

The crystal structure of kiddcreekite solved using micro X-ray diffraction and the *EPCryst* program

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ABSTRACT

Abundant kiddcreekite grains were identified in the Zijinshan Cu-Au epithermal deposit in Fujian Province, China. The mineral occurs as polycrystalline grains, 5–300 µm in size, associated with colusite, enargite, stannoidite, mawsonite, vinciennite, hemusite, tennantite and wolframite in a predominantly covellite ore. Based on electron microprobe analysis, the empirical formula of the kiddcreekite is $\text{Cu}_{6.2}\text{Sn}_{0.97}\text{W}_{0.95}\text{S}_{7.83}$, without significant Se or Te contents. The crystal structure of kiddcreekite was solved using the direct-space method (*EPCryst*) from laboratory micro X-ray diffraction (μXRD) data and refined by the Rietveld method. The R values of the final Rietveld refinement were $R_p = 9.06\%$, $R_{wp} = 8.31\%$, $R_B = 3.16$ and $R_F = 2.17\%$. Kiddcreekite has a cubic structure, space group $F\bar{4}3m$ and lattice parameter $a = 10.8178(3) \text{ \AA}$ ($Z = 4$, $V = 1265.95(6) \text{ \AA}^3$). In the unit cell, W, Sn and Cu atoms occupy the $4a$, $4c$ and $24f$ Wyckoff positions, respectively, and S atoms occupy two sets of $16e$ Wyckoff positions. The structure of kiddcreekite consists of stacked double MeS_4 layers (giving a W–Sn–Cu tier and a Cu–vacancy tier) as in the sphalerite substructure. This study also demonstrates the possibility of using laboratory μXRD data coupled with the direct-space method to solve inorganic structures in cases where samples are too small for conventional powder and single-crystal diffraction.

KEYWORDS: kiddcreekite, crystal structure, micro X-ray diffraction, *EPCryst*, Zijinshan Cu-Au deposit.

Introduction

KIDDCREEKITE, ideally Cu_6SnWS_8 , was first discovered in bornite-rich ore in the Kidd Creek mine at Timmins, Ontario, Canada, and identified subsequently in the Campbell orebody at Bisbee, Arizona, USA (Thorpe *et al.*, 1976; Harris *et al.*, 1984). The mineral occurred as irregular fine grains associated with scheelite, clausenthalite, tennantite and tungstenite at the Kidd Creek mine and with pyrite, colusite, stuetzite and altaite at the Bisbee mine. In China, this mineral was first found in the Hongshan porphyry-copper deposit

in Jiangxi Province (Zhang *et al.*, 1996) and then in the Bitian epithermal Au-Ag deposit in Fujian Province (Chen *et al.*, 1998). The intimately associated minerals in the Hongshan samples were colusite, bornite, chalcocite and tennantite, while in the Bitian deposit, the associated minerals were mawsonite and chalcopyrite. Electron microprobe analysis suggested that kiddcreekite had the ideal formula Cu_6SnWS_8 , with traces of Se, Te and Fe (Harris *et al.*, 1984; Chen *et al.*, 1998). The lattice parameters of kiddcreekite were first investigated by indexing a Gandolfi powder pattern with reference to hemusite, which suggested a cubic F lattice of an unknown space group with $a = 10.856(2) \text{ \AA}$ and $Z = 4$ (Harris *et al.*, 1984). Hemusite, the molybdenum analogue of kiddcreekite, ideal

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formula $\text{Cu}_6\text{SnMoS}_8$, was first found in the Chelopech deposit in Bulgaria and is a cubic mineral with $a = 10.821 \text{ \AA}$ (Terziev, 1971; Shimizu *et al.*, 1988, 1991). However, the powder X-ray data for these two minerals were obtained from small amounts of polycrystalline, multi-component, impure material. The absence of suitably large single crystals prevented crystal-structure determination by single-crystal XRD methods, and thus their structures have remained unclear (Putz *et al.*, 2006).

It is extremely difficult to find crystals suitable for single-crystal X-ray diffraction experiments. Also, no attempt to synthesize kiddcreekite has been successful, to our knowledge. Thus, in this present work, an alternative method is presented for solving the crystal structure of kiddcreekite by laboratory powder μXRD combined with the direct-space and Rietveld methods.

Occurrence of kiddcreekite

The Zijinshan mine field is a porphyry-epithermal Cu-Au-Mo-Ag mineralization system located in the southwestern part of the Fujian Province of

China (Zhang *et al.*, 2003). The mineral field consists of the Zijinshan high-sulfidation epithermal Cu-Au deposit, the Luoboling porphyry Cu-Mo deposit, the Yueyang low-sulfidation epithermal Au-Ag-Cu deposit (Bitian), the Longjiangting mesothermal Cu deposit and the Wuziqilong mesothermal Cu deposit. The Zijinshan Au-Cu deposit is the first recognized example of a high-sulfidation epithermal deposit of Cretaceous age in mainland China and is characterized by the occurrence of assemblages of alunite, digenite, covellite and enargite/luzonite (Zhang *et al.*, 1991; So *et al.*, 1998). Recently, grains of kiddcreekite were identified in the Zijinshan Cu-Au epithermal deposit (Liu *et al.*, 2012). Kiddcreekite in the Zijinshan mine occurs mostly as subhedral to irregular grains in covellite-dominated ore with a maximum grain size of $300 \mu\text{m}$ (Fig. 1c). This ore is characterized by a complex mineral association of covellite, colusite, enargite, stannoidite and alunite in the upper level of the ore body, in which kiddcreekite is cut by euhedral stannoidite (Fig. 1d). In the lower level of the drilled sections, kiddcreekite is associated with covellite, mawsonite, vinciennite, hemusite,

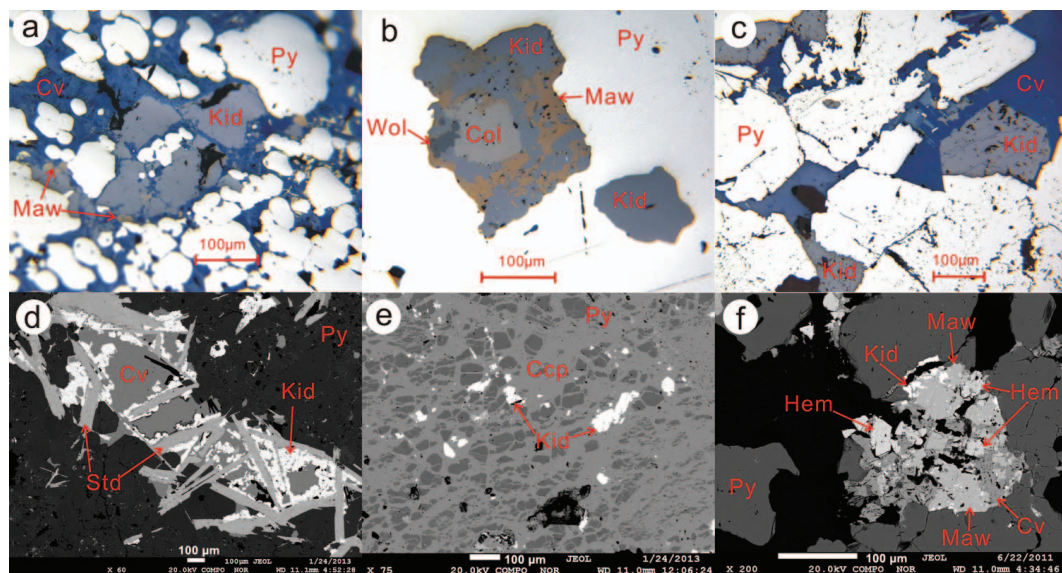


FIG. 1. (a) Anhedrall kiddcreekite grains in covellite-dominated ore in the lower-level of drilled sections (reflected light). (b) Kiddcreekite and colusite replaced by mawsonite and wolframite (reflected light). (c) Subhedral kiddcreekite in upper-level covellite-dominated ore (reflected light). (d) Kiddcreekite grains cut by euhedral stannoidite (BSE, backscattered electron image). (e) Anhedrall kiddcreekite grains in chalcopyrite-rich ore (BSE image); (f) Kiddcreekite associated with hemusite and replaced by covellite and mawsonite (BSE image). Key: Kid: kiddcreekite; Maw: mawsonite; Wol: wolframite; Cv: covellite; Py: pyrite; Hem: hemusite; Std: stannoidite; Ccp: chalcopyrite.

tennantite and wolframite, and replaced by mawsonite, wolframite and covellite (Fig. 1*a,b,f*). In addition, small grains of kiddcreekite (<50 µm) occur in bornite-rich ore in the adjacent intermediate epithermal deposit (Longjiangting mine), associated with chalcopyrite, pyrite and bornite (Fig. 1*e*). The large kiddcreekite grains from the upper covellite-dominated ore were chosen for crystal-structure determination.

Chemical composition

Quantitative chemical data for kiddcreekite and its associated minerals were obtained with an electron microprobe (JEO-JXA 8230) installed at Fuzhou University. The major elements were determined at 20 kV accelerating voltage and 10 nA beam current, with an estimated beam diameter of 5 µm and a counting time of 20 s. The following standards and spectroscopic lines were used: Ag-pure element (Ag*Lα*), W-pure element (W*Mα*), Sn-pure element (Sn*Lβ*), V-pure element (V*Kα*), pyrite (Fe*Kα*, S*Kα*), chalcopyrite (Cu*Kα*), sphalerite (Zn*Kα*), stibnite (Sb*Lα*), synthetic GaAs (As*Lα*), synthetic GeS (Ge*Lα*), synthetic Bi₂S₃ (Bi*Mβ*) and synthetic CdSe (Cd*Lβ*, Se*Lα*).

The crystal grains of kiddcreekite were found to be homogeneous within analytical error. The average chemical composition of kiddcreekite (36 points), together with the atomic ratios, is shown in Table 1. On the basis of 16 atoms, the

empirical formula of kiddcreekite was established as Cu_{6.20}Sn_{0.97}W_{0.95}S_{7.83}, with trace amounts of Fe and V. Small amounts of Se and Te were reported in kiddcreekite by a previous study (Harris *et al.*, 1984; Chen *et al.*, 1998); however, this present study found that the characteristic X-ray lines Se*Kα*₁ and Te*Lα*₁ overlapped with higher-order lines W*Mz*₁ and Sn*Lβ*₃. When lines without interference were chosen for quantitative analysis, the results suggested an absence of significant Se and Te content in kiddcreekite.

Experimental methods

Crystal fragments (>50 µm) of kiddcreekite were extracted from thin slices and polished sections, and several fragments were measured with a single-crystal X-ray diffractometer (Bruker SMART APEX-CCD X) installed at the China University of Geoscience (Beijing); however, no satisfactory results were obtained due to the lack of suitable single crystals. Consequently, three large crystal fragments of kiddcreekite (>100 µm) were selected for powder µXRD. The three grains were crushed into powders (1–2 µm), concentrated in an area 300 µm × 300 µm (~50 µg) on double-sided tape and then mounted on a zero-background sample stage.

The powders were analysed with an X-ray micro-diffractometer (Rigaku D/MAX-RAPID-R)

TABLE 1. Average electron microprobe analyses (36 points) and atomic ratios for kiddcreekite on the basis of 16 atoms.

	Ave (wt.%)	Max (wt.%)	Min (wt.%)	S.D	Atomic ratios
Ge	0.01	0.03	0.00	0.01	0.00
As	0.01	0.03	0.00	0.01	0.00
W	18.64	18.84	18.53	0.13	0.95
S	26.69	26.79	26.37	0.18	7.83
Bi	0.02	0.02	0.01	0.00	0.00
Ag	0.02	0.03	0.01	0.01	0.00
Cd	0.03	0.04	0.01	0.01	0.00
Sn	12.42	12.59	12.28	0.11	0.97
V	0.03	0.06	0.01	0.02	0.01
Fe	0.04	0.09	0.02	0.03	0.02
Cu	42.09	42.30	41.85	0.16	6.20
Zn	0.02	0.05	0.01	0.01	0.00
Sb	0.02	0.06	0.00	0.02	0.00
Total	100.05	100.34	99.51	0.32	16.00

S.D.: standard deviation

installed at Central South University and equipped with a curved image plate detector using graphite-monochromatized rotating anode $\text{CuK}\alpha$ radiation (18 kW). The DmaX Rapid II Microdiffraction system utilizes a finely collimated X-ray beam (with pinhole collimators 800 to 30 μm in diameter) aligned precisely with a CCD camera directed at the area to be analysed with the resultant diffraction signal collected on a 46.5 cm $\times$ 25.6 cm curved image plate detector with exposure times ranging between 5 min and several hours. The diffraction system was configured for the collection of monochromatic two-dimensional Debye-ring images in reflection mode, enabling the collection of a powder pattern simply by sample in-plane rotation. Specimens are mounted on a manually adjusted X-Y-Z stage, with each axis adjustable over a ± 5 mm range (a 30 mm thick sample can be handled). The operating conditions were $\text{CuK}\alpha$ X-rays (40 kV, 250 mA), 50 μm collimator with $\omega = 10^\circ$, χ (tilt)

axis fixed at 45° , 2θ interval of $10\text{--}160^\circ$, exposure time of 8 h.

Data collection and reduction

The diffraction data were collected using Rigaku *RapidXRD* software, which also processed the 2D image plate data, producing a digital Debye-ring image of the exact area from which data were collected and saved with reference and documentation information. Rigaku *2DP* software was then used to process digitally the 2D diffraction data into a standard 2θ diffraction pattern vs. intensity dataset that can be analysed with standard and specialized powder diffraction analysis software (Fig. 2). The diffraction patterns showed a small amount of covellite in the sample (Figs 2 and 3). Diffraction data reduction and indexing were performed with the *PowderX* program (Dong, 1999). The non-symmetric microabsorption effect on the diffraction intensity data was corrected

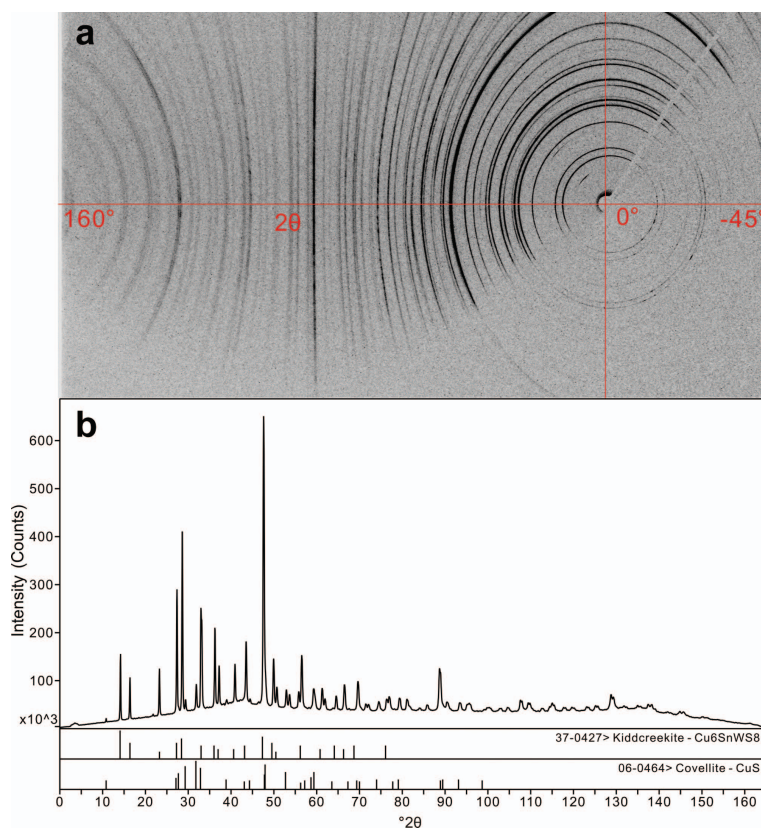


FIG. 2. (a) 2-D Debye-ring image of kiddcreekite. (b) 2-D image of kiddcreekite converted into a 2θ -I diffraction pattern plot with a small amount of covellite.

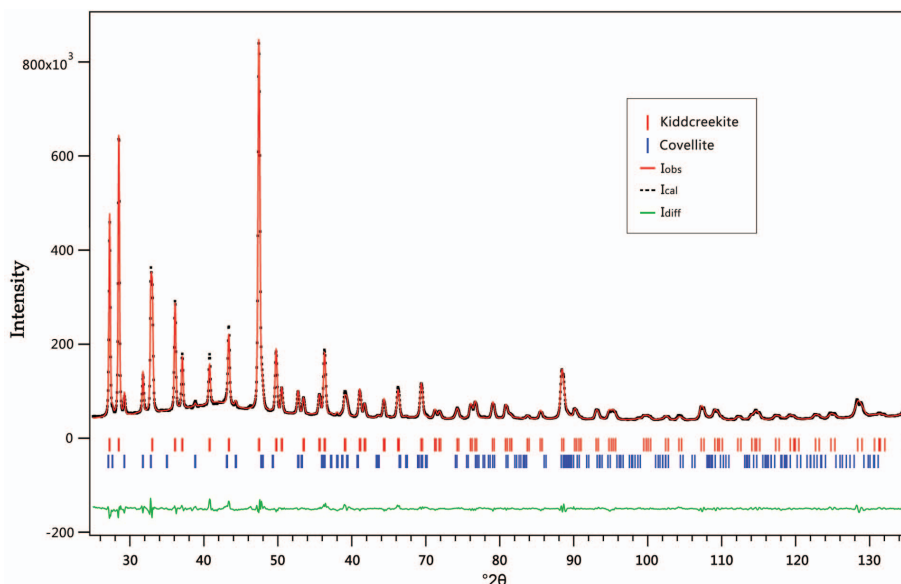


FIG. 3. Experimental and calculated diffraction patterns from Rietveld refinement for the kiddcreekite sample with a small amount of covellite impurity. The positions of the Bragg reflections are indicated by vertical bars ($\downarrow$). Red bars are reflection positions of kiddcreekite; green bars are for covellite. The observed, I_{obs} (black spots), calculated, I_{cal} (red curve), and difference, I_{diff} (green line), diffraction patterns are shown.

using the equation given by Collazo *et al.* (1997). After subtraction of the covellite impurity, indexing suggested an F -centred cubic cell with $a = 10.8178(3) \text{ \AA}$, $V = 1265.95(6) \text{ \AA}^3$, $Z = 4$ and a calculated density, with ideal formula, of 4.934 g cm^{-3} . From the observed extinction conditions (hkl : $h + k, h + l, k + l = 2n$; $0kl$: $k = 2n, l = 2n$; hhl : $h + l = 2n$; $00l$: $l = 2n$), five space groups are possible for kiddcreekite ($F23$, $Fm\bar{3}$, $F432$, $F43m$ and $Fm\bar{3}m$).

Structure solution and refinement

Structure determination from powder diffraction data (SDPD) has developed over the last 30 years from an art to an almost routine technique and is a powerful alternative when samples are available as only crystalline powders (Le Bail *et al.*, 1988). One of the most important advances with SDPD is the development of the direct-space strategy. The program *EPCryst* (Deng and Dong., 2011) is one of the latest tools that can be used to solve a crystal structure using the direct-space method. The program *EPCryst* first applies an algorithm to generate a full set of trial structure models (TSMs) by enumerating all possible equivalent position combinations (EPCs) based on the unit-

cell content and space-group information (Deng and Dong, 2011). Then, the crystal structure can be solved by global optimization based on grid search or simulated annealing.

The program *Fullprof* was used initially to extract diffraction intensities for kiddcreekite by whole-pattern profile fitting, which considered the covellite impurity as the second phase. The program *EPCryst* then used the diffraction data obtained for kiddcreekite as the input to solve the crystal structure. After several trial calculations with the five possible space groups, space group $F43m$ was chosen because it gave the best intensity fit (minimal R_{Bragg}). The equivalent position combinations were also determined. In the unit cell, W, Sn and Cu atoms occupy the $4a$, $4c$ and $24f$ Wyckoff positions, respectively, and S atoms occupy two sets of $16e$ Wyckoff positions. There are only three variable structural parameters: one for the Cu atoms at $24f(x,0,0)$ positions and two for the two sets of S atoms at $16e$ positions (x,x,x). Approximate positional parameters were obtained by the grid-search method with *EPCryst* and these parameters were refined using the Rietveld method with *Fullprof*. The R values of the final Rietveld refinement are $R_p = 9.06\%$, $R_{wp} = 8.31\%$, $R_B = 3.16$ and $R_F = 2.17\%$. The results of the Rietveld

TABLE 2. Refinement details for kiddcreekite.

Formula	CuSnWS ₆
Crystal system	Cubic
Space Group	F $\bar{4}3m$
Cell parameter (<i>a</i>)(Å)	10.8178(3)
Volume (Å ³)	1265.95(6)
Z	4
Density (g cm ⁻³)	4.934
Step size (°)	0.045
Wavelength	1.5406
2θ of data collection (°)	10–160°
2θ of refinement (°)	25–135°
<i>R_p</i>	9.06%
<i>R_{wp}</i>	8.31%
<i>R_B</i>	3.16%
<i>R_F</i>	2.17%

refinement are given in Table 2 and the atom coordinates in Table 3. The final Rietveld refinement plot is shown in Fig. 3.

Structure description

The crystal structure of kiddcreekite contains three different types of metal–sulfur (Me–S) coordination tetrahedra, CuS₄, WS₄ and SnS₄ (Fig. 4). According to the classification of Makovicky (2006), it has an adamantine structure with tetrahedral coordination of cations and anions. There are two distinct sulfur sites (S1 and S2) in the structure of kiddcreekite. Both SnS₄ and WS₄ form tetrahedra in which the Sn and W atoms are each coordinated by four S1 and S2 atoms, respectively. In the CuS₄ tetrahedra, each Cu atom is coordinated by two S1 and two S2 atoms. Kiddcreekite is a derivative of a tetrahedral MeS structure with a stacking of double layers along the <111> direction, according to the sphalerite principle (Fig. 4). These double layers display a cubic stacking of component layers

inside them, in the direction of tetrahedron apices; the top layers are composed of Cu tetrahedra and octahedral cavities, and the second layers are composed of Cu, Sn and W tetrahedra (Fig. 4). In the second layer, an inverted W tetrahedron shares edges with three Cu tetrahedra in the same layer, organized around a common vertex, and with three Cu tetrahedra of the first layer above them. In contrast, the Sn tetrahedra only share vertices with surrounding Cu tetrahedra. Along the <111> direction, a cluster of six Cu tetrahedra that share edges with the central W tetrahedron appears as a ‘supertetrahedron’ with Cu tetrahedra forming each face and the Sn tetrahedra in four corners (Fig. 4). Thus, the structure of kiddcreekite is a three-dimensional stacking of W-based ‘super-tetrahedra’ with common Sn vertices.

Selected Me–S bond distances and angles for kiddcreekite are presented in Table 4 and Fig. 4b. Because of the mutual interaction from the highly charged small W⁶⁺ cations and highly charged large Sn⁴⁺ cations, the Cu tetrahedra are slightly irregular, with two different Cu–S distances and bond angles. The Cu–S distances to the S1 shared with the Sn tetrahedron are 2.308 Å and the subtended S1–Cu–S1 angles are close to 102.2°, whereas the Cu–S distances to the S2 shared with the W tetrahedron are 2.325 Å and the bond angle of S2–Cu–S2 are close to 108.9°. The Sn–S1 distances are 2.485 Å, with S1–Sn–S1 bond angles close to 109.47°. The W–S2 distances are 2.316 Å, with S2–W–S2 bond angles close to 109.47°. In the current structure, the formation of supertetrahedra is a consequence of the strong drive of W to form a short Me–Me interaction. The metals Cu and W form a regular octahedron with Cu–W distances equal to 2.689 Å and the bond angle close to 90°.

Furthermore, the essential crystal-structure information (space group *F* $\bar{4}3m$ and atomic positions) refined for kiddcreekite (Cu₆SnWS₈) can be used for the isostructural mineral hemusite

TABLE 3. Fractional atom coordinates for kiddcreekite.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (Å ²)
Cu	0.2486(2)	0.0	0.0	0.98
W	0.0	0.0	0.0	0.44
Sn	0.25	0.25	0.25	0.31
S1	0.3826(3)	0.3826(3)	0.3826(3)	0.81
S2	0.8764(3)	0.8764(3)	0.8764(3)	0.11

CRYSTAL STRUCTURE OF KIDDCREEKITE

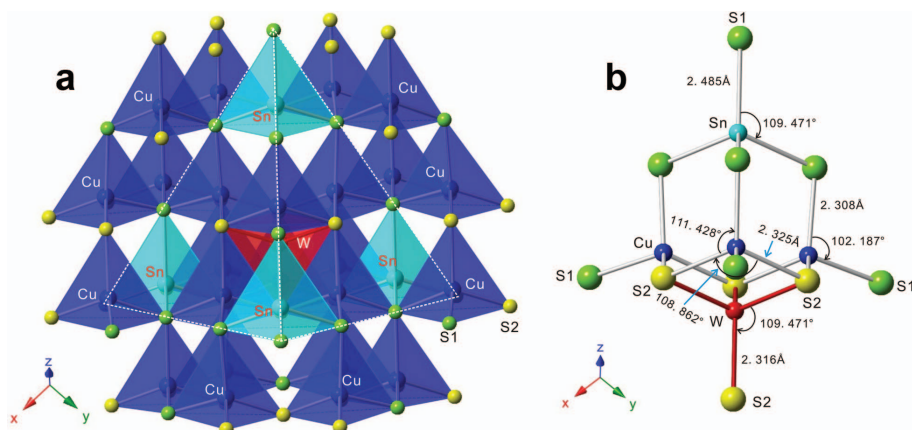


FIG. 4. The crystal structure of kiddyckite in a polyhedral representation. (a) A fragment of two layers stacking along (111) with W-based ‘supertetrahedra’. (b) Me–S coordination tetrahedra with interatomic distances and angles.

(Cu₆SnMoS₈) with lattice parameter $a = 10.821 \text{ \AA}$ (Terziev, 1971). A dataset indexed more recently of hemusite has the lattice parameter $a = 10.800 \text{ \AA}$ (Shimizu *et al.*, 1988), which is slightly smaller than for kiddyckite ($a = 10.818 \text{ \AA}$). Due to the similar electronic configurations, ionic radii and valence states of Mo⁶⁺ (0.41 Å) and W⁶⁺ (0.42 Å) (Shannon, 1976), kiddyckite and hemusite crystallize in the same space group and are isostructural with small differences in cell parameters. The substitution between Mo⁶⁺ and W⁶⁺ also causes a complete solid-solution series like that, for example, from scheelite (CaWO₄) to powellite (CaMoO₄) (Tyson *et al.*, 1988). Both endmembers in this case crystallize in the same space group ($I4_1/a$) and are isostructural (Hazen *et al.*, 1985).

In contrast, the mineral catamarcaite (Cu₆GeWS₈) which is related chemically to kiddyckite and hemusite, has a different structure with space group $P6_3mc$, and consists of a double layer of packets of ABAC type, stacking along the

c axis to give a combined $hchc...$ sequence. The two-layer packets with cubic layer stacking are separated invariably by a boundary based on the hexagonal stacking of tetrahedral layers, and with the [001] vertex of the W-based ‘supertetrahedron’ truncated (Putz *et al.*, 2006). The different crystallography of kiddyckite and catamarcaite is due, apparently, to differences in the Me⁴⁺ tetrahedra; the radius of Sn⁴⁺ (0.55 Å) is appreciably larger than that of Ge⁴⁺ (0.39 Å) (Putz *et al.*, 2006; Makovicky, 2006).

Conclusions and discussion

Kiddyckite has space group $F\bar{4}3m$ and the F -centred cubic structure is visualized as a stacking of double layers (W–Sn–Cu tier and Cu–vacancy tier) according to the sphalerite principle. The structure of kiddyckite refined in this present study is close to the structure model inferred from the structure of catamarcaite by Putz *et al.* (2006). The essential crystal structural

TABLE 4. Selected bond lengths and angles for kiddyckite.

Atom	Bonding atoms	Bond length (Å)	Bond angle (°)
Cu	2S1	2.308 ± 0.004	102.2
Cu	2S2	2.325 ± 0.004	108.9
Cu	S1–S2		111.4
W	S2	2.316 ± 0.003	109.5
Sn	S1	2.485 ± 0.003	109.5

information refined for kiddcreekite (Cu_6SnWS_8) can be used for the isostructural mineral hemusite ($\text{Cu}_6\text{SnMoS}_8$). The different crystallography of kiddcreekite and catamarcaite is caused apparently by the tetrahedral radius of Sn^{4+} being larger than that of Ge^{4+} (Putz *et al.*, 2006; Makovicky, 2006).

A wide range of important crystalline solids cannot be prepared in the form of single crystals of suitable size and quality for structural determination by conventional single-crystal XRD methods. In such cases, when only polycrystalline powders of a material are available, it is instead necessary to tackle structure determination using powder X-ray data (Harris and Cheung, 2004). Micro-diffraction is well adapted to phase identification, but it can also be used for structure determination. The laboratory μXRD used in this present study produces high-quality diffraction data for tiny samples that are perfectly adequate for structure solution. Consequently, the crystal structure of kiddcreekite was solved successfully. Furthermore, this study also demonstrates the possibility of laboratory μXRD data coupled with the direct-space method for solving inorganic structures (especially for those with high symmetry) in cases of samples too small for conventional powder and single-crystal diffraction.

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CRYSTAL STRUCTURE OF KIDDCREEKITE

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