

K₂CdSnS₄ 的溶剂热合成与晶体结构

白音孟和^{*,1,2} 刚 刚¹ 娜仁吉如嘎¹

(¹ 内蒙古师范大学化学与环境科学学院, 呼和浩特 010022)

(² 内蒙古自治区功能材料物理与化学重点实验室, 呼和浩特 010022)

摘要: 利用溶剂热法合成了层状硫代锡(Ⅲ)酸镉(Ⅱ)化合物 K₂CdSnS₄。单晶 X-射线衍射分析结果表明, 化合物属单斜晶系, C2/c 空间群, $a=1.102\ 1(5)\ \text{nm}$, $b=1.103\ 0(5)\ \text{nm}$, $c=1.515\ 1(10)\ \text{nm}$, $\alpha=90^\circ$, $\beta=100.416(12)^\circ$, $\gamma=90^\circ$, $V=1.811\ 4(17)\ \text{nm}^3$, $Z=8$, $D_c=3.209\ \text{g}\cdot\text{cm}^{-3}$, $M_r=437.60$, $\mu=6.853\ \text{mm}^{-1}$, $F(000)=1\ 600$, $\lambda=0.071\ 073\ \text{nm}$, $R=0.104\ 2$, $wR=0.200\ 8$ 。该化合物由类金刚烷[Cd₂Sn₂S₁₀]⁸⁻结构单元互相连接形成层状结构。紫外-可见漫反射光谱研究表明, 化合物为半导体, 带隙为 2.2 eV。

关键词: 溶剂热合成; 晶体结构; 四元硫代锡酸盐; 光学性质

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Solvothermal Synthesis and Crystal Structure of K₂CdSnS₄

BAIYIN Meng-He^{*,1,2} GANG Gang¹ NAREN Ji-Ru-Ga¹

(¹ College of Chemistry & Environmental Science, Inner Mongolia Normal University, Hohhot 010022, China)

(² Key Laboratory for Physics and Chemistry of Functional Materials, Inner Mongolia, Hohhot 010022, China)

Abstract: Layered K₂CdSnS₄ (**1**) was synthesized solvothermally and characterized by X-ray single crystal diffraction. The crystals belong to the space group C2/c, with $a=1.102\ 1(5)\ \text{nm}$, $b=1.103\ 0(5)\ \text{nm}$, $c=1.515\ 1(10)\ \text{nm}$, $\alpha=90^\circ$, $\beta=100.416\ (12)^\circ$, $\gamma=90^\circ$, $V=1.811\ 4\ (17)\ \text{nm}^3$, $Z=8$, $D_c=3.209\ \text{g}\cdot\text{cm}^{-3}$, $M_r=437.60$, $\mu=6.853\ \text{mm}^{-1}$, $F(000)=1\ 600$, $\lambda=0.071\ 073\ \text{nm}$, and the final $R=0.104\ 2$ and $wR=0.200\ 8$ for all observed reflections. The compound is comprised of sheets with adamantane-like [Cd₂Sn₂S₁₀]⁸⁻ units. UV-Vis reflectance spectrum of compound **1** reveals that **1** is a semiconductor with a band gap of 2.2 eV. CCDC: 424763.

Key words: solvothermal synthesis; crystal structure; quaternary thiostannate; optical property

0 Introduction

In recent years the coordination chemistry of metal-chalcogenides has been an active area of research^[1-6]. One reason for this is the remarkable ability of metal-chalcogenides to exist in many sizes and participate in various bonding modes, in an extremely large variety of structure types with transition and main group metals. Multinary chalcogenides now represent one of

the most structurally diverse classes in inorganic chemistry. They possess very diverse and interesting structures, and exhibit useful physical and chemical properties which are promising for application in magnetism, electronics, photoluminescence, nonlinear optics and ion exchange^[1,7-9]. In the last two decades, the syntheses of binary and ternary thiostannates have been extensively investigated via high-temperature solid state, intermediate-temperature flux, and low-

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*通讯联系人。E-mail: baiymh@163.com

temperature solvothermal techniques, but relatively little is known about quaternary thioannates which may also exhibit interesting properties^[10-16]. Up to now most known quaternary thioannates have been prepared with the molten alkali-metal polychalcogenide flux technique^[16-21], however, low-temperature solvo(hydro)thermal reactions produce a limited number of quaternary thioannates^[7,9,22-27]. We demonstrated that the integration of transition metal cations into thioannate networks can successfully be achieved using a mineralizer, which does not coordinatively saturates transition metal cations, thus enabling bond formation to the thioannate networks. Applying this synthetic strategy the cations Ag^+ and Hg^{2+} could be successfully integrated in thiometallate networks^[28-33]. Recently, we have presented a new mercury-containing thioannate synthesized under solvothermal conditions^[33]. In our continuing work on the solvothermal syntheses of transition metal containing thioannates, the cadmium containing compound K_2CdSnS_4 was obtained. Here we present the synthesis, crystal structure and semiconductor properties of this new quaternary thioannate.

1 Experimental

1.1 Materials and characterization

All materials were commercially purchased and used without further purification. Energy dispersive spectroscopy (EDS) was performed on an F-3400N scanning electronic microscope. Elemental analysis was conducted on a Vario MICRO elemental analyzer. Optical diffuse reflectance measurement for the powder sample was done at room temperature with a Shimadzu UV-2500 double beam, double monochromator spectrophotometer equipped with an integrating sphere (27 mm in diameter). The diffuse reflectance data were recorded in UV-Vis region. BaSO_4 powder was used as reference (100% reflectance). The absorption spectra were calculated from reflectance spectra by using the Kubelka-Munk function: $\alpha/S=(1-R)^2/2R$ where α is the absorption coefficient, S is the scattering coefficient which is practically independent of wavelength when

the particle size is larger than 5 μm , and R is the reflectance.

1.2 Synthesis of K_2CdSnS_4 (1)

The synthesis of compound **1** was as follows. First CdI_2 (0.052 g, 1 mmol), K_2CO_3 (0.072 g, 1 mmol), Sn (0.015 g, 1 mmol) and $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (0.120 g, 1 mmol) were put into a Pyrex glass tube, to which 1.0 mL of a mixture of pyridine-1, 2-ethanedithiol(2:1, V/V) was added. The glass tube was sealed with a 10% filling, placed into a Teflon-lined stainless steel autoclave, and heated at 170 $^\circ\text{C}$ for seven days. The products were washed with ethanol and water, respectively, and pure yellow crystals were obtained. Elemental analysis Calcd.(%) for K_2CdSnS_4 (**1**): S 29.31; Found: S 29.03. A composition analysis by an energy-dispersive spectrum collected by a scanning electron microscope indicates the presence of K, Sn, and Cd in a molar ratio of 22.52:11.64:13.23, which are consistent with that expected from the following crystal structure determination.

The presence of 1,2-ethanedithiol is essential for the synthesis; otherwise cadmium sulfide will always form, and K_2CdSnS_4 will not be obtained. 1, 2-ethanedithiol appears to serve as a mineralizer in this solvothermal synthesis, not simply as a solvent, because 1,2-ethanedithiol is a chelating agent, which can form stable and soluble chelates with heavy metals such as cadmium and mercury under the alkaline conditions. By the above method, a pure K_2CdSnS_4 was obtained.

1.3 X-ray crystallography

A suitable yellow block-shaped single crystal with dimensions of 0.22 mm \times 0.18 mm \times 0.16 mm was used in diffraction measurement on a Bruker APEX-II CCD diffractometer equipped with graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at 293 (2) K. A total of 4 587 reflections and 1 741 unique one were collected in the range of $2.63^\circ\leq\theta\leq 26^\circ$ with $R_{\text{int}}=0.050\ 5$ complexe **1**, respectively, of which 1 453 reflections with $I>2\sigma$ were considered as observes and used in the succeeding structural calculations. The absorption corrections were applied using the multiscan technique. The structure was

solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX97 program package^[34]. The crystallographic data and structural refinement details are summarized in Table 1. The

selected bond lengths and angles in Table 2.

CCDC: 424763.

2 Results and discussion

Table 1 Crystal data and structure refinement parameters for **1**

Empirical formula	K_2CdSnS_4	$D_c / (g \cdot cm^{-3})$	3.209
Formula weight	437.60	Volume / nm^3	1.811 4(17)
Temperature / K	293(2)	Absorption coefficient / mm^{-1}	6.853
Wavelength / nm	0.071 073	$D_c / (Mg \cdot m^{-3})$	3.209
Crystal system	Monoclinic	$F(000)$	1 600
Space group	$C2/c$	Data / restraints / parameters	1 741/12/74
a / nm	1.1021(5)	Goodness-of-fit on F^2	1.074
b / nm	1.103 0(6)	Final R indices [$I > 2\sigma(I)$]	$R_1=0.104$ 2, $wR_2=0.200$ 8
c / nm	1.515 1(10)	R indices (all data)	$R_1=0.118$ 6, $wR_2=0.207$ 5
Z	8	Largest diff. peak and hole / ($e \cdot nm^{-3}$)	2 413, -2 365

Table 2 Selected bond lengths(nm) and bond angles($^\circ$) for compound **1**

Cd(1)-S(2)	0.245 9(7)	Sn(1)-S(2)i	0.241 5(8)	S(2)-Sn(1)iii	0.241 5(8)
Cd(1)-S(3)	0.246 8(5)	Sn(1)-S(1)	0.241 5(8)	S(3)-Cd(1)ii	0.246 8(5)
Cd(1)-S(1)	0.247 2(6)	Sn(1)-S(5)	0.247 9(5)	S(4)-Sn(1)ii	0.249 7(11)
Cd(1)-S(4)	0.248 7(11)	Sn(1)-S(4)ii	0.249 7(11)	S(5)-Sn(1)ii	0.247 9(5)
S(2)-Cd(1)-S(3)	107.8(3)	S(2)i-Sn(1)-S(1)	105.0(2)	Sn(1)-S(1)-Cd(1)	103.3(3)
S(2)-Cd(1)-S(1)	106.3(2)	S(2)i-Sn(1)-S(5)	108.7(3)	Sn(1)iii-S(2)-Cd(1)	107.9(3)
S(3)-Cd(1)-S(1)	112.5(2)	S(1)-Sn(1)-S(5)	112.4(3)	Cd(1)-S(3)-Cd(1)ii	107.1(3)
S(2)-Cd(1)-S(4)	108.0(4)	S(2)i-Sn(1)-S(4)ii	107.5(4)	Cd(1)-S(4)-Sn(1)ii	104.9(3)
S(3)-Cd(1)-S(4)	108.9(3)	S(1)-Sn(1)-S(4)ii	113.6(4)	Sn(1)ii-S(5)-Sn(1)	106.2(3)
S(1)-Cd(1)-S(4)	113.04(4)	S(5)-Sn(1)-S(4)ii	109.3(3)		

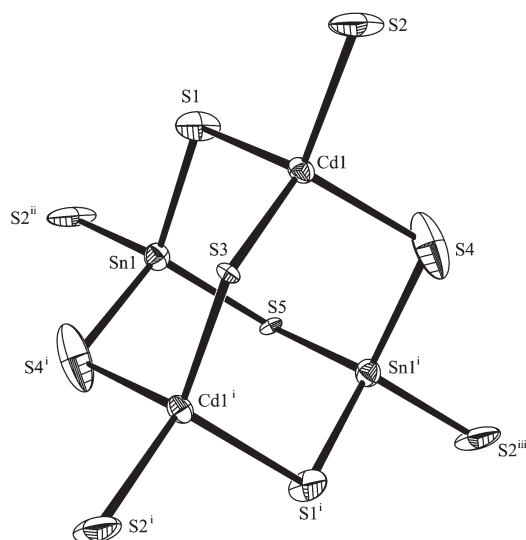
Symmetry transformations used to generate equivalent atoms: ⁱ $x-1/2, y+1/2, z$; ⁱⁱ $-x, y, -z+1/2$; ⁱⁱⁱ $x+1/2, y-1/2, z$

2.1 Crystal structure description

Crystal structure analysis shows that compound **1** is sheet structure, consisted of adamantane-like cluster $[Cd_2Sn_2S_{10}]^{8-}$ anions as building block as shown in Fig. 1. The anionic building blocks, which are closely related to those found in K_2MnSnS_4 ^[35], can be viewed as the Mn atoms from an adamantane-like cluster $[Mn_2Sn_2S_{10}]^{8-}$ in which Mn atoms are completely replaced by Cd atoms. The structure of $[Cd_2Sn_2S_{10}]^{8-}$ contains a crystallographic independent Cd and Sn atoms. Cd and Sn atoms are both coordinated by four S atoms at the corners of a tetrahedron. Each Cd atom is coordinated by S(1), S(2), S(3), S(4) atoms, each Sn

atom is coordinated by S(1), S(2), S(4), S(5) atoms. A pair of CdS_4 tetrahedra and a pair of SnS_4 tetrahedra are condensed into an adamantine-like cluster $[Cd_2Sn_2S_{10}]^{8-}$ via corner-sharing, i.e., S(3), S(5), $2 \times S(1)$, $2 \times S(4)$. In the structure of compound **1** each S atom connects two metal atoms. Each adamantine-like cluster $[Cd_2Sn_2S_{10}]^{8-}$ connect other four adamantine-like clusters $[Cd_2Sn_2S_{10}]^{8-}$ through four S (2) atoms to construct a sheet of the formula type ${}^\infty[Cd_2Sn_2S_{10}]^{8-}$ (Fig.2).

The charge-balancing alkali-metal cations are stuffed into the channels created by the packing of these anionic $[Cd_2Sn_2S_{10}]^{8-}$ clusters (Fig.3). Cd and Sn



30% thermal ellipsoids, symmetry codes: ⁱ $x-1/2, y+1/2, z$; ⁱⁱ $-x, y, -z+1/2$; ⁱⁱⁱ $x+1/2, y-1/2, z$

Fig.1 Geometric details of linkage of CdS_4 , SnS_4 and atom labeled in an adamantane-like cluster $[\text{Cd}_2\text{Sn}_2\text{S}_{10}]^{8-}$

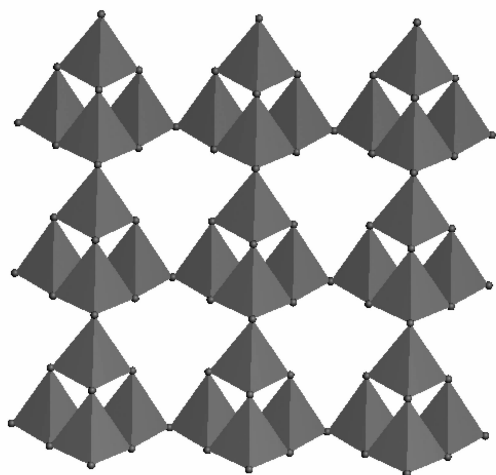


Fig.2 Polyhedral plot of compound **1** in which the adamantane-like $[\text{Cd}_2\text{Sn}_2\text{S}_{10}]^{8-}$ units are linked into sheets via common terminal S atoms

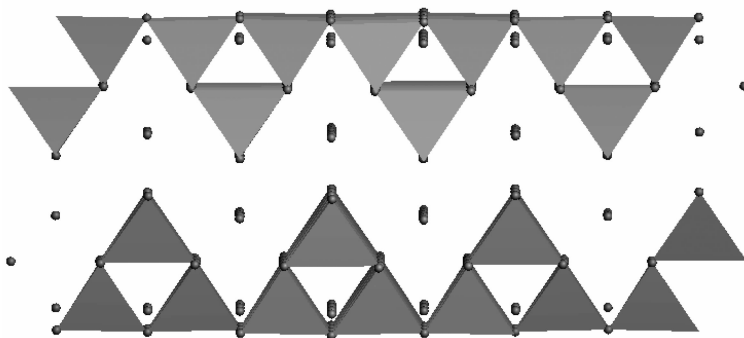
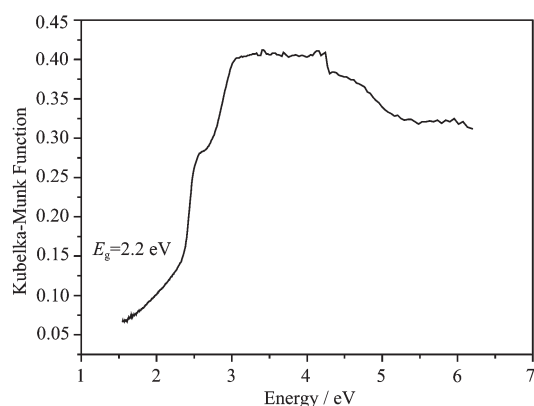


Fig.3 Polyhedral plot of the projected view of compound **1**

atoms are tetrahedrally coordinated, geometries of CdS_4 units are distorted slightly: CdS_4 with Cd-S bond distances ranging from 0.245 9 (7) nm to 0.248 7(11) nm, S-Cd-S angles from 106.3 (2)° to 113.0 (4)°; SnS_4 with Sn-S bond distances ranging from 0.241 5 (8) nm to 0.249 7 (11) nm, S-Sn-S angles from 105.0 (2)° to 113.6 (4)°. The metal-sulfur bond lengths for the compound **1**, in general, in agreement well with those reported in the literature^[7,17].

The compound **1** with an adamantane-like cluster $[\text{Cd}_2\text{Sn}_2\text{S}_{10}]^{8-}$ is the first example of A/Cd/Sn/S systems (A=Ba, Li, Na, K, Rb, Cs) containing kalium and is structurally different from other A/Cd/Sn/ systems compounds reported^[7,17,36] so far. Compound **1** is distinctly different from the layered $[\text{CdSnS}_4]^{2-}$ framework of BaCdSnS_4 , wherein CdS_4 and SnS_4 tetrahedra are connected through both corners and edges^[36]; the two-dimensional $\text{Li}_2\text{CdSnS}_4$ and three-dimensional $\text{Na}_2\text{CdSnS}_4$ are built from the corner-connection of tetrahedra CdS_4 and SnS_4 ^[17]; the layered $\text{Na}_2\text{CdSnS}_{12}$ is composed of octahedral coordination CdS_6 and SnS_6 ^[17]; the compound $\text{Cs}_{10}\text{Cd}_4\text{Sn}_4\text{S}_{17}$ exists discrete molecular $[\text{Cd}_4\text{Sn}_4\text{S}_{17}]^{10-}$ clusters^[7].

The structure of A/Cd/Sn/S systems compounds could be imagined to have resulted from the different ways of ordering Ba/Li/Na/K/Rb/Cs, Cd^{2+} and Sn^{2+} ions in either the octahedral or tetrahedral sites in the arrays of sulfur atoms and this ordering is essentially due to the difference in sizes and charges of the structure direction ions. The building block of adamantane-like building unit $[\text{Cd}_2\text{Sn}_2\text{S}_{10}]^{8-}$ is very rare in the known thioannates and has never been found in quaternary thioannates before our work. Compared

Fig.4 UV-Vis reflectance spectrum of compound **1**

with that of germanium sulfide-based adamantane-like clusters^[37-45], the quantity of known tin sulfide-based adamantane-like clusters^[28,33,35] is much less, and quaternary thiostannates are usually prepared by molten alkalimetal polychalcogenide flux or high-temperature solid state techniques.

The syntheses of sulfide-based adamantane-like clusters have been extensively investigated with organic amines as structure directing cations, but relatively little is known alkali-metal cations as structure directing agent.

2.2 Optical property

UV-Vis reflectance spectrum of compound **1** (Fig. 4) reveals that **1** is a semiconductor with the band gap of 2.2 eV. This value falls in between those of $\text{Na}_2\text{CdSnS}_4$ (1.52 eV)^[17] and $\text{Cs}_{10}\text{Cd}_4\text{Sn}_4\text{S}_{17}$ (3.16 eV)^[7].

3 Conclusions

We have shown that $\text{HSCH}_2\text{CH}_2\text{SH}$ is a very effective mineralizer for the solvothermal synthesis of K_2CdSnS_4 . The successful synthesis suggests the possibility of synthesizing new quaternary sulfides containing other heavier transition metals and deciphering the structure of materials containing new quaternary sulfides by this novel method.

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