Synthesis, crystal structure and optical properties of $K_2Cu_2GeS_4$

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A B S T R A C T

A new compound $K_2Cu_2GeS_4$ was successfully synthesized by using molten thiourea reactive flux method. The structure was determined by single crystal X-ray diffraction. The compound crystallizes in the monoclinic system of space group $P2/c$ with a unit cell of $a = 7.063$ (3) Å, $b = 5.435$ (3) Å, $c = 11.037$ (6) Å and $\beta = 112.83$ (3)°. The crystal structure of $K_2Cu_2GeS_4$ is composed of defective *anti*-PbO like $[Cu_2GeS_4]^{2-}$ layers which are interleaved by K^+ cations. This compound is a semiconductor with an indirect band gap of 2.3 (1) eV, which is derived from optical absorption spectrum. First principles calculations reveal that $K_2Cu_2GeS_4$ has interesting intermediate bands consisting of Ge-4s and S-3p orbitals. This new semiconductor is potentially suitable for solar photocatalytic and photoelectric applications.

1. Introduction

Quaternary sulfides with the formula of $A/M/M'/S$ (A = alkali metal; M = group IB elements; M' = Ge, Sn) have received much attention for their intriguing structures as well as potential applications for photocatalysts, photoluminescence, and photoresponse. The variable coordination numbers of IB metals (2, 3 and 4) allow for different construction moieties (linear, triangle and tetrahedron) and more structure diversity. Many unique structures are seen in these compounds, such as the interesting $[Cu_8S_{12}]^{16-}$ cages in $A_4Cu_8Ge_3S_{12}$ (A = K, Rb) [1] and the $[M_2M'_2S_6]^{2-}$ anion chains in $K_2M_2M'_2Q_6$ (M = Ag, Au; M' = Ge, Sn; Q = S, Se) [2–4].

Recently, exfoliated nanosheets from layered chalcogenides were shown to always have excellent catalytic, optical, electronic and spin-electronic properties [5–14]. Therefore, the discovery of new layered chalcogenides is of scientific significance. There are some layered chalcogenides in the $A-M-Sn-S$ (A = alkali metal, M = group IB metals) system [1–4,15–21]. For instance, $Rb_2Cu_2SnS_4$ [19] and $K_2Ag_2SnSe_4$ [16] contain interesting $[Cu_2SnS_4]^{2-}$ and $[Ag_2SnSe_4]^{2-}$ layers, respectively, with defective *anti*-PbO-like structure. The system of $A-M-Ge-S$ (A = alkali metal, M = group IB metals) is also ideal to explore new layered chalcogenides because of the similarity between Ge and Sn. Moreover, physical properties of semiconductors with similar structure are expected to change with element substitution. For example, the band gap (E_g) of $K_4Cu_8Ge_3S_{12}$ (2.2 eV) [1] is larger than that of isostructural $K_4Cu_8Sn_3S_{12}$ (1.9 and 1.52 eV) [22]. Yet, only a few $A-M-Ge-S$ compounds are found [1,4,18].

Here, the system of K–Cu–Ge–S was investigated by using molten thiourea as a reactive flux to grow crystals. At the low reaction temperature of 220 °C, a new $K_2Cu_2GeS_4$ compound was synthesized. The crystal structure was studied by single crystal and powered X-ray diffractions. The compound crystallizes in the monoclinic system (space group: $P2/c$), whose structure contains defective *anti*-PbO-like $[Cu_2GeS_4]^{2-}$ layers, which are more regular than those in the reported Sn compounds [16,19]. The semiconducting properties were measured by optical absorption spectrum and an interesting intermediate band consisting of Ge/S valence orbitals was found by first-principles calculations.

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2. Experimental

2.1. Synthesis of the $K_2Cu_2GeS_4$ crystals

Single crystals of $K_2Cu_2GeS_4$ were synthesized by using molten thiourea as a reactive flux. The reactants including Ge powder (0.363 g, 5 mmol, AR, 3N), Cu powder (0.318 g, 5 mmol, AR, 2.5N), thiourea ($SC(NH_2)_2$, 7.612 g, 0.1 mol, 3N) and KOH (10 g, AR, 2N) were grinded directly in an agate mortar. The mixture was then transferred into a 50 mL Teflon-lined stainless steel autoclave. The reaction was carried out at 220 °C for 3 days. After the autoclave cooled down to room temperature, the as-reacted mixtures were taken out and washed with deionized water for several times. After dried in acetone, the final products were collected.

2.2. Morphology characterization and powder X-ray diffraction (PXRD)

The morphology of the obtained crystals was investigated using a JEOL (JSM6510) scanning electron microscope (SEM) and their elementary composition was analyzed by energy dispersive X-ray spectroscopy (EDXS). Fine powder of the as-synthesized crystalline sample was prepared before testing. Powder X-ray diffraction was carried out using a Bruker D8 Focus diffractometer equipped with mirror-monochromated Cu K_α radiation (λ = 1.54178 (1) Å, 40 kV, 40 mA). The pattern was measured in a slow scanning mode from 10° to 60° (2θ) at a scan rate of 6° min^{-1}.

2.3. Single crystal X-ray diffraction

A single crystal with good crystallinity was selected for crystallographic data collections using a Bruker D8 Quest single crystal X-ray diffractometer equipped with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å, 50 kV, 10 mA) at room temperature. The crystal structure of $K_2Cu_2GeS_4$ was solved and refined using the Bruker APEX 3 program. The crystal was twinned with high K values at small $F_c/F_c(max)$. The data were then treated as twin crystal with two integrated components. The structural was originally solved using the hkl4 file and finally refined using hkl5 file format. The actual numbers of measured, independent and observed [$I > 2\sigma(I)$] reflections are 16535, 898, and 776.

2.4. Solid-state UV–visible spectroscopy

UV–vis reflectance spectrum of the $K_2Cu_2GeS_4$ powder was measured using a Hitachi UV-4100 spectrophotometer. The scanning range and velocity were 1000–400 nm and 120 nm·min^{-1}, respectively. The reflectance data were converted to absorbance data using the Kubelka-Munk equation [23] to calculate its band gap.

2.5. Electronic band structure calculations

First-principles calculations were carried out using the Vienna Ab-initio Simulation Package (VASP) based on density functional theory (DFT) [24,25]. The projector augmented wave (PAW) [24] was used in this work and the exchange-correlation functional was applied in the generalized-gradient approximation (GGA) [26] method using the Perdew-Burke-Ernzerhof (PBE) [26] scheme. We chose 350 eV as the plane-wave cutoff energy. For the structure optimizations, $6 \times 6 \times 6$ Monkhorst-Pack grids were used for the conventional cell. Relaxation of the geometry optimization was performed until the total energy changes were within 10^{-6} eV per atom and the Hellmann-Feynman force on all atomic sites was less than 0.01 eV/Å. The valence states of K, Cu, Ge and S are $3s$, $3p^*$, $3p$ and $4s$; $3p^*$, $3p$, $3d^*$, $3d$ and $4s$; $3d^*$, $3d$, $4s$, $4p^*$ and $4p$; $3s$, $3p^*$ and $3p$, respectively.

3. Results and discussions

3.1. Synthesis and structure description

Thiourea is a good flux for synthesizing sulfides at low temperature because it can gradually release S when heated above its melting point (182 °C) [27]. With the assistance of KOH, we successfully synthesized a new quaternary compound $K_2Cu_2GeS_4$. The final products are orange crystals and no impurity was found by the SEM examination, as shown in Fig. 1. The crystals are block-like and about 30 μm in size on average with an average yield of 40% (based on Cu element). The statistical ratio of K, Cu, Ge and S is 22.4(3):21.5(4):11.0(1):45.0(4) from the EDXS result shown in the inset, which is close to 2:2:1:4.

The crystal structure of $K_2Cu_2GeS_4$ is isostructural to $K_2Ag_2SnSe_4$ [16], which crystallizes in the monoclinic space group $P2/c$. There are one independent Cu site ($4g$), one independent Ge site ($2f$), two independent K sites (K1: $2e$; K2: $2a$) and two independent S sites (S1: $4g$; S2: $4g$), as shown in Table 2. Since Cu and Ge atoms are both at tetrahedral sites, there is a possibility that they could be disordered. Cu and Ge atoms were first assigned based on the bond lengths and charge balance. The resulting occupancies of Cu and Ge sites are 98.2% and 98.5%, respectively. The bond valence sums of the Cu and Ge sites were calculated to be 1.02 and 4.01, respectively, which are the same as for the regular oxidation states of Cu$^+$ and Ge^{4+}. Therefore, the Cu and Ge sites can be concluded to be ordered. The displacement parameters for the Ge site are low compared to the other sites (Table 2). Similar cases are also seen in $Rb_2Cu_2SnS_4$ and $K_2Ag_2SnSe_4$ where Sn atoms have smallest displacement parameters. This might relate to the large atomic masses and regular coordination polyhedra of Ge or Sn atoms in these compounds.

The structure features defective *anti*-PbO like $[Cu_2GeS_4]^{2-}$ 2D layers separated by K$^+$ ions. K$^+$ ions are in similar cubic interstices between the layers as those in KFe_2Se_2 [28] as shown in Fig. 2c–d. Similar defective *anti*-PbO like layers are also found in $K_2Ag_2SnSe_4$ [16], $Rb_2Cu_2SnS_4$ [19], and $A_2M_2TiQ_4$ (A = K, Rb, Cs; M = Cu, Ag) [29] compounds. The crystallographic data and detailed refinement parameters are shown in Table 1.

The $[Cu_2GeS_4]^{2-}$ 2D layers can be derived from the *anti*-PbO layers, as shown in Fig. 2a–c. The Cu and S atoms replace the Pb and O sites in PbO, respectively, to form an *anti*-PbO-like "CuS" layer.
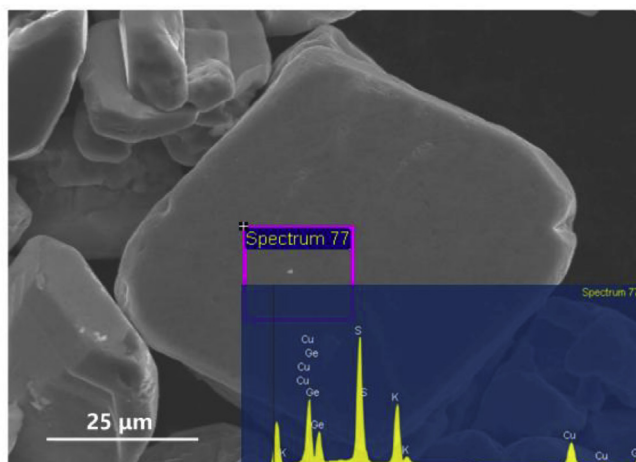

Fig. 1. SEM image of the $K_2Cu_2GeS_4$ crystals and elemental analysis (insert).