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ARTICLE TYPE

Synthesis and Characterization of $Cd_4YbO(BO_3)_3$ – A Congruent Melting Cadmium-oxyborates with Large Nonlinear Optical Properties

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A nonlinear optical crystal cadmium-ytterbium oxyborates $Cd_4YbO(BO_3)_3$ has been synthesized through high-temperature solid-state reactions. In the crystal structure, CdO_n (n = 6, 8) , YbO_6 distorted polyhedra and π-delocalization BO_3 groups interconnect via shared edges and corners to form a complicated three-dimensional (3D) network. The second harmonic generation (SHG) measurement shows that $Cd_4YbO(BO_3)_3$ possesses a large SHG response about four times as that of KH_2PO_4 (KDP) and is phase-matchable in the visible region. In addition, it exhibits a wide transparent regions ranging from near UV to middle IR. The title compound melts congruently suggesting that this material is a promising NLO material.

Introduction

Nonlinear-optical (NLO) materials,[1] as frequency conversion devices for providing coherent radiation in a wide-wavelength range, play an indispensable role in laser science and technology. Thus, they have attracted much attention. However it is particularly difficult to search for suitable materials with high NLO coefficients and wide transparency. It presents a great challenge to design new crystal materials with a preset function by an inorganic crystal engineering method. Employing noncentrosymmetric (NCS)[2] chromophores as building units offers a great strategy for synthesizing new NLO materials. Noncentrosymmetric (NCS) building units consist of distorted polyhedra with a d^0 cation center resulting from a second-order Jahn–Teller effect,[3] polar displacement of a d^{10} cation center,[4] or distortion from the stereochemically active lone pair (SCALP) effect of the cation,[5] or borate π-orbital systems.[6] It has been demonstrated that the combination of the above two types of polarization groups can produce compounds with excellent SHG properties such as $Pb_2B_5O_9I$,[7] $BaMo_2TeO_9$,[3a] $BaNbO(IO_3)_6$.[8]

In the past decades, borates[9] with π-conjugated systems have been widely considered as an ideal candidate for designing new NLO materials because of their wide transparency, noncentrosymmetric (NCS) structure types, high damage threshold, and high optical quality. In order to further enhance the second harmonic generation (SHG), Chen's group[4a] employed the d^{10} cation Cd^{2+} with polar displacement and the Bi^{3+} cation with SCALP effect to be incorporated in borates, resulting in the discovery of a new NLO material $Cd_4BiO(BO_3)_3$ with strong SHG responses which is 6 times as that of KDP. However, it is known that introducing the BiO_6 distorted octahedron into borates may make the UV absorption edge shift sharply towards the red. In the present research, we introduced rare earth (Re) to substitute for bismuth in the Bi_2O_3-CdO-B_2O_3 system because the NLO materials containing rare earth elements are with shorter UV absorption edge and excellent physicochemical properties such as $YAl_3(BO_3)_4$ (YAB),[10] $Y_{0.57}La_{0.72}Sc_{2.71}(BO_3)_4$ (YLSB)[11] and $GdCa_4(BO_3)_3$ (GCOB).[12] Guided by this idea, our exploration of the CdO-B_2O_3-Re_2O_3 (Re = La, Sc, Yb) system leads to the discovery of a new UV NLO material, $Cd_4YbO(BO_3)_3$ with a wide transparent regions ranging from UV to middle IR and a large SHG effect, measured on ground crystals, about four times that of KDP. Herein we report the syntheses, crystal structures, and optical properties.

Experimental Section

Reagents

$CdCO_3$ (99%), H_3BO_3 (99%) and Yb_2O_3 (99.99%) were purchased from Sinopharm and used as received.

Synthesis

Single crystals of $Cd_4YbO(BO_3)_3$ was grown through high-temperature solid state reactions. A mixtures of $CdCO_3$ (8.0 mmol), H_3BO_3 (6.0 mmol) and Yb_2O_3 (1.0 mmol) in a molar ratio of 8 : 6 : 1 were ground and loaded into platinum crucibles. The synthesis was performed in four steps. First, the mixtures were heated at 500 ℃ for one day in order to decompose H_3BO_3 and $CdCO_3$. Second, the resulting mixtures were further heated for one day at 1200 °C until transparent and clear melts were formed. Third, the melts were allowed to cool slowly (3 °C/h) to the final crystallization temperature (1100 °C). Finally, the obtained mixtures were quenched to room temperature. Colorless, transparent crystals were obtained for struture determination. After proper structural analysis, pure powder samples of $Cd_4YbO(BO_3)_3$ were obtained in quantitative yield through the

Table 1. Crystal Data and Structure Refinement for $Cd_4YbO(BO_3)_3$.

Formula	$Cd_4YbO(BO_3)_3$
Formula Mass (amu)	815.07
Crystal System	Monoclinic
Space Group	*Cm*
a (Å)	7.938 (4)
b (Å)	15.794 (7)
c (Å)	3.4414(15)
β (°)	99.992(9)
V(Å^3)	424.9(3)
Z	2
ρ(calcd) (g/cm^3)	6.370
Temperature (K)	293(2)
λ(Å)	0.71073
F(000)	714
μ (mm^{-1})	20.79
Final R indices (I>2σ (I))^a R_1/wR_2	0.0527/0.1367
R indices (all data)^a R_1/wR_2	0.0545/0.1380
GOF on F^2	1.11
Absolute Structure Parameter	0.00

$^a R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

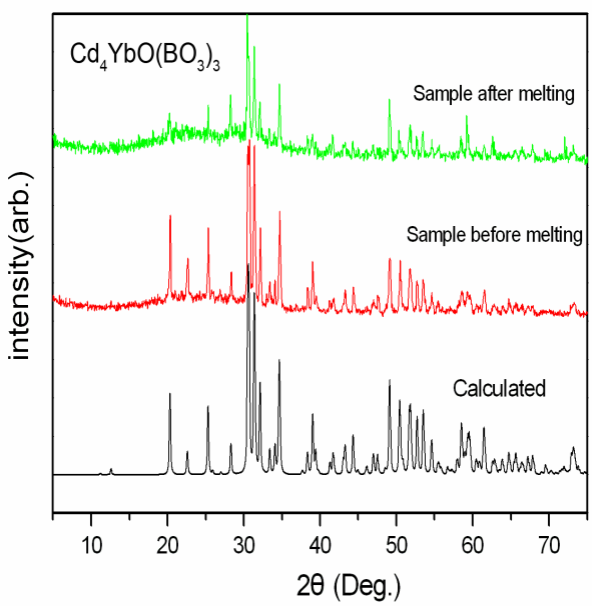

Figure 1: Experimental and calculated XRD patterns for $Cd_4YbO(BO_3)_3$. The black curve is the calculated one, the red is the pattern of sample before melting and the green is the pattern of sample after melting.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for $Cd_4YbO(BO_3)_3$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

atom	x	y	z	U_{eq}(Å^2)	BVS
Yb(1)	0.0227(2)	0.5000	0.6932(3)	0.015(1)	2.615
Cd(1)	0.3790(2)	0.3879(1)	0.3596(3)	0.002(1)	2.068
Cd(2)	0.2642(1)	0.1738(1)	0.0552(5)	0.009(1)	1.717
O(1)	0.1990(30)	0.5000	0.2750(40)	0.008(3)	1.809
O(2)	0.5490(30)	0.2719(13)	0.3900(50)	0.021(2)	1.876
O(3)	0.2370(30)	0.3213(11)	0.8070(60)	0.010(2)	1.936
O(4)	0.0670(20)	0.0768(11)	-0.0590(40)	0.012(3)	2.123
O(5)	0.4360(20)	0.1414(12)	-0.3880(40)	0.016(3)	1.944
O(6)	-0.1700(18)	0.5000	1.1070(90)	0.029(3)	1.700
B(1)	0.1400(20)	0	-0.0190(50)	0.004(6)	2.884
B(2)	0.0770(30)	0.3005(17)	0.6110(70)	0.006(4)	2.815

solid-state reactions from the stoichiometric mixtures of $CdCO_3$, H_3BO_3 and Yb_2O_3 at 950 ℃ for 5 days.

Single Crystal X-ray Diffraction

Single crystal X-ray diffraction data were collected at room temperature on a Rigaku Mercury CCD diffractometer with graphite-monochromatic Mo Kα radiation (λ = 0.71073 Å). A transparent block of crystal was mounted on a glass fiber with epoxy for structure determination. A hemisphere of data was collected using a narrow-frame method with the ω-scan mode. The data were integrated using the CrystalClear program, and the intensities were corrected for Lorentz polarization, air absorption, and absorption attributable to the variation in the path length through the detector faceplate. Absorption corrections based on the Multiscan technique[13] were also applied. The structure was solved by the direct methods and refined by full-matrix least-squares fitting on F^2 using SHELX-97.[14] All of the structures were verified using the ADDSYM algorithm from the program PLATON,[15] and no higher symmetries were found. Relevant crystallographic data and details of the experimental conditions for $Cd_4YbO(BO_3)_3$ are summarized in Table 1. Atomic coordinates and isotropic displacement coefficients are listed in Table 2. Selected bond lengths and angles (deg) for $Cd_4YbO(BO_3)_3$ are listed in Table 3.

Powder X-ray Diffraction

X-ray diffraction patterns of polycrystalline materials were obtained on a Rigaku Dmax2500 powder X-ray diffractometer by using Cu Kα radiation (λ=1.540598 Å) at room temperature in the angular range of 2θ = 5-75° with a scan step width of 0.05° and a fixed time of 0.2 s. The powder XRD patterns for the pure

Table 3. Selected bond lengths (Å) and angles (deg) for $Cd_4YbO(BO_3)_3$.[a]

Yb1—O1	2.17 (2)	Yb1—O6^{ii}	2.31 (3)
Yb1—O1^{i}	2.24 (2)	Yb1—O5^{iii}	2.340 (19)
Yb1—O6	2.26 (3)	Yb1—O5^{iv}	2.340 (19)
Cd1—O1	2.263 (15)	B1—O4^{xiii}	1.34 (2)
Cd1—O2	2.27 (2)	B1—O6^{ix}	1.49 (5)
Cd1—O3^{ii}	2.291 (19)	B2—O2^{viii}	1.37 (3)
Cd1—O3	2.310 (19)	B2—O5^{iii}	1.45 (3)
Cd1—O4^{vi}	2.314 (15)	O4^{xiii}—B1—O4	129 (3)
Cd1—O4^{vii}	2.346 (15)	O4^{xiii}—B1—O6^{ix}	115.3 (17)
Cd2—O5^{i}	2.226 (18)	O4—B1—O6^{ix}	115.3 (17)
Cd2—O4	2.228 (18)	O2^{viii}—B2—O3	121 (2)
Cd2—O5	2.289 (17)	O2^{viii}—B2—O5^{iii}	119 (2)
Cd2—O2^{viii}	2.356 (19)	O3—B2—O5^{iii}	120 (2)
Cd2—O3ii	2.413 (18)		

[a] Note. Symmetry transformations used to generate equivalent atoms: (i) x, y, z+1; (ii) x, y, z−1; (iii) x−1/2, −y+1/2, z+1; (iv) x−1/2, y+1/2, z+1; (v) x, −y+1, z; (vi) x+1/2, −y+1/2, z; (vii) x+1/2, −y+1/2, z+1; (viii) x−1/2, −y+1/2, z; (ix) x+1/2, y−1/2, z−1; (x) x+1/2, y−1/2, z; (xi) x−1/2, −y+1/2, z−1; (xii) x+1/2, −y+1/2, z−1; (xiii) x, −y, z.

powder samples of $Cd_4YbO(BO_3)_3$ showed good agreement with the calculated XRD patterns from the single-crystal models (Figure 1).

Thermal Analysis

Differential thermal analysis (DTA) was performed under nitrogen atmosphere on a NETZSCH DTA404PC. The sample and reference (Al_2O_3) were enclosed in Pt crucibles, heated from room temperature to 1200 °C for $Cd_4YbO(BO_3)_3$ and then allowed to cool to 100 °C at a rate of 10 °C/min.

Infrared Spectroscopy

IR spectra were recorded on a Magna 750 Fourier transform infrared (FT-IR) spectrometer as KBr pellets in the range of 4000-400 cm^{-1}.

UV-vis Diffuse Reflectance Spectroscopy

The UV-vis diffuse reflection data were recorded at room temperature using a powder sample with $BaSO_4$ as a standard (100% reflectance) on a PerkinElmer Lamda-900 UV/vis/NIR spectrophotometer and scanned at 200-2500 nm. Reflectance spectra were converted to absorbance using the Kubelka-Munk function.[16]

Second-Harmonic Generation

Powder second-harmonic generation (SHG) signals were measured using the experimental method adapted from that reported by Kurtz and Perry[17] with the wavelength of the fundamental (1064 nm doubled to 532 nm). Since SHG efficiencies were known to be strongly dependent on particle size, polycrystalline samples were ground and sieved into the following particle size ranges: 20-44, 44-74, 74-105, 105-149, and 149-210 μm. In order to make relevant comparisons with known SHG materials, crystalline KDP were also ground and sieved into the same particle size ranges. The samples were pressed between glass microscope cover slides and secured with tape in 1-mm thick aluminum holders containing an 8-mm diameter hole. They were subsequently placed in a light-tight box and irradiated with a pulsed infrared beam (10 ns, 3 mJ, 10 Hz) from a Q-switched Nd: YAG laser at a wavelength of 1064 nm. A cutoff filter was used to limit background flash-lamp light on the sample, and an interference filter (530 ± 10 nm) was used to select the second harmonic for detection with a photomultiplier tube attached to a RIGOL DS1052E 50-MHz oscilloscope. This procedure was then repeated using the standard nonlinear optical material KDP, and the ratio of the second-harmonic intensity outputs was calculated. No index-matching fluid was used in any of the experiments.

Computational Descriptions.

First principle band structure and density of states (DOS) calculations were carried out by employing the plane-wave basis pseudopotential method as implemented in the CASTEP.[18] The exchange and correlation effects were considered by Perdew−Burke−Ernzerhof (PBE) in the generalized gradient approximation (GGA).[19] Norm-conserving pseudopotentialsare selected to describe the interactions between the ionic cores and the valence electrons.[20] In the atoms, B: $2s^22p^1$, O: $2s^22p^4$, Cd: $4d^{10}5s^2$, Yb:$4f^{14}5s^25p^66s^2$, were treated as valence electrons. A kinetic-energy cutoff of 700 eV was set for the self-consistent-field convergence of the total electronic energy. Monkhorst–Pack k-point meshes with a density of 4 × 4 × 7 points in the Brillouin zone of the $Cd_4YbO(BO_3)_3$unit cell are chosen. The other parameters and convergence criteria were adopted the default values of the CASTEP code.

Results and Discussion

Crystal Structure

$Cd_4YbO(BO_3)_3$ is isostructural to its Bi derivative $Cd_4BiO(BO_3)_3$ and crystallize into a monoclinic crystal system with an acentric space group of *Cm*. Its structure is an intricate three-dimensional (3D) framework of interconnecting $Cd1O_6$, $Cd2O_8$ and$Yb1O_6$ distorted polyhedra, and π-delocalization BO_3 planar triangles as shown in Figures 2a and 2b. There are two kinds of boron sites, B(1) and B (2), with three-fold coordination. BO_3 planar triangles with B-O bond lengths ranging from 1.34 (2) to 1.49 (5) Å lie

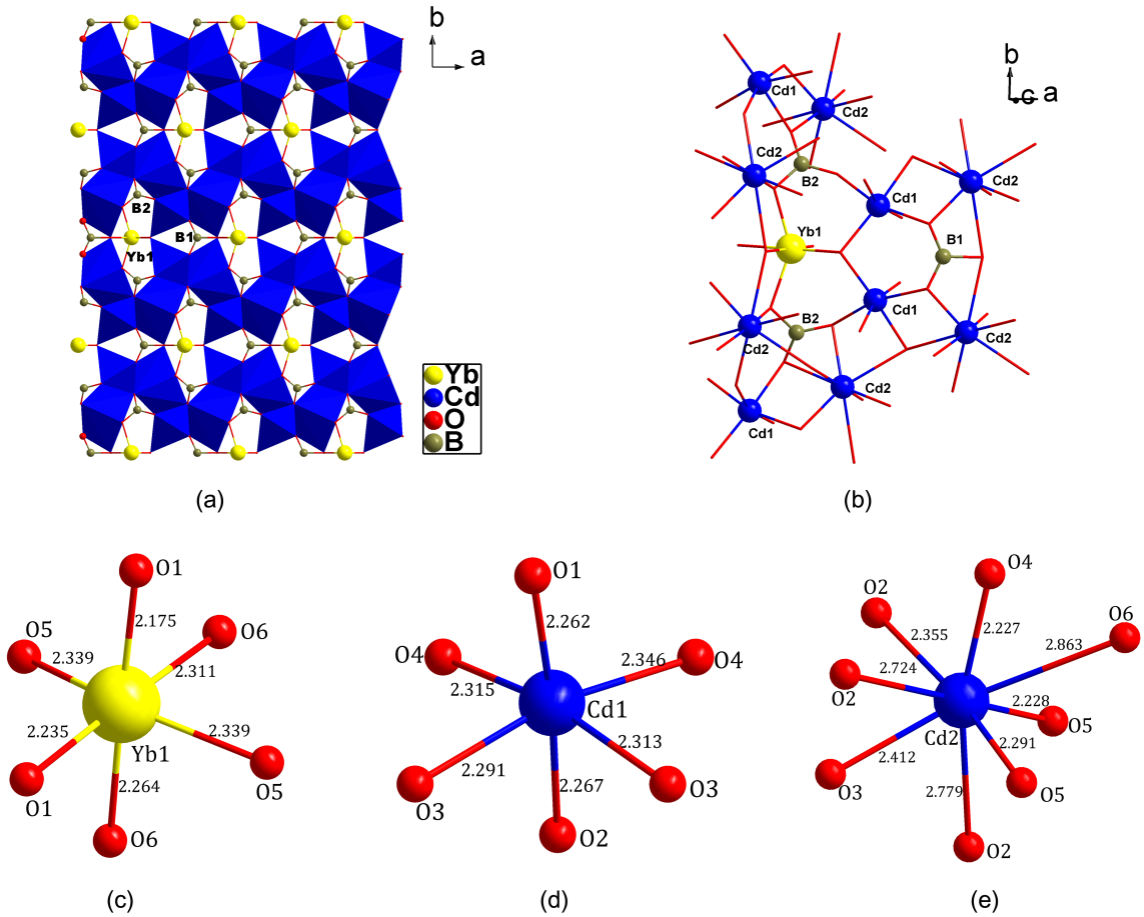

Figure 2: View of the structure of $Cd_4YbO(BO_3)_3$ down the c axis (a) and cation coordinate environments (b), and the coordination of oxygen atoms around Yb1 (c), Cd1 (d), and Cd2 (e) cations.

approximately parallel to the (001) plane. In this structure, all the BO_3 planar triangles are approximately parallel along the c axis that produces cooperative contribution to the macroscopic SHG effect. There are two types of Cd^{2+} ions that occupy distorted polyhedra sites: $Cd1O_6$, $Cd2O_8$ distorted polyhedra (Figure 2c). The Cd–O bond lengths range from 2.262 – 2.346 Å in $Cd1O_6$ distorted polyhedra, and 2.227 – 2.863 Å in $Cd2O_8$ distorted polyhedra. Each $Cd1O_6$ distorted octahedron shares corners with five BO_3 triangles, while every $Cd2O_8$ distorted dodecahedron shares corners with two and edges with three BO_3 triangles. Along the c axis, $Cd1O_6$ and $Cd2O_8$ distorted polyhedra interconnect via sharing edges and corners into 1D double chains. The double chains are further interconnected via sharing corners and edges into a 3D framework with the eight-member and four-member tunnels. Then, the B2 and Yb atoms are located in eight-member tunnels, while the B1 atoms are located in four-member tunnels. The Yb^{3+} cation is surrounded by six oxygen atoms, forming a YbO_6 distorted octahedron with Yb-O bond lengths ranging from 2.175 to 2.339 Å, and the octahedron shares corners with four BO_3 triangles.

The bond valence sums for $Cd_4YbO(BO_3)_3$ is calculated using the formula

$$V_i = \sum_j S_{ij} = \sum_j \exp\left\{\left(r_0 - r_{ij}\right)/B\right\} \qquad (1)$$

where S_{ij} is the bond valence associated with bond length r_{ij} and r_0 and B (usually 0.37) are empirically determined parameters.[21] The calculated total bond valence for Cd, Yb, B, and O atoms are summarized in Table 2. These valence sums are in good agreement with the expected oxidation states which suggest that the reported crystal structure is correct.

Thermal Properties

The DSC diagrams of $Cd_4YbO(BO_3)_3$ exhibit one endothermic peak in the heating curves and one exothermic peaks in the cooling curves, revealing that it melts congruently at around 1150 ℃ (Figure 3). To verify that $Cd_4YbO(BO_3)_3$ melts congruently, $Cd_4YbO(BO_3)_3$ powders were placed into a platinum crucible and heated to 1200 ℃ until the powders melted completely. The powders were allowed to cool to room temperature. Analysis of the powder XRD patterns of the solidified melts reveals that the solid products exhibit a diffraction pattern identical to that of the initial compound powders (Figure 1), further demonstrating that

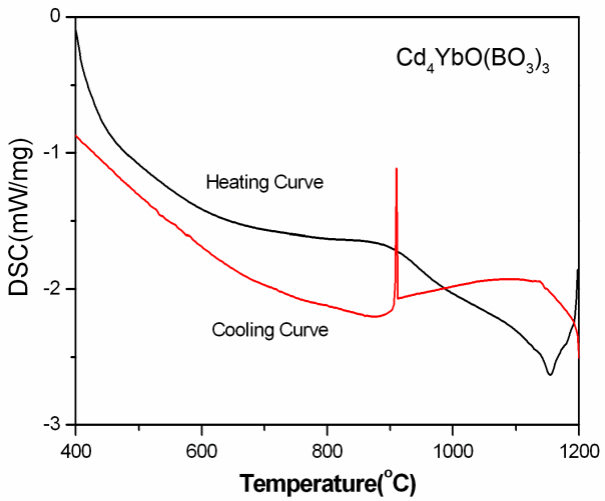

Figure 3: DSC curves of $Cd_4YbO(BO_3)_3$

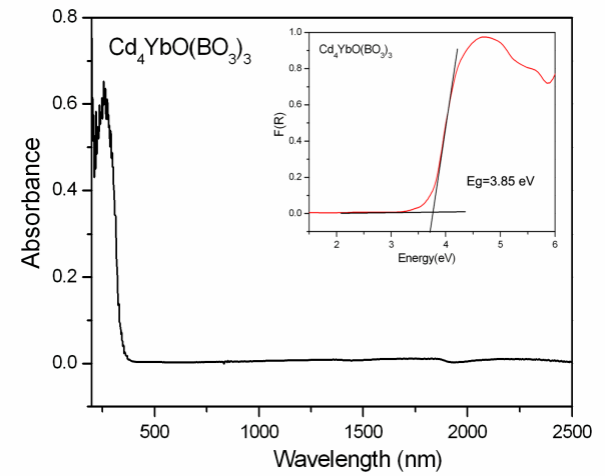

Figure 4: UV absorption spectra and Optical diffuse reflectance spectra of $Cd_4YbO(BO_3)_3$

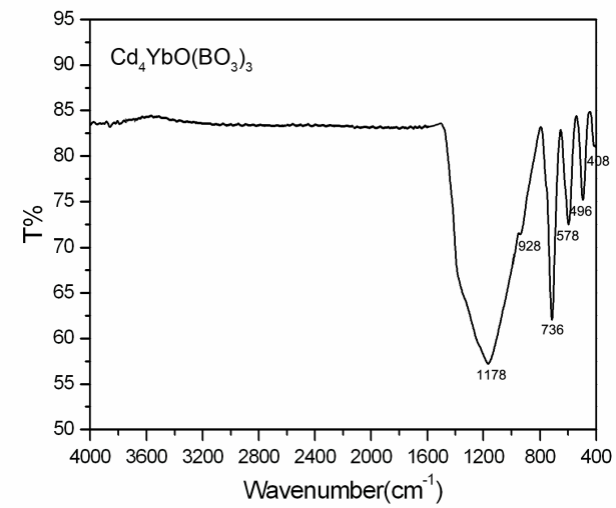

Figure 5: IR spectra for $Cd_4YbO(BO_3)_3$.

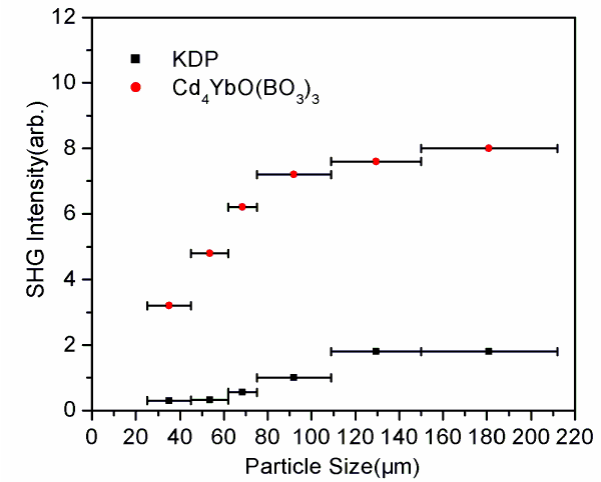

Figure 6: SHG measurements of $Cd_4YbO(BO_3)_3$ ground crystals (solid circle) with KDP (open circle) as a reference (1064 nm doubled to 532 nm).

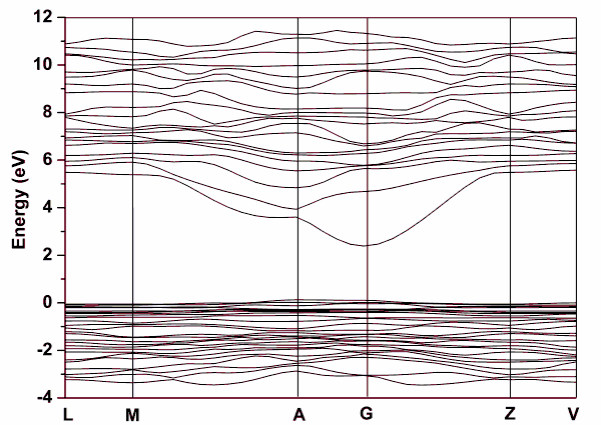

Figure 7: Band structure for $Cd_4YbO(BO_3)_3$.

$Cd_4YbO(BO_3)_3$ is congruent melting compounds. This behavior indicates that its single crystals with large size and high quality could be grown by the Czochralski method.

Optical Properties

UV-Vis diffuse reflectance spectra was collected for $Cd_4YbO(BO_3)_3$. Absorption (K/S) data were calculated from the following Kubelka-Munk function: $F(R) = (1-R)^2/2R = K/S$, where R is the reflectance, K is the absorption, and S is the scattering. In the (K/S)-versus-E plots, extrapolating the linear part of the rising curve to zero provides the onset of absorption. UV absorption spectra of $Cd_4YbO(BO_3)_3$ reveals that it has wide transparent regions ranging from near UV to middle IR (Figure 4). Optical diffuse reflectance spectrum studies indicate that the optical band gap for $Cd_4YbO(BO_3)_3$ are approximately 3.85 eV with UV cut-off edge of 322 nm (Figure 4). Compared with its isostructural compound $Cd_4BiO(BO_3)_3$ whose UV cut-off edge is about 392 nm, $Cd_4YbO(BO_3)_3$ has a shorter UV cut-off edge that demonstrates the introduction of rare earth to substitute for bismuth can effectively produce the blue shift of the UV absorption edge.

Figure 5 presents the IR spectra of $Cd_4YbO(BO_3)_3$. Referring

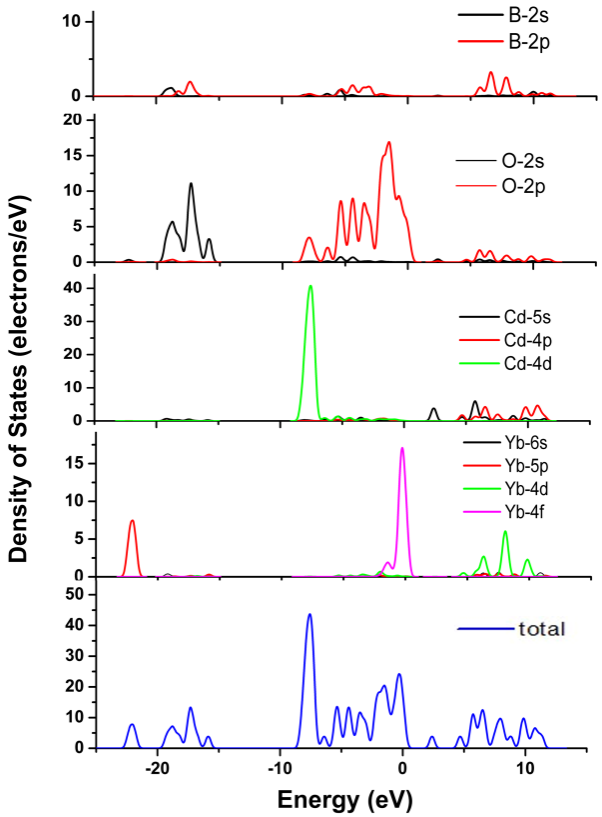

Figure 8: Total and partial densities of states for $Cd_4YbO(BO_3)_3$.

to the literature,[22] the peaks at 1178 and 928 cm^{-1} for $Cd_4YbO(BO_3)_3$ can be assigned to asymmetric stretching and symmetric stretching vibrations of BO_3, while the peaks located at 736 cm^{-1} is likely from the out-of-plane bending of B–O in BO_3. The peaks at 578,496 and 408 cm^{-1} are attributed to bending vibrations.

NLO Properties

The curves of SHG signal as a function of particle size from the measurements made on ground crystals for $Cd_4YbO(BO_3)_3$ are shown in Figure 6. The results are consistent with phase-matching behaviors according to the rule proposed by Kurtz and Perry.[17] A KDP sample is selected as a reference. The second-harmonic signal is found to be 4 × KDP for $Cd_4YbO(BO_3)_3$. Since the reported d_{36} coefficient for KDP is 0.39 pm/V,[23] the derived d_{eff} coefficients for $Cd_4YbO(BO_3)_3$ is 1.56 pm/V. In the $Cd_4BiO(BO_3)_3$,[4a] the main sources of the SHG response are from the cooperation of the 3-chromophore asymmetric structures composed of the polar displacement of the d^{10} Cd^{2+} ion, SCALP effect of Bi^{3+}, and π-delocalization of BO_3. So we believe that the cooperation effects of the asymmetric π-delocalization of the triangular BO_3 groups and the polar displacement of the d^{10} cation Cd^{2+} and YbO_6 distorted octahedron in $Cd_4YbO(BO_3)_3$ make the material exhibit a large SHG response.

Calculations

To gain further insight the bonding interactions in $Cd_4YbO(BO_3)_3$, theoretical calculations were performed based on DFT methods. As plotted in Figure 7, the calculated band structure along high-symmetry points of the first Brillouin zone information was presented. It is clear that both the conduction band minimum and the valence band maximum are localized at the G point, with a direct band gap of 2.28 eV.The total and partial densities of states, DOS and PDOS are presented in Figure 8. The occupied part of the valence band can be subdivided into four regions separated by energy gaps. The bands in the lowest region, from -51.0eV to -49.0 eV, have most of the contribution from the s orbital of Yb. The valence bands (VB) spanning over -23.0 eV to -21.0 eV originate predominately fromYb-5p, while from -20eV to -15.0 eV have the most of the contributions from O-2s, B-2s and B-2p states. In the vicinity of the Fermi level, namely, from -9.0 eV to 0 eV in the valence band, Cd-4d, O-2p, Yb-4d4f, and B-2p states are mainly involved and overlap fully, indicative of the strong covalent interactions of Cd−O, Yb-O, B-O bonds. Energy band around 2.5 eV regions is made up of the Cd-5s state. Ranging from 4.3 eV to 11.0 eV in the conduction band, the Yb-5d,O-2p, B-2p, and Cd-4p5s states are mainly involved.

Conclusions

In summary, we discovered a novel ultraviolet nonlinear-optical material $Cd_4YbO(BO_3)_3$ in the CdO-Yb_2O_3-B_2O_3 system. In the crystal structure, $Cd1O_6$, $Cd2O_8$ and YbO_6 distorted polyhedra interconnect via shared edges and corners into a three dimensional framework with tunnels along the c axis, where all B atoms are located. Isolated BO_3 planar triangles lie approximately parallel to the (001) plane in the space of the framework. The second harmonic generation test shows that the compound exhibits a large second harmonic generation response about four times that of KH_2PO_4. Moreover, the ultraviolet – visible – infrared diffuse reflectance spectrum indicates that $Cd_4YbO(BO_3)_3$ has a wide transparent region from the ultraviolet to near infrared regions. It is congruent melting compounds with excellent physicochemical properties. These features promise $Cd_4YbO(BO_3)_3$ great applications as a nonlinear-optical material.

Acknowledgments

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Notes and references

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