Syntheses of six and twelve membered borophosphate ring structure with nonlinear optical activity

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ABSTRACT

Two new noncentrosymmetric borophosphates, $Li_3Cs_2Ba_2B_3P_6O_{24}$, **1** and $RbBaBP_2O_8$, **2**, have been synthesized via solid-state reactions at high temperature. The single crystal X-ray diffraction technique shows a cubic system, space group $P2_13$ (No 198) for **1** with a $= 12.8530(5)$ Å and tetragonal system $I\bar{4}2d$ (No 122) for **2** with $a = 7.2810(18)$ Å, $c = 14.330(5)$ Å. The main structure motif attributes a 3D framework formed of BO_4 and PO_4 tetrahedra in both compounds. The powder samples exhibit second harmonic generation (SHG) response, using Kurtz and Perry technique, demonstrated that **1**, **2** are about 0.2, 0.5 and 2, 2.5 times than that of KDP and SiO_2 in particle size range of 106–150 μm, 46−74 μm respectively.

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1. Introduction

Nonlinear optics covers a broad area of research and technology that playing a dynamic role in various fields of chemistry, physics, biology and engineering [1]. Borates and Phosphates are important benchmarks of outstanding inorganic NLO materials. For example, β-BaB_2O_4 (BBO) [2], LiB_3O_5 (LBO) [3], $CsLiB_6O_{10}$ (CLBO) [4], CsB_3O_5 (CBO) [5], $KTiOPO_4$ (KTP) [6], and KH_2PO_4(KDP) [7]. These materials show high damage threshold, broad Ultra violet transparency, a moderate birefringence and excellence nonlinearity which make them applicable to various fields. Recently, scientists paid much attention to metal borophosphates due to their interesting structural chemistry and potential applications [8,9]. Borate and phosphate consisting materials are divided into two classes. The anionic groups of borates and phosphates are connected in *borophosphate* while there is no connection between borate and phosphate anionic units in *borate-phosphate* [10] and these are constructed by complex anionic groups such as BO_3, BO_4, and PO_4 groups. Among them, the trigonal planar BO_3 shows distinct properties including large SHG effect and contributing more in deep UV NLO property than BO_4 groups [11]. Thus borophosphate showing wide variation in their chemical structure offers great interest for exploration of new compounds.

To date, few materials comprising both borate and phosphate groups are known, for example, $Co_5BP_3O_{14}$ the first borophosphate having BO_3 and PO_4 groups [12], $M_2BP_3O_{12}$ [M=Fe, Cr] with magnetic properties [13a, b]. Similarly, $BiM_2BP_2O_{10}$ [M=Co, Ni] having a quasi-1D linear chain structure [14], $SrCo_2BPO_7$ with a four-column ribbon structure [15], $A(ZnBP_2O_8)$ [A=NH_4, K, Rb, Cs] exhibit zeolite like microporous structures [16]. $Li_2Cs_2B_2P_4O_{15}$, $LiK_2BP_2O_8$, $Li_3M_2BP_4O_{14}$ [M=K, Rb] comprising various fundamental building units [17]. $Ba_3(ZnB_5O_{10})PO_4$ [18], Cd_3BPO_7 [19], BPO_4 [20], β-Zn_3BPO_7 [21], $MBPO_5$ (M=Sr and Ba)[22a, b, c], $Na_3Cd_3B(PO_4)_4$ [23] and $AXBP_2O_8$ (A=K, X=Sr, Ba and A=K, Rb, X=Pb) are potential NLO materials [24a, b, c]. Other examples include $K_7B_2P_5O_{19}$ [25], $Na_3B_6PO_{13}$ and $Na_3BP_2O_8$, [26], $Li_2B_3PO_8$ [27], $Li_3BP_2O_8$ [28], $Sr_6BP_5O_{20}$ [29], $Li_2NaBP_2O_8$ and $LiNa_2B_5P_2O_{14}$ [30], $Li_3Cs_2M_2B_3P_6O_{24}$ (M=Pb, Sr) [31], and so on. Also Kniep and coworkers, in their review article, put forwarded the detailed study of all borophosphate compounds [8].

Borophosphates are new and an important class that having unique structural properties and applications in modern technology. Because of their fascinating chemistry, our attentions are directed towards the design, syntheses, and characterization of such compounds. Mostly borophosphate have been synthesized under hydrothermal condition. Anhydrous compounds of borophosphate are rare and synthesized via solid state reaction at high temperature. So herein, two borophosphate compounds i.e., $Li_3Cs_2Ba_2B_3P_6O_{24}$, **1** and $RbBaBP_2O_8$, **2** having 3D framework of 6 and 12 membered ring structures have been successfully

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synthesized and these anhydrous compounds containing BO_4 and PO_4 tetrahedra with B:P (1:2) related with alkali and alkaline earth metals. Synthesis of these compounds has been carried out by solid-state reaction while characterization is done using ICP, single crystal X-ray diffraction analysis, IR, UV–vis, TG, and second harmonic generation measurements.

2. Experimental section

2.1. Synthesis of $Li_3Cs_2Ba_2B_3P_6O_{24}$, 1

Li_2O (99.99%), BaO (99.95%), B_2O_3 (99.9%), CsCl (99%) and P_2O_5 (99.99%) were obtained from Aladdin (China) and used as received. All manipulations were carried out in an Ar-filled glovebox with controlled oxygen and moisture level less than 0.1 ppm. For $Li_3Cs_2Ba_2B_3P_6O_{24}$, a total weight of 300 mg of Li_2O, BaO, B_2O_3 and P_2O_5 in ratio of 0.5:1:0.5:1 respectively was mixed with extra 300 mg of CsCl in a graphite crucible in glovebox. Such a graphite crucible was sealed in vacuum fused-silicon tubes below 10^{-3} Pa, and thereby heated in a tube furnace up to 250 °C within 15 h, sustained at that temperature for 1 d, then heated to 620 °C for 20 h, and to 850 °C in 28 h. Maintained at this temperature for 4 days, the reaction mixture was cooled to 450 °C in 80 h prior to switching off the furnace. The excess flux was first washed off with distilled water and then dried with ethanol. $Li_3Cs_2Ba_2B_3P_6O_{24}$, 1 was obtained as colorless crystals.

2.2. Synthesis of $RbBaBP_2O_8$, 2

Reagents were crushed thoroughly in an agate mortar in 0.5:1:1:2 ratio respectively and filled in a platinum crucible. The temperature was increased to 400 °C within 4 h, following a dwell time of 5 h, and then products were cooled to room temperature and ground up again and heated to 800 °C for 8 h and kept at this temperature for 2 days with intermediate grinding and mixing which ensures the completion of solid-state reaction.

Single crystals of 2 were found out by following a stoichiometric composition of Rb_2CO_3, $BaCO_3$, H_3BO_3, and $NH_4H_2PO_4$ in a platinum crucible. The first step of the growth involved, the increase in temperature to 400 °C within 4 h, and then product was cooled to room temperature after 5 h at 400 °C while the second step involved the transfer of mixture to a graphite crucible packed in a fused silica tube under vacuum. Then, the temperature was increased to 850 °C at the same rate as in 1. Finally, transparent crystals were attained.

2.3. Single crystal structure determination

Single crystals of both compounds were selected for diffraction data collection with the aid of Rigaku Mercury CCD automatic diffractometer furnished with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Both compounds were subjected to absorption corrections applying multi-scan methods and their structures were solved by direct methods [32], then refined on F^2 by a full-matrix least-squares method, which was performed in SHELXL-97/PC programs [33]. Anisotropic thermal parameters of all atoms were refined. Crystallographic measurements and structural refinements for the two title compounds are summarized in Table 1, atomic coordinates, important bond distances and angles are listed in (supporting Information Table S1-S2). The final refined solutions obtained were tested with the ADDSYM algorithm in the PLATON program and no higher symmetry was observed [34]. Microprobe elemental analysis of the single crystals and inductively coupled plasma (ICP) spectrometry was performed to ensure chemical composition of the compounds

Table 1.
Crystal Data and Structure Refinements for $Li_3Cs_2Ba_2B_3P_6O_{24}$ and $RbBaBP_2O_8$.

Formula	$Li_3Cs_2Ba_2B_3P_6O_{24}$	$RbBaBP_2O_8$
fw	1163.135	423.54
crystal system	Cubic	Tetragonal
crystal color	colorless	colorless
space group	$P2_13$ (No 198)	$I\bar{4}2d$ (No 122)
a (Å)	12.8530(5)	7.2810 (18)
c (Å)		14.330(5)
$\alpha = \beta = \gamma$ (deg)	90	90
V (Å^3)	2123.3(14)	759.6(4)
Z	4	4
μ (mm^{-1})	7.635	12.025
GOOF on F^2	1.045	1.242
R_1, wR_2 $(I > 2\sigma(I))^a$	0.0292, 0.0782	0.0198,00.0499
R_1, wR_2 (all data)	0.0295, 0.0784	0.0191,00.0606
largest diff. peak and hole (e/Å^3)	1.070, −2.388	0.567, −1.089
Flack parameter	0.00(3)	0.19(3)

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

which showed the presence of Li, Cs, Ba, B, P and O elements in 1 and Rb, Ba, B, P and O elements in 2.

2.4. Powder X-ray diffraction

XRD data for finely powdered patterns were collected on a RigakuMiniFlex II diffractometer at 298 K with Cu Kα radiation in 2θ range of 10 − 70° using a profile fitting by a least-squares method utilizing the computer program GSAS apply with EXPGUI [35].

2.5. Elemental analysis

The ratio of the elements was measured by an energy dispersive X-ray spectroscope (EDX, Oxford INCA) on a field emission scanning electron microscope (FESEM, JSM6700F) for polycrystalline 1, 2 (Supporting Information Fig. S1a, S1b; Table S3a, S3b). The Cs/Ba/P molar ratio was measured to be approximately 2.0:1.9:6.7 (1); Rb/Ba/P=1.0:0.9:2.7 (2). Semiquantitative elemental analyses of both compounds were performed with the aid of an Ultima-2 inductively coupled plasma emission spectrometer (ICP-OES) which provided mass percentages for $Li_3Cs_2Ba_2B_3P_6O_{24}$, 1 as; 1.6% Li, 20.6% Ba, 2.7% B, 14.3% P, and for $RbBaBP_2O_8$, 2 as; 30.1% Ba, 2.9% B, 13.0% P. These results were in good agreement with the calculated value.

2.6. UV − vis-near-IR diffuse reflectance spectra

The optical diffuse reflectance spectra of powdered polycrystalline samples were recorded at room temperature in the range of 200–2500 nm using a Perkin Elmer Lambda 950 UV − vis spectrophotometer fitted with an integrating sphere attachment and $BaSO_4$ plates as reference on which finely ground powdered samples were coated. The absorption spectra were calculated by using Kubelka − Munk function: $\alpha/S = (1-R)^2/2 R$, in which α, S, R are the absorption coefficient, scattering coefficient, and reflectance, respectively [36].

2.7. Thermal analysis

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were performed on a NETZSCH STA 449 °C simultaneous analyzer. The sample was encased in Al_2O_3 crucible, thereby heated at a rate of 10 °C/min up to 1100 °C under continuous flow of nitrogen gas.