

Preparation and Characterization of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$

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The preparation and crystal structure of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ is presented. $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ crystallizes in the tetragonal space group $I\bar{4}c2$ ($a = 18.003(2)$ Å, $c = 11.203(3)$ Å, $Z = 4$) with a unique halide structure where Cd is found in both tetrahedral and octahedral coordination. © 1992 Academic Press, Inc.

Introduction

$\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ was first isolated by V. K. Filipov, K. A. Agafonova, and M. A. Yakimov in 1974 during an investigation of the solubilities of halides in water at room temperature (1). Unlike CsCdBr_3 and Cs_2CdBr_4 , two well known ternary compositions in the $\text{CsBr}-\text{CdBr}_2$ system, there is little known about $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$. It has never been observed as a product of solid-state reactions between the binary halides at elevated temperatures. We report here a convenient route for the preparation of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ as a pure phase by precipitation from concentrated HBr.

The stoichiometry of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ can be described as $3\text{Cs}_2\text{CdBr}_4 \cdot \text{CsBr}$. From this representation one might expect the compound to bear a strong resemblance to Cs_2CdBr_4 . Like Cs_2CdBr_4 , Cd is found in tetrahedral coordination in the $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ structure. But this compound is also related to the CsCdBr_3 structure because these two

halides share a common structural feature: linear chains of Cd octahedra. The coexistence of two Cd coordinations, tetrahedral and octahedral, is an unusual feature of the $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ structure. In the following sections the crystal structure of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ is described, and the structural relationships between $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$, CsCdBr_3 , and Cs_2CdBr_4 are discussed. In addition, thermal and optical properties of the title compound are presented.

Experimental

X-ray powder diffraction patterns of samples were obtained with an Enraf-Nonius FR552 Guinier camera with a rotating sample holder, Cu radiation, and silver metal as an internal standard. It was found that $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ is a friable material and will disorder upon grinding. Sharp powder patterns of these materials were obtained by minimizing the handling of the compounds and mounting the samples on a rotating sample holder. Powder diffraction patterns were indexed with the aid of the program LAZY

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PULVERIX (2). Cell parameters were calculated from the x-ray powder diffraction patterns by a least-squares technique with a computer program. Intensities of powder diffraction patterns were determined by comparison with a calibrated photographic step wedge. Data for the single crystal structure were collected on an Enraf-Nonius CAD4 diffractometer at room temperature. Empirical absorption corrections were made using the program DIFABS (3). The structure was solved by direct methods and refined by the full-matrix least-squares method (4). A list of observed and calculated structure factors for $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ has been deposited with the National Auxiliary Publications Service (NAPS) (5).

Differential thermal analysis was carried out on a Harrop Industries DT-736 differential thermal analyzer with a Cyber 702 control and data acquisition system. All experiments were conducted in air. The heating rate was $10^\circ\text{C}/\text{min}$.

The absorption spectra of powders were measured with a scanning reflectometer which was designed to exclude sample fluorescence during measurement. It utilizes an integrating sphere for light collection and monochromators to provide both narrow band input light and narrow band detection.

Preparation of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$

$\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ was prepared by precipitation from hot concentrated HBr. In a typical preparation 0.035 moles CsBr (Johnson Matthey/AESAR: Grade 1) and 0.015 moles of Cd metal (Johnson Matthey/AESAR Cd shot: 99.9999%) were dissolved in 20 ml of hot concentrated HBr (Eastman Kodak Company: reagent ACS grade). The resulting mixture was brought to a boil with constant stirring, then allowed to cool to room temperature with no agitation. White, acicular crystals of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ formed readily during cooling. The precipitate was collected, washed with ethyl alcohol, and allowed to dry in air. The material shows

weak orange luminescence when exposed to 254-nm excitation. The white product does not appear to be hygroscopic and may be stored in air.

Results and Discussion

$\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ can be precipitated from either aqueous solution or concentrated aqueous hydrobromic acid. Experiments carried out in water under the conditions described by Filippov *et al.* (1) gave a low yield, (approximately 10%), of impure $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$. Preparations of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ from concentrated HBr gave yields of around 70% of single-phase material. Concentrated HBr, rather than water, is preferred as the solvent for the preparation of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ because both the yield and the product purity are higher when HBr is used.

Examination of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ crystals under crossed polarizing filters showed that the crystals are uniaxial. The observation that the crystals show clear extinctions every 90° when rotated under crossed polarizers indicated that $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ crystallizes in either the tetragonal or hexagonal crystal system. The acicular crystal habit as well as the orthogonal prismatic form of the precipitated $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ crystals also suggest either tetragonal or hexagonal symmetry.

The structure of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ was determined from a single crystal obtained by precipitation of the compound from concentrated HBr. The crystal data and refinement parameters are summarized in Table I. Analysis of the initial data set led to the selection of a tetragonal unit cell having cell constants of $a = 18.003(2) \text{ \AA}$ and $c = 11.203(3) \text{ \AA}$. The space group was established as either $I4/mcm$ or $I4c2$. The unexpected size of the lattice led us to take precession photographs which confirmed the tetragonal symmetry and the systematic absences indicated by the space groups. While the centrosymmetric space group $I4/mcm$ and the noncentrosymmetric $I4c2$ show the

TABLE I
SUMMARY OF CRYSTAL DATA AND REFINEMENT PARAMETERS FOR Cs₇Cd₃Br₁₃

M.W.: 2306.35 g/mol	D_{calc} : 4.219 g/cc	$Z = 4$
Space group: $I4c2$	a (Å): 18.003(2)	c (Å): 11.203(3)
Cell volume (Å ³): 3631(2)		
Absorption coeff. (μ , MoK α) cm ⁻¹ : 227.84		
Scan technique: $\omega - 2\theta$		Scan rate, deg 2θ min ⁻¹ : 2 to 20
2θ limit, deg: 46		hkl range: 0-19, 0-19, 0-12
No. Unique data measured: 711		
No. of data used in refinement ($I > \sigma(I)$): 602		
No. of parameters: 54		
$R = \sum F_o - K F_c / \sum F_o $: 0.046		
$R_w = (\sum w(F_o - K F_c)^2 / \sum wF_o^2)^{1/2}$: 0.059		
$S = [(\sum w(F_o - K F_c)^2 / (n_o - n_v))]^{1/2}$: 1.190		
Wtg. parameters ($w^{-1} = \sigma^2(F_o) + (pF_o)^2 + q$): $p = 0.03$, $q = 2.0$		
Maximal shift in final cycle, (Δ/σ): 0.08		

same systematic absences, the latter space group was chosen based on the comparison of the statistical averages of the normalized structure factors with the theoretical values obtained assuming a random distribution of atoms (6). Both the statistical averages and the distribution of normalized structure factors (7) strongly indicated that the space group is acentric. The structure was successfully refined in space group $I4c2$. The

atomic positions and thermal parameters are given in Table II. The results indicate that there are no strong anisotropic thermal motions of the atoms in Cs₇Cd₃Br₁₃.

Table III compares bond distances and angles involving Cd polyhedra with reported values for similar geometries. The tetrahedral geometry around Cd(1) is somewhat distorted, similar to that found in Cs₂CdBr₄ (8, 9). The octahedral geometry around

TABLE II
POSITIONAL AND THERMAL PARAMETERS (esd's) FOR Cs₇Cd₃Br₁₃

Wyckoff position	Atom	x	y	z	$U(1,1)$	$U(2,2)$	$U(3,3)$	$U(1,2)$	$U(1,3)$	$U(2,3)$
c	Cs(1)	0.20961(8)	0.20961	0.250	0.0243(6)	0.0243	0.0198(9)	0.0036(9)	-0.003(3)	-U(1,3)
i	Cs(2)	0.20036(8)	0.5004(4)	0.4992(7)	0.0190(7)	0.0409(8)	0.0337(8)	-0.002(3)	0.002(4)	-0.0001(8)
b	Cs(3)	0.0	0.0	0.0	0.072(2)	0.072	0.045(2)	0	0	0
e	Cd(1)	0.37251(9)	0.37251	0.25	0.0226(8)	0.0226	0.024(1)	-0.005(1)	-0.012(2)	-U(1,3)
c	Cd(2)	0.5	0.0	0.25	0.0146(9)	0.0146	0.012(1)	0	0	0
i	Br(1)	0.3210(2)	0.3263(2)	0.4490(2)	0.065(2)	0.041(2)	0.019(1)	-0.002(1)	0.009(2)	0.005(2)
d	Br(2)	0.5	0.0	0.5	0.020(1)	0.020	0.013(2)	0.002(8)	0	0
i	Br(3)	0.3435(2)	0.5124(1)	0.253(1)	0.047(2)	0.019(1)	0.067(2)	0.000(1)	0.016(5)	0.005(5)
i	Br(4)	0.3896(1)	0.1090(1)	0.2510(9)	0.020(1)	0.022(1)	0.031(1)	0.0066(9)	-0.004(4)	0.006(4)

Note. The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^2U(1,1) + k^2b^2U(2,2) + l^2c^2U(3,3) + 2hkabU(1,2) + 2hlacU(1,3) + 2klbcU(2,3))]$, where a , b , and c are reciprocal lattice constants.

TABLE III
COMPARATIVE BOND DISTANCES AND ANGLES
AROUND Cd IN CsCdBr₃, Cs₂CdBr₄, AND Cs₇Cd₃Br₁₃

Cd in tetrahedral geometry		
Distances	Cs ₇ Cd ₃ Br ₁₃	Cs ₂ CdBr ₄ (8)
Cd(1)–Br	2 × 2.553(3) Å 2 × 2.572(3) Å	2.531 Å 2 × 2.558 Å 2.566 Å
Angles	Cs ₇ Cd ₃ Br ₁₃	Cs ₂ CdBr ₄ (8)
Br–Cd–Br	2 × 103.4(4)° 2 × 107.6(4)° 113.4(1)° 121.7(2)°	2 × 104.7° 107.4° 2 × 111.4° 116.7°
Cd in octahedral geometry		
Distances	Cs ₇ Cd ₃ Br ₁₃	CsCdBr ₃ (11)
Cd(2)–Br	4 × 2.801(1) Å 2 × 2.793(2) Å	6 × 2.824 Å
Angles	Cs ₇ Cd ₃ Br ₁₃	CsCdBr ₃ (11)
Br–Cd–Br	4 × 89.9(2)° 4 × 90.2(2)° 4 × 90° 2 × 179.5(4)° 180°	6 × 88.2° 6 × 91.8° 2 × 180° 180°

Cd(2) is essentially undistorted and similar to that found in CsCdBr₃ (10, 11).

X-ray powder diffraction patterns of Cs₇Cd₃Br₁₃ could be completely indexed on the basis of the tetragonal unit cell. The calculated cell parameters from Guinier powder photographs are $a = 18.007(5)$ Å and $c = 11.194(5)$ Å. The calculated density of Cs₇Cd₃Br₁₃ from the X-ray powder diffraction results is 4.22 g/cc. Table IV lists the indices, d -spacings, and observed intensities for the first 15 lines of the X-ray powder diffraction pattern of Cs₇Cd₃Br₁₃.

Discussion of the Structure

The structure of Cs₇Cd₃Br₁₃ is closely related to the structures of both CsCdBr₃,

which crystallizes with the CsNiCl₃ structure, and Cs₂CdBr₄, which crystallizes with the low K₂SO₄ structure. The most notable feature of the Cs₇Cd₃Br₁₃ structure is the presence of two distinct types of cadmium coordination, octahedral and tetrahedral. Figure 1 shows the Cs₇Cd₃Br₁₃ structure projected onto the ab -plane. The two different coordinations of Cd are clearly seen when the structure is viewed along the c -axis. A more detailed description of the structural similarities between Cs₇Cd₃Br₁₃, CsCdBr₃, and Cs₂CdBr₄ is given below.

The structure of CsCdBr₃ has been reported by Knakkegaard-Moeller (10) and McPherson *et al.* (11). CsCdBr₃ adopts the CsNiCl₃ structure. The local coordination geometry around the Cd cation in the CsCdBr₃ structure is slightly distorted octahedral, and the most notable feature of the structure is the $[MX_3^-]_n$ anionic chain consisting of Cd octahedra, which share opposite faces. The $[MX_3^-]_n$ chains in compounds crystallizing with the CsNiCl₃ structure type suggest that some one-dimensional charac-

TABLE IV
OBSERVED POWDER DIFFRACTION DATA FOR
Cs₇Cd₃Br₁₃

hkl	d -space	Intensity
(200)	8.98285	44.0
(211)	6.53305	96.6
(310)	5.69329	159.6
(002)	5.58725	65.0
(321)	4.55572	180.6
(330)	4.24048	54.5
(222)	4.20001	233.1
(312)	3.98704	233.1
(402)	3.50443	359.2
(431)	3.42579	621.8
(332)	3.38029	1000.0
(422)	3.26593	317.2
(521)	3.20093	201.6
(440)	3.18123	275.1
(530)	3.08541	359.2

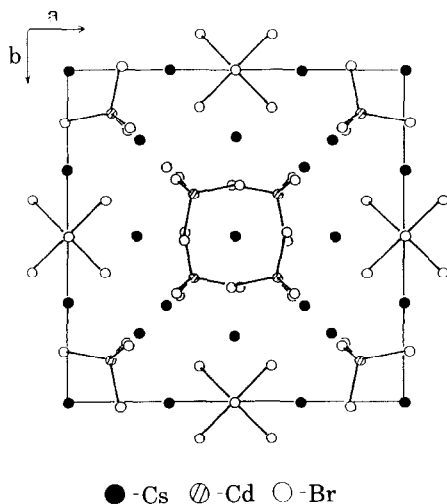


FIG. 1. The structure of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ as viewed along the c -axis. The solid balls are cesium atoms, the hatched balls are cadmium atoms, and the open balls are bromine atoms.

ter may be found in the physical properties of these materials. $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ shares a common structural feature with the CsCdBr_3 ; infinite linear anionic chains of cadmium octahedra run parallel to the c -axis in both structures.

The chains of Cd octahedra in CsCdBr_3 and $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ differ by how the octahedra are linked together in the anionic chains. In the CsCdBr_3 structure, Cd octahedra share opposite faces to form linear chains and the charge of the $[\text{MX}_3^-]_n$ anionic chains is balanced by monovalent Cs cations (11). In the $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ structure, Cd octahedra share opposite corners, forming linear anionic chains which can be described as having stoichiometry $[\text{MX}_3^{3-}]_n$. Figure 2 shows the two types of infinite anionic chains in the CsCdBr_3 and $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ structures. The positions of the linear $[\text{MX}_3^{3-}]_n$ anionic chains of cadmium octahedra in $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ show fourfold symmetry and the chains are isolated from each other by cadmium tetrahedra, as is clearly shown in Fig. 1. As with CsCdBr_3 , one might expect to observe

some anisotropic physical properties in $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ due to the presence of the one-dimensional $[\text{MX}_3^{3-}]_n$ anionic chains. The difference between the chains of octahedra in the two structures can be stated very succinctly: the CsCdBr_3 structure has $[\text{CdBr}_3^-]_n$ anionic chains and the $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ structure has $[\text{CdBr}_3^{3-}]_n$ anionic chains.

The crystal structure of Cs_2CdBr_4 was reported by Altermatt *et al.* in 1979 (8). Cs_2CdBr_4 crystallizes at room temperature with the low K_2SO_4 structure. The most notable feature of this structure is the unusual coordination of Cd. The local coordination of Cd in Cs_2CdBr_4 is tetrahedral and all Cd cations are found as CdBr_4^{2-} anions. Altermatt *et al.* (8) reported in 1979 that Cs_2CdBr_4 and $(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$ were the only two bromide compounds where tetrahedral coordination of Cd had been verified by direct structure determination. The structure reported here demonstrates that the CdBr_4^{2-} anion is also found in $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$.

The $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ structure is similar to the room temperature structure of Cs_2CdBr_4 in that isolated CdBr_4^{2-} tetrahedra occupy special positions in both structures. Although

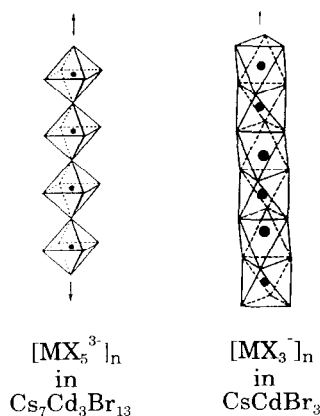


FIG. 2. An illustration showing the differences between $[\text{MX}_3^{3-}]_n$ and $[\text{MX}_3^-]_n$ chains found in cesium cadmium halide structures.

the Cs_2CdBr_4 structure has an orthorhombic unit cell, the isolated CdBr_4^{2-} tetrahedra form a pseudo-hexagonal arrangement when viewed along the a -axis (8). The arrangement of tetrahedrally coordinated Cd is visible when the $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ structure is viewed along the c -axis. The CdBr_4^{2-} tetrahedra appear to form infinite columns parallel to the c -axis. The columns of CdBr_4^{2-} tetrahedra are stuffed with Cs ions to help maintain charge balance, and the columns effectively isolate the $[\text{MX}_3^-]_n$ anionic chains from each other. The unusual arrangement of the tetrahedral groups in $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ reinforces the notion that this structure should exhibit anisotropic physical properties.

Thermal Stability of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$

The thermal stability of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ was examined by differential thermal analysis. Investigations of the high-temperature phase diagram of the CdBr_2 - CsBr ternary system by Il'yasov (12) and Il'yasov and Bergman (13) revealed only two congruently melting phases in the cesium-cadmium-bromide system: CsCdBr_3 and Cs_2CdBr_4 . Other investigations of the Cs-Cd-Br system by Tovmas'yan *et al.* (14) and Il'yasov *et al.* (15) have used X-ray powder diffraction to verify that only CsCdBr_3 and Cs_2CdBr_4 are formed from the melt. These results suggest that $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ should not be stable at elevated temperatures. The results of the DTA experiment are shown in Fig. 3.

The differential thermal analysis trace of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ shows two endothermic peaks, which indicates that the compound melts incongruently. The incongruent melting of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ suggests that the compound is less stable than other cesium cadmium halides at elevated temperatures. X-ray powder diffraction patterns of the residue from the DTA experiment showed Cs_2CdBr_4 as the major phase, consistent with incongru-

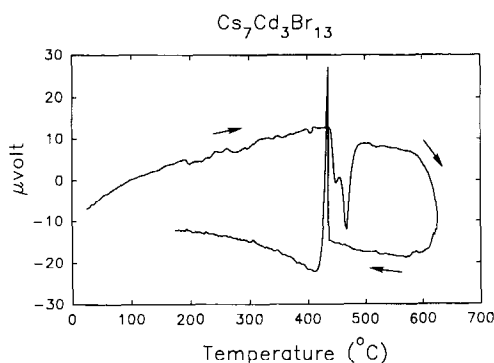


FIG. 3. Differential thermal analysis plot for $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$.

ent melting of the compound. These results are also in agreement with the report of Filippov and Agafonova (16), who commented that $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ melts incongruently but provided no further details. I.I. Il'yasov and Bergman (13) have shown that eutectic compositions exist on either side of the composition Cs_2CdBr_4 , (mp, 457°C), so the exothermic peak with an onset temperature of between 435 and 440°C observed in the cooling curve of the DTA trace can be attributed to the crystallization of Cs_2CdBr_4 from the melt.

It is interesting to note that although $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ can be readily precipitated from acid solution, the compound cannot be prepared from the melt. Filippov and Agafonova (16) have reported that the calculated Gibbs free energy change for the crystallization of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ from aqueous solution is around -8.15 kcal/mole CdBr_2 . The change in free energy for formation of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ from the binary halides is not known, but $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ can be observed as a transient impurity during solid state reactions of the binary halides if the temperature is kept below the melting point of the halides. Unfortunately, conditions for the formation of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ as a single phase material by solid-state reaction above room temperature could not be determined. The

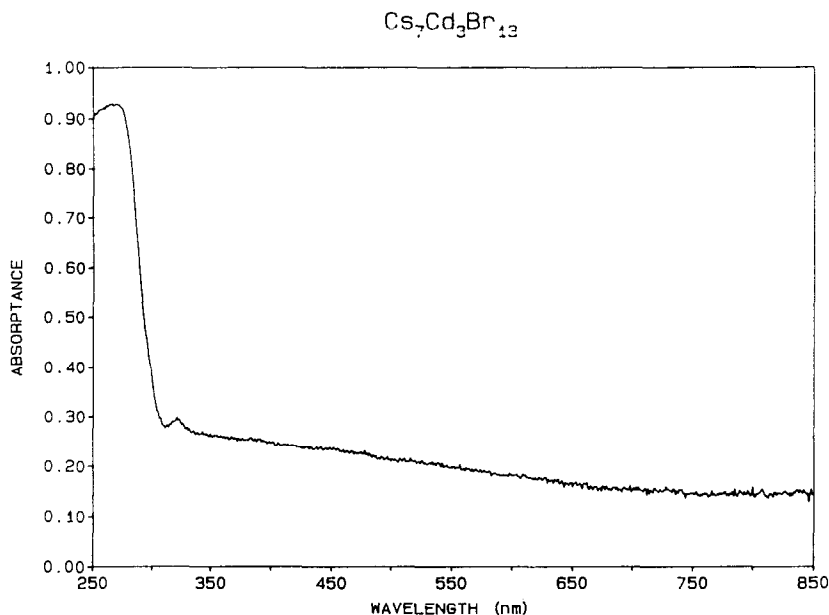


FIG. 4. Optical absorption spectrum for $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$.

solid-state reaction of a 7/3 $\text{CsBr}/\text{CdBr}_2$ molar ratio always led to the formation of Cs_2CdBr_4 in the temperature region between 200 and 500°C.

Optical Properties of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$

Figure 4 shows the optical absorption spectrum of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ prepared as described in the experimental section. The onset of the primary optical absorption in $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ is approximately 300 nm. The weak absorption band located near 320 nm is an optical absorption which is believed to be caused by structural defects in $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ (17). The 320-nm band disappears with annealing and the onset of optical absorption shifts toward higher energies, indicating that electronic interactions related to structural disorder are important in this material (17). Similar phenomena have been observed in CsCdBr_3 (18).

Conclusions

The preparation and structure of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ has been presented. $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ crystallizes in a unique tetragonal structure which accommodates both octahedral and tetrahedral coordination of Cd. The compound melts incongruently at 440°C, and to date has only been prepared as a pure phase by precipitation from solution. $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$ has an optical absorption edge at around 300 nm and is an attractive host material for investigations of the optical properties of cations in different coordinations. Many studies of the luminescent, magnetic, and optical properties of substitutional cations in the CsCdBr_3 structure have been reported (19). It will be interesting to study the properties of compounds resulting from the substitution of optically and magnetically active cations on the different coordination sites of $\text{Cs}_7\text{Cd}_3\text{Br}_{13}$. These investigations will give us a better understanding of the electronic interactions in this unique structure.

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5. See NAPS document No. 04946 for 5 pages of supplementary material. Order form ASIS/NAPS. Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75 up to 20 pages plus \$.30 for each additional page. All orders must be prepaid. Institutions and Organizations may order by purchase order. However, there is a billing and handling charge for this service of \$15. Foreign orders add \$4.50 for postage and handling, for the first 20 pages and \$1.00 for additional 10 pages of material, \$1.50 for postage of any microfiche orders.
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