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Synthesis and Crystal Structure of $Ba_6Cu_{12}Fe_{13}S_{27}$

Jaime Llanos,*[1] Carlos Mujica,* Oscar Wittke,† Pedro Gómez-Romero,‡ and Rafael Ramírez§

*Departamento de Química, Facultad de Ciencias, Universidad Católica del Norte, Casilla 1280, Antofagasta, Chile; †Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 487-3, Santiago, Chile; ‡Instituto de Ciència de Materials de Barcelona (CSIC), Campus de la Universitat Autónoma de Barcelona, 08193 Bellaterra, Barcelona, Spain; and §Instituto de Ciencia de Materiales de Madrid, CSIC, Campus Cantoblanco, 28049 Madrid, Spain

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The new phase $Ba_6Cu_{12}Fe_{13}S_{27}$, a new djerfisherite-like compound, has been prepared by solid state reaction of BaS_3 and $CuFeS_2$ at 1273 K. This compound crystallizes in the cubic system with space group $Pm\bar{3}m$ (No. 221), $Z = 1$, and cell constant $a = 1037.9(1)$ pm. The discrepancy indices of the single crystal structure refinement were $R = 0.023$ and $R_w = 0.030$. The structure was determined using three-dimensional single crystal X-ray diffraction data and consists of a three-dimensional cubic framework of edges and corners sharing Cu- and Fe-centered tetrahedra forming large interconnecting tunnels and octahedral cages; one iron atom and a Ba_6S octahedron per crystallographic unit cell are located in the cages and the channels, respectively. Consequently, were found two different geometrical environments for the transition metal atoms. XPS analysis reveal the presence of one valence state for copper, Cu(I), whereas iron exists as Fe(II) and Fe(III). © 1997 Academic Press

INTRODUCTION

In our investigation of the solid state chemistry of alkali metal copper–iron chalcogenides, we have reported on the structural features and electronic structure of phases containing Li (1, 2), Na (3, 4), K (5, 6), and Cs(7). As a continuation of this work, we have investigated phases with alkaline earth metals. We report here on the synthesis and crystal structure of $Ba_6Cu_{12}Fe_{13}S_{27}$.

EXPERIMENTAL

Synthesis. $CuFeS_2$ and BaS_3 constitute the starting materials for the preparation of the compound. Synthetic chalcopyrite was prepared as described in the literature (8). The X-ray powder diffraction of $CuFeS_2$ did not show any extraneous lines. BaS_3 was prepared from BaO, which was heated in an alumina crucible at 900 K under continous flow of CS_2 carried by Ar. After 20 h, no diffraction lines of the starting material was found in the powder diagram of BaS_3. The parent compounds were mixed together in an oxygen-free argon-filled dry box. The mixture was heated in a tightly sealed graphite crucible at 1273 K in a vertical furnace for 48 h under an Ar atmosphere. The sample was then allowed to cool over a period of 3 days at room temperature. Quantitative elemental analysis, using ICP, agreed quite well with the formula $Ba_6Cu_{12}Fe_{13}S_{27}$ (Ba 26.01%, Cu 24.30%, Fe 22.80%, and S 26.89%). The product is stable in air and water and forms crystals readily under the above conditions.

The X-ray powder diffraction diagram of the product was inspected, looking for peaks from the starting matrials, from binary or ternary (Cu, Fe) sulfides, and from the known related alkali-metal-containing compounds. The X-ray powder pattern did not reveal any relationship between the above-mentioned compounds and $Ba_6Cu_{12}Fe_{13}S_{27}$. In addition, a single crystal was selected and a complete crystal structure analysis was carried out.

X-ray powder diffraction. The samples were examined using a Siemens D-5000 diffractometer fitted with a graphite monochromator, using Cu$K\alpha$ radiation ($\lambda = 154.057$ pm) with quartz as an internal standard. The experimental powder patterns were in almost perfect agreement with those calculated from the single crystal data using the program Lazy-Pulverix (9).

Differential thermal analysis. Thermal analysis was performed in a Netzsch 404-EP apparatus under an Ar atmosphere at a heating and cooling rate of 10 °C/min; α-Al_2O_3 was used as the reference for all analysis. The samples obtained from the DTA runs after cooling were examined by X-ray diffraction using Cu$K\alpha$ radiation.

X-ray photoelectron spectroscopy. The XPS spectra of $Ba_6Cu_{12}Fe_{13}S_{27}$ were recorded on a Perkin–Elmer spectrometer. Mg$K\alpha$ X-rays were used for the measurements. Powder samples were pressed onto indium foil and then mounted in an aluminum sample holder. Crystals (approximately 0.5 cm^2) were fixed on a sample holder with an

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[1] To whom correspondence should be addressed.

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TABLE 1
Crystallographic Data and Details of the Structure Analysis for $Ba_6Cu_{12}Fe_{13}S_{27}$

Formula	$Ba_6Cu_{12}Fe_{13}S_{27}$
Crystal system	Cubic
Space group	$Pm\bar{3}m$ (No. 221)
a (pm)	1037.9(1)
Z	1
Volume (10^6 pm^3)	111.81(5)
μ Mo$K\alpha$ (cm^{-1})	159.68
Transmission factors	0.263–1.000
Diffractometer	Siemens R3m/V
Radiation, monochromator	Mo$K\alpha$, highly oriented graphite crystal
Scanning mode	ω–2θ
θ max.	50
Measured reflections	1179
Unique reflections	244 ($R_{\text{int}} = 0.065$)
Number of refined parameters	24
S = goodness of fit	0.98
Weighting schema	$w = 1/[\sigma^2(F) + 0.0015F^2]$
Final R,[a] R_w[b]	0.023, 0.030

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$.
[b] $R_w = \{\sum[w(|F_o| - |F_c|)^2]/\sum(wF_o^2)\}^{1/2}$.

TABLE 3
Selected Interatomic Distances (pm) and Angles (°) with Standard Deviation Given in Parentheses (M = Cu, Fe)

Interatomic distances		Bond angles	
Fe1–S1	250.1(3) × 6	S1–M2–S2	106.6(1) × 2
M2–S1	234.9(2)	S2–M2–S2	105.2(1)
M2–S2	236.2(1) × 2	S2–M2–S3	105.2(1) × 2
M2–S3	230.5(2)	S1–M2–S3	126.4(1)
S4–Ba	314.4(1) × 6		
Ba–S3	332.4(2) × 4		
Ba–S2	325.8(2) × 4		
Ba–S4	314.4(1)		
M2–M2	280.7(1) × 2		
M2–M2	286.3(2)		

organic glue. All the samples were sputtered with an Ar ion beam before the spectra were recorded.

Structure determination. A single crystal of $Ba_6Cu_{12}Fe_{13}S_{27}$ was selected and mounted into a glass capillary for X-ray analysis with a four circles diffractometer (Siemens R3m/V) using graphite monochromated Mo$K\alpha$ radiation. Cell parameters were refined from 20 centered reflections. Intensities were measured in the ω–2θ scan mode and the absorption correction was done empirically by ψ-scanning.

The structure was solved by the direct method in the space group $Pm3m$ and subsequently refined by the full least-squares method using the SHELXTL PLUS program system (10). The anisotropic refinement converged to $R = 0.023$ and $R_w = 0.030$. The highest residual electron density peak has a height which is 1.5% that of barium atom. List of observed and calculated structure factors can be obtained upon request from the authors. The bond lengths and angles were calculated using the program ORFFE (11). The crystallographic data as well as details of the structure analysis of $Ba_6Cu_{12}Fe_{13}S_{27}$ are given in Table 1.

The refined atomic coordinates, displacement factors and site occupation factors are given in Table 2. The S.O.F. of copper and iron in position 24 m was refined and values consistent with 50% occupancy for both Cu and Fe were found. Selected interatomic distances and angles are given in Table 3.

RESULTS AND DISCUSSION

The new phase $Ba_6Cu_{12}Fe_{13}S_{27}$ is isostructural to djerfisherite. The common structural feature for djerfisherite-like compounds has 24 tetrahedra. Three edges of tetrahedron are shared with other tetrahedra, forming a cluster of eight tetrahedra. Each cluster is linked to other clusters by corner-sharing of a tetrahedron. The transition

TABLE 2
Fractional Atomic Coordinates, and Equivalent and Anisotropic Displacement Parameters (in pm^2)

Atom	Position	x	y	z	S.O.F.	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba	6e	0.3030(6)	0	0	1	97(3)	65(5)	112(4)	U_{22}	0	U_{23}	U_{23}
Fe1	1b	1/2	1/2	1/2	1	75(4)	75(7)	U_{11}	U_{11}	0	U_{23}	U_{23}
Fe2	24m	0.3648(6)	0.3648(6)	0.1379(7)	0.51(1)	154(3)	140(5)	U_{11}	181(6)	− 5(2)	U_{23}	− 12(0)
Cu2	24m	0.3648(6)	0.3648(6)	0.1379(7)	0.49(1)	154(3)	140(5)	U_{11}	181(6)	− 5(2)	U_{23}	− 12(0)
S1	6f	1/2	0.2590(3)	1/2	1	94(11)	134(27)	74(15)	U_{22}	0	U_{23}	U_{23}
S2	12h	1/2	0.2444(2)	0	1	91(6)	90(10)	70(9)	113(11)	0	U_{23}	U_{23}
S3	8g	0.2184(1)	0.2184(1)	0.2184(1)	1	104(4)	104(6)	U_{11}	U_{11}	38(4)	U_{23}	U_{23}
S4	1a	0	0	0	1	70(8)	70(14)	U_{11}	U_{11}	0	U_{23}	U_{23}

Note. Standard deviations are given in parentheses.

metal atoms at the center of each tetrahedron form a primitive cubic arrangement like the antifluorite structure type (12, 13).

The structure of $Ba_6Cu_{12}Fe_{13}S_{27}$ consists of a three-dimensional cubic framework of edge and corner sharing MS_4 (M = Cu, Fe) tetrahedra which form large interconnecting tunnels and octahedral cages. One iron atom and a $[Ba_6S]$ octahedron per crystallographic unit cell were found to reside in these large channels and cages, respectively. A projection of the structure is shown in Fig. 1.

There are two distinct coordination geometries of the iron atoms. Fe1 is surrounded by six S1 atoms forming a regular octahedron with Fe–S distances of 250.1 pm, whereas Fe2 and Cu2 atoms are tetrahedrally coordinated by three different crystallographic sulfur atoms. In fact, the $[CuS_4]$ and $[FeS_4]$ tetrahedra are slightly distorted with Cu–S and Fe–S distances ranging from 230.5 to 236.2 pm. This distortion results in an S1–Fe2–S3 or S1–Cu2–S3 angle of 126.4°.

The $[Ba_6S]$ octahedron is regular with Ba–S distances of 314.5 pm. The six barium atoms of the unit cell form the coordination sphere of the S4 atom.

On the other hand, the Ba^{+2} are coordinated to nine sulfur ions, six located at the corners of a trigonal prism and three approximately above the rectangular faces with Ba–S distances ranging from 314.5 to 332.4 pm. All distances are comparable with those found in other barium–transition metal–sulfur compounds (14, 15).

There is no S–S bonding in $Ba_6Cu_{12}Fe_{13}S_{27}$; the shortest S–S distance is 354.2 pm, significantly longer than the 200.0 pm, expected for S–S single bonds (16, 17). It is therefore reasonable to assign the oxidation state of sulfur as 2-.

The DTA curve showed two peaks, one endothermic during the heating period and the other exothermic while the sample was cooling, both starting at 1023 K. After the DTA analysis the sample gave the characteristic XRD pattern of $Ba_6Cu_{12}Fe_{13}S_{27}$. That means that the two peaks corrrespond to the fusion and crystallization temperatures, respectively.

The X-ray photoelectron spectral (XPS) studies were carried out to examine the oxidation state of the transition metals in $Ba_6Cu_{12}Fe_{13}S_{27}$. The observed values of the binding energies for Cu ($2p_{3/2}$) and Cu ($2p_{1/2}$) are in good agreement with those in the literature (18). The full width at half maximum (FWHM) calculated for Cu ($2p_{3/2}$) is 1.8 eV, also in good agreement with the reported value (19), and confirms that only Cu^{+1} is present in the title compound. The XPS spectrum of Cu ($2p$) is shown in Fig. 2. For consistency with the usual electron counting rules, one would expect that $Ba_6Cu_{12}Fe_{13}S_{27}$ contains iron atoms with both +2 and +3 oxidation states. The formula of this compound can be then written as $Ba_6Cu_{12}(I)Fe_9(II)Fe_4(III)S_{27}$ and the Fe can be considered as having average oxidation number 2.31.

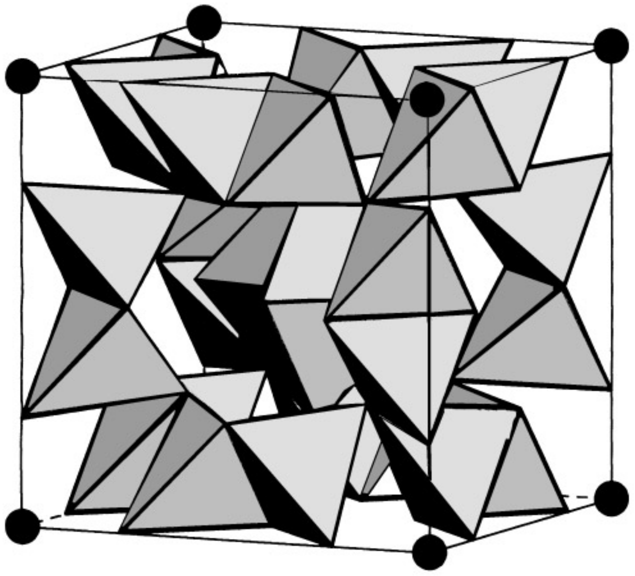

FIG. 1. Polyhedral representation of the crystal structure of $Ba_6Cu_{12}Fe_{13}S_{27}$. Black circles represent Fe1 atoms. The origin of the structure figure is translated in 1/2, 1/2, 1/2 relative to the atomic coordinates in Table 2.

It is well known that sulfides containing trivalent iron in a tetrahedral environment are difficult to prepare (20). Therefore, it could be assumed that Cu(I) and Fe(II) atoms preempt 21 tetrahedral sites, the other three are occupied by Fe(III) atoms, and the Fe(III) atom is confined to the octahedral site.

CONCLUSIONS

The new $Ba_6Cu_{12}Fe_{13}S_{27}$, a new djerfisherite-like compound, may be representative of a yet undiscovered family of alkaline earth metals copper iron sulfides. The structure

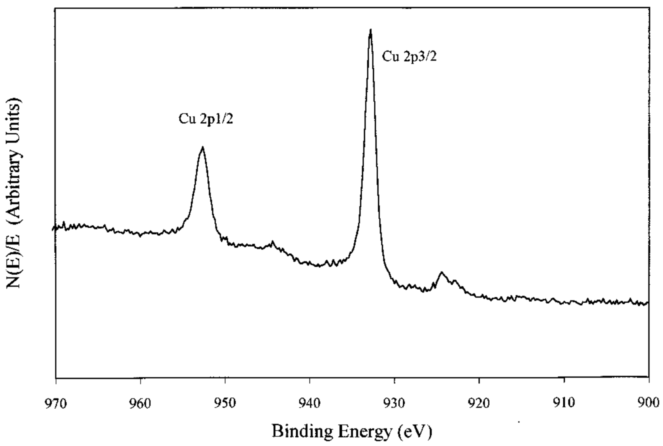

FIG. 2. X-ray photoelectron spectrum of Cu ($2p$) of $Ba_6Cu_{12}Fe_{13}S_{27}$ after bombardment with argon ions.

of this new compound contains interconnecting channels similar to that of framework silicates. A framework is built up of edge- and corner-sharing transition metal tetrahedra forming large channels running parallel to the crystallographic axes of the cubic unit cell. In $Ba_6Cu_{12}Fe_{13}S_{27}$, two octahedral holes per crystallographic unit cell are occupied, one by an S atom in the octahedral hole (1a) formed by the six Ba atoms, and one by an Fe atom in the octahedral hole (1b) formed by six S atoms.

It is hoped that further work, in progress, will lead to the preparation and characterization of new members of this interesting new family of compounds.

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