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A Novel Nonlinear Optical Crystal for the IR Region: Noncentrosymmetrically Crystalline $CsCdBr_3$ and Its Properties

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A noncentrosymmetric crystal structure of $CsCdBr_3$ has been successfully observed with X-ray single-crystal structure analysis. It crystallizes in the hexagonal space group *P*6(3)*mc*, with $a = 7.7281(14)$ Å, $b = 7.7281(14)$ Å, $c = 6.742(2)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$, $Z = 2$. It was obtained by a new preparation procedure different from that reported in the literature that gave a centrosymmetric structure. The structure contains Cd–Br octahedrons, which are connected in a plane-sharing way to form one-dimensional long chains. Each octahedron is slightly distorted, as the three Cd–Br bond lengths are 2.774 Å, while the other three Cd–Br bond lengths are 2.804 Å. The distortion directions of all of the octahedrons are almost parallel and give rise to the accumulation of the microcosmic nonlinear optical (NLO) coefficient. The Kurtz powder technique shows that $CsCdBr_3$ has a powder second harmonic generation of about 2 times as large as that of potassium dihydrogen phosphate (KDP). It shows excellent transparency in the visible and infrared regions. The thermal stability is also good. Therefore it may be utilized as a potential nonlinear optical crystal for the IR region.

Second-order nonlinear optical (NLO) materials have played a key role in optical fields such as laser frequency conversion and optical parameter oscillators.[1] According to the application wavelength ranges, second-order NLO crystal materials can be divided into three main groups, which are ultraviolet NLO crystals, visible NLO crystals, and infrared NLO crystals. In the past decades, several NLO crystal materials used in the UV and visible regions have been found, such as KDP, KTP, $LiNbO_3$, BBO, LBO, etc. But in the IR region the current materials, such as $AgGaSe_2$ and $ZnGeP_2$, are less suitable for applications mainly due to their low laser damage threshold, as their band gaps are narrow.[2] On the other hand, infrared NLO crystals are very important due to their potentially wide applications in many fields such as molecular spectroscopy. So the research for new infrared NLO crystals with excellent properties, especially a high damage threshold, has become one of the key research areas in NLO material science and technology.

In order to obtain materials with a high laser damage threshold, we choose halide compounds as our jumping-off point because of their excellent electrical insulating characteristics, which will be beneficial to the improvement of the laser damage threshold. In the guidance of this principle, this group[3a,b] and an American research group[3c] have independently found an excellent NLO material, $CsGeCl_3$, whose second harmonic generation (SHG) is 5 times as large as that of KDP, and its damage threshold reaches 200 MW/cm.[3d] Recently, in an attempt to synthesize mixed-halide compounds, $CsCdBr_nI_{3-n}$, we mixed the aqueous solutions of CdI_2 and CsBr together to form prism crystals.[4] Elemental analysis shows that the crystal is $CsCdBr_3$, which was synthesized before to adopt centrosymmetric space group *P*6(3)/*mmc*.[5] But our Kurtz powder SHG measurement showed that it is SHG-active (2×KDP).[6] It is well-known that only a noncentrosymmetric structure may possess second-order

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(4) Detailed experimental procedure: 0.74 g of CdI_2 (2 mmol) and 0.43 g of CsBr (2 mmol) were mixed in 3 mL of distilled water. The mixture was refluxed for about 2 h and cooled naturally to get colorless prism-like crystals. Yield: 0.30 g. A large single crystal with size up to 20 × 2 × 2 mm^3 can be grown utilizing a solvent slow evaporation technique in water. Elemental analysis was performed on ICP-JY38 (for metal analysis) and IC-DionicAIX-1 (for halide analysis). Calcd (%): Br, 49.44; Cd, 23.16; Cs, 27.40. Found: Br, 49.42; Cd, 23.00; Cs, 27.22.

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Table 1. Selected Bond Lengths (Å) and Angles (deg)

Cs-Br	3.8641(7)	Cs−Br#11[a]	4.056(10)
Cs−Br#2	3.8641(7)	Cd−Br#12	2.774(6)
Cs−Br#3	3.8641(7)	Cd−Br#10	2.774(6)
Cs−Br#4	3.8641(7)	Cd−Br#13	2.774(6)
Cs−Br#5	3.8641(7)	Cd−Br	2.804(6)
Cs−Br#6	4.039(10)	Cd−Br#14	2.804(6)
Cs−Br#7	4.039(10)	Cd−Br#1	2.804(6)
Cs−Br#8	4.039(10)	Cd−Cd#12	3.371(10)
Cs−Br#9	4.056(10)	Cd−Cd#15	3.371(10)
Cs−Br#10	4.056(10)	Br−Cd#15	2.774(6)

Br#12−Cd−Br#10	87.8(2)	Br#13−Cd−Br#14	92.75(2)
Br#12−Cd−Br#13	87.8(2)	Br−Cd−Br#14	86.7(2)
Br#10−Cd−Br#13	87.8(2)	Br#12−Cd−Br#1	92.75(2)
Br#12−Cd−Br	179.2(3)	Br#10−Cd−Br#1	92.75(2)
Br#10−Cd−Br	92.75(2)	Br#13−Cd−Br#1	179.2(3)
Br#13−Cd−Br	92.75(2)	Br−Cd−Br#1	86.7(2)
Br#12−Cd−Br#14	92.75(2)	Br#14−Cd−Br#1	86.7(2)
Br#10−Cd−Br#14	179.2(3)	Br#12−Cd−Cd#12	53.22(16)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x + y, -x, z$; #2 $-y, x - y - 1, z$; #3 $-y + 1, x - y, z$; #4 $x, y - 1, z$; #5 $-x + y + 1, -x, z$; #6 $y, -x + y, z + {}^1/_2$; #7 $-x + 1, -y, z + {}^1/_2$; #8 $x - y, x - 1, z + {}^1/_2$; #9 $x - y, x - 1, z - {}^1/_2$; #10 $y, -x + y, z - {}^1/_2$; #11 $-x + 1, -y, z - {}^1/_2$; #12 $-x, -y, z - {}^1/_2$; #13 $x - y, x, z - {}^1/_2$; #14 $-y, x - y, z$; #15 $-x, -y, z + {}^1/_2$; #16 $x, y + 1, z$.

NLO effects. So there exist two possibilities. One is that the centrosymmetric structure reported in the reference was incorrect. The other is that what we have obtained is $CsCdBr_3$ with a new structure type. In order to validate our hypothesis, we synthesized $CsCdBr_3$ over again according to the method in the reference, that is, to use CsBr and $CdBr_2$ as the reactants. The product we obtained is also prism-like, but exhibits no SHG. So we can confirm that what we have prepared from CdI_2 and CsBr is $CsCdBr_3$ with a new structure type. The X-ray single crystal structure analysis was thus conducted and proved that it is really noncentrosymmetric with a space group *P*6(3)*mc*.[7] Table 1 lists some bond lengths and bond angles. In the structure, one cadmium atom and six bromide atoms form an octahedron. The cadmium−bromide octahedrons are connected in a plane-sharing way to form one-dimensional long chains (Figure 1). Figure 2 is the crystal packing along the *c* axis. Each octahedron is slightly distorted, as three Cd−Br bond lengths are 2.774 Å, while the other three Cd−Br bond lengths are 2.804 Å, 0.03 Å longer. It is notable that all the Cd−Br bond lengths are the same (2.824 Å) in the centrosymmetric $CsCdBr_3$ crystal.[5] In our case, the distortion directions of all the octahedrons are almost parallel as indicated in Figure 1, which is beneficial to the accumulation of the microscopic nonlinear optical (NLO) coefficient.

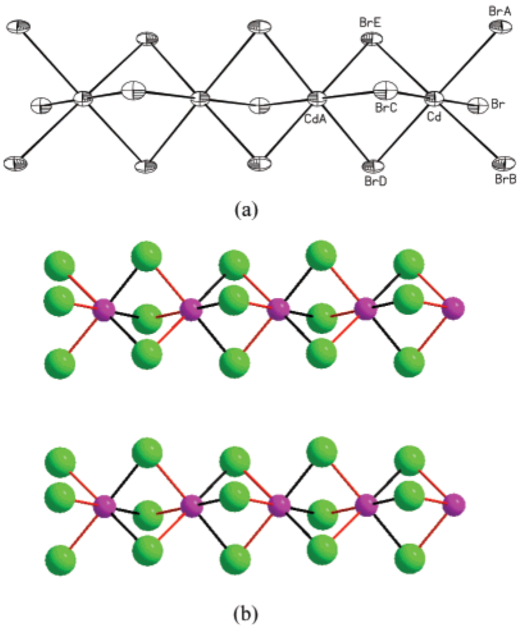

Figure 1. (a) The structure of a one-dimensional cadmium−bromide octahedron long chain with 30% thermal ellipsoids. (b) Representation of the cadmium−bromide octahedron distortion (the green balls represent bromide atoms, while the purple ones represent cadmium atoms; the red bond length is 2.804 Å, while the black bond length is 2.774 Å).

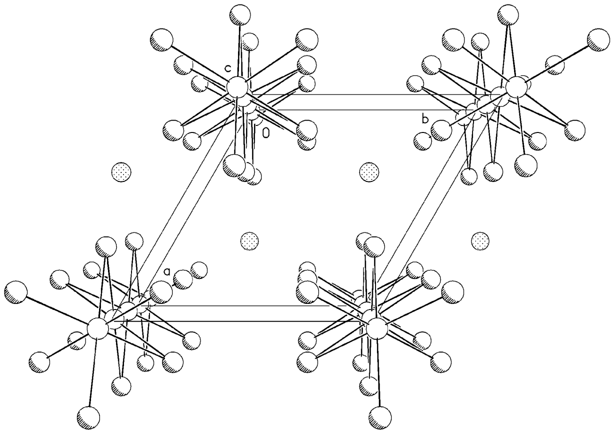

Figure 2. Crystal packing along the *c* axis.

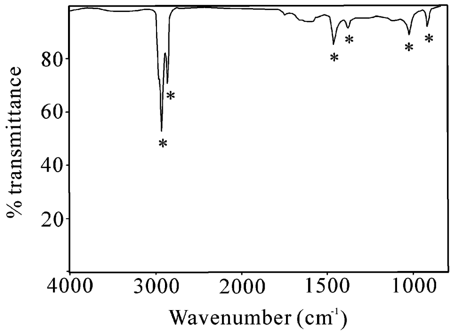

Figure 3. IR spectrum of $CsCdBr_3$ in paraffin oil [the peaks with an asterisk (∗) belong to the vibrations of paraffin oil].

The infrared and UV−visible−near-infrared electronic absorption spectra were performed on a NICOLET 170SX FT-IR spectrophotometer with a KBr pellet in the region 4000−400 cm^{-1} and a Hitachi 3400 UV−vis spectrophotometer, respectively. The infrared spectrum shows that $CsCdBr_3$ is transparent in the middle-infrared region and does not show any additional absorption (Figure 3). In addition, it is transparent in the visible region and even down to about

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(6) The optical SHG effect was investigated using the Kurtz powder technique. A Nd:YAG laser was utilized to generate fundamental 1064 nm light. Microcrystalline KDP served as the standard.

(7) The data were collected at 293 K using the $\omega/2\theta$ scan mode and corrected for Lorentz and polarization effects as well as absorption during data reduction using Enraf-Nonius Molen/VAX software. The structure refinement method was based on full-matrix least-squares on F^2. Crystal data for $CsCdBr_3$: hexagonal, *P*6(3)*mc* (No. 186); $a = 7.7281(14)$ Å, $b = 7.7281(14)$ Å, $c = 6.742(2)$ Å; $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$; $V = 348.74(14)$ Å^3; $Z = 2$; $D = 4.619$ g/cm^3; $\mu = 25.326$ mm^{-1}; $F(000) = 416$; $\lambda = 0.71073$ Å; R1 = 0.0558, wR2 = 0.1383; and GOF on F^2 is 1.063.

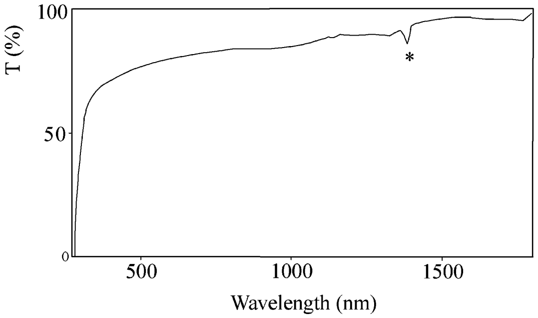

Figure 4. UV−vis−near-IR spectrum of $CsCdBr_3$ in solution [the small peak with an asterisk (∗) is an instrumental artifact signal].

300 nm (Figure 4), which is the absorption edge of $CsCdBr_3$ in solution. We can calculate approximately the band gap of the compound to be 4.1 eV, which is at least similar to the band gap of $LiNbO_3$ (3.5 eV). It is known that the band gap is consistent with the laser damage threshold. The larger the band gap is, the higher the laser damage threshold will be. So we may expect that $CsCdBr_3$ will exhibit excellent laser damage threshold properties.

The thermogravimetric analysis (TGA) measurement was carried out in static air on a Shimadzu DT-40 at a scan rate of 20 °C/min. It is clear that $CsCdBr_3$ has excellent thermal stability as there is no obvious weight loss up to 440 °C (Figure 5).

In summary, we have reported the preparation of a new form of $CsCdBr_3$ crystal with a noncentrosymmetric structure. It exhibits an SHG effect of about 2 times as large as that of KDP. It is transparent in the middle- and near-IR region and the visible region. Absorption edge calculation indicates that it may exhibit a high laser damage threshold. It is expected that $CsCdBr_3$ may be used as an excellent candidate for second-order NLO application in the IR region.

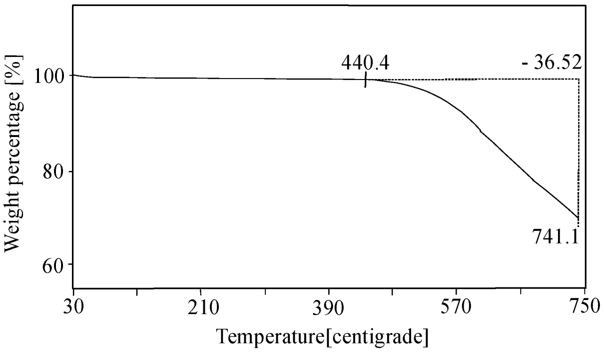

Figure 5. TGA curve of $CsCdBr_3$.

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Supporting Information Available: Crystallographic file in CIF format for $CsCdBr_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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