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Syntheses, crystal and electronic structures of three new potassium cadmium(II)/zinc(II) tellurides: $K_2Cd_2Te_3$, K_6CdTe_4 and K_2ZnTe_2

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ABSTRACT

Three new ternary potassium(I) zinc(II) or cadmium(II) tellurides, namely, $K_2Cd_2Te_3$, K_6CdTe_4 and K_2ZnTe_2, were synthesized by solid-state reactions of the mixture of pure elements of K, Cd (or Zn) and Te in Nb tubes at high temperature. $K_2Cd_2Te_3$ belongs to a new structure type and its structure contains a novel two-dimensional $[Cd_2Te_3]^{2-}$ layers perpendicular to the *b*-axis. K(5) cation is located at the center of five member rings of the 2D $[Cd_2Te_3]^{2-}$ layer, whereas other K^+ cations occupy the interlayer space. K_6CdTe_4 with a K_6HgS_4 type structure features a "zero-dimensional" structure composed of isolated $CdTe_4$ tetrahedra separated by the K^+ ions. K_2ZnTe_2 in the K_2ZnO_2 structural type displays 1D $[ZnTe_2]^{2-}$ anionic chains of edge sharing $[ZnTe_4]$ tetrahedra separated by the potassium(I) ions. $K_2Cd_2Te_3$, K_6CdTe_4 and K_2ZnTe_2 revealed a band gap of 1.93, 2.51 and 3.0 eV, respectively.

1. Introduction

The studies on metal chalcogenides have received lots of research attentions in recent years. This class of compounds may exhibit a variety of open-framework structures with good ion exchange properties [1–5]. Some of metal chalcogenides show excellent thermoelectric properties [6–8]. Furthermore metal chalcogenides are usually semiconductors and they can also form non-centrosymmetric structures with large second harmonic generation (SHG) response and excellent transmission properties in the mid-IR and far-IR region [9–11]. Compared with metal sulfides and selenides, tellurides are much less explored. We focus on the alkali-Zn/Cd–Te systems in order to explore new SHG materials used in the mid-IR and far-IR region. So far reports on this class of compounds are still very limited, the structurally characterized ternary phases include $K_2Cd_3Te_4$ (*Pnma*) [12], $Cs_2Cd_3Te_4$ (*Ibam*) and $Rb_2Cd_3Te_4$ (*C*2/*c*) [13]. In addition, a number of lanthanide(III)-containing quaternary phases such as $CsLnZnTe_3$ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Y), $AYbZnTe$ (A = Rb, Cs) and $CsLnCdTe_3$ (Ln = La, Pr, Nd, Sm, Gd–Tm and Lu) have also been isolated by the Ibers group and the Wu group [14–16]. Our explorations on the ternary phases in K–Zn(Cd)–Te systems afforded three new compounds, namely, $K_2Cd_2Te_3$ with a new structural type, K_6CdTe_4 with a K_6HgS_4 type structure [17] and K_2ZnTe_2 with a K_2ZnO_2 type structure [18]. Herein we report their syntheses, crystal structures, band structures and optical properties.

2. Experimental

2.1. Materials and methods

All of chemicals were obtained from commercial sources and used without further purification. Microprobe elemental analyses on K, Zn, Cd and Te elements were performed on a field emission scanning electron microscope (FESEM, JSM6700F) equipped with an energy dispersive X-ray spectroscope (EDS, Oxford INCA). X-ray powder diffraction (XRD) patterns (Cu*Kα*) were collected on an XPERT-MPD θ–2θ diffractometer. Optical diffuse reflectance spectrum was measured at room temperature with a PE Lambda 900 UV–visible spectrophotometer. The instrument was equipped with an integrating sphere and controlled by a personal computer. $BaSO_4$ plate was used as a standard (100% reflectance). The absorption spectrum was calculated from reflectance spectrum using the Kubelka–Munk function: $\alpha/S=(1-R)^2/2R$ [19], where α is the absorption coefficient, S is the scattering coefficient which is practically wavelength-independent when the particle size is larger than 5 μm, and R is the reflectance.

2.2. Synthesis of $K_2Cd_2Te_3$

Due to the air sensitive nature of the three compounds, all synthetic operations were performed under an argon atmosphere

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within a glove box. Red single crystals of $K_2Cd_2Te_3$ were initially obtained by the solid state reaction of a mixture of K (Alfa Aesar, 99.95%, bulk), Cd (Alfa Aesar, 99.95%, shot), Sn (Alfa Aesar, 99.5%, shot) and Te (Alfa Aesar, 99.99%, broken ingot) in a molar ratio of 1:1:1:2 in our attempt to synthesize a K–Cd–Sn–Te quaternary phase. The mixture was loaded into a niobium tube within an argon-filled glove box and then the Nb tube was arc-welded under an argon atmosphere. The Nb tube was subsequently sealed into an evacuated quartz tube ($\sim 10^{-4}$ Torr) and placed into a furnace. The sample was heated to 573 K in 6 h, kept at 573 K for 1 day, and then heated to 773 K in 6 h, kept at 773 K for 4 days, and then cooled to 473 K in 6 days at 2 K/h, before switching off the furnace. Microprobe elemental analyses on several single crystals indicate the absence of the Sn element and gave a molar ratio of K/Cd/Te of 2.1(2)/2.0(2)/3.2(2), which is very close to that from single-crystal structural analyses. After proper structural determination, a lot of efforts were tried to prepare the single phase product of $K_2Cd_2Te_3$, but were unsuccessful. The reaction of pure elements of K, Cd and Te in stoichiometric molar ratio gave $K_2Cd_3Te_4$ (*Pnma*) as the main product [12]. Changing reaction temperatures or starting materials (K_2Te and CdTe) also lead to $K_2Cd_3Te_4$ as the main product. The sample used for optical diffuse reflectance spectrum measurements are single crystals selected based on shape and color.

2.3. Syntheses of K_6CdTe_4 and K_2ZnTe_2

Single crystals of K_6CdTe_4 and K_2ZnTe_2 were initially prepared by reactions of a mixture of pure elements of K, Cd (or Zn) and Te in a molar ratio of 6:1:4 for K_6CdTe_4, or 2:1:2 for K_2ZnTe_2. The mixture was loaded into a niobium tube in an argon-filled glove box and then the Nb tube was arc-welded under an argon atmosphere. The Nb tube was subsequently sealed within an evacuated quartz tube ($\sim 10^{-4}$ Torr) and placed into the furnace. The samples were heated at 523 K for 1 day and then heated at 1023 (for K_6CdTe_4) or 973 K (for K_2ZnTe_2) for 1 day, and then cooled to 773 K at 2 K/h, kept at 773 K for 3 days, and then cooled to 473 K in 5 days at 2 K/h, before switching off the furnace. Results of EDS microprobe elemental analyses on several single crystals of K_6CdTe_4 and K_2ZnTe_2 gave a K/Cd(or Zn)/Te molar ratios of 6.1(2)/1.0(2)/4.2(2) and 2.2(2)/1.0(2)/2.2(2), respectively, for K_6CdTe_4 and K_2ZnTe_2. After structural analyses, the mono-phase products of K_6CdTe_4 and K_2ZnTe_2 were obtained quantitatively by the solid state reactions of a stoichiometric mixture of K/Cd (or Zn)/Te at 1023 (for K_6CdTe_4) or 973 K (for K_2ZnTe_2) for 5 days. Their purities were confirmed by XRD powder diffraction studies (see Supporting Materials).

2.4. Crystal structure determination

Data collections for $K_2Cd_2Te_3$, K_6CdTe_4 and K_2ZnTe_2 were performed on a Rigaku mercury CCD diffractometer equipped with a graphite-monochromated Mo*K*α radiation ($\lambda = 0.71073$ Å) at 293 K. The data sets were corrected for Lorentz and polarization factors as well as for absorption by multi-scan method [20]. All three structures were solved by the direct methods and refined by full-matrix least squares fitting on F^2 by SHELXTL 97 [21]. All atoms were refined with anisotropic thermal parameters. All of the atomic sites in the three compounds were fully occupied according to the site occupancy refinements. Final difference Fourier maps showed featureless residual peaks of 3.484 and -1.791 eÅ^{-3} (0.92 and 0.61 Å, respectively, away from Cd(6)) for $K_2Cd_2Te_3$, 0.779 and -1.304 eÅ^{-3} (0.96 and 1.05 Å from Te(1) and Cd(1), respectively) for K_6CdTe_4, 0.593 and -0.480 eÅ^{-3} (0.06 and 1.53 Å from Te(1) and K(1), respectively) for K_2ZnTe_2. Data collection and refinement parameters were summarized in Table 1, the atomic coordinates, important bond lengths and angles were listed in Tables 2 and 3 respectively.

Crystallographic data in CIF format for $K_2Cd_2Te_3$, K_6CdTe_4 and K_2ZnTe_2 have been given as Supporting Materials. These data can also be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen,

Table 1
Crystal data and structure refinement for $K_2Cd_2Te_3$, K_6CdTe_4 and K_2ZnTe_2.

Chemical formula	$K_2Cd_2Te_3$	K_6CdTe_4	K_2ZnTe_2
Formula weight	685.80	857.40	398.77
Crystal system	Monoclinic	Hexagonal	Orthorhombic
Space group	$P2_1/c$ (no. 14)	$P6_3mc$ (no. 186)	*Ibam* (no. 72)
a (Å)	13.259(3)	11.050(1)	7.303(3)
b (Å)	15.785(3)	11.050(1)	14.022(5)
c (Å)	14.266(3)	8.292(2)	6.921(2)
β (deg)	94.033(4)	90	90
V (Å^3)	2978.5(1)	876.9(2)	708.7(4)
Z	12	2	4
D_{calcd} (g/cm^3)	4.588	3.247	3.737
μ (Mo*K*α)/mm^{-1}	13.674	9.150	12.575
Reflections collected	22928	6203	2569
Unique reflections	6745	764	442
Reflections ($I > 2\sigma(I)$)	5824	735	427
T (K)	293	293	293
GOF on F^2	1.078	1.190	1.049
$R1$, w$R2$ [$I > 2\sigma(I)$]^a	0.0329, 0.0661	0.0294, 0.0655	0.0153, 0.0342
$R1$, w$R2$ (all data)	0.0407, 0.0701	0.0310, 0.0663	0.0165, 0.0346

[a] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$; $wR_2 = \sum w[(F_o)^2 - (F_c)^2]^2 / \sum w[(F_o)^2]^{21/2}$.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters ($\times 10^3$ Å^2) for $K_2Cd_2Te_3$, K_6CdTe_4 and K_2ZnTe_2.

Atom	*Wyck*	x	y	z	U (eq)^a
$K_2Cd_2Te_3$					
K1	4*e*	0.1424(2)	0.0379(2)	0.4399(2)	43(1)
K2	4*e*	0.3572(2)	0.0247(2)	0.0459(2)	35(1)
K3	4*e*	0.2486(2)	0.0295(2)	0.7328(1)	43(1)
K4	4*e*	0.4748(2)	0.0262(2)	0.3542(2)	46(1)
K5	4*e*	0.7351(2)	0.2706(2)	0.2324(2)	46(1)
K6	4*e*	0.0189(1)	0.0536(1)	0.1225(1)	48(1)
Cd1	4*e*	0.4429(1)	0.2306(1)	0.1808(1)	27(2)
Cd2	4*e*	0.6302(1)	0.2907(1)	0.4812(1)	30(2)
Cd3	4*e*	0.8621(1)	0.1917(1)	0.4905(1)	28(2)
Cd4	4*e*	0.1776(1)	0.2497(1)	0.0954(1)	27(2)
Cd5	4*e*	0.3189(1)	0.2535(1)	0.3863(1)	27(2)
Cd6	4*e*	0.9935(1)	0.2898(1)	0.3236(1)	34(2)
Te1	4*e*	0.5845(1)	0.1114(1)	0.1387(1)	24(2)
Te2	4*e*	0.2604(1)	0.1384(1)	0.2387(1)	23(2)
Te3	4*e*	0.1562(1)	0.1397(1)	0.9328(1)	24(1)
Te4	4*e*	0.4906(1)	0.3452(1)	0.3328(1)	24(2)
Te5	4*e*	0.0125(1)	0.3503(1)	0.1374(1)	27(2)
Te6	4*e*	0.8345(1)	0.3668(1)	0.4405(1)	26(2)
Te7	4*e*	0.9330(1)	0.1223(1)	0.3255(1)	31(2)
Te8	4*e*	0.6702(1)	0.3797(1)	0.0158(1)	33(2)
Te9	4*e*	0.3526(1)	0.3480(1)	0.0499(1)	23(2)
K_6CdTe_4					
K(1)	6*c*	0.4766(1)	0.9532(1)	0.9774(1)	38(1)
K(2)	6*c*	0.7021(1)	0.8510(1)	0.2912(1)	54(2)
Cd(1)	2*b*	1/3	2/3	0.5983(1)	24(1)
Te(1)	6*c*	0.6178(1)	0.8089(1)	0.7025(1)	24(1)
Te(2)	2*b*	1/3	2/3	0.2537(1)	34(1)
K_2ZnTe_2					
K(1)	8*j*	0.1799(1)	0.3579(1)	0	28(1)
Zn(1)	4*a*	0	0	1/4	19(1)
Te(1)	8*j*	0.1947(1)	0.1071(1)	0	20(1)

[a] U (eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.