Zeitschrift für Kristallographie 189, 77–87 (1989)

Structure of $BaCuInF_7$: The interpretation between a pyrochlore-like edge-sharing network of octahedra and a defect fluorite structure

Complex copper(II) fluorides – XI.

A. de Kozak and M. Samouël

Laboratoire de Cristallochimie du Solide, Université P. et M. Curie, Tour 54,
4 Place Jussieu, 75252 Paris Cedex 05, France

J. Renaudin and G. Férey*

Laboratoire des Fluorures, UA CNRS 449, Faculté des Sciences,
Route de Laval, 72017 Le Mans Cedex, France

Received: December 5, 1988; accepted in final form: February 23, 1989

Copper and indium ions in statistical distribution / Crossed chains of* Cu/In *edge-sharing octahedra / Pyrochlore-like subnetwork / Barium ions in cubic coordination / Defect fluorite structure

Abstract. $BaCuInF_7$ is tetragonal [space group $I4_1/amd$, $a = 6.843(1)$ Å, $c = 12.001(3)$ Å, $Z = 4$]. Its room temperature crystal structure was solved from 327 unique reflections to $R = 0.035$. The $8c$ sites of the structure are statistically occupied by both copper and indium ions in octahedral coordination. The three-dimensional network is built up from infinite chains of edge-sharing octahedra. These rutile-like chains lie along the $\boldsymbol{a}$ and b axes and form a four-layer tetragonal packing. Barium ions (eightfold coordinated) ensure also a three-dimensional subnetwork described as a defect fluorite structure in the tunnels of which octahedral chains are inserted. The original topology is discussed in terms of scale of disorder since it allows a strict cationic ordering in a chain and a disorder between two chains.

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* Author to whom correspondence should be addressed.

Table 1. Crystallographic data and details of the intensity measurements.

Symmetry: tetragonal
Space group: $I4_1/amd$ (cell choice 2)
Cell parameters from 32 reflections within the range $15 < \theta < 16°$: $a = 6.843(1)$ Å, $c = 12.001(3)$ Å, $V = 522.0$ Å^3 $Z = 4$, $M = 448.69$ g mole^{-1}
Density = 5.30 g cm^{-3}
Crystal dimensions: 0.065 mm × 0.055 mm × 0.040 mm
Radiation: MoK_α ($\lambda = 0.71073$ Å)
Linear absorption coefficient: 150 cm^{-1}
Intensity measurements up to $\theta_{max} = 40°$
Indices: $-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $0 \leq l \leq 21$, 40 steps per reflection, 2 s per step, step width: 0.03°
Standard reflections: 200/020/112 measured every hour with an intensity variation: 0.70% max., 4383 measured reflections (with only lattice I condition), 2274 rejected with $I/\sigma(I) < 3$, 327 independent reflections ($R_{int} = 0.035$), 19 refined parameters
Weighting scheme: $w = 3.1/[\sigma(F)^2 + 10^{-6} F^2]$
Electron density in final difference Fourier synthesis: maximum = 2.3, minimum $= -2.2\ e\ Å^{-3}$ [close to F(3) ions]
Secondary extinction factor: $g = 5(2) \times 10^{-8}$.

Introduction

This paper is a part of a general study concerning the crystal structure of barium and copper(II) fluorides which were evidenced from the ternary systems $BaF_2-CuF_2-MF_3$ with M = Fe (Samouël et al., 1985), M = V (Samouël et al., 1988) and M = In (Samouël et al., 1989). The Jahn-Teller Cu^{2+} ions associated with small trivalent metals in octahedral coordination lead to new crystalline architectures (Renaudin et al., 1985; 1986; 1987). Therefore the choice of In^{3+} is due to its larger ionic radius and the various coordination numbers (C.N.) that this ion can adopt: C.N. = 6 in Cs_2NaInF_6 (Schneider and Hoppe, 1970), C.N. = 6 + 7 in $RbIn_3F_{10}$ (Champarnaud-Mesjard et al., 1977) and $Rb_2In_3F_{11}$ (Champarnaud-Mesjard and Frit, 1978), C.N. = 7 in KIn_2F_7 (Champarnaud-Mesjard and Frit, 1977), Pb_2InF_7 (Senegas et al., 1987), Sr_2InF_7 (Scheffler and Hoppe, 1984) and $Ba_3In_2F_{12}$ (Scheffler and Hoppe, 1985). The only compound isolated so far in the ternary system, $BaCuInF_7$, exhibits a new structural type in the series $BaM^{II}M^{III}F_7$ with M^{II} = Ca, Mn, Fe, Co, Ni, Cu, Zn, Cd and M^{III} = Al, Ga, V, Cr, Fe. Its crystal structure is described below and correlated with other structural types.

Experimental

Several crystals were obtained under conditions described elsewhere (Samouël et al., 1989). A very small single crystal was selected for X-ray data collection on a Siemens-STOE AED2 four-circle diffractometer. The crystallographic characteristics are reported in Table 1. No absorption correction was applied owing to the quasi-spherical shape and the small dimensions (coefficient $\mu R < 0.5$) of the crystal. Atomic scattering factors for Ba^{2+}, Cu^{2+}, In^{3+}, F^- and anomalous dispersion corrections were taken from International Tables for Crystallography (Ibers and Hamilton, 1974).

Table 2. Atomic coordinates and parameters of anisotropic thermal motion ($\times 10^{-4}$) with e.s.d. in parentheses (origin choice 2 of space group $I4_1/amd$).

Atom	Site	x	y	z	U_{11}
Ba	$4b$	0	1/4	3/8	226(3)
Cu, In	$8c$	0	0	0	94(2)
F(1)	$16f$	0.2854(7)	0	0	213(23)
F(2)	$8e$	0	1/4	0.0937(6)	398(47)
F(3)	$4a$	0	3/4	1/8	573(57)

Atom	Site	U_{22}	U_{33}	U_{13}	U_{13}	U_{12}	B (Å^2)
Ba	$4b$	226(3)	229(6)	0	0	0	1.81
Cu, In	$8c$	84(2)	370(7)	−36(4)	0	0	1.47
F(1)	$16f$	358(28)	324(24)	−120(23)	0	0	2.35
F(2)	$8e$	175(35)	327(41)	0	0	0	2.37
F(3)	$4a$	573(57)	414(80)	0	0	0	4.10

The vibrational coefficients U_{ij} relate to the expression: $T = \exp [-2\pi^2 (h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$

All calculations were performed using the SHELX-76 program (Sheldrick, 1976). The structure was solved from 3D-Patterson map and refined in space group $I4_1/amd$ to the final residuals: $R = 0.035$ and $R_w = 0.033$. The final parameters are listed in Table 2 with a statistical occupancy of $8c$ site by indium and copper ions [their standard occupancy factor was refined to 0.127(3)]. Refinements performed in the sub-groups of $I4_1/amd$ (especially in $Imma$ to separate the eight cations Cu^{2+} and In^{3+} in two distinct sites) all led to increase the R factors. Moreover, the thermal motion of Cu^{2+} becomes negative and very high for In^{3+}, confirming the statistical distribution of the two cations. The list of structure factors is deposited.[1]

According to the Jahn-Teller effect on cupric ions, the $(Cu,In)F_6$ octahedra are elongated with an orthorhombic distortion (Table 3): the three metal — fluorine distances are in good agreement with the wide range of Cu — F and In-F distances previously observed in similar fluorides (Tables 4 — 5).

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[1] Additional material to this paper can be ordered referring to the no. CSD 53557, names of the authors and citation of the paper at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG.

Table 3. Interatomic distances (Å) and bond angles with c.s.d. in parentheses.

Cu/In	F(1)	F(1)	F(2)	F(2)	F(3)	F(3)
F(1)	**1.953(5)**	3.905(7)	2.829(4)	2.829(4)	2.998(3)	2.998(3)
F(1)	180.0(4)	**1.953(5)**	2.829(4)	2.829(4)	2.998(3)	2.998(3)
F(2)	90.0(4)	90.0(4)	**2.047(2)**	4.095(3)	3.442(1)	2.625(7)
F(2)	90.0(4)	90.0(4)	180.0(2)	**2.047(2)**	2.625(7)	3.442(1)
F(3)	90.0(2)	90.0(2)	105.4(1)	74.6(3)	**2.275(1)**	4.550(1)
F(3)	90.0(2)	90.0(2)	74.6(3)	105.4(1)	180.0(1)	**2.275(1)**

⟨Cu/In – F⟩ = 2.092 Å, d(Cu/In – Cu/In) = 3.421 Å

Ba Polyhedron:

8 × Ba – F(1) = 2.709(8)
2 × Ba – F(2) = 3.376(8)
4 × Ba – F(2) = 3.44(1)

4 × F(1) – F(1) = 2.940
4 × F(1) – F(1) = 3.020
4 × F(1) – F(1) = 3.421

Ionic Radii (Shannon, 1976):
F^- : 1.285 Å, 1.30 Å and 1.31 Å [resp. 2-, 3- and 4-fold coord.]
Cu^{2+} : 0.73 Å and In^{3+} : 0.80 Å [6-fold coord.]
Ba^{2+} : 1.42 Å [8-fold coord.]

Table 4. Comparison of Cu – F distances (Å) in copper fluorides exhibiting an orthorhombic distorsion of the CuF_6 octahedra.

Compound	Cu – F distances			Mean ⟨Cu – F⟩	References
$KCuF_3$	2 × 1.888	2 × 1.962	2 × 2.258	⟨2.036⟩	Müller, 1987
$CuPtF_6$	2 × 1.930	2 × 2.007	2 × 2.122	⟨2.020⟩	Müller, 1987
$CuAuF_5$	2 × 1.854	2 × 2.021	2 × 2.221	⟨2.032⟩	Müller, 1987
$KCuCrF_6$	1.872 1.878	1.999 2.007	2.239 2.261	⟨2.043⟩	Kissel and Hoppe, 1988
α-$Ba_2Cu_5F_{14}$	1.875 1.898	1.914 1.943	2.232 2.372	⟨2.055⟩	de Kozak et al., 1986
	2 × 1.865	2 × 2.056	2 × 2.148	⟨2.023⟩	
$BaCuFeF_7$[a]	1.877 1.931	1.990 2.015	2.099 2.111	⟨2.004⟩	Renaudin et al., 1985
$Ba_2CuV_2F_{12}$[a]	1.859 1.886	1.978 1.990	2.022 2.122	⟨1.976⟩	Renaudin et al., 1986

[a] The two last compounds exhibit also a statistical occupancy for copper and trivalent metal.

Discussion

This structure is very particular with respect to many aspects:

- the original topology of the octahedral subnetwork of Cu^{2+} and In^{3+} surrounding the tetragonal net of these cations,
- the defect fluorite network of barium polyhedra,
- the interconnection of these two sublattices.

Table 5. Comparison of In – F distances (Å) in indium fluorides with octahedral coordination for In.

Compound	In – F distances			Mean ⟨In – F⟩	References
InF_3		6 × 2.04		⟨2.04⟩	Schneider and Hoppe, 1970
$In(OH)F_2$	2 × 2.08 (In-OH)	2 × 2.06	2 × 2.11	⟨2.08⟩	Forsberg, 1957
$(NH_4)_3InF_6$		2 × 2.05		⟨2.05⟩	Schneider and Hoppe, 1970
Cs_2NaInF_6		6 × 2.03		⟨2.03⟩	Schneider and Hoppe, 1970
$RbIn_3F_{10}$	2 × 2.00	2 × 2.09	2 × 2.10	⟨2.06⟩	Champarnaud-Mesjard et al., 1977
$Rb_2In_3F_{11}$	1.93	2.05 2 × 2.07	2.10 2.17	⟨2.06⟩	Champarnaud-Mesjard and Frit, 1978

1. The Cu-In octahedral subnetwork and rod packings

The $(Cu,In)F_6$ octahedra form infinite rutile-like chains by sharing F(2) – F(3) edges (Fig. 1). Owing to the disorder, the elongation axis due to the Jahn-Teller effect is distributed equally on all the octahedra and corresponds to the M – F(3) distances. These long axes alternate in a chain whereas they are parallel within the rutile chains of CuF_2. The chains run along [010] at the $z = 0$ and $z = 1/2$ levels and along [100] at $z = 1/4$ and $z = 3/4$, according to the 4_1 axis and form a tetragonal Cu – In cationic subnetwork. The chains are linked together via F(3) ions which therefore connect four octahedra (Fig. 2). This last feature may be one of the reasons explaining the large thermal motion of F(3) ions; the other one concerns the cationic disorder which mainly affects the Jahn-Teller elongation axis.

The topology of the octahedral sublattice is similar to that existing in the ordered modified pyrochlore structure of $NH_4Fe_2F_6$ (Férey et al., 1985). In both cases, it is built up from orthogonal chains whose linkage ensures a 3D network. These chains were considered as rods in a famous paper (O'Keeffe and Andersson, 1977) concerning a simple description of crystal structures. They were described as four-layer tetragonal packing of rods (hereafter noted 4L-tp) with the symmetry $I4_1/amd$ (Fig. 3a); this is the very case in $BaCuInF_7$ whereas $NH_4Fe_2F_6$ adopts space group *Pnma*. The main difference between the two structures is that the rods consist of corner-sharing octahedra with composition $MF_{6/2}$ (or MF_3) in $NH_4Fe_2F_6$ and edge-sharing octahedra with composition $MF_{2/1}F_{2/2}F_{2/4}$ (or $MF_{3.5}$) in $BaCuInF_7$. If one considers that the octahedral network is the basic building unit, the latter compound must be written $Ba[CuF_{3.5}InF_{3.5}]$, the barium ions being inserted between the rods (Fig. 3b).

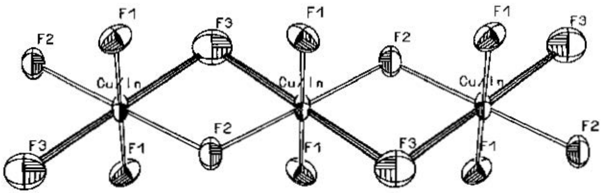

Fig. 1. Perspective view of a [CuInF$_7$] chain of edge-sharing octahedra (thermal ellipsoids: 50% probability).

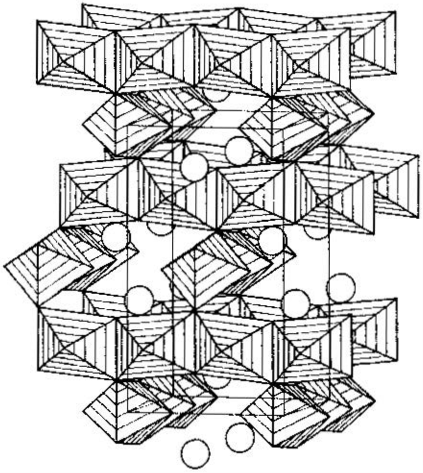

Fig. 2. Perspective view of the crossed chains of Cu/In edge-sharing octahedra with insertion of Ba^{2+} ions.

2. The defect fluorite subnetwork of barium polyhedra

The barium ions possess a first shell of eight F(1) neighbours at 2.71 Å which form a slightly distorted cube. A second shell of F(2) neighbours appears at nearly 3.4 Å (Table 3). These cubes ensure also a three-dimensional subnetwork by sharing four edges as shown in Figure 4c.

This subnetwork can be clearly understood starting from an AX network: the cubic CsCl structural type. The latter will be further described

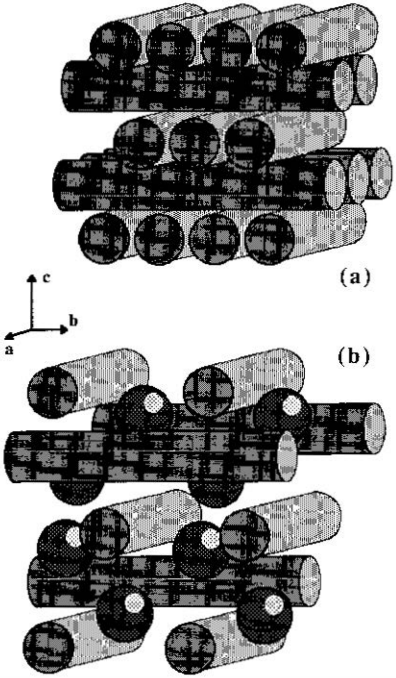

Fig. 3. A four-layer tetragonal packing of rods (a) compared to the BaCuInF$_7$ structure (b) represented as [CuInF$_7$] rods and Ba^{2+} spheres.

using a multiple cell (2a, 2a, 4a) similar to that of BaCuInF$_7$. This cell contains 16 anions X and 16 cations A which occupy the following positions of space group $I4_1/amd$: A(1) in 4*a*, A(2) in 4*b*, A(3) in 8*e* ($z = 0.125$) and X in 16*f* ($x = 0.25$). If A(3) sites become empty, the electrical neutrality requires for the remaining A(1) and A(2) cations to become divalent (for example, Ba instead of Cs). This leads to the classical fluorite BaF$_2$ (Fig. 4a) which can therefore be written as $Ba_8\square_8F_{16}$ or, more explicitly, as $Ba_{4a}Ba_{4b}\square_{8e}F_{16f}$. If one creates new vacancies on the 4*a* barium sites (Fig. 4b), the resulting network $(Ba_4F_{16})^{8-}$ (namely $\square_{4a}Ba_{4b}\square_{8e}F_{16f}$) corresponds to the very situation occurring in BaCuInF$_7$, the fluorine involved being all F(1) ions (Fig. 4c). The vacancies open large rectangular

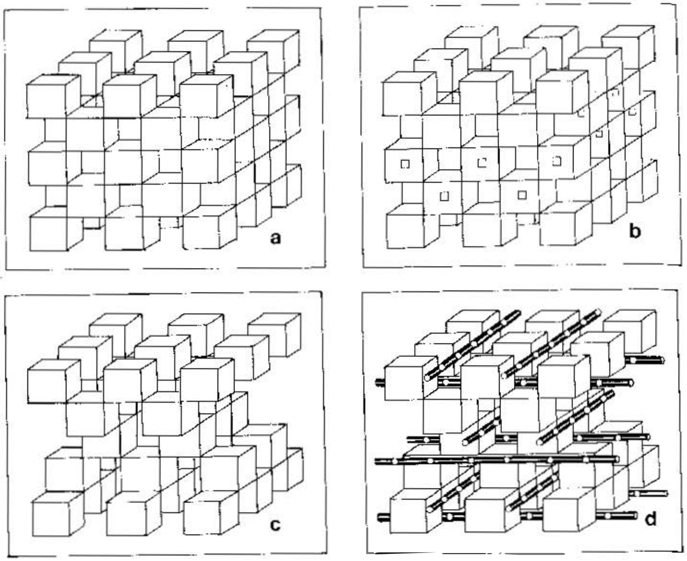

Fig. 4. Perspective view of two cells of the fluorite structure (a), the defective fluorite structure with (4a) vacancies (b), the barium polyhedra sublattice of $BaCuInF_7$ (c) and the interpenetration of the $[BaF_4]^{2-}$ subnetwork and $[CuInF_3]^{2+}$ rods (d).

windows surrounded by the anionic sublattice of the structure. The rods described above run through these tunnels (Fig. 4d). However, their composition becomes $[CuInF_3]^{2+}$ instead of $[CuInF_7]^{2-}$ and they are formally described from edge-sharing square planes since the F(1) ions are now attributed to the fluorite network.

Attention must be paid now to the location of F(2) and F(3) ions within the defect fluorite sublattice: F(3) occupy 4*a* sites, on which one created before barium vacancies; F(2) are located on 8*e* sites, filled in CsCl structural type and empty in BaF_2. Therefore Ba^{2+} and F^- ions build centered cubes and a substructure Ba_4F_{28}, intermediate between CsCl type and a pure centered cubic lattice of F^- ions. Cu^{2+} and In^{3+} ions are inserted in the octahedral vacancies centered on some edges of the cubes. A full occupancy of all edges would correspond to a rocksalt structure in the same way as f.c.c. FeO originates from cubic centered Fe_α. $BaCuInF_7$ is therefore a relatively dense structure (packing ratio from barium and fluorine: 0.61).

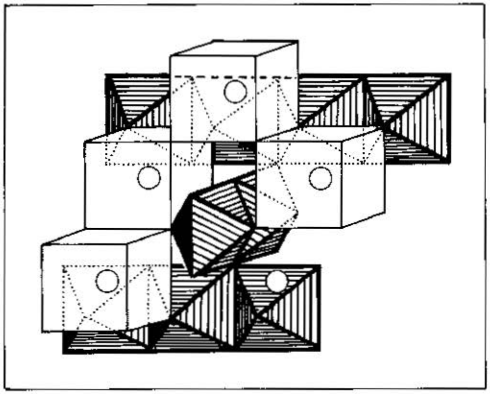

Fig. 5. Illustration of the connection between the two sets of polyhedra Ba^{2+} cubes and Cu/In octahedra.

To summarize, $BaCuInF_7$ can be described either as barium ions inserted in a 4L-tp of edge-sharing octahedra rods of composition $[CuInF_7]^{2-}$ (Fig. 3b) or as the interpretation of a defect fluorite sublattice $[BaF(1)_4]^{2-}$ with a 4L-tp of edge-sharing square planes rods of composition $[CuInF(2,3)_3]^{2+}$ (Fig. 4d). The existence of M – F(1) bonding transforms the square planes into octahedra whose linkage to the defect fluorite sublattice is shown in Fig. 5.

3. Comparison with homologous compounds

This compound corresponds to a new structural type in the series of barium heptafluorometallates $BaM^{II}M^{III}F_7$ which can be divided in three main subgroups:

— The first one involves small divalent and trivalent cations (M^{II} = Mn, Fe, Co, Ni and M^{III} = V, Cr, Fe). Their common structural feature is the existence of edge-sharing bioctahedral units: Mn_2F_{10} separated by isolated Fe^{III} octahedra in $BaMnFeF_7$ (Holler et al., 1981); $ZnFeF_{10}$ groups in the high temperature form of $BaZnFeF_7$ (Holler and Babel, 1982), the linkage between two bioctahedral units occurring by vertices via Zn – F – Fe bonds; $CuFeF_{10}$ groups in $BaCuFeF_7$ (Renaudin et al., 1985) linked one to the other via corners with alternatively Cu – F – Cu and Fe – F – Fe bonds.

— The second subgroup concerns large divalent and small trivalent cations (M^{II} = Ca, Mn, Cd and M^{III} = Cr, Ga). The structures are charac-

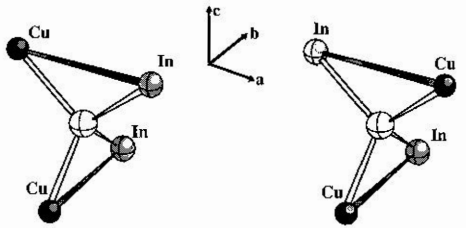

Fig. 6. The two symmetrical arrangements for ordered Cu/In chains around F(3) ions.

terized by two types of coordination polyhedra for M^{II}: octahedral and eightfold. This is the case for $BaMnGaF_7$ (Holler et al., 1984) and $BaCaGaF_7$ (Holler and Babel, 1985).

– The third subgroup evidenced in this paper relates to a larger trivalent cation.

A question arises finally: is the Cu^{2+}/In^{3+} subnetwork really disordered as it appears from diffraction data of the bulk? The original topology of the chains of octahedra leads to a very interesting case in which, even if there is a strict cationic ordering between Cu^{2+} and In^{3+} within one chain, the whole structure appears as disordered. Indeed, F(3) ions linking two chains are surrounded tetrahedrally by two Cu^{2+} and two In^{3+}, each containing one Cu^{2+} and one In^{3+}. Therefore, starting from a given order within a chain, two energetically equivalent arrangements arise related by the (100) mirror plane (Fig. 6). This alternative is encountered at every connection along the *c* axis and explains that only a statistical distribution is observed at the macroscopic scale. This last feature is confirmed by Buerger photographs which show no supplementary spots, even when overexposed during 72 h.

Acknowledgement. The authors are very indebted to Dr. M. Leblanc for his help in X-ray data collection.

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