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$Na_3Cd_3B(PO_4)_4$: A New Noncentrosymmetric Borophosphate with Zero-Dimensional Anion Units

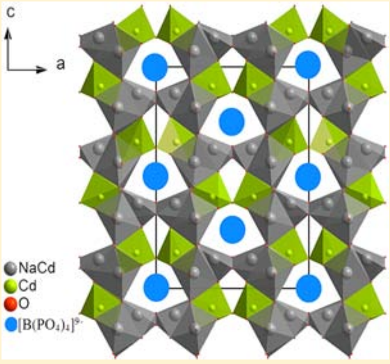
Yunjing Shi,[†,‡] Shilie Pan,*[,†] Xiaoyu Dong,[†,‡] Ying Wang,[†,‡] Min Zhang,[†,‡] Fangfang Zhang,[†] and Zhongxiang Zhou[†]

[†]Xinjiang Key Laboratory of Electronic Information Materials and Devices, Xinjiang Technical Institute of Physics & Chemistry, Chinese Academy of Sciences, 40-1 South Beijing Road, Urumqi 830011, China

[‡]University of the Chinese Academy of Sciences, Beijing 100039, China

S *Supporting Information*

ABSTRACT: A new noncentrosymmetric borophosphate, $Na_3Cd_3B(PO_4)_4$, has been successfully synthesized by conventional solid state reaction for the first time. It crystallizes in the orthorhombic space group $Pmc2_1$ with unit cell parameters of a = 13.6854(3) Å, b = 5.3346(11) Å, c = 18.2169(4) Å, and Z = 4. $Na_3Cd_3B(PO_4)_4$ features zero-dimensional $[B(PO_4)_4]^{9-}$ anion units with Cd^{2+} and Na^+/Cd^{2+} cations located around them, in which the BO_4 tetrahedron is surrounded by four PO_4 tetrahedra by sharing the vertexes of O atoms. Second harmonic generation (SHG) measurements show that $Na_3Cd_3B(PO_4)_4$ exhibits a SHG response 1.1 times larger than that of KH_2PO_4 (KDP) and is phase matchable.



■ INTRODUCTION

In recent years, nonlinear optical (NLO) materials have been widely researched because of their potential application in multitudinous fields such as frequency doubling laser, electro-optic phase modulation, parametric oscillation, and holographic storage.[1−9] Most excellent inorganic NLO materials are based on borate or phosphate. For example, β-BaB_2O_4 (BBO),[2a] LiB_3O_5 (LBO),[2b] CsB_3O_5 (CBO),[10] $CsLiB_6O_{10}$ (CLBO),[11] KH_2PO_4 (KDP),[12] and $KTiOPO_4$ (KTP)[13] have been applied broadly due to their enhanced UV transparency and excellent nonlinearity. It is expected that the borophosphate, which combines the borate anionic group with phosphate anionic group, may generate a new class of NLO materials with excellent properties, such as $M[BPO_5]$ (M = Ca, Sr, Ba),[14] $M_3[BPO_7]$ (M = Zn, Mg),[15] $KMBP_2O_8$ (M = Sr, Ba),[16] and $Na_5B_2P_3O_{13}$.[17] In addition, according to second-order Jahn−Teller (SOJT) effect,[18] the polar displacement of a d^{10} cation center likely leads to asymmetric bonding configurations.[19] Consequently, we expect that the combination of Cd polyhedra, borates, and phosphates in the same compound may generate new NLO materials.

In this study, we carried out systematic explorations in the $Na_2O-CdO-B_2O_3-P_2O_5$ system to expand the structural chemistry of borophosphate and identify novel materials. A new noncentrosymmetric borophosphate, $Na_3Cd_3B(PO_4)_4$, which is the first compound in the $Na_2O-CdO-B_2O_3-P_2O_5$ system, has been found. In this paper, the synthesis, crystal structure, and optical properties of the title compound have been described.

■ EXPERIMENTAL SECTION

Synthesis. Polycrystalline $Na_3Cd_3B(PO_4)_4$ was prepared by solid-state reaction techniques. All reagents were of analytical grade. A mixture of Na_2CO_3 (Tianjin Baishi Chemical Reagent Co., Ltd., 99.0%), CdO (Tianjin Baishi Chemical Reagent Co., Ltd., 99.0%), H_3BO_3 (Tianjin Baishi Chemical Reagent Co., Ltd., 99.0%), and $NH_4H_2PO_4$ (Tianjin Baishi Chemical Co., Ltd., 99.5%) in the molar ratio of 1.5:3:1:4 was ground and loaded into a fused-silica crucible. The mixture was preheated at 200 °C for 2 h to decompose the $NH_4H_2PO_4$ and eliminate the water. Then the temperature was raised to 400 °C to decompose the carbonate, and the products were cooled to room temperature and ground. Finally the sample was calcined at 680 °C for 3 days with several intermediate grindings until a single-phase powder was obtained. X-ray powder diffraction analysis of $Na_3Cd_3B(PO_4)_4$ was performed at room temperature in the angular range of $2\theta = 10°-70°$ with a scan step width of 0.02° and a fixed counting time of 1 $s \cdot step^{-1}$ using an automated Bruker D2 PHASER X-ray diffractometer equipped with a diffracted beam monochromator set for Cu Kα radiation (λ = 1.5418 Å). The experimental powder X-ray diffraction pattern did not match any pattern in the database and was later found to be in agreement with the calculated pattern on the basis of the single-crystal crystallographic data of $Na_3Cd_3B(PO_4)_4$ (Figure 1).

Single Crystal Growth. Single crystals of $Na_3Cd_3B(PO_4)_4$ were grown by a spontaneous crystallization method. The solution was prepared in a platinum crucible by melting a mixture of $Na_2CO_3/H_3BO_3/CdO/NH_4H_2PO_4$ in the molar ratio of 1:1:1:2. The Pt crucible was placed in the center of a vertical programmable temperature furnace. It was held at 850 °C for 10 h until the solution

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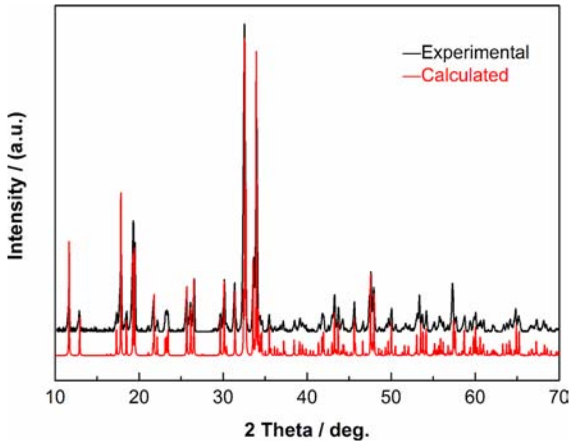

Figure 1. Powder X-ray diffraction patterns of $Na_3Cd_3B(PO_4)_4$.

Table 1. Crystal Data and Structure Refinement for $Na_3Cd_3B(PO_4)_4$

empirical formula	$Na_3Cd_3B(PO_4)_4$
formula weight	796.86
temp [K]	296(2)
wavelength [Å]	0.71073
cryst syst	orthorhombic
space group	$Pmc2_1$
unit cell dimensions [Å]	a = 13.6854 (3) b = 5.3346(11) c = 18.2169(4)
vol [$Å^3$]	1329.9(5)
Z	4
density (calculated) [mg/cm^3]	3.980
abs coeff [mm^{-1}]	5.430
$F(000)$	1480
cryst size [mm^3]	0.219 × 0.14 × 0.068
limiting indices	$-15 \le h \le 17, -6 \le k \le 6, -23 \le l \le 21$
reflns collected/unique	9685/3026 [R(int) = 0.0285]
completeness to theta = 27.49 [%]	99.8
refinement method	full-matrix least-squares on F_o^2
data/restraints/params	3026/8/270
GOF on F_o^2	1.108
final R indices [$F_o^2 > 2\sigma(F_o^2)$]^a	R_1 = 0.0389, wR_2 = 0.1018
R indices (all data)^a	R_1 = 0.0423, wR_2 = 0.1049
extinction coeff	0.00081(16)
largest diff. peak and hole [$e \cdot Å^{-3}$]	2.553 and −1.869

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$.

became transparent and clear and then quickly cooled to 700 °C. The temperature was further decreased to 650 °C at a rate of 1 °C/h; then the temperature was allowed to cool to room temperature at a rate of 10 °C/h. Some colorless, transparent block crystals were obtained for structure determination.

Structure Determination. A single crystal of $Na_3Cd_3B(PO_4)_4$ with dimensions 0.219 mm × 0.14 mm × 0.068 mm was selected for structure determination. The crystal structure of $Na_3Cd_3B(PO_4)_4$ was determined by single-crystal X-ray diffraction on an APEX II CCD diffractometer using monochromatic Mo Kα radiation (λ = 0.71073 Å) at 296(2) K and intergrated with the SAINT program.[20] The numerical absorption corrections were carried out using the SCALE[20] program for area detector. All calculations were performed with programs from the SHELXTL[21] crystallographic software package. The structure was checked for missing symmetry elements with PLATON.[22] All atoms were refined using full matrix least-squares techniques with isotropic thermal parameters, and final least-squares refinement is on F_o^2 with data having $F_o^2 \geq 2\sigma(F_o^2)$. During the refinement, Na and Cd atoms were set to share the same sites, due to the large U(eq) and R values with these sites set as Cd atoms. Four fractional occupancies were refined for the Na(1) disordered with Cd(3), Na(2) disordered with Cd(4), Na(3) disordered with Cd(5), and Na(4) disordered with Cd(6), respectively. To retain charge balance, the total molar ratio of Na/Cd is set as 3:1 in the disorder sites. In order to confirm the chemical composition of Na and Cd in the single crystal, we performed elemental analysis. The result indicates that the sodium content is 8.56 wt % and the cadmium content is 42.68 wt %, which are consistent with the calculated ones (see Elemental Analysis section). Crystal data and structure refinement information are given in Table 1. The final refined atomic positions and isotropic thermal parameters are summarized in Table 2. The main interatomic distances and angles are listed in Table S1 in the Supporting Information.

Infrared Spectroscopy. The sample was mixed thoroughly with dried KBr (5 mg samples mixed with 500 mg of KBr). Infrared spectrum ranged from 400 to 4000 cm^{-1} was recorded on Shimadzu IR Affinity-1 Fourier transform infrared spectrometer to specify and compare the coordination of boron and phosphorus atoms in $Na_3Cd_3B(PO_4)_4$.

UV−Vis−NIR Diffuse-Reflectance Spectroscopy. UV−vis−NIR diffuse-reflectance spectra of $Na_3Cd_3B(PO_4)_4$ crystalline samples were collected with a Solid Spec-3700DUV spectrophotometer using fluororesin as a standard in the wavelength range from 270 to 2600 nm.

NLO Measurements. Powder SHG tests were carried out on $Na_3Cd_3B(PO_4)_4$ by the Kurtz−Perry method using 1064 nm radiation.[23] $Na_3Cd_3B(PO_4)_4$ compound was powdered and graded by standard sieves to obtain distinct particle size ranges, 20−38, 38−55, 55−88, 88−105, 105−150, and 150−200 μm. The samples were then placed in 0.2 mm thick quartz cells and irradiated by a Q-switched Nd:YAG solid-state laser (1064 nm, 10 kHz, 10 ns). We measured the intensity of the frequency-doubled output emitted from the sample using a photomultiplier tube. A digital oscilloscope was used to view the SHG signal and $I^{2\omega}/I^{2\omega}_{(KDP)}$ was taken for a particle size range from 55 to 88 μm. The second harmonic efficiency of the $Na_3Cd_3B(PO_4)_4$ sample was compared with that of a standard powder sample of KDP.

Elemental Analysis. Elemental analysis of single crystal $Na_3Cd_3B(PO_4)_4$ was measured by using a VISTA-PRO CCD simultaneous ICP-OES. The crystal samples were dissolved in nitric acid. Calculated for the $Na_3Cd_3B(PO_4)_4$: Na, 8.65; Cd, 42.32; B, 1.36; P, 15.55. Found: Na, 8.56; Cd, 42.68; B, 1.22; P, 15.67.

■ RESULTS AND DISCUSSION

Crystal Structure. $Na_3Cd_3B(PO_4)_4$ crystallizes in the space group $Pmc2_1$ of the orthorhombic system. It has a three-dimensional framework that is built up of zero-dimensional $[B(PO_4)_4]^{9-}$ anion groups, CdO_6 octahedra, and Na/CdO_n (n = 6, 7, and 8) polyhedra. There are 2 unique cadmium atoms, 2 unique boron atoms, 6 unique phosphorus atoms, and 20 unique oxygen atoms in the asymmetric unit (Table 2). Na^+ cations and Cd^{2+} cations share the same sites in Na/CdO_n (n = 6, 7, and 8) polyhedra (Table 2), in which their ratio is in good agreement with the results of the elemental analysis.

In the BO_4 tetrahedron, each B atom is coordinated by four O atoms forming a BO_4 distorted tetrahedron with an average B−O bond length of 1.4795 Å. In the PO_4 tetrahedron, each P atom is coordinated by four O atoms forming a PO_4 distorted tetrahedron with an average P−O bond length of 1.548 Å, which is in good agreement with other borophosphates reported previously.[24] The BO_4 tetrahedron is surrounded by four PO_4 tetrahedra by sharing the vertexes of O atoms, forming zero-dimensional $[B(PO_4)_4]^{9-}$ anionic units (Figure

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $Na_3Cd_3B(PO_4)_4$

atom	Wyck.	*x*	*y*	*z*	U_{eq}[a]	occ.
Cd(1)	4c	6354(1)	5590(1)	4104(1)	18(1)	1
Cd(2)	4c	8687(1)	995(1)	6591(1)	21(1)	1
Na(1)/Cd(3)	4c	7535(2)	5551(3)	5690(1)	22(1)	0.66/0.34
Na(2)/Cd(4)	4c	8780(1)	4781(4)	8801(1)	33(1)	0.747/0.253
Na(3)/Cd(5)	4c	6237(2)	308(5)	6292(2)	45(1)	0.806/0.194
Na(4)/Cd(6)	4c	7468(2)	113(5)	8153(1)	30(1)	0.787/0.213
B(1)	2b	5000	3690(20)	2210(7)	6(2)	1
B(2)	2a	10000	−720(20)	4673(7)	8(2)	1
P(1)	2b	5000	5457(5)	5691(2)	7(1)	1
P(2)	2b	5000	746(5)	3458(2)	8(1)	1
P(3)	2a	10000	−3753(5)	5905(2)	9(1)	1
P(4)	2a	10000	−31(6)	8151(2)	8(1)	1
P(5)	4c	6964(1)	5283(4)	7341(1)	8(1)	1
P(6)	4c	8040(1)	416(3)	4838(1)	8(1)	1
O(1)	2a	10000	−3073(15)	5060(4)	20(2)	1
O(2)	2b	5000	2705(15)	5904(5)	18(2)	1
O(3)	2b	5000	1265(14)	2611(4)	15(2)	1
O(4)	2a	10000	−2778(15)	8343(5)	16(2)	1
O(5)	4c	9075(4)	810(12)	7761(3)	19(1)	1
O(6)	2a	10000	−1264(14)	6328(4)	12(2)	1
O(7)	4c	5921(4)	6270(12)	5288(3)	19(1)	1
O(8)	4c	7329(4)	3189(12)	6856(4)	31(2)	1
O(9)	2a	10000	1599(14)	8887(4)	9(2)	1
O(10)	2b	5000	3281(15)	3862(4)	12(2)	1
O(11)	4c	7775(4)	8198(12)	4370(3)	19(1)	1
O(12)	2b	5000	7130(13)	6418(4)	10(2)	1
O(13)	4c	9080(4)	−5213(11)	6071(4)	18(1)	1
O(14)	4c	4070(4)	−669(11)	3638(3)	18(1)	1
O(15)	4c	4158(4)	5204(11)	2380(4)	15(1)	1
O(16)	4c	7565(5)	2806(12)	4587(5)	36(2)	1
O(17)	4c	7199(4)	7824(11)	7032(4)	22(1)	1
O(18)	4c	7348(5)	5040(16)	8112(4)	31(2)	1
O(19)	4c	7768(5)	−88(14)	5622(3)	26(1)	1
O(20)	4c	9157(4)	902(10)	4810(3)	14(1)	1

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

2), which can be described as 5 □: [□] □ | □ | □ | □ | using the fundamental building units (□ is represented as a BO_4 or PO_4 unit).[25] Such a $[B(PO_4)_4]^{9-}$ anionic unit has only been found in $Pb_6[BP_4O_{16}][PO_4]$[26a] and $Sr_6[BP_4O_{16}][PO_4]$[26b] in inorganic borophosphates.

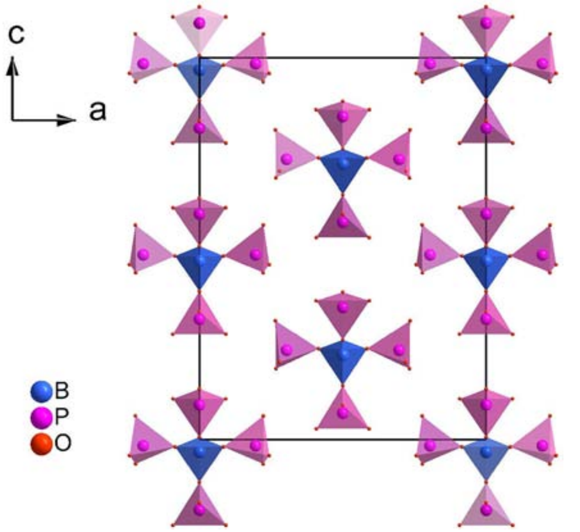

Figure 2. Zero-dimensional $[B(PO_4)_4]^{9-}$ anionic units. The BO_4 and PO_4 groups are shown in blue and pink, respectively.

Of the two unique Cd atoms, each Cd atom is surrounded by six O atoms to form a CdO_6 distorted octahedral geometry, in which the Cd(1)−O bond distances range from 2.250(5) to 2.442(5) Å and the Cd(2)−O bond distances range from 2.200(6) to 2.766(5) Å. Of the four Na/Cd atoms, the site of Na/Cd atom is coordinated by O atoms to form distorted $Na(1)/Cd(3)O_6$, $Na(2)/Cd(4)O_8$, $Na(3)/Cd(5)O_7$, and $Na(4)/Cd(6)O_7$ polyhedra, respectively. The two different Na/CdO_n ($n = 6$, 7, and 8) polyhedra arrange alternatively with one CdO_6 octahedron to form a one-dimensional chain along the *c* axis by sharing edges and faces (Figure 3a). Furthermore, the one-dimensional chains arrange in parallel along the *b* axis by sharing edges and vertexes to form planes (Figure 3b); the one-dimensional chains arrange in parallel along the *a* axis by the mirror operation to form planes (Figure S1 in the Supporting Information), and these planes interconnect with each other forming a three-dimensional framework with tunnels along *b* axis. The zero-dimensional $[B(PO_4)_4]^{9-}$ anionic groups reside in the tunnels (Figure 4).

IR Spectroscopy. Figure S2 in the Supporting Information shows IR spectrum of $Na_3Cd_3B(PO_4)_4$ at room temperature.

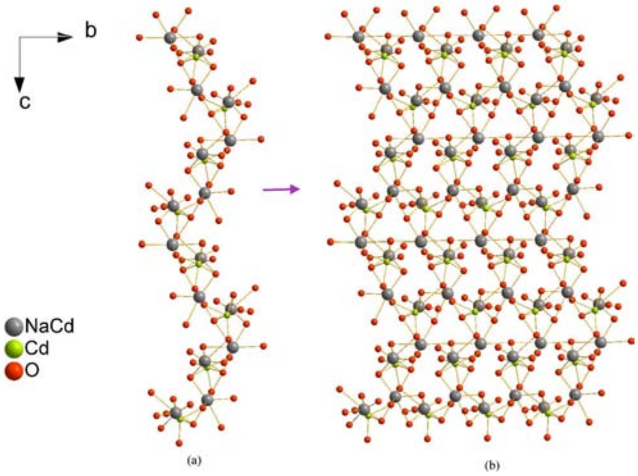

Figure 3. The CdO_6 and Na/CdO_n ($n = 7$, 8, and 9) polyhedra chain (a) and plane (b), viewed along the *a* axis.

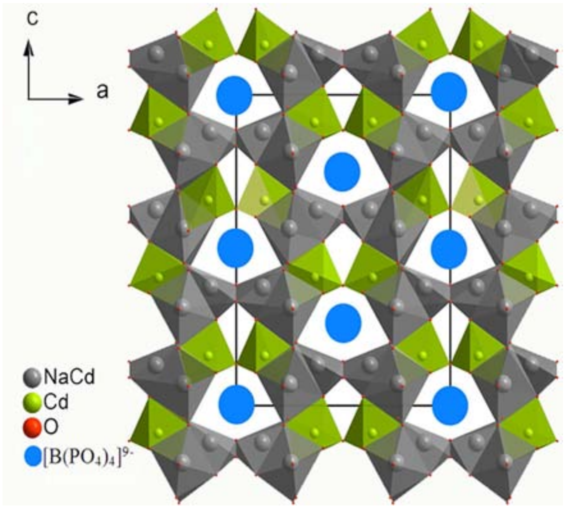

Figure 4. Crystal structure of $Na_3Cd_3B(PO_4)_4$. The CdO_6 and Na/CdO_n ($n = 7$, 8, and 9) polyhedra and $[B(PO_4)_4]^{9-}$ anionic groups are shown in green, gray, and blue, respectively.

The IR spectrum of $Na_3Cd_3B(PO_4)_4$ displays features similar to those of other metal borophosphates.[27] The main IR absorption region between about 1100 and 590 cm^{-1} reveals several absorption bands owing to stretching and bending frequencies of B−O and P−O bonds in BO_4 and PO_4 groups. The bands at 1107, 976, and 912 cm^{-1} are due to the asymmetric and symmetric stretching of B−O in BO_4 and P−O in PO_4, whereas the bands at 632 and 545 cm^{-1} are the out-of-plane bending of B−O in BO_4 and P−O in PO_4.

UV−Vis−NIR Diffuse-Reflectance Spectroscopy. UV−vis−NIR diffuse-reflectance spectrum of $Na_3Cd_3B(PO_4)_4$ crystalline sample was converted to absorbance with the Kubelka−Munk function.[28] It has a cutoff edge at about 360 nm (Figure 5).

SHG Measurements. The noncentrosymmetric structure of $Na_3Cd_3B(PO_4)_4$ prompts us to measure its second-order NLO properties. Figure 6 shows the curve of the SHG signal intensity versus particle size for sieved sample $Na_3Cd_3B(PO_4)_4$. As is shown, the material is phase-matchable and exhibits a SHG response 1.1 times larger than that of KDP. According to the anionic group theory of NLO activity,[29] BO_4 and PO_4 groups may make contributions to the SHG effect.[14b] In addition, based on the structural data, the CdO_6 octahedra exhibit obvious distortions. Therefore, the influence of the CdO_6 octahedra with a polar displacement of the d^{10} Cd^{2+} ion should also be considered.[19e,30]

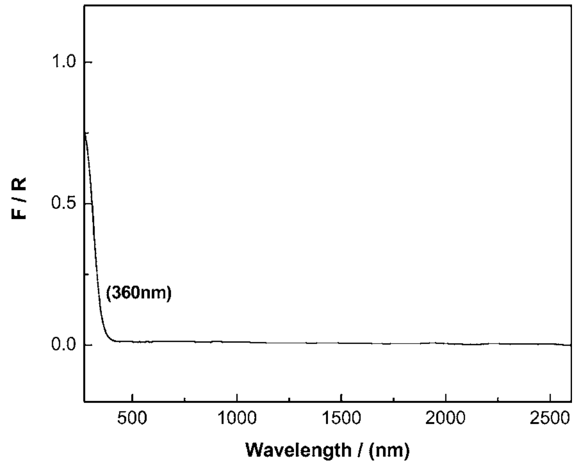

Figure 5. UV−vis−NIR absorption spectrum of $Na_3Cd_3B(PO_4)_4$.

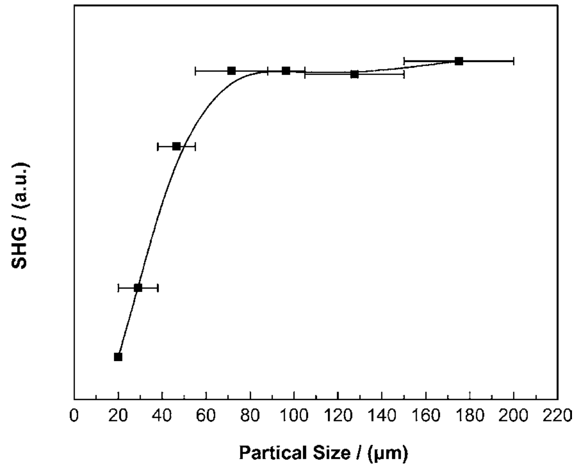

Figure 6. Phase-matching curve, particle size vs SHG intensity, for $Na_3Cd_3B(PO_4)_4$. The solid curve drawn is to guide the eye and is not a fit to the data.

The direction and magnitude of the distortions in BO_4, PO_4, CdO_6, and Na/CdO_n ($n = 6$, 7, and 8) polyhedra have been quantified by determining the local dipole moments to analyze the structure−property relation of $Na_3Cd_3B(PO_4)_4$. A bond-valence approach has been used to calculate the direction and magnitude of the dipole moment.[31] With the Debye equation, the dipole moment of individual B−O, P−O, Na/Cd−O, and Cd−O bonds have been calculated. The entire calculation process has been described in detail previously.[31] The total polarization of $Na_3Cd_3B(PO_4)_4$ in the unit cell and the contributions from BO_4, PO_4, CdO_6, and Na/CdO_n ($n = 6$, 7, and 8) polyhedra to the total polarization have been shown in Table 3. It is clear that the polarizations of BO_4, PO_4, CdO_6, and Na/CdO_n ($n = 6$, 7, and 8) polyhedra along the *a* and *b* axes are almost canceled, and their vector sum is well enhanced along the *c* axis (Figure S3 in the Supporting Information), which leads to the SHG response of $Na_3Cd_3B(PO_4)_4$. According to the data in Table 3, the polarization of CdO_6 octahedra and PO_4 groups is in the positive direction along the

Table 3. The Direction and Magnitude of the Dipole Moments in the BO_4 and PO_4 Tetrahedra and CdO_6 and Na/CdO_n (n = 6, 7, and 8) Polyhedra, And Their Contributions to the Polarization in the Unit Cell

species	x (a)	y (b)	z (c)	magnitude: debye	magnitude: 10^{-4} esu·cm/A^3
$B(1)O_4$	0	0	−1.8570	1.8570	56
$B(2)O_4$	0	0	−8.2241	8.2241	247
$P(1)O_4$	0	0	3.9076	3.9076	118
$P(2)O_4$	0	0	−2.4345	2.4345	73
$P(3)O_4$	0	0	−4.5897	4.5897	138
$P(4)O_4$	0	0	19.7137	19.7137	593
$P(5)O_4$	0	0	1.3337	1.3337	40
$P(6)O_4$	0	0	3.9829	3.9829	120
$Cd(1)O_6$	0	0	2.5478	2.5478	77
$Cd(2)O_6$	0	0	0.9810	0.9810	30
$Na(1)/Cd(3)O_6$	0	0	1.0138	1.0138	30
$Na(2)/Cd(4)O_8$	0	0	−14.5591	14.5591	438
$Na(3)/Cd(5)O_7$	0	0	−8.6921	8.6921	261
$Na(4)/Cd(6)O_7$	0	0	2.6904	2.6904	81
BO_4 tetrahedra	0	0	−10.0811	10.0811	303
PO_4 tetrahedra	0	0	21.9137	21.9137	659
CdO_6 octahedra	0	0	3.5288	3.5288	106
Na/CdO_n polyhedra	0	0	−14.547	14.547	437
total	0	0	0.8144	50.071	1505

c axis, while that of BO_4 groups and Na/CdO_n (n = 6, 7, and 8) polyhedra is along the c axis in the negative direction. The total direction of the unit cell polarization is in the positive direction along the c axis, which means that the SHG effect may originate from the combinations of BO_4, PO_4, CdO_6, and Na/CdO_n (n = 6, 7, and 8) polyhedra.

CONCLUSIONS

By the combination of the d^{10} Cd^{2+} ion and BO_4 and PO_4 groups, a new noncentrosymmetric borophosphate, $Na_3Cd_3B(PO_4)_4$, has been prepared successfully. $Na_3Cd_3B(PO_4)_4$ has a three-dimensional framework that is built up of CdO_6 and Na/CdO_n (n = 6, 7, and 8) polyhedra and zero-dimensional $[B(PO_4)_4]^{9-}$ anion units, in which each BO_4 tetrahedron is surrounded by four PO_4 tetrahedra forming a zero-dimensional $[B(PO_4)_4]^{9-}$ anionic unit. The zero-dimensional $[B(PO_4)_4]^{9-}$ anionic groups reside in the tunnels of the three-dimensional cation frameworks. UV−vis−NIR diffuse-reflectance spectroscopy indicates that $Na_3Cd_3B(PO_4)_4$ has a wide transparent region with the cutoff edge at about 360 nm. $Na_3Cd_3B(PO_4)_4$ exhibits SHG effect 1.1 times larger than that of KDP and is phase-matchable. In the future, we will continue to explore the new compounds with interesting NLO properties in the $A_2O-CdO-B_2O_3-P_2O_5$ system (A = K, Rb, and Cs).

ASSOCIATED CONTENT

Ⓢ Supporting Information

Selected bond distances (Å) and angles (deg) of $Na_3Cd_3BP_4O_{16}$, view of the cation framework in the ac plane, IR absorption spectrum, and the direction of the distortions of the BO_4, Na/CdO_n (n = 6, 7, and 8), PO_4, and CdO_6 polyhedra. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Phone: (86)991-3674558. Fax: (86)991-3838957. E-mail: slpan@ms.xjb.ac.cn.

Notes

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