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A NOTE ON THE CRYSTAL STRUCTURE OF MARSHITE

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ABSTRACT

The crystal structure of untwinned marshite, CuI, a 6.6063(1) Å, V 222.9(1) Å^3, space group $F\bar{4}3m$, $Z = 2$, has been refined to an R index of 2.0% on the basis of 98 observed reflections measured with Mo$K\alpha$ X-radiation. Untwinned marshite is isostructural with sphalerite and with γ-CuI, and must have crystallized below 367°C, the temperature of the β-CuI → CuI transition.

Keywords: marshite, crystal structure, sphalerite.

SOMMAIRE

La structure d'un cristal non maclé de marshite, CuI, a 6.6063(1) Å, V 222.9(1) Å^3, groupe spatial $F\bar{4}3m$, $Z = 2$, a été affiné jusqu'à un résidu R de 2.0% en utilisant 98 réflexions observées, mesurées avec rayonnement Mo$K\alpha$. La marshite non maclée a la même structure que la sphalérite et la forme γ de CuI, et doit donc avoir cristallisé à moins de 367°C, température de la transition β-CuI → CuI.

(Traduit par la Rédaction)

Mots-clés: marshite, structure cristalline, sphalérite.

INTRODUCTION

Marshite, CuI, occurs as pale pink to brownish red tetrahedra. Where fresh, it is colorless to pale shades of yellow, but becomes pink to red on exposure. It is found at Broken Hill, New South Wales, Australia, where it is associated with "wad", cerussite, cuprite, native copper and limonite, and at Chuquicamata, Chile, where it is associated with atacamite, leightonite and gypsum. Marshite was originally reported as being tetragonal, but was later recognized as cubic.

The temperature-dependent phase transitions in CuI have been investigated extensively, and earlier work is summarized by Yude *et al.* (1990). At room temperature, CuI is isostructural with sphalerite (ZnS, $F\bar{4}3m$). At 367°C, CuI becomes hexagonal ($P\bar{6}m2$), and at 407°C, it becomes cubic again [$Fm3m$, although $F\bar{4}3m$ was suggested by Bührer & Hälg (1977)]. As the synthetic system is very well characterized, we thought it worthwhile to test the low-temperature origin of marshite.

EXPERIMENTAL

The material used in this work is from Broken Hill, New South Wales, Australia, and was obtained from the Royal Ontario Museum, sample number M12531. It is associated with spessartine, another pale pink cubic mineral. Most of the marshite is moderate pink-to-orange, and appears twinned (on {111}); a small fraction of marshite is translucent yellow-to-pink and is not twinned. A cleavage plate [indexed as $(01\bar{1})$] was used to collect the X-ray intensity data on a Nicolet $R3m$ instrument according to the procedure of Hawthorne & Groat (1985). A psi-scan absorption correction reduced R(azimuthal) from 18.4 to 3.3%. A total of 98 reflections was collected over two asymmetric units, and all reflections were observed at the 5σ level. The structure refined to an R index of 2.0% for 47 unique observed (5σ) reflections and four variable parameters. Cell dimensions and information pertinent to data collection and refinement are given in Table 1, and final atom parameters and

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TABLE 1. SINGLE-CRYSTAL X-RAY DIFFRACTION DATA-COLLECTION AND REFINEMENT INFORMATION FOR MARSHITE

a (Å)	6.063(1)	Crystal size (mm)	0.22 x 0.38 x 0.09
V (Å^3)	222.9(1)	Radiation/Mono.	Mo$K\alpha$
		Total no. $\|F\|$	98
Space group	$F\bar{4}3m$	No. $\|F_o\|$	47
		R(azimuthal) %	18.4 → 3.3
Cell content	4[CuI]	R(observed) %	2.0
		wR(observed) %	2.0

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$; $wR = [\Sigma w(|F_o|-|F_c|)^2/\Sigma F_o^2]^{½}$, $w = 1$

TABLE 2. FINAL ATOM PARAMETERS, SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR MARSHITE

	x	y	z	*U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Cu	1/4	1/4	1/4	336(8)	336(8)	336(8)	0	0	0	336(5)
I	0	0	0	194(5)	194(5)	194(5)	0	0	0	194(3)

Cu–I	x4	2.625(1)	I–Cu–I	109.5(1)
I–Cu	x4	2.625(1)	Cu–I–Cu	109.5(1)

*U x 10^4

selected bond-lengths and angles are given in Table 2. Structure factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

DISCUSSION

The results of the current refinement show marshite to have the space group $F\bar{4}3m$ and to be isostructural with sphalerite. Marshite is thus γ-CuI in the nomenclature of Yude *et al.* (1990). There is no evidence for any disorder of the Cu and I atoms, as occurs for high-temperature cubic α-CuI. The powder neutron-diffraction structure-refinement of Yude *et al.* (1990) gives the isotropic-displacement factors for the *Cu* and *I* sites as 2.20(8) and 1.41(1) Å^2, respectively. Conversions of the corresponding U_{eq} values (Table 2) to B-values (*via* multiplication by $8\pi^2$) gives 2.65(4) and 1.53(2) Å^2, respectively. Thus the X-ray values are somewhat higher than the neutron values, as expected: neutron scattering occurs effectively from a point source, and the displacement parameters represent true thermal and zero-point motion (presuming that no positional disorder is present), whereas X-ray scattering occurs from the much larger volume of the electron density. Moreover, the relative sizes of the two displacement factors are similar in each structure, suggesting that there is no Cu–I disorder at the two sites. Thus untwinned marshite must crystallize below the β-CuI → γ-CuI transition temperature of 367°C.

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