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$KMBP_2O_8$ (M = Sr, Ba): A New Kind of Noncentrosymmetry Borophosphate with the Three-Dimensional Diamond-like Framework

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Two new isotypic anhydrous borophosphates, $KMBP_2O_8$ (M = Sr, Ba), have been prepared under high temperature solution growth (HTSG). Investigation of single-crystal X-ray diffraction shows that they crystallize in noncentrosymmetric space group $I\bar{4}2d$ with the following lattice parameters: $a = 7.1095(18)$, $c = 13.882(5)$ Å for $KSrBP_2O_8$ and $a = 7.202(2)$, $c = 14.300(6)$ Å for $KBaBP_2O_8$. The fundamental building block (FBB) of title borophosphates with B:P ratio = 1:2 is 12□:⟨12□⟩ (symbol □ represents BO_4 and PO_4 tetrahedra). The FBBs are further interlocked together to form the final 3D diamond-like architecture. Second-harmonic generation (SHG) on powder samples has been measured using Kurtz and Perry technique, which indicates that they are phase-matchable materials, and their SHG coefficients are measured to be about 1/5 (for $KSrBP_2O_8$) and 1/3 (for $KBaBP_2O_8$) times as large as that of KDP.

Introduction

With the development of technology and science, there are increasing needs for new multifunctional magnetic materials, ultraviolet (UV) phosphors, scintillators, and laser materials. Accordingly, searching for new second-order nonlinear optical (NLO) materials is of current interest and great importance due to their applications in photonic technologies.[1] The practical potential of materials is mostly associated with their structural characteristics. The necessary structural prerequisite for second harmonic generation (SHG) is crystallographic noncentrosymmetry (NCS), which is often a consequence of the acentric coordination of certain cations. It is reported [2] that the π-conjugated system based on trigonal $[BO_3]$ groups is responsible for the second harmonic generation (SHG) properties of the borates, such as LiB_3O_5 (LBO),[3] β-BaB_2O_4 (BBO),[4] and $LnM_3(BO_3)_4$ (Ln = rare-earth element; M = Al, Ga, Cr, Fe, Sc).[5] On the other hand, introducing transition-metal ions susceptible to second-order Jahn−Teller (SOJT) distortions (d^0 transition metal ions, such as Ti^{4+}, Nb^{5+}, Mo^{4+}, or W^{6+}) and cations with nonbonded electron pairs (Se^{4+}, Te^{4+}, or Sb^{3+}) into NCS compounds might also be SHG effective, such as $KTiPO_5$(KTP) and so forth.[6] Metal borophosphates containing both borate and phosphate groups are also promising NLO materials. The asymmetric coordination polyhedron adopted by the B(III) or P(V) atom may result in noncentrosymmetric structures with consequent interesting properties. Borophosphates can adopt many unusual structures, and the presence

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of delocalized electron systems and metal−oxygen coordination polyhedra susceptible to distortions may bring microscopic nonlinearity; hence, nonlinear optical materials have been also obtained in this system several times, such as $MBPO_5$ (M = Ca, Sr, Ba).[7] Furthermore, many more structural types are available for borophosphates since the complex anionic structures built of BO_4, BO_3, and PO_4 groups can be interconnected into a variety of polymeric boron−phosphor−oxide anions with extended structures under high temperature solid state reactions ($T > 600$ °C) and supercritical hydrothermal or solvothermal conditions. So far, a large number of borophosphates containing complex anionic structures extending from isolated species, oligomers, rings, and chains to layers and frameworks have been reported. The compounds known to date are systemically classified in terms of reviews by Kniep et al.[8] For example, $Co_5BP_3O_{14}$ is the first compound containing interconnected planar $[BO_3]$ groups and $[PO_4]$ tetrahedra; $Sc(H_2O)_2[BP_2O_8]\cdot H_2O$ contains intriguing one-dimensional (1D) infinite helices ${}^{1}_{\infty}[BP_2O_8]^{3-}$ along the *c*-axis;[9] zincoborophosphate $Na[ZnBP_2O_8]\cdot H_2O$ and $(C_4N_3H_{16})[Zn_3B_3P_6O_{24}]\cdot H_2O$ feature CZP topology framework.[10] In addition, the reported borophosphates include $Na_5B_2P_3O_{13}$,[11] $Co(C_2H_{10}N_2)(B_2P_3O_{12})(OH)$,[12] $M^IM^{II}(H_2O)_2(BP_2O_8)\cdot H_2O$ (M^I = Na, K; M^{II} = Mg, Mn, Fe, Co Ni, Zn) and $M^IM^{II}(H_2O)(BP_2O_8)$,[13] $A(ZnBP_2O_8)$ (A = NH_4^+, K^+, Rb^+, Cs^+),[14] $Na_3B_6PO_{13}$ and $Na_3BP_2O_8$,[15] $Sr_6BP_5O_{20}$,[16] $Na_2[VB_3P_2O_{12}(OH)]\cdot 2.92H_2O$,[17] $M^{II}[BPO_4(OH)_2]$ (M^{II} = Mn, Fe, Co),[18] $Na_2[M^{II}B_3P_2O_{11}(OH)]\cdot 0.67(H_2O)$ (M^{II} = Mg, Mn, Fe, Co, Ni, Cu,Zn),[19] $Cu(H_2O)_2(B_2P_2O_8(OH)_2)$,[20] $NH_4[BPO_4F]$,[21] $KAl(BP_2O_8(OH))$,[22] $NaInBP_2O_8(OH)$,[23] $Na_8[Cr_4B_{12}P_8O_{44}(OH)_4][P_2O_7]\cdot nH_2O$,[24] $Fe(H_2O)_2BP_2O_8\cdot(H_2O)$,[25] and so on.

As we know, novel borophosphates were mostly obtained through hydrothermal synthesis, and anhydrous phases are rare by high temperature solid reaction, which might have better chemical and thermal stability than the hydrated phase ones to ensure the feasibility of the industrial applications. High temperature solution growth (HTSG) of single crystal has been extensively explored as an effective and powerful tool in solid-state chemistry. Many mixed-metal oxides, sulfides, and complex intermetallics have been successfully obtained under molten conditions.[26] In our work, reactions of K_2CO_3, H_3BO_3, $NH_4H_2PO_4$, and $SrCO_3$ or $BaCO_3$ afforded two new potassium alkaline-earth borodiphosphate compounds, namely, $KMBP_2O_8$ (M= Sr, Ba). As far as our knowledge goes, the two compounds represent the first example of anhydrous borophosphate associate with alkali and alkaline-earth metals. Herein, we will report the synthesis by HTSG method in the open air, structural determination by single-crystal X-ray diffraction analysis, EDS, IR, UV−vis, TGA, and powder frequency-doubling measurements for the title compounds.

Experimental Section

Materials and Instrumentation. All of the chemicals were analytically pure from commercial sources and used without further purification. $NH_4H_2PO_4$, H_3BO_3, K_2CO_3, $SrCO_3$, and $BaCO_3$ were purchased from the Shanghai Reagent Factory. Microprobe elemental analyses were performed by using a field-emission scanning electron microscope (FESEM, JSM6700F) equipped with an energy-dispersive X-ray spectroscope (EDS, Oxford INCA). X-ray powder diffraction (XRD) patterns were collected on an XPERT-MPD $\theta-2\theta$ diffractometer by using graphite-monochromated Cu Kα radiation in the angular range $2\theta = 5-65$ °C with a step size of 0.05°. Thermogravimetric analyses (TGA) and differential thermal analyses (DTA) were carried out with a NETZSCH STA 449C unit under an air atmosphere. The samples were placed in Al_2O_3 crucibles and heated from 35 to 1100 °C at the rate of 10.0 K/min. IR spectra were recorded by using a Magna 750 FTIR spectrometer with samples as KBr pellets in the range of 3000−400 cm^{-1}. An optical diffuse reflectance spectrum was measured at room temperature with a Perkin-Elmer Lambda 900 UV/vis spectrophotometer. A $BaSO_4$ plate was used as a standard (100% reflectance). The UV−vis absorption spectrum was calculated from reflectance spectra by using the Kubelka−Munk function: $F(R) = (1 - R)^2/2R$,[27] where R is the reflectance and $F(R)$ is the Kubelka−Munk remission function. The measurement of the powder frequency-doubling effect was carried out on the powder samples of $KMBP_2O_8$ (M = Sr, Ba) by means of the modified method of Kurtz and Perry.[28] The fundamental wavelength was 1064 nm, which was generated by a Q-switched Nd:YAG

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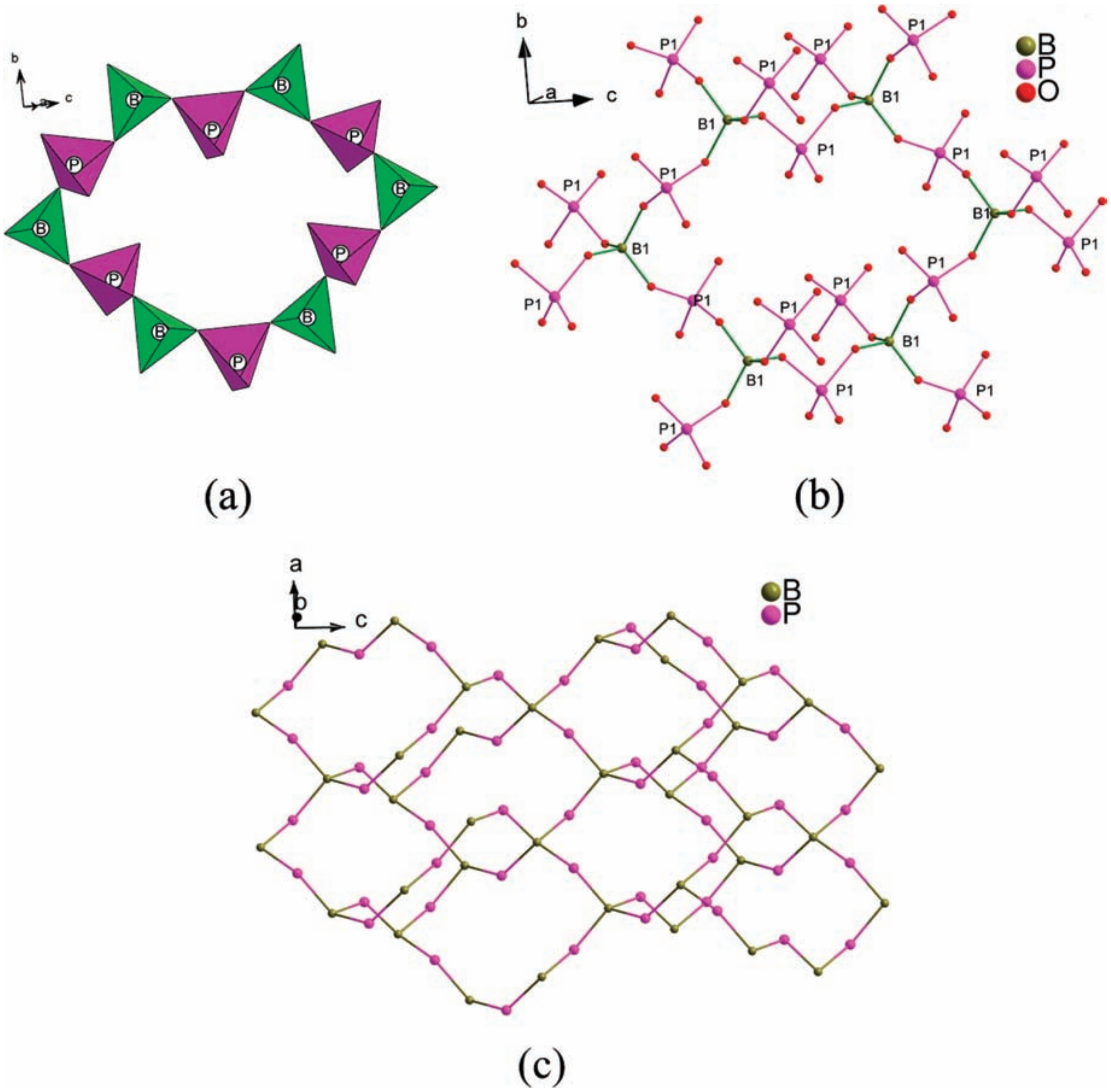

Figure 1. (a) Combined polyhedral representation of $[(BO_4)_6(PO_4)_6]$ 12-member ring; (b) view of the coordination sphere of a 12-member ring; and (c) view of the 3D anionic framework of ${}^{3}_{\infty}[BP_2O_8]^{3-}$ (oxygen atoms are omitted for clarity).

laser. The sample was ground and sieved by using a series of mesh sizes in the range of 25−250 μm. A sample of KDP (KH_2PO_4) was prepared as a reference material in an identical fashion.

Synthesis. Single crystals of $KSrBP_2O_8$ were initially obtained by the HTSG method. At room temperature, K_2CO_3 (0.8940 g, 6.468 mmol), $SrCO_3$ (0.7958 g, 5.390 mmol), H_3BO_3 (2.000 g, 32.34 mmol), and $NH_4H_2PO_4$ (0.6199 g, 5.390 mmol) with the molar ratio of K/Sr/B/P = 12/5/30/5 were mixed. Then the reaction mixture was thoroughly ground in an agate mortar and pressed into a pellet to ensure the best homogeneity and reactivity, which was put into a platinum crucible. Subsequently the crucible was put into an oven and heated at 1050 °C in the air for 2 days. In this stage, the mixture oxide of $K_2O-SrO-B_2O_3-P_2O_5$ was completely melted. Afterward, it was allowed to cool at a rate of 0.05 °C /min to 500 °C before switching off the furnace. After boiling for 24 h in water, prism-shaped colorless crystals were obtained in very low yield (< 5%). Attempts to produce the barium analogy of $KSrBP_2O_8$ led to the isolation of a few prism-shaped colorless crystals of $KBaBP_2O_8$. The starting materials of K_2CO_3, $BaCO_3$, H_3BO_3, and $NH_4H_2PO_4$ were also weighed in the molar ratio K/Ba/B/P = 12/5/30/5, with the same subsequent procedure.

The polycrystalline samples of $KMBP_2O_8$ (M = Sr, Ba) were synthesized by solid-state reactions of analytical reagents with stoichiometric amounts (K/M/B/P = 1:1:1:2). The powdered mixtures were ground in an agate mortar and then calcined at 900 °C for 7 days with several intermediate grindings to ensure solid-state reactions completely. On the basis of powder XRD diffraction studies, they have been successfully obtained as single phase (Figure S1 of Supporting Information).

Single-Crystal Structure Determination. Single crystals of $KMBP_2O_8$ (M = Sr, Ba) with dimensions of 0.25 mm × 0.20 mm × 0.15 mm (Sr) and 0.18 mm × 0.14 mm × 0.10 mm (Ba) were selected for single-crystal X-ray diffraction determination. The diffraction data of $KSrBP_2O_8$ were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), while the data of $KBaBP_2O_8$ were collected on a Rigaku Saturn70 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Intensity data were collected by the narrow frame method at 293 K. The data were corrected for lorentz factor, polarization, air absorption, and absorption due to variations in the path length through the detector faceplate.

Table 1. Crystal Data Collection and Structural Refinement Parameters for $KMBP_2O_8$ (M = Sr, Ba)[a]

formula	$KSrBP_2O_8$	$KBaBP_2O_8$
formula weight	327.47	377.19
wavelength (Å)	0.71073	0.71073
crystal system	tetragonal	tetragonal
space group	$I\bar{4}2d$	$I\bar{4}2d$
unit cell dimensions	$a = 7.1095(18)$ $c = 13.882(5)$	$a = 7.202(2)$ $c = 14.300(6)$
volume, Z	701.7(3), 4	741.7(4), 4
D_{calcd} ($g \cdot cm^{-3}$)	3.100	3.378
absorption corretion	multiscan	multiscan
absorption coeffient (mm^{-1})	8.743	6.356
$F(000)$	624	696
crystal size (mm)	0.250 × 0.200 × 0.150	0.180 × 0.140 × 0.100
θ range (deg)	3.22—27.41	3.17—27.46
limiting indices	(−9,−9,−13) to (9,4,18)	(−9,−9,−18) to (9,9,17)
R_{int}	0.0403	0.0272
reflections collected	2121	2749
independent reflections	378	415
parameter/restraints	32/0	32/0
goodness-of-fit on F^2	1.043	1.006
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0389$ $\omega R_2 = 0.0944$	$R_1 = 0.0132$ $\omega R_2 = 0.0311$
R indices (all data)	$R_1 = 0.0402$ $\omega R_2 = 0.0956$	$R_1 = 0.0140$ $\omega R_2 = 0.0314$
largest difference peak and hole ($e \cdot A^{-3}$)	0.904 and −0.468	0.326 and −0.237

[a] $R_1 = \sum||F_{obs}| - |F_{calc}||/\sum|F_{obs}|$, $wR_2 = [\sum w(F_{obs}^2 - F_{calc}^2)^2/\sum w(F_o^2)]^{1/2}$.

Absorption corrections based on the Multiscan technique were also applied.[29] The single-crystal refinements of $KMBP_2O_8$ (M = Sr, Ba) were performed with the program SHELX-97.[30] The space groups of them were all initially determined to be $I\bar{4}2d$ based on systematic absences as well as E value statistics. Both structures were solved by the direct methods, and the metal and phosphorus atoms were revealed. Subsequent difference Fourier syntheses by full-matrix least-squares fitting on F^2 allowed localization of all boron and oxygen atoms. To confirm that the chemical composition was stoichiometric $KMBP_2O_8$ (M = Sr, Ba), we do microprobe elemental analyses of the single crystals, indicating the presence of K, Sr, and P elements in a molar ratio of 2.65:2.53:7.22 in $KSrBP_2O_8$ and K, Ba, and P in a molar ratio of 2.74:2.85:7.40 in $KBaBP_2O_8$. Since samples were unpolished and X-ray corrections may be approximate especially for light elements, the EDS results were in agreement with those from single crystal X-ray structural analyses. In this structure, the K and M (M = Sr, Ba) atoms were in substitutional disorder, and the atomic position and anisotropic displacement parameters of K and M were therefore constrained to be identical at K/M sites in the initial refinements. The refined site occupation factors converge to 0.48699/0.51301 for K/Sr and 0.48581/0.42419 for K/Ba. Then they were fixed to 1/1 in the final refinement, which was consistent with the EDS results and achieved electroneutrality. The final structure refinement performed by least-squares methods with atomic coordinates and anisotropic thermal parameters resulted in the satisfactory residuals and crystal chemical parameters of $S = 1.043$, $R_1 = 0.0389$, and $\omega R_2 = 0.0944$ ($KSrBP_2O_8$) and $S = 1.006$, $R_1 = 0.0132$, $\omega R_2 = 0.0311$ ($KBaBP_2O_8$) for observed data ($I > 2\sigma(I)$). The flack parameters (x) were close to zero in the refinement, that is, 0.00(4) and −0.01(2) for $KSrBP_2O_8$ and $KBaBP_2O_8$, respectively. It should be noted that the absolute structure of the two isotypical compounds is reversed (Figure 1a,b). If an instruction was used to reverse their absolute structure (input move 1 0.5 0.25 −1 in the *.ins file on the process of refinement), the crystallographic results were low precision and flack parameters closed to 1.0. In addition, the final refined solutions obtained for $KMBP_2O_8$ (M = Sr, Ba) were checked with the ADDSYM algorithm in the program PLATON,[31] and no higher symmetries were found; hence, the model with the noncentrosymmetrical space group was reasonable. Furthermore, the acentricity of the structures could also be confirmed by second harmonic generation experiments. The data collection and refinement parameters are summarized in Table 1. The atomic coordinates and selected bond lengths are listed in Tables 2 and 3, respectively.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Compounds $KMBP_2O_8$ (M = Sr, Ba)

atom	Wyck.	S.O.F.	x/a	y/b	z/c	U_{eq}[a] (Å)
			$KSrBP_2O_8$			
K(1)	8d	0.5	0.36187(13)	0.2500	0.1250	0.0229(4)
Sr(1)	8d	0.5	0.36187(13)	0.2500	0.1250	0.0229(4)
B(1)	4a	1.0	1.0000	0.0000	0.0000	0.022(3)
P(1)	8d	1.0	0.8382(3)	0.2500	0.1250	0.0274(6)
O(1)	16e	1.0	0.7239(11)	0.3958(8)	0.0767(5)	0.070(2)
O(2)	16e	1.0	0.9926(12)	0.1679(10)	0.0549(6)	0.074(2)
			$KBaBP_2O_8$			
K(1)	8d	0.5	0.36538(4)	0.7500	0.1250	0.01776(13)
Ba(1)	8d	0.5	0.36538(4)	0.7500	0.1250	0.01776(13)
B(1)	4a	1.0	1.0000	1.0000	0.0000	0.0114(10)
P(1)	8d	1.0	0.84906(11)	0.7500	0.1250	0.01408(19)
O(1)	16e	1.0	0.7340(3)	0.6029(3)	0.07887(13)	0.0274(4)
O(2)	16e	1.0	0.9951(3)	0.8303(3)	0.05442(14)	0.0248(4)

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

Results and Discussion

Crystal Structure. X-ray analysis revealed that the compounds $KSrBP_2O_8$ and $KBaBP_2O_8$ are isotypic and crystallize in the tetragonal system with space group $I\bar{4}2d$; hence, only the structure of $KSrBP_2O_8$ will be discussed in detail as a representation.

The asymmetric unit of $KSrBP_2O_8$ is $K_{1/4}Sr_{1/4}B_{1/2}PO_4$ with unique crystallographically different boron and

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(29) *CrystalClear*, version 1.3.5.; Rigaku Corp.: Woodlands, TX, 1999.

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Table 3. Selected Bond Distances (Å) and Angles (deg) for $KMBP_2O_8$ (M = Sr, Ba)

		$KSrBP_2O_8$[a]			
K(1)$\vert$Sr(1)—O(1)^{i}	2.676(7)	K(1)$\vert$Sr(1)—O(2)^{vi}	2.860(9)	B(1)—O(2)^{ix}	1.417(7)
K(1)$\vert$Sr(1)—O(1)^{ii}	2.676(7)	K(1)$\vert$Sr(1)—O(2)^{vii}	2.860(9)	B(1)—O(2)^{x}	1.417(7)
K(1)$\vert$Sr(1)—O(1)^{iii}	2.817(8)	(K1$\vert$Sr1—O(2)^{iv})	3.334(10)	P(1)—O(1)^{v}	1.478(6)
K(1)$\vert$Sr(1)—O(1)^{iv}	2.817(8)	(K1$\vert$Sr1—O(2)^{iii})	3.334(10)	P(1)—O(1)	1.478(6)
K(1)$\vert$Sr(1)—O(1)	2.854(8)	B(1)—O(2)^{viii}	1.417(7)	P(1)—O(2)^{v}	1.579(7)
K(1)$\vert$Sr(1)—O(1)^{v}	2.854(8)	B(1)—O(2)	1.417(7)	P(1)—O(2)	1.579(7)
O(1)^{v}—P(1)—O(1)	113.3(6)	O(1)—P(1)—O(2)^{v}	113.7(3)	O(1)—P(1)—O(2)	111.2(5)
O(1)^{v}—P(1)—O(2)^{v}	111.2(5)	O(1)^{v}—P(1)—O(2)	113.7(3)	O(2)^{v}—P(1)—O(2)	91.9(6)
O(2)^{viii}—B(1)—O(2)	106.8(3)	O(2)—B(1)—O(2)^{ix}	114.9(7)	O(2)—B(1)—O(2)^{x}	106.8(3)
O(2)^{viii}—B(1)—O(2)^{ix}	106.8(3)	O(2)^{viii}—B(1)—O(2)^{x}	114.9(7)	O(2)^{ix}—B(1)—O(2)^{x}	106.8(3)
		$KBaBP_2O_8$[b]			
K(1)$\vert$Ba(1)—O(1)^{i}	2.721(2)	K(1)$\vert$Ba(1)—O(1)^{vii}	2.934(2)	B(1)—O(2)^{x}	1.4492(19)
K(1)$\vert$Ba(1)—O(1)^{ii}	2.721(2)	K(1)$\vert$Ba(1)—O(1)	2.934(2)	B(1)—O(2)	1.4492(19)
K(1)$\vert$Ba(1)—O(2)^{iii}	2.910(2)	(K(1)$\vert$Ba(1)—O(2)^{vi})	3.418(2)	P(1)—O(1)	1.498(2)
K(1)$\vert$Ba(1)—O(2)^{iv}	2.910(2)	(K(1)$\vert$Ba(1)—O(2)^{v})	3.418(2)	P(1)—O(1)^{vii}	1.498(2)
K(1)$\vert$Ba(1)—O(1)^{v}	2.927(2)	B(1)—O(2)^{viii}	1.4492(19)	P(1)—O(2)^{vii}	1.568(2)
K(1)$\vert$Ba(1)—O(1)^{vi}	2.927(2)	B(1)—O(2)^{ix}	1.4492(19)	P(1)—O(2)	1.568(2)
O(1)^{vii}—P(1)—O(2)	113.16(10)	O(1)—P(1)—O(1)^{vii}	112.86(18)	O(1)^{vii}—P(1)—O(2)^{vii}	110.38(12)
O(2)^{vii}—P(1)—O(2)	95.78(15)	O(1)—P(1)—O(2)^{vii}	113.16(10)	O(1)—P(1)—O(2)	110.38(12)
O(2)^{viii}—B(1)—O(2)^{ix}	106.76(8)	O(2)^{ix}—B(1)—O(2)^{x}	115.03(17)	O(2)^{ix}—B(1)—O(2)	106.76(8)
O(2)^{viii}—B(1)—O(2)^{x}	106.76(8)	O(2)^{viii}—B(1)—O(2)	115.03(17)	O(2)^{x}—B(1)—O(2)	106.76(8)

[a] (i) $1-x, -0.5+y, 0.25-z$; (ii) $1-x, 1-y, z$; (iii) $y, -0.5+x, 0.25+z$; (iv) $y, 1-x, -z$; (v) $x, 0.5-y, 0.25-z$; (vi) $-1+x, y, z$; (vii) $-1+x, 0.5-y, 0.25-z$; (viii) $1-y, -1+x, -z$; (ix) $2-x, -y, z$; (x) $1+y, 1-x, -z$; (xi) $1+x, y, z$; (xii) $1+y, -x, -z$; (xiii) $1-x, -y, z$; (xiv) $1-y, x, -z$; and (xv) $0.5+y, 0.5-x, 0.5-z$. [b] (i) $1-x, 1-y, z$; (ii) $1-x, 0.5+y, 0.25-z$; (iii) $-1+x, y, z$; (iv) $-1+x, 1.5-y, 0.25-z$; (v) $1-y, 1.5-x, 0.25+z$; (vi) $1-y, x, -z$; (vii) $x, 1.5-y, 0.25-z$; (viii) $2-x, 2-y, z$; (ix) $y, 2-x, -z$; (x) $2-y, x, -z$; (xi) $1+x, y, z$; (xii) $y, 1-x, -z$; and (xiii) $1.5-y, 0.5+x, 0.5-z$.

phosphor atom sites. Each B atom is tetrahedrally coordinated by four oxygen atoms, forming nearly ideal BO_4 tetrahedron geometry with four equal B—O bond lengths of 1.417(5) Å, while each P atom is also coordinated by four oxygen atoms in a tetrahedral geometry with two types of P—O distances (1.579(7) Å and 1.478(6) Å). BO_4 and PO_4 groups are connected to each other alternatively via corner-sharing O(2) atoms, leading to a unbranched 12-member ring of $[(BO_4)_6(PO_4)_6]$, as shown in Figure 1a. Such 12-member rings are the fundamental building block (FBB) of borophosphate $KSrBP_2O_8$ (B:P ratio = 1:2), which can be written as 12□:⟨12□⟩ (symbol □ represents BO_4 and PO_4 tetrahedra).[32] Then each adjacent 12-member ring is connected by the BO_4 tetrahedra, forming the three-dimensional (3D) anionic framework of $^{3}_{\infty}[BP_2O_8]^{3-}$, as shown in Figure 1b,c. It is worth noting here that all BO_4 tetrahedra participate in bridging functions of 12-member rings whereas each PO_4 tetrahedron is only owned by one ring; in other words, each BO_4 group is surrounded by four PO_4 groups resulting in four uniform B—O bond lengths, whereas each PO_4 group only connects to two BO_4 groups resulting in the P—O bonds of the ring oxygen atoms O(2) considerably longer (1.579(7)Å) than the terminal oxygen atoms O(1) (1.478(6)Å). By considering the B atoms as tetrahedral nodes, the framework of $KSrBP_2O_8$ can be described as a four-connected diamondoid topology net with a short vertex symbol $6^{6}_{(2)}$ (Figure 2). Furthermore, the anionic open framework of $^{3}_{\infty}[BP_2O_8]^{3-}$ delimits large cages in which K^+ and Sr^{2+} cations reside to ensure the cohesion and the neutrality of the structure, resulting in the final 3D open framework. The distances of adjacent boron nodes are the same (4.968 Å). Compared with previously reported borophosphates, such a 12□:⟨12□⟩ ring has only been seen in the compound $Cs(B_2P_2O_8(OH))$,[33] and such a 3D anionic framework with diamondoid topology is not found in other borophosphates up to now.

In the structure of $KMBP_2O_8$ (M = Sr, Ba), it is impossible to separate K^+ and M^{2+} cations at the respective octahedron site. This case is comparable to the other one of reported potassium—strontium or potassium—barium oxides containing K/M substitutional disorder.[34] Accordingly, each K/M site has an average charge of +1.5 which is just to provide charge compensation of anionic $^{3}_{\infty}[BP_2O_8]^{3-}$ framework to form the final 3D structure of $KMBP_2O_8$. Considering the coordination of K/M atoms, they have an eightfold coordination of oxygen atoms for both $KSrBP_2O_8$ and $KBaBP_2O_8$, in which six oxygen atoms (O(1)) connect to five PO_4 polyhedra (four of them in a unidentate fashion and one of them through edge-sharing oxygen atoms), and two oxygen (O(2)) atoms connect to three groups (two BO_4 polyhedra through corner-sharing and one PO_4

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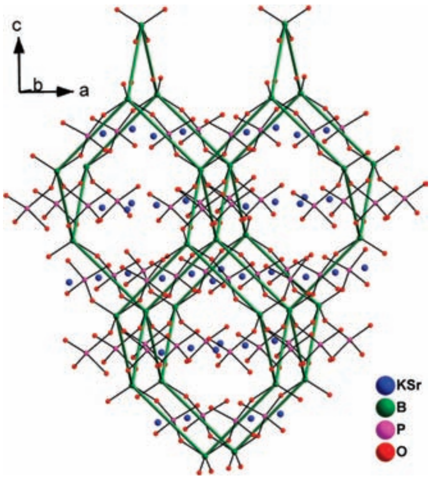

Figure 2. View of the 3D structure of $KSrBP_2O_8$. Boron atoms are considered as the nodes and linked by thick wires to show the 3D diamondoid topological net.

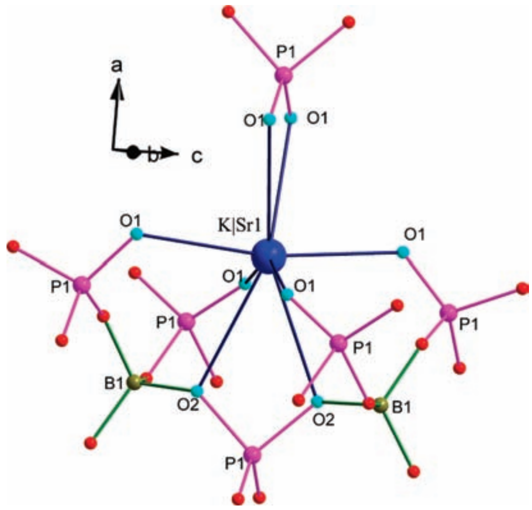

Figure 3. Coordinated environment of mixed occupied K/Sr atoms.

polyhedron through edge-sharing), as shown in Figure 3. In comparison of $KSrBP_2O_8$ and $KBaBP_2O_8$, the Ba^{2+} cation is larger than the Sr^{2+} one. As a consequence, the K/Sr−O distances are in the range of 2.676(7)−2.860(9)Å while the K/Ba−O bond distances range from 2.721(2) to 2.934(2)Å. On the other hand, there are also two weak K/M−O contacts which can be considered as secondary bonds to complete the extended coordination spheres of these very large cations (coordination number up to 10). Interestingly, the two weak K/Ba−O contacts (3.418(2) Å) are significantly longer than that of K/Sr−O (3.334(10) Å).

Thermal Analysis and Optical Properties of $KMBP_2O_8$ (M = Sr, Ba). Thermal stability studies were done for $KMBP_2O_8$ (M = Sr, Ba). There was no obvious weight loss before 1100 °C, indicating that it is thermally stable up to the high temperature (Figure S2 of Supporting Information).

Furthermore, we take $KSrBP_2O_8$ as a representation to measure its IR and UV−vis properties. IR studies indicated that $KSrBP_2O_8$ is transparent in the range of 3000−400 cm^{-1}(Figure S3 of Supporting Information). The absorption bands in the region 558−1173 cm^{-1} can be assigned to the asymmetric stretching and bending vibrations of the PO_4, BO_4, and B−O−P groups. From the UV−vis absorption spectra mesurament (Figure S4 of Supporting Information), we can notice that compound $KSrBP_2O_8$ has no absorption in the range from 350 to 800 nm. The absorption edge is around 313 nm (3.97 eV), indicating that $KSrBP_2O_8$ is an insulator with an optical band gap of 3.97 eV. According to the above discussion, the title compounds exhibit remarkable thermal stability and is transparent in the range of 350−800 nm and insoluble in common solvents, making it a potential candidate for practical applications.

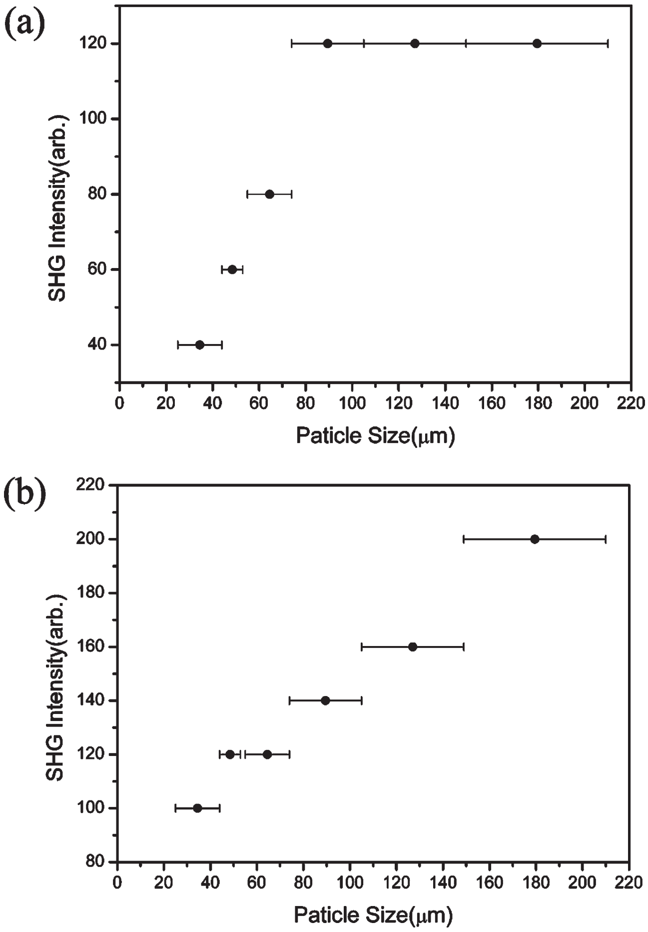

Figure 4. SHG measurements of $KSrBP_2O_8$(a) and $KBaBP_2O_8$(b) powder patterns.

Second Harmonic Generation (SHG) Measurements. Compounds $KMBP_2O_8$ (M = Sr, Ba) have the same space group as KH_2PO_4 (KDP), which belongs to the point group $\overline{4}2m$ (D_{2d}). Such a noncentrosymmetric structure prompts us to measure their second-order nonlinear optical (NLO) properties. Figure 4a,b gives the curves of the SHG signal for powder samples of $KMBP_2O_8$ (M = Sr, Ba), which are consistent with phase-matching behavior according to the rule proposed by Kurtz and Perry.[28] Since the powder SHG signal strongly depends on coherent length, a KDP sample was selected as a reference to ensure the accuracy of measurements because the coherent lengths for them may be approximately equal. The second-harmonic signal produced by powder samples with a 1064-nm fundamental corresponds to 1/5 and 1/3 times that of KDP, respectively, for $KSrBP_2O_8$ and

$KBaBP_2O_8$. In return, the SHG signal provides a highly sensitive and definitive test for the absence of a center of symmetry in the compound.

Conclusions

In this work, compounds $KMBP_2O_8$ (M = Sr, Ba) representing a new type of anhydrous borophosphate are synthesized by the HTSG method and structurally characterized by means of the single-crystal X-ray diffraction. They are isotypic and crystallize in the tetragonal crystal system with space group $I\bar{4}2d$ (No. 122). The fundamental building block of them is 12-member rings composed of alternatively connected BO_4 and PO_4 tetrahedra, denoted as $12\square{:}\langle 12\square \rangle$. Further interlocking of such rings leads to the 3D anionic framework of ${}^3_\infty[BP_2O_8]^{3-}$. Considering all boron atoms as the nodes in this structure, the framework can be denoted as hexagonal diamondoid topology, that is, $6^6{}_{(2)}$ mode. K^+ and M^{2+} (M = Sr, Ba) cations reside in the 3D framework, and K/M positions show substitutional type disorder. On the other hand, NCS structure of title compounds results in a fascinating second-order nonlinear optical effect. SHG measurements on powder samples reveal that $KSrBP_2O_8$ and $KBaBP_2O_8$ exhibit a weak SHG signal about 1/5 and 1/3 times that of KDP, respectively.

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Supporting Information Available: X-ray crystallographic files (CIF and CheckCIF); full results of elemental analysis; experimental and simulated X-ray powder diffraction patterns; thermal analysis (TGA, DTA); and IR and UV−vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.