe3—O22 ^{viii}	1.982 (6)	Fe2—O13 ^{ix}	1.958 (5)
Fe3—O22 ^{vii}	1.982 (6)	Fe2—O21	2.034 (6)
Fe3—O23 ^v	1.999 (5)	Fe2—O21 ^v	2.034 (6)

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

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.

For both compounds, data collection: XSCANS (Siemens, 1991a); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structures: SHELXS86 (Sheldrick, 1990); program(s) used to refine structures: 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: BR1123). 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.
- Boutfessi, A., Boukhari, A. & Holt, E. M. (1996). *Acta Cryst.* **C52**, 1597–1599.
- 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.
- Vst'yantsev, 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**, 1597–1599

Copper(II) Diiron(III) Pyrophosphate

AICHA BOUTFESSI,^a ALI BOUKHARI^a AND ELIZABETH M. HOLT^{b*}

^aLaboratoire de Chimie du Solide Appliquée, Département de Chimie, Faculté des Sciences, Université Mohammed V, Avenue Ibn Batouta, Rabat, Morocco, and ^bDepartment of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, USA. E-mail: chememh@osucc.bitnet

(Received 23 November 1995; accepted 16 January 1996)

Abstract

The crystalline structure of $\text{CuFe}_2^{\text{II}}(\text{P}_2\text{O}_7)_2$ [copper(II) diiron(III) bis(diphosphate)] is characterized by isolated and centrosymmetric $\text{Fe} \cdots \text{Cu} \cdots \text{Fe}$ trimers. The Cu^{II} atom has square-planar coordination geometry, with Cu—O distances in the range 1.920(3)–1.934(3) Å, while the Fe^{III} atom is octahedrally coordinated, with an average Fe—O distance of 2.000(3) Å.

Comment

Studies of mixed-valence pyrophosphates of the type $A^{\text{II}}B^{\text{III}}\text{P}_2\text{O}_7$ are limited in the literature. $\text{Fe}_3(\text{P}_2\text{O}_7)_2$ ($\text{Fe}_{0.5}^{\text{II}}\text{Fe}_{2.5}^{\text{III}}\text{P}_2\text{O}_7$) crystallizes in space group *Pnma*, with linear $\text{Fe}_3\text{O}_{12}^{6-}$ trimers composed of $\text{Fe}^{\text{III}} \cdots \text{Fe}^{\text{II}} \cdots \text{Fe}^{\text{III}}$ units [Fe^{II}—Fe distances 2.924(1) Å]. The central Fe^{II} atom has trigonal bipyramidal coordination geometry, sharing opposite faces with octahedrally coordinated Fe^{III} atoms. The solid shows antiferromagnetic behavior

(Ijjaali, Venturini, Gerardin, Malaman & Gleitzer, 1991; Ijjaali, Venturini, Malaman & Gleitzer, 1990).

The isotopic pyrophosphates BaTi^{IV}₂(P₂O₇)₂ (Wang & Hwu, 1991) and BaV^{III}₂(P₂O₇)₂ (Benhamada, Grandin, Borel, Leclaire & Raveau, 1991) crystallize in space group *C2/c*. PbFe^{II}₂(P₂O₇)₂ (Wanklyn, Wondre, Davison & Salmon, 1983) and MgCr^{II}₂(P₂O₇)₂ (Ust'yantsev & Tretnikova, 1974) have also been reported, but only in the powder form.

SrFe^{III}₂(P₂O₇)₂ crystallizes in space group *P1̄* (Boutfessi, Boukhari & Holt, 1995), with metal atoms distributed in two types of column oriented along the [001] axis. The repeat unit within one column is ...Sr...Fe...Sr...Fe... [Sr...Fe 3.915 (2) Å] and within the second is ...Fe...Fe... [Fe...Fe 7.830 (2) Å]. Fe atoms in adjacent columns are widely separated. The Fe atoms have octahedral coordination geometry [average Fe—O 1.996 (3) Å].

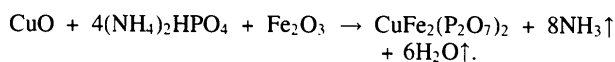
CuFe^{III}₂(P₂O₇)₂ is characterized by centrosymmetric Fe^{III}...Cu^{II}...Fe^{III} trimers in which the central Cu atoms with square-planar coordination geometry share two O atoms with each of two neighboring octahedrally coordinated Fe atoms [Cu...Fe 3.145 (3), average Cu—O 1.927 (3), average Fe—O 2.000 (3) Å] (Fig. 1). Thus, there is a structural similarity to the trimers found in Fe_{0.5}Fe^{III}P₂O₇, but with a change of coordination

geometry for the central divalent atom. Studies of the magnetic properties of this material are underway.

A projection view of CuFe^{III}₂(P₂O₇)₂ (Fig. 2) shows the trimers to be situated in a parallel arrangement with P₂O₇ groups occupying the intermediate space. The pyrophosphate groups have a staggered conformation, with bond angles and distances similar to those seen in other diphosphate-containing structures.

Experimental

The title pyrophosphate, CuFe^{III}₂(P₂O₇)₂, was synthesized by mixing stoichiometric quantities of (NH₄)₂HPO₄, CuO and Fe₂O₃ according to:



The reaction mixture was ground together and heated progressively to 1273 K. After 24 h at this temperature, the molten mixture was cooled slowly (5 K h⁻¹) to 573 K and then in an uncontrolled manner to room temperature in air. Blue single crystals were thus obtained.

Crystal data

CuFe₂(P₂O₇)₂
M_r = 523.1
 Monoclinic
P2₁/n
a = 6.589 (1) Å
b = 5.163 (1) Å
c = 15.633 (3) Å
 β = 91.99 (3)°
V = 531.52 (8) Å³
Z = 2
D_x = 3.269 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 45 reflections
 θ = 9.5–17.2°
 μ = 5.364 mm⁻¹
T = 298 K
 Chunk
 0.2 × 0.2 × 0.2 mm
 Blue-green

Data collection

Syntex *P4* four-circle diffractometer
 $\theta/2\theta$ scans
 Absorption correction: semi-empirical *via* ψ scan (*XEMP*; Siemens, 1991*b*)
 T_{\min} = 0.28, T_{\max} = 0.45
 2303 measured reflections
 1553 independent reflections
 1253 observed reflections [$F > 6.0\sigma(F)$]

R_{int} = 0.0534
 θ_{max} = 23.5°
 h = -9 → 9
 k = 0 → 7
 l = 0 → 21
 3 standard reflections monitored every 97 reflections
 intensity decay: negligible

Refinement

Refinement on *F*
 R = 0.0420
 wR = 0.0541
 S = 1.26
 1253 reflections
 98 parameters
 $w = 1/[\sigma^2(F) + 0.0008F^2]$
 $(\Delta/\sigma)_{\text{max}}$ = 0.001

$\Delta\rho_{\text{max}}$ = 0.25 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.75 e Å⁻³
 Extinction correction: none
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

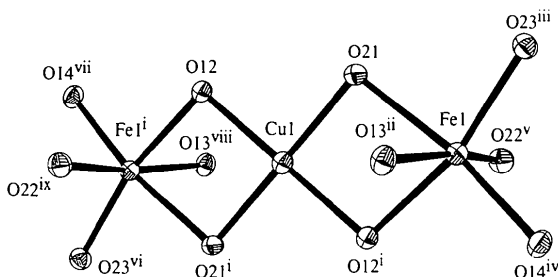


Fig. 1. A projected view of the metallic trimers in CuFe^{III}₂(P₂O₇)₂ with displacement ellipsoids shown at 50% probability levels [symmetry codes: (i) $-x, -y, -z$; (ii) $-x, 1-y, -z$; (iii) $1-x, -y, z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $1-x, 1-y, -z$; (vi) $-1+x, -1+y, z$; (vii) $-\frac{1}{2}-x, -\frac{1}{2}+y, -\frac{1}{2}-z$; (viii) $x, -1+y, z$; (ix) $-1+x, y, z$].

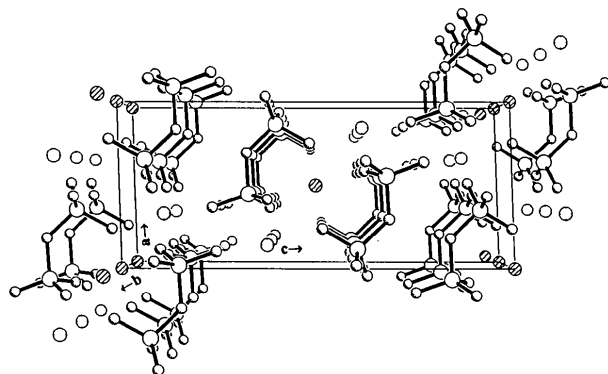


Fig. 2. A view of CuFe^{III}₂(P₂O₇)₂ projected onto the *ac* plane.

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