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Synthesis and Structural Characterization of Ba_2CdTe_3

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The new ternary compound Ba_2CdTe_3 has been prepared by the reaction of a stoichiometric mixture of elements at 700°C. Its structure was determined via the Rietveld refinement method using powder X-ray diffraction with $R_p/R_{wp}(\%) = 6.54/8.67$. Ba_2CdTe_3 crystallizes in space group *Pnma* (No. 62) of the orthorhombic system with $Z = 4$ and $a = 9.8198(2)$ Å, $b = 4.7436(1)$ Å, $c = 19.0638(5)$ Å. It is isotypic to Ba_2MnS_3 and K_2AgI_3. The structure consists of one-dimensional chains of $^1_\infty[CdTe_{2/2}Te_2]^{4-}$ separated by Ba^{2+} cations. The chain is made of corner-sharing $CdTe_4$ tetrahedra. Each Ba atom is coordinated to seven tellurium atoms to form a trigonal prism with one rectangular face capped by a Te atom. © 1999 Academic Press

***Key Words*: chalcogenide; cadmium telluride; Rietveld method; X-ray diffraction.**

INTRODUCTION

Extensive interest has been devoted to CdTe for its application in short wavelength optical devices, solar cells, room temperature semiconductor X- and γ-ray detectors, thermoelectric materials, nanotechnology, and other fields (1–5). Synthesis and characterization studies of ternary cadmium chalcogenides containing electropositive cations (*A*–Cd–Q, *A* is an alkali metal or alkaline earth metal) have been reported (5–8). As the three dimensional cadmium chalcogen network of CdTe is broken into layers, chains, or blocks, interesting physical properties may result (5–8). However, a search of *A*–Cd–Te ternaries in the ICSD 2.01 database (9) yields only one compound, $K_2Cd_3Te_4$ (5). This work reports the synthesis and structural characterization of the first alkaline earth metal-containing ternary cadmium telluride Ba_2CdTe_3.

EXPERIMENTAL

All manipulations were carried out in an argon-filled glove box. The starting materials were (1) barium, distilled dendritic pieces (Aldrich) of 99.9 + % purity, ampouled under argon, (2) cadmium shot (Cerac), 99.999%, and (3) tellurium granules (Cerac), 99.999%. Elemental mixtures with the stoichiometric ratio 2Ba/Cd/3Te were placed in a vitreous carbon crucible (EMC) sealed in a quartz tube, heated at 700°C for 100 h, and slow cooled to 500°C over 80 h. X-ray (Scintag XDA 2000, Cu*Kα*, 25°C) and microprobe (JEOL 733) analysis were performed on a chunk of the product. A homogeneous dark orange phase with the formula Ba_2CdTe_3 was identified. White amorphous powder appeared on the surface of the bulk materials after a month's exposure in air. Two other stoichiometries were also tried, Ba/Cd/2Te, and Ba/2Cd/3Te. The same heating profile was applied. Both contained CdTe and Ba_2CdTe_3 in their products based on the X-ray and microprobe analysis. The powder X-ray diffraction pattern of Ba_2CdTe_3 suggested that it is isostructural to Ba_2CdSe_3 (*Pnma*). Based on this model, the structure was refined by the Rietveld method using GSAS (10). The X-ray linewidths of the peaks are relatively broad (approximately twice as wide as for our polycrystalline Si standard with FWHM = 0.08° at 28.46°). The background was refined by using the fixed background feature of GSAS to fit the fluctuating component of the background and the cosine Fourier series to fit the remainder. GOF is lower than 1 due to the relatively high background intensity. No constraints were imposed. The profile refinement is shown in Fig. 1. The relevant refinement and crystal data are listed in Tables 1 and 2.

RESULTS AND DISCUSSION

Ba_2CdTe_3 is isotypic to Ba_2CdSe_3 and Ba_2CdS_3. Ba_2MnS_3, Ba_2MnSe_3, and Ba_2MnTe_3 (11) adopt the same structural type. They are isotypic to K_2AgI_3 (8, 12). The electron counting of Ba_2CdTe_3 can be understood in the framework of the Zintl–Klemm concept (13). The formal oxidation states can be assigned as Ba^{2+}, Cd^{2+}, and Te^{2-}. $(CdTe_3)^{4-}$ constitutes the anionic network, which is a one-dimensional chain as shown in Fig. 2. The chain $^1_\infty[CdTe_{2/2}Te_2]^{4-}$ runs in the *y* direction. It is composed of corner-sharing $(CdTe_4)$ tetrahedra. The two Ba^{2+} cations

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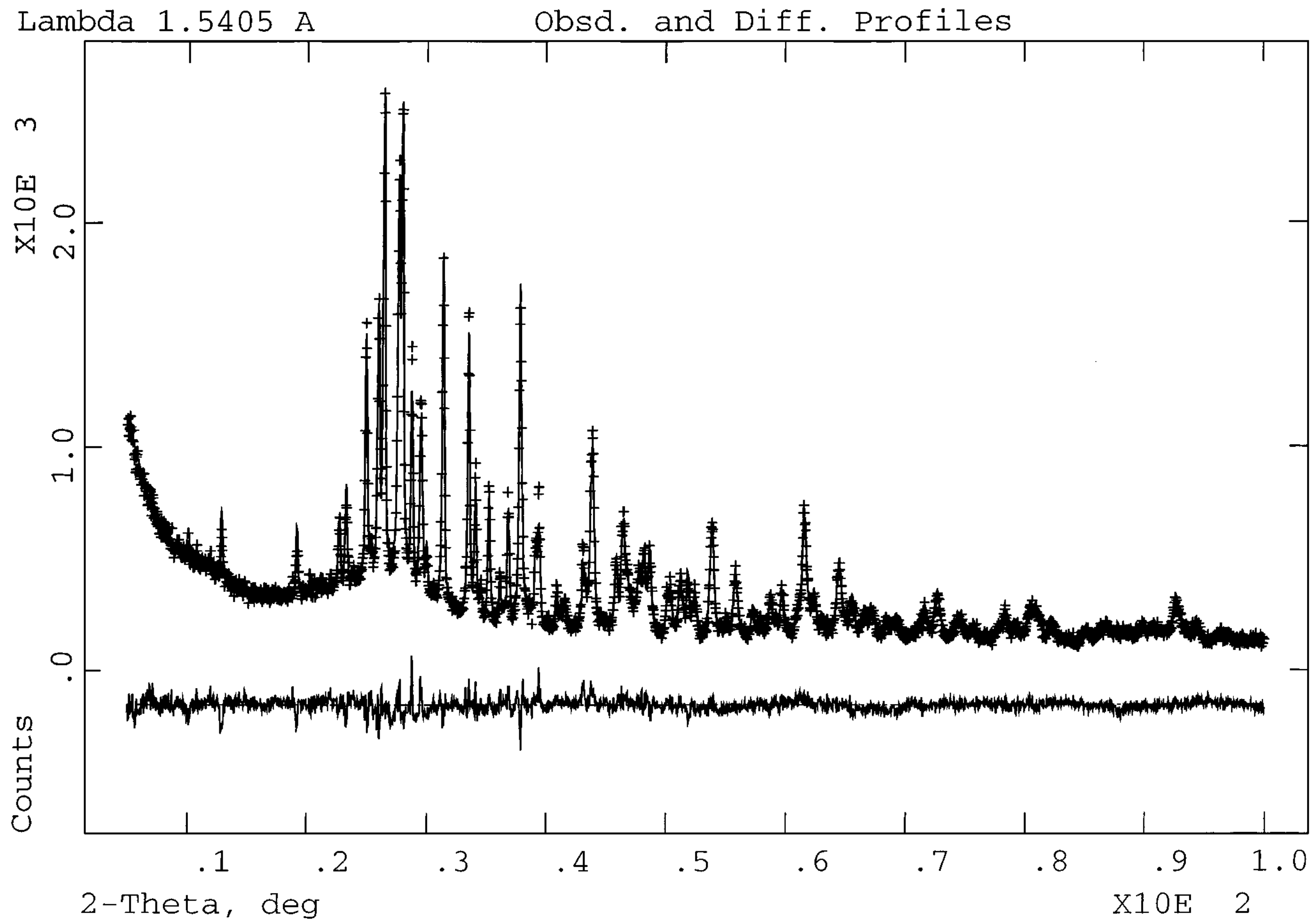

FIG. 1. Observed (+), calculated, and difference (bottom) X-ray powder diffraction pattern of Ba_2CdTe_3 by using GSAS (10).

are coordinated to seven Te^{2-} anions, which can be described as a trigonal prism with one rectangular face capped with a Te^{2-} ion (Fig. 3).

The $CdTe_4$ tetrahedrons in Ba_2CdTe_3 are slightly distorted. Around each Cd, the two Cd–Te bonds participating in the corner-sharing are stretched along the chain direction. Those bond lengths are 2.843 Å, which is longer than the lengths of the other two Cd–Te bonds that are not involved in the corner-sharing of tetrahedrons, 2.808 and 2.806 Å (Table 3). The six bonding angles of Te–Cd–Te

TABLE 1
Summary of Refinement Data and Lattice Parameters of Ba_2CdTe_3

Formula	Ba_2CdTe_3
Space group	*Pnma*
a (Å)	9.819(1)
b (Å)	4.743(1)
c (Å)	19.062(2)
V (Å^3)	887.8(2)
Z	4
Calculated density	5.760 gm/cm^3
Detector	HP Ge low-energy photon spectrometer
Counting time	4 s
Step	0.01°
Profile function	pseudo-Voigt
Number of profile points	9500
Number of parameters refined	36
R_p (%)	5.97
R_{wp} (%)	7.94
R_B	9.28
$R_{exp}{}^a$	8.82
Durbin–Watson statistic	0.979
GOF	0.90

[a] $R_{exp} = R_{wp}/GOF$.

TABLE 2
Atomic Parameters and Standard Deviation for Ba_2CdTe_3

	Wyckoff	X	Y	Z	$100U_{iso}$	Occ.
Ba1	4c	0.4267(3)	0.25	0.7141(2)	2.24(11)	1.00
Ba2	4c	0.2565(2)	0.25	0.4618(1)	1.37(8)	1.00
Cd	4c	0.3707(2)	0.25	0.1354(2)	1.49(8)	1.00
Te1	4c	0.3059(3)	0.25	0.2788(2)	1.64(13)	1.00
Te2	4c	0.1135(3)	0.25	0.0712(2)	1.35(11)	1.00
Te3	4c	0.9875(3)	0.25	0.5977(2)	2.26(10)	1.00

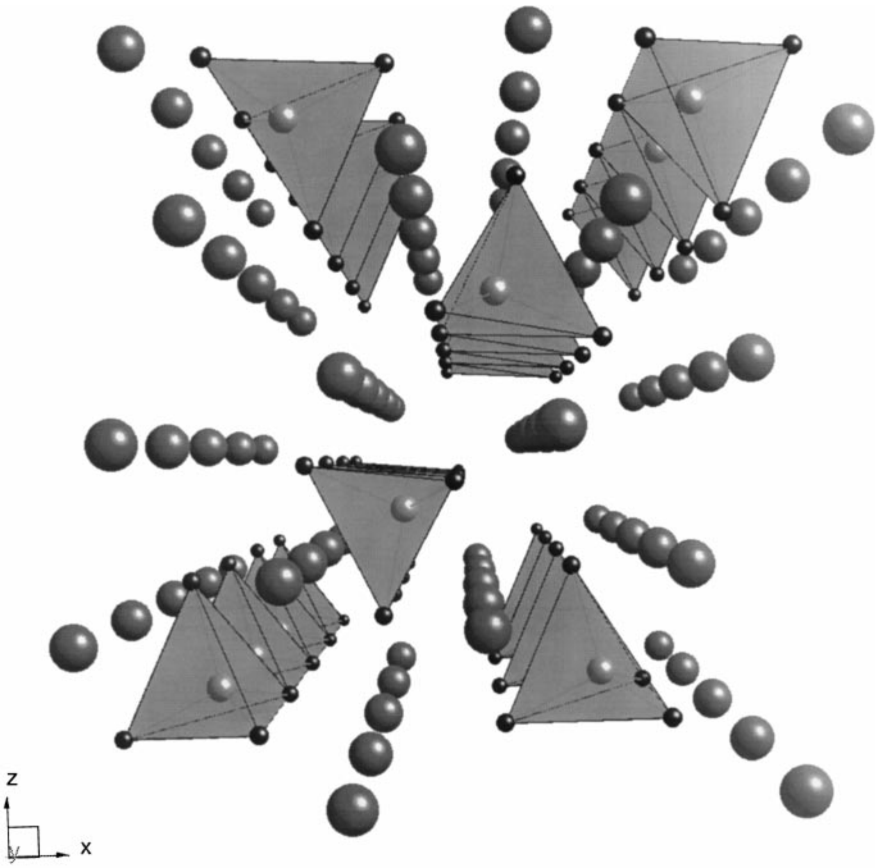

FIG. 2. The structure of Ba_2CdTe_3 viewed along the *y* direction. The discreet dots are Ba. The corner-sharing tetrahedrons of $CdTe_4$ are also shown here. In the middle of each tetrahedron is Cd.

deviate from 109.5° by up to several degrees. A similar tetrahedral distortion also occurs in Ba_2CdSe_3 and Ba_2CdS_3 (8).

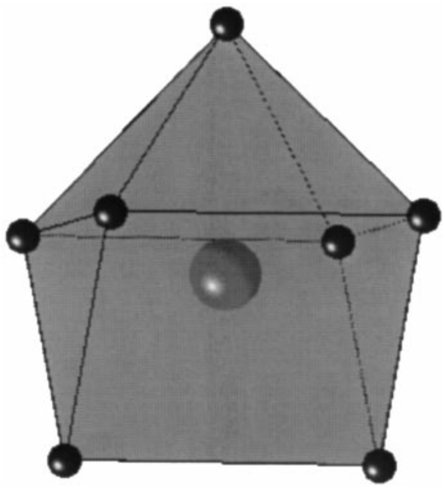

FIG. 3. Monocapped trigonal prism $BaTe_7$.

In order to describe the tetrahedral distortion in a quantitative way, we introduce "distortionality *d*," which is defined according to Eq. [1],

$$d^2 = \sum(\theta_i - 109.5^\circ)^2/N, \qquad [1]$$

where θ_i is the *i*th bond angle around the center atom in the tetrahedron and *N* is the number of bonding angles at each center. The *d* values for the three isostructural chalcogenides

TABLE 3
Selected Bond Distances and Angles for Ba_2CdTe_3

	Distances (Å)		
Ba1–Cd	4.050(3)	Cd–Te1	2.808(4)
Ba1–Te1	3.516(3), 3.541(3)	Cd–Te2	2.806(3)
Ba1–Te2	3.633(3)	Cd–Te3	2.843(2)
Ba1–Te3	3.638(5)		
Ba2–Te1	3.521(4)		
Ba2–Te2	3.406(3), 3.562(3)		
Ba2–Te3	3.556(3)		
	Angles (°)		
Te1–Cd–Te2	102.77(11)	Te2–Cd–Te3	109.30(9)
Te1–Cd–Te3	110.93(9)	Te3–Cd–Te3	113.09(13)

TABLE 4

Bonding Distances Cd−Te, Bond Angles Te−Cd−Te Around Cd, and Tetrahedral Distortionality *d* in Ba_2CdS_3, Ba_2CdSe_3, and Ba_2CdTe_3

	Ba_2CdS_3	Ba_2CdSe_3	Ba_2CdTe_3
Cd–Q1 (Å)	2.53(1)	2.634(3)	2.806(5)
2Cd–Q2 (Å)	2.48(1)	2.613(3)	2.802(4)
Cd–Q3 (Å)	2.57(1)	2.663(3)	2.840(2)
Q1–Cd–Q2 (°)	101.7(4)	101.8(1)	102.8(1)
2(Q1–Cd–Q3) (°)	109.6(4)	110.2(1)	110.9(1)
2(Q2–Cd–Q3) (°)	109.8(4)	109.6(1)	109.3(1)
Q3–Cd–Q3 (°)	115.3(4)	114.6(1)	113.1(1)
d (°)	3.972	3.793	3.211

Note. Q represents S, Se, or Te.

Ba_2CdQ_3 are tabulated in Table 4. Ba_2CdS_3 to Ba_2CdSe_3 and Ba_2CdTe_3 display a slightly decreasing trend of distortion from an ideal tetrahedron with 109.5° bonding angles.

In summary, a new compound Ba_2CdTe_3 was synthesized and its structure was refined by the Rietveld method. A one-dimensional chain $^{1}_{\infty}[\mathrm{CdTe}_{2/2}\mathrm{Te}_2]^{4-}$ with corner-sharing tetrahedra is found to exist in this compound, which is reminiscent of the three-dimensional corner-sharing $CdTe_4$ tetrahedrons in CdTe but different from the layered $(Cd_3Te_4)^{2-}$ net with corner-sharing and edge-sharing tetrahedrons in $K_2Cd_3Te_4$ (5).

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