SYNTHETIC CUBANITE CuFe$_2$S$_3$: PRESSURE-INDUCED TRANSFORMATION TO ISOCUBANITE

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Abstract

Cubanite, the orthorhombic polymorph of CuFe$_2$S$_3$, is very sensitive to temperature, pressure and compositional variations. This sensitivity has prevented its successful synthesis in a controlled laboratory environment. We report here the first successful synthesis of cubanite and its high-pressure Mössbauer spectroscopic and electrical properties up to 7 GPa. We also compare the Mössbauer spectroscopic and electrical resistivity results on our synthetic cubanite with the behavior of naturally occurring cubanite under identical conditions. The magnetic hyperfine field, a sensitive Mössbauer parameter of the synthetic sample, corresponds to that of orthorhombic cubanite. We report here the pressure-induced transformation of the magnetic sextet (cubanite) to a paramagnetic doublet (isocubanite) at ~4 GPa at room temperature. This transformation has been confirmed independently by our electrical resistivity measurements up to 7 GPa. The present results could be useful in estimating the metamorphic pressure conditions of cubanite-bearing carbonaceous chondrites.

Keywords: cubanite, isocubanite, high-pressure transition, diamond anvil cell (DAC), Mössbauer spectroscopy, electrical properties.

Sommaire

La cubanite, polymorphe orthorhombique de CuFe$_2$S$_3$, est très sensible aux variations en température, pression et composition. A cause de cette sensibilité, il a été jusqu'à maintenant impossible de la synthétiser au laboratoire sous conditions contrôlées. Nous avons réussi cette synthèse pour la première fois, et nous avons déterminé son spectre Mössbauer et ses propriétés électriques à pression élevée, jusqu'à 7 GPa. Aussi, nous comparons nos résultats avec le comportement de la cubanite naturelle à conditions identiques. Le champ magnétique hyperfin, un paramètre Mössbauer sensible de l'échantillon synthétique, correspond à celui de la cubanite. Nous avons découvert une transformation sensible à la pression du sextet magnétique (cubanite) au doublet paramagnétique (isocubanite) à ~4 GPa à température ambiante. Cette transformation a été confirmée de façon indépendante par nos mesures de la résistivité électrique jusqu'à 7 GPa. Nos résultats pourraient s'avérer utiles pour estimer la pression du métamorphisme des chondrites carbonacées porteuses de cubanite.

(Traduit par la Rédaction)

Mots-clés: cubanite, isocubanite, transition à haute pression, cellule à enclume de diamant, spectroscopie de Mössbauer, propriétés électriques.

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INTRODUCTION

In mineral deposits, cubanite occurs in a chalcopyrite + pyrrhotite matrix as the orthorhombic polymorph of $CuFe_2S_3$. In nature, the exsolution of the cubic polymorph, isocubanite, in a chalcopyrite host is followed by its transformation into cubanite (orthorhombic). Sulfide minerals are common in mantle rocks, and likely to control the budget of platinum-group elements, siderophile and chalcophile elements, and their behavior during melting, but very little is known about the origin of mantle-derived sulfides. There are few high-pressure studies on sulfide minerals, and most are focused on the system Fe–FeS, which is relevant to understand the seismic properties of the core of the Earth, Mars and other planetary bodies (Dobson 2000, Fei & Bertka 2005, Sanloup & Fei 2004, Sata et al. 2008).

In this report, synthetic $CuFe_2S_3$ is characterized under high pressures up to 7 GPa using Mössbauer spectroscopy and measurements of electrical resistivity. The high-pressure behavior is compared to that of the naturally occurring mineral to unravel the genesis of cubanite in natural conditions.

BACKGROUND INFORMATION

Primary sulfides occur both as micro-inclusions in major silicate and oxide minerals and as individual millimetric grains in mantle-derived spinel lherzolites and pyroxenite xenoliths (Guo et al. 1999). The discovery of cubanite in CI chondrites and in the stardust of Comet Wild 2 clarified the mechanism about the large-scale mixing of low-temperature assemblages in the early solar system (MacDugall & Kerridge 1977, Bullock et al. 2005, Berger & Lauretta 2008, Berger et al. 2009). The high-pressure stability of sulfide minerals has important bearings in understanding the redox conditions in some shergottites (Lorand et al. 2005).The phase relations in the system Cu–Fe–S determine the compositions of coexisting phases as a function of temperature and point to the formation of cubanite at unique combinations of temperature and composition (Yund & Kullerud 1966, Sugaki et al. 1975). Owing to the unique physicochemical conditions needed, orthorhombic $CuFe_2S_3$ cannot be synthesized in the laboratory environment. The crystal structure of cubanite is orthorhombic, with an ordered distribution of tetrahedrally coordinated cations and S atoms in an approximately hexagonal packing. The Fe atoms occupy adjacent edge-shared tetrahedra as Fe^{2+} and Fe^{3+}, with a rapid exchange of an electron between them. The low-temperature polymorph of $CuFe_2S_3$ transforms to the high-temperature cubic form (isocubanite) at 210°C. Isocubanite does not revert to cubanite upon cooling (Putnis 1977, Miyamoto et al. 1988, Pruseth et al. 1999).

Naturally occurring cubanite has been investigated using single-crystal X-ray diffraction, Mössbauer spectroscopy and measurements of the temperature-dependent electrical resistivity in a diamond-anvil cell (DAC) to register an insulator – metal phase-transition in the range of 3.4–5.8 GPa, coinciding with a structural transition to a hexagonal NiAs-type structure (McCammon et al. 1992, McCammon 1994, 1995, Rosenberg et al. 1997). The valence of Cu is 1+ on the basis of neutron-diffraction measurements (Winterberger et al. 1974), consistent with the rapid exchange of an electron between Fe^{2+} and Fe^{3+}. The nature of the electron configuration of Fe is sensitive to cation–anion bond lengths; the Fe–S distance remains constant up to 3.6 GPa (McCammon et al. 1992). Pearce et al. (2006) concluded that one of the two inequivalent tetrahedra in chalcopyrite is occupied by a high-spin nominally trivalent Fe atom, and the other, by a monovalent Cu atom, resulting in the formula $Cu^{1+}Fe^{3+}S_2$. In contrast, in cubanite, each pair of tetrahedra contains a random distribution of Fe^{3+} and Fe^{2+} (Szymański 1974). According to electrical resistivity data, cubanite is a semiconductor (Sleight & Gillson 1973). The response of the structure of cubanite to an increase in pressure is seen in its unusually low bulk modulus due to shortening of Cu–S bonds with significant tilting of the tetrahedra, the mean Fe–S distances remaining virtually constant.

EXPERIMENTAL DETAILS

A stoichiometric proportion of Cu, Fe, S was initially kept at l80°C for 4–6 hours to prevent sudden increase in vapor pressure of sulfur in an evacuated silica tube using a resistance furnace. The temperature was slowly raised to 800°C under controlled rate of heating and kept at the same temperature for 12 hours. The samples thus prepared were then cooled down to room temperature in various steps described elsewhere (Pareek et al. 2008). The sample was characterized and analyzed by recording X-ray-diffraction patterns using a Philips diffractometer with Cu$K\alpha$ radiation. The composite pattern was analyzed with a specific program for mineral analysis using ICDD reference data for the respective minerals, chalcopyrite and polymorphs of $CuFeS_2$, pyrrhotite, cubanite and isocubanite.

X-ray-fluorescence (XRF) measurements were carried out on the sample using a Philips Analytical system. Three sets of independent measurements were taken to determine the average composition.

Ambient Mössbauer measurements were performed using a 10 mCi $^{57}Co(Rh)$ point source with an active area of 0.5×0.5 mm^2 operating in a constant-acceleration mode on a Wissel transducer, a Si–PIN solid-state detector (Amptek XR–100CR with a resolution of 250 eV), and a CMCA–550 Wissel data-acquisition module. The velocity scale was calibrated with reference

to α-Fe. For high-pressure Mössbauer measurements, a Merrill–Bassett-type diamond-anvil cell (DAC) was used (Chandra *et al*. 2001, 2005, 2010, Chandra 2007). The DAC sample assembly was prepared in a tantalum gasket hole of ~200 μm in diameter using 4:1 methanol : ethanol mixture as a pressure-transmitting fluid and a few tiny crystals of ruby as a pressure calibrant. The shift in the R_1 and R_2 lines of ruby, which vary linearly with pressure, was used to determine pressure on the sample. Mössbauer measurements in steps of ~0.7 GPa were carried out with long exposure-times (more than one week each) to achieve an appreciable signal-to-noise ratio. The patterns were analyzed by least-square fits to Lorentzian lines using the program of Jernberg & Sundquist (1983). For comparison, natural pure cubanite was also studied at ambient conditions and at high pressures up to 6 GPa. The error in the pressure measurements is ~0.3 GPa up to 7 GPa.

Electrical resistivity measurements were carried out in an opposed anvil system using MgO as pressure-transmitting medium (Parthasarathy 2007). The details of the apparatus and calibration are discussed elsewhere (Parthasarathy 2006). The typical uncertainty associated with pressure measurements is 0.2 GPa in the pressure region of 6 GPa (Chandra *et al*. 2010).

RESULTS AND DISCUSSIONS

The characterization of $CuFe_2S_3$ prepared under controlled conditions (Pareek *et al*. 2008) indicates the importance of methods of preparation to achieve an abundant yield of cubanite. We found that the quenching process results in the formation of pyrrhotite in abundance. Dutrizac *et al*. (1970) used X-ray-diffraction analysis on a synthetic sample and suggested that the compound with a pale brass yellow color synthesized by sintering pellets of CuS and FeS (1:2) is cubanite, along with small inclusions of pyrrhotite (<0.5 vol.%). However, further microscopic examination of the same sample revealed a "chalcopyrite-like phase" finely exsolved from a matrix of isocubanite. X-ray-diffraction results also confirmed that the phases are apparently "chalcopyrite" and isocubanite (Dutrizac 1976).

Differential thermal analysis (DTA) measurements acquired by heating natural cubanite at 5°C/min. indicates an exothermic reaction between 250 and 300°C associated with the transformation of cubanite to isocubanite. Another transformation is observed at 900°C, at which point the sulfide melts incongruently. In our study, the sample slowly cooled to room temperature (hereafter named "synthetic cubanite") is made the subject of further analyses. An analysis of its X-ray-diffraction pattern shows a mixture of isocubanite in abundance (85%), pyrrhotite (8%) and copper iron sulfide (7%) in small quantities without any signature of the orthorhombic cubanite (Fig. 1, Table 1). The pattern was analyzed through a program identifying minerals with the help of ICDD reference cards. The lines on top

of the diffraction peaks identify the compositions. A few of the diffraction peaks are characterized with more than one composition owing to equivalent *d* values. In Table 1, we also compare the normalized intensity of various peaks of our sample with the standard values reported. The chemical composition of our sample, determined by the X-ray-fluorescence technique, is represented as $Cu_{0.98}Fe_{2.02}O_{3.0}$.

Mössbauer spectroscopy is a sensitive technique to distinguish various iron-containing minerals by their parameters, especially magnetic hyperfine field (HF) and isomer shift (IS). Greenwood & Whitfield (1968) compared orthorhombic cubanite and chalcopyrite, and found the magnetic field of chalcopyrite to be larger (~ 36 T) than that of cubanite (~ 33 T). Vaughan & Tossell (1973) studied chalcopyrite in pellet form and powdered material, and observed a six-line spectrum with an isomer shift of 0.24 mm/s, a quadrupole splitting of 0.03 mm/s and a magnetic field of 34 T, along with a central peak having an isomer shift identical to that of the magnetic spectrum. On applying a pressure of 1.6 GPa, only faint traces of the magnetic spectrum remain, whereas the doublet broadens, with all other parameters remaining the same. The spectrum has been interpreted to be due to the presence of antiferromagnetically ordered high-spin Fe^{3+} in the tetrahedral sites

TABLE 1. POWDER X-RAY DIFFRACTION
OF SYNTHETIC CUBANITE, $CuFe_2S_3$

Position °2θ	d value Å	I in % ICDD card	I in % our data	Phase identification through ICDD card
29.1	3.06	100	81.8	Isocubanite
29.3	3.04		100	Isocubanite +
		100		Copper iron sulfide
29.9	2.98	30	4.7	Pyrrhotite
33.8	2.65	4	6.5	Isocubanite +
		80		Pyrrhotite
43.8	2.06	100	2.1	Pyrrhotite
48.5	1.87	63.8	34.3	Isocubanite +
		16.4		Copper iron sulfide
48.9	1.86	31.7	26.8	Copper iron sulfide
53.2	1.72	35.0	2.9	Pyrrhotite
57.7	1.6	25.7	13.3	Isocubanite +
				Copper iron sulfide
58.3	1.58	18.3	4.3	Copper iron sulfide
71.1	1.32	6.7	2.1	Isocubanite +
				Pyrrhotite
78.5	1.22	7.1	2.7	Isocubanite
79.3	1.21		2.3	Copper iron sulfide
91.2	1.07		2.4	Copper iron sulfide
98.1	1.02		1.5	Copper iron sulfide

Name	Composition and phase	ICDD ref. no.
Copper iron sulfide	Tetragonal $CuFeS_2$	03-065-1573
Pyrrhotite	Hexagonal $Fe_{1-x}S$	00-029-0724
Isocubanite	Cubic $CuFe_2S_3$	01-081-1378

Cubanite was synthesized by resistive heating up to 800°C, then slowly cooled to room temperature. Phase identification is given using ICDD cards. The standard intensity value is given for comparison. *I*: relative intensity.
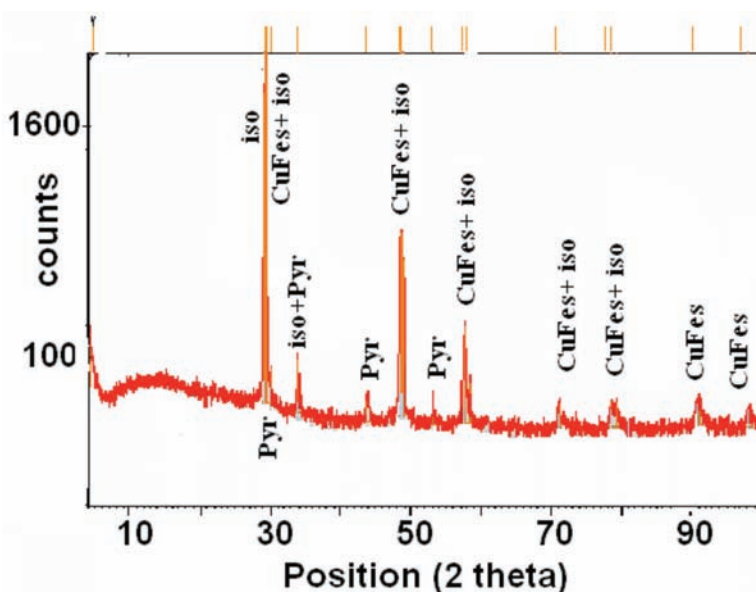
FIG. 1. Powder X-ray-diffraction pattern of cubanite, $CuFe_2S_3$, synthesized through resistive heating up to 800°C and slowly cooled to room temperature acquired using $CuK\alpha$ radiation. The marker on top of the figure indicates peaks corresponding to the various phases present (Table 1). Symbols: Iso: isocubanite, Po: pyrrhotite, CuFeS: tetragonal $CuFe_2S_3$.

of the sphalerite-type structure of chalcopyrite. Similar experiments on pyrrhotite samples also show a magnetic to nonmagnetic transformation at 1.6 GPa (Vaughan & Tossell 1973). The cations in cubanite are tetrahedrally coordinated to sulfur. Therefore, the isomer shift is an important parameter to give information regarding the coordination; 0.60 mm/s and 0.20 mm/s are the typical values of isomer shifts of high-spin tetrahedrally coordinated Fe^{2+} and Fe^{3+} ions, respectively (Hoggins & Steinfink 1976).

To confirm the presence of the orthorhombic structure, the room-temperature Mössbauer spectrum of the synthetic sample was analyzed in two ways. Firstly considering two magnetic sextets with fields of 33 T and 27 T, respectively and a nonmagnetic doublet with IS = 0.46 mm/s (Fig. 2a, Table 2), manifesting the average isomer shift corresponding to Fe^{2+} and Fe^{3+} ions in tetrahedral coordination. The sextet with a magnetic field of 33 T seems to be well defined and sharper, whereas the second sextet is wider and could not be resolved further. One can conclude, therefore, that the sextet with a magnetic field of 33 T corresponds to cubanite (orthorhombic), whereas the wider pattern with the 27 T field belongs to pyrrhotite and other sulfide components. The Mössbauer pattern of hexagonal pyrrhotite is reported with three sextets having magnetic hyperfine fields of 30 T, 27 T and 25 T, respectively (Ovanesyan *et al.* 1971).

Secondly, the pattern was analyzed as a single sextet with a magnetic field of 33 T (neglecting the contribution of pyrrhotite) and two singlets with isomer shifts of 0.24 and 0.78 mm/s. They match well the values of high-spin tetrahedrally coordinated Fe^{3+} and Fe^{2+}, respectively (Fig. 2b, Table 2). The wider line-widths imply a rapid fluctuation of electrons between Fe^{3+} and Fe^{2+} ions in the cubanite structure. For chalcopyrite, the isomer shift value would be equivalent to that of high-spin Fe^{3+} ion.

Room-temperature Mössbauer measurements on the sample of natural cubanite show a sextet with magnetic field of ~33 T and an isomer shift ~0.3 mm/s (Fig. 2c, Table 2). The presence of the single sextet instead of two superimposed magnetic sextets expected for Fe^{3+} and Fe^{2+} ions is attributed to the rapid exchange of electrons between them (Greenwood & Whitfield 1968).

High-pressure Mössbauer spectra of the synthesized cubanite at various pressures in the diamond-anvil cell (DAC) are shown in Figure 3a, and analyzed parameters are represented in Table 3. At 0.7 GPa, a magnetic sextet (with field ~33 T) and a broader unresolved doublet with a lower isomer shift are seen. The nonmagnetic component is wider and could not be resolved into Fe^{2+} and Fe^{3+} configurations. At 2.8 GPa and up to 3.6 GPa, the quadrupole split doublet could be resolved with the average isomer shift corresponding to the values
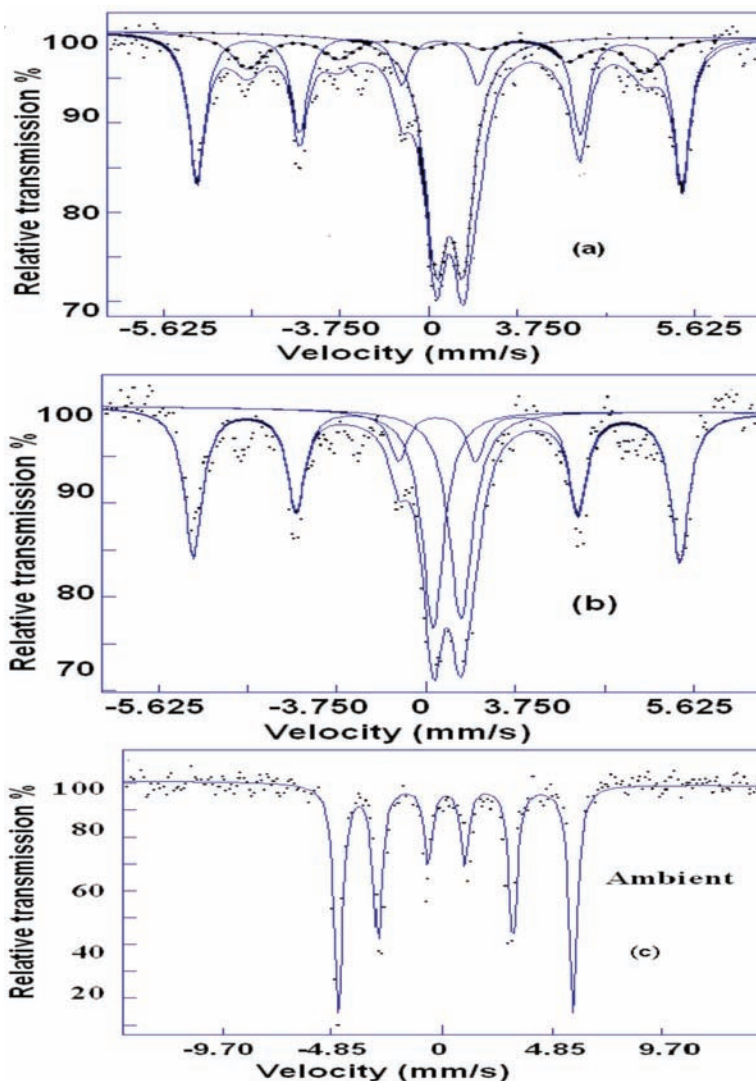
FIG. 2. Room-temperature Mössbauer spectra of samples outside DAC. (a) Synthetic cubanite analyzed as two sextets and a nonmagnetic doublet corresponding to cubanite, pyrrhotite and isocubanite, respectively. (b) Synthetic cubanite analyzed as one sextet corresponding to cubanite and two singlets representing Fe^{3+} and Fe^{2+} ions in tetrahedral coordination. (c) Natural cubanite analyzed as a sextet with a magnetic field of ~33T.

for Fe^{2+} and Fe^{3+} configurations, whereas the intensity of magnetic component has decreased. The sextet pattern of low intensity is visible (shown by a marker) and could be analyzed as a broad line spreading over the sextet with a lower isomer shift. At 4.2 GPa, the magnetic component vanishes completely, and only the nonmagnetic component can be fitted with two singlets having isomer shifts ~0.22 and 0.75 mm/s, attributed

to tetrahedrally coordinated Fe^{3+} and Fe^{2+} ions. The variation of isomer shift with pressure shows a decrease in isomer shift of one component, and then a sharp increase at 4.2 GPa where the magnetic component totally vanishes (Fig. 4). The new value corresponds to the tetrahedrally coordinated Fe^{3+} ion. The isomer shift of second component goes on increasing, corresponding to high-spin Fe^{2+}. Bulk magnetization, represented by

TABLE 2. MÖSSBAUER PARAMETERS OF SYNTHETIC CUBANITE MEASURED
AT ROOM TEMPERATURE, COMPARED TO THOSE OF NATURAL CUBANITE

Sample description	Components	Isomer shift* mm/s ±0.01	Quadrupole split mm/s ±0.01	Width mm/s ±0.01	Intensity % ±2	Magnetic hyperfine field Tesla ±0.1
Synthetic cubanite						
Analyzed with two sextets and one doublet	Magnetic sextet P1	0.23	-0.01	0.44	40	33.9
	Magnetic sextet P2	0.46	-0.16	0.91	19	27.1
	Nonmagnetic doublet	0.46	0.61	0.60	39	-
Analyzed with one sextet and two singlets	Magnetic sextet P1	0.17	-0.14	0.51	54	34.4
	Nonmagnetic singlets	0.24	-	0.32	22	-
		0.78	-	0.37	23	-
Natural cubanite						
	Magnetic sextet	0.38	0.46	0.22	100	32.8

The cubanite was synthesized through resistive heating up to 800°C, then slowly cooled to room temperature. The room-temperature Mössbauer spectra were analyzed in two different ways, as described in the text. The Mössbauer parameters of natural cubanite are given for comparison.

TABLE 3. MÖSSBAUER PARAMETERS OF SYNTHETIC AND
NATURAL CUBANITE MEASURED AT ROOM TEMPERATURE

Pressure GPa ±0.3	Isomer shift* mm/s ±0.01	Quadrupole splitting mm/s ±0.01	Line width mm/s ±0.01	Magnetic field tesla ±0.1	Popu- lation % ±2
Synthetic cubanite					
0.7	0.03	0.09	0.79	33.0	52.4
	0.37	0.00	2.07	-	47.5
2.8	-0.31	0	very wide	-	79.1
	0.51	0.58	0.30	-	20.9
3.6	-0.79	0	wide	-	60.9
	0.54	0.49	0.45	-	39.0
4.2	0.22	0	0.60	-	58.3
	0.75	0	0.34	-	41.7
5.6	0.21	0	0.58	-	53.4
	0.79	0.1	0.29	-	46.6
6.3	0.22	-	0.34	-	51.0
	0.76	-	0.22	-	48.9
Natural cubanite					
1.4	0.46	0.481	0.45	-	89.2
	0.69	-	0.39	-	10.8
3.6	0.16	-	0.23	-	38.5
	0.72	-	0.33	-	61.5
5.6	0.18	-	0.25	-	48.8
	0.78	-	0.23	-	51.2

We measured the room-temperature parameters for cubanite, $CuFe_2S_3$, both synthetic and natural, at various pressures in a diamond-anvil cell. Cubanite was synthesized through resistive heating up to 800°C and slowly cooled to room temperature. * With respect to α-Fe.

the magnetic hyperfine field, depends on the strength of the exchange interaction and the size of the magnetic moment through an increase in covalence. Careful inspection of the magnetic sextet up to 3.6 GPa does not show any change in the positions of the peaks. The covalence of the Fe–S bonds thus does not increase significantly at high pressures. The decrease in isomer shift might be caused by the increased efficiency of the charge-transfer process (McCammon 1995). We observed a sudden increment in the isomer-shift values between 3.6 to 4.2 GPa.

The high-pressure Mössbauer measurements carried out on the natural sample of cubanite under identical conditions (Fig. 3b) shows reminiscences of a magnetic contribution (marked with arrows) up to 3.6 GPa, which at 4.2 GPa transforms into a pure doublet. The values of the isomer shift of synthetic cubanite $Cu_{0.98}Fe_{2.02}O_{3.0}$ and the natural sample are found to be in close agreement (Table 3). Both samples show a nonmagnetic component at 4.2 GPa and higher pressures. Had the synthesized sample contained sulfides other than the orthorhombic phase (cubanite), especially chalcopyrite, the pressure-induced magnetic to nonmagnetic transformation would have occurred at ~1.6 GPa (Vaughan & Tossell 1973, Pitt & Vyas 1974, Hoggins & Steinfink 1976), not at 4.2 GPa, as observed in the present study. Moreover, the Mössbauer patterns after release of the pressure for synthesized $Cu_{0.98}Fe_{2.02}O_{3.0}$ and natural cubanite demonstrate an irreversible high-pressure phase transition for both natural and synthetic
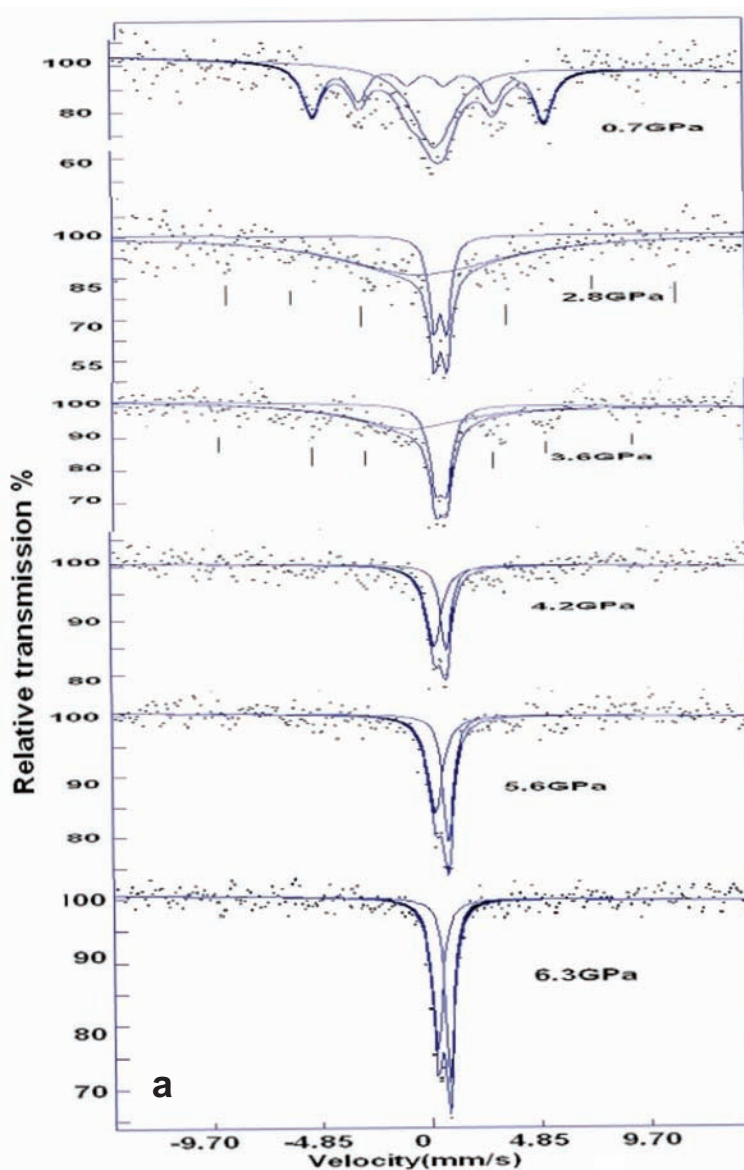
FIG. 3. (a) Room-temperature Mössbauer spectra of the cubanite $CuFe_2S_3$, synthesized through resistive heating up to 800°C and slowly cooled to room temperature, at various pressures (ambient, 0.7, 2.8, 3.6, 4.2, 5.6 and 6.3 Gpa).

$Cu_{0.98}Fe_{2.02}O_{3.0}$ (Fig. 5). Electrical resistivity measurements under pressure on the synthesized $Cu_{0.98}Fe_{2.02}O_{3.0}$ sample also confirm the pressure-induced phase transition, with a discontinuous decrease of electrical resistivity at ~3.8 GPa (Fig. 6), confirming that the sample consists of the pure cubanite phase. The value of the transition pressure suggested for cubanite is in the range of 3.6–5 GPa, whereas for chalcopyrite, the electrical resistivity transitions are observed at 2.8 GPa and ~6.7 GPa (McCammon *et al*. 1972, Pitt & Vyas 1974).
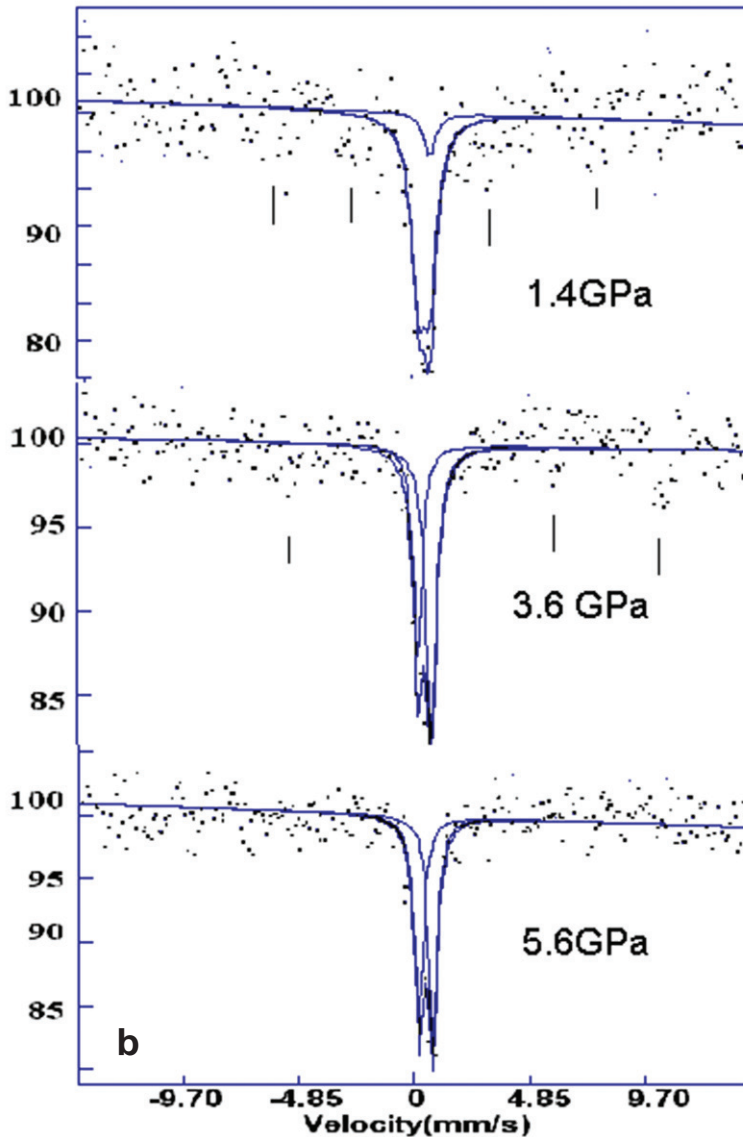
FIG. 3. (b) Room-temperature Mössbauer spectra of the natural cubanite at various pressures: 1.4, 3.6 and 5.6 GPa.

CONCLUSIONS

We have used ^{57}Fe Mössbauer spectroscopy, a sensitive technique, to determine the chemical characteristics of compounds containing iron, to successfully characterize the synthetic cubanite, $CuFe_2S_3$. The abundance of the orthorhombic phase seems strongly dependent on the conditions of the preparation. A slowly cooled sample shows more of the orthorhombic phase than

a quenched one. The identical crystal structures and subtle differences in XRD patterns of cubanite and chalcopyrite make their identification difficult using X-ray-diffraction technique. The Mössbauer parameters (magnetic hyperfine field and isomer shift) clearly demarcates these two sulfides. The high-pressure phase transition at ~4 GPa for the synthetic material, documented by Mössbauer spectroscopy and high-precision electrical resistivity studies, also confirm it to
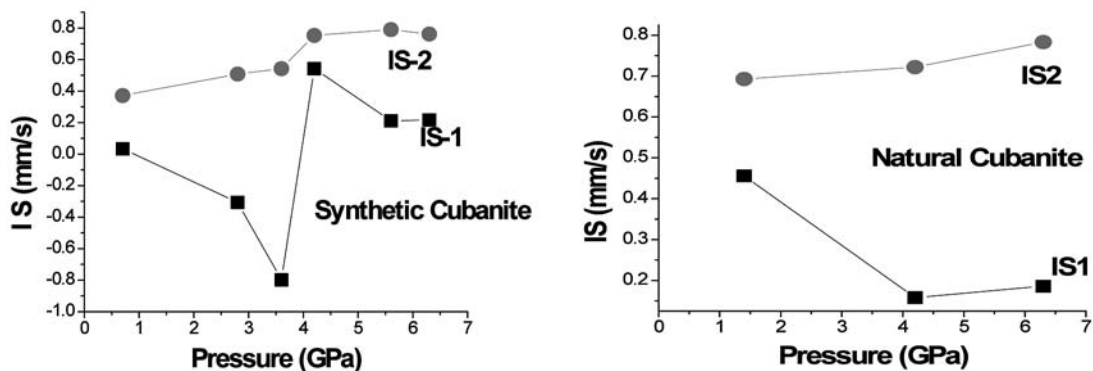
FIG. 4.   Variation of isomer shift with pressure of the cubanite $CuFe_2S_3$, synthesized through resistive heating up to 800°C and slowly cooled to room temperature, and natural cubanite.
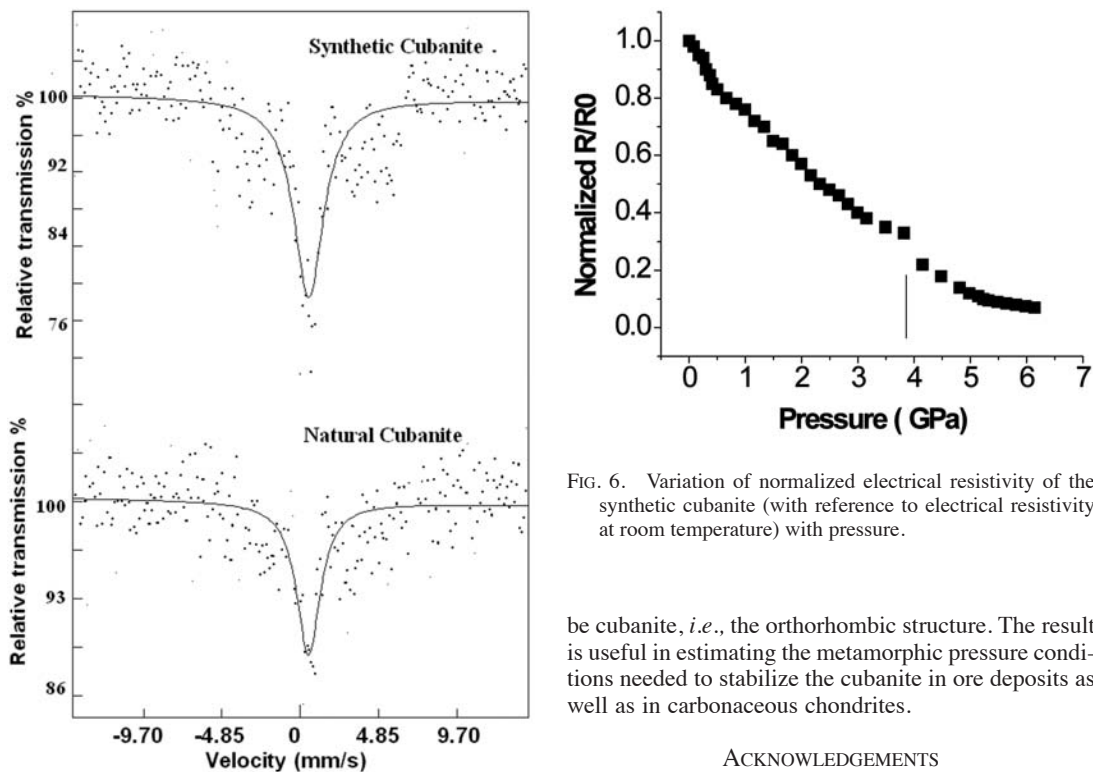

FIG. 5.   Room-temperature Mössbauer spectra of cubanite synthesized through resistive heating up to 800°C and slowly cooled to room temperature, and natural cubanite after release of pressure in DAC.

FIG. 6.   Variation of normalized electrical resistivity of the synthetic cubanite (with reference to electrical resistivity at room temperature) with pressure.

be cubanite, *i.e.*, the orthorhombic structure. The result is useful in estimating the metamorphic pressure conditions needed to stabilize the cubanite in ore deposits as well as in carbonaceous chondrites.

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