Refinement of the crystal structure of dipotassium tricadmium(II) tetraselenide, $K_2Cd_3Se_4$

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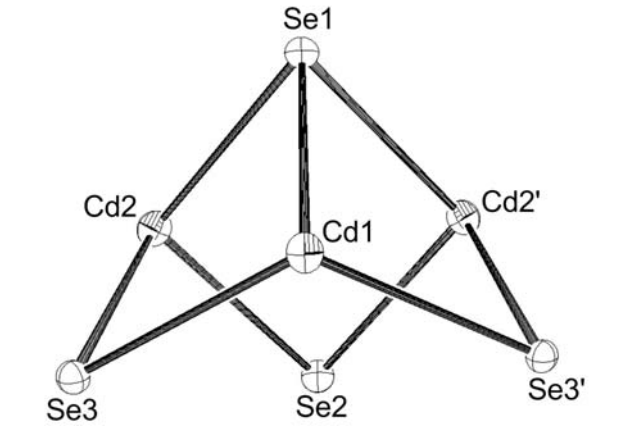

Abstract

$Cd_3K_2Se_4$, orthorhombic, *Pnma* (no. 62), a = 14.312(4) Å, b = 10.604(3) Å, c = 6.839(2) Å, V = 1037.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.027, $wR_{ref}(F^2)$ = 0.065, T = 290 K.

Source of material

$CdCl_2$ (0.020 g, 0.11 mmol) and K_2Se_2 (0.078 g, 0.33 mmol) were charged to a Pyrex tube with diameter of 9 mm under an argon atmosphere, and about 0.5 ml ethylenediamine was added as a solvent. While the solvent was being frozen, the Pyrex tube was evacuated (about 2.0×10^{-3} torr) and sealed with the use of a flame. The sealed tube was placed in a furnace and heated at 160 °C for 24 h, then cooled to room temperature. Yellow crystals were isolated and washed with diethyl ether several times (36 % yield, based on $CdCl_2$ used). The compound is insoluble in water and common organic solvents.

Discussion

Ternary low-dimensional cadmium chalcogenides, $A_2Cd_3Q_4$ (A = alkali metal; Q = S, Se, Te) were explored in particular to achieve the dimensional reduction in II-VI materials [1-2]. Dimensional reduction of CdQ by the incorporation of A_2Q resembles size reduction of CdQ particles into the nanometer range [2]. Nanometer-sized CdQ materials have attracted extensive research efforts last two decades and are still garnering a lot of attention [3-5]. The title compound is the first example of A/Cd/Q (A = alkali metal; Q = S, Se, Te) ternary compounds to be prepared by a hydro (or solvo) thermal method. Until now, only the lattice parameters for $K_2Cd_3Se_4$ were reported, no complete structure determination was made [1].

The title crystal structure is composed of two-dimensional anionic layers $(Cd_3Se_4)_n^{2n-}$ and charge-balancing cations K^+, representing the same structure as the other analogues of $A_2Cd_3Q_4$ (A = K, Q = S, Te; A = Rb, Q = S, Se) [1]. Other structurally characterized $A_2Cd_3Q_4$ compounds are $Rb_2Cd_3Te_4$ and $Cs_2Cd_3Te_4$, which crystallize in $K_2Zn_3O_4$ type and $Cs_2Zn_3S_4$ type, respectively [6]. The $(Cd_3Se_4)_n^{2n-}$ layer spreads out along the crystallographic b and c axes, with the repeating unit of a $Cd_3Se_4^{2-}$ cluster (figure, top). The $Cd_3Se_4^{2-}$ cluster is geometrically shaped as a truncated cube with one corner missing and consists of three Cd(II) metal ions and four Se^{2-} monoselenide ligands. In the truncated cube cluster, one Se atom could be regarded to be sitting on the apex and coordinating to the three Cd metal atoms in the puckered 6-member ring Cd_3Se_3. Three-coordinated Cd atoms and two-coordinated Se atoms in the $Cd_3Se_4^{2-}$ cluster are connected to Se and Cd atoms of adjacent clusters to form a layered structure (figure, bottom). As a result, all Cd atoms are tetrahedrally coordinated and all Se atoms are triply coordinated. Tetrahedral coordination of Cd atoms is distorted as the ∠Se–Cd–Se angles are ranging from 95.8° to 140.3°, and trigonal pyramidal coordination of Se atoms is encountered with the ∠Cd–Se–Cd angles ranging from 73.6° to 108.1°.

Table 1. Data collection and handling.

Crystal:	yellow plate, size 0.04 × 0.10 × 0.48 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	208.42 cm^{-1}
Diffractometer, scan mode:	MacScience MXC3, φ/ω
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1207, 1207
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1067
$N(param)_{refined}$:	50
Programs:	SHELXS-97, SHELXL-97 [7], ORTEP-3 [8]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K(1)	4*a*	½	½	½	0.020(1)	0.018(1)	0.024(1)	0.0023(8)	–0.009(1)	–0.0014(9)
K(2)	4*c*	0.5333(2)	¼	–0.0218(3)	0.020(1)	0.018(1)	0.023(1)	0	–0.000(1)	0
Cd(1)	4*c*	0.29692(5)	¼	0.2710(1)	0.0160(4)	0.0130(3)	0.0108(3)	0	–0.0015(3)	0
Cd(2)	8*d*	0.24665(3)	0.40651(4)	–0.16373(7)	0.0149(2)	0.0139(2)	0.0119(2)	0.0014(2)	–0.0014(2)	0.0007(2)
Se(1)	4*c*	0.13853(7)	¼	0.0690(1)	0.0109(4)	0.0127(4)	0.0134(5)	0	0.0002(4)	0
Se(2)	4*c*	0.35560(7)	¼	0.6292(1)	0.0145(5)	0.0141(4)	0.0096(4)	0	0.0012(4)	0
Se(3)	8*d*	0.36723(5)	0.46791(6)	0.11281(9)	0.0116(3)	0.0113(3)	0.0121(3)	–0.0007(2)	0.0001(3)	–0.0014(2)

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