

CsB₃GeO₇ and K₂B₂Ge₃O₁₀: Explorations of New Second-Order Nonlinear Optical Materials in the Borogermanate Systems

Fang Kong, Hai-Long Jiang, Ting Hu, and Jiang-Gao Mao*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, P. R. China

Received July 9, 2008

Two novel alkali(l) borogermanates with noncentrosymmetric structures, namely, CsB₃GeO₇ and K₂B₂Ge₃O₁₀, have been synthesized by high-temperature solid-state reactions in a platinum crucible. The structure of CsB₃GeO₇ features a novel three-dimensional (3D) framework composed of cyclic B₃O₇⁵⁻ groups that are interconnected by Ge(IV) cations, whereas the structure of K₂B₂Ge₃O₁₀ is a new 3D network based on cap-shaped [Ge₃B₂O₁₄]¹⁰⁻ clusters that are interconnected via Ge–O–B bridges. CsB₃GeO₇ exhibits a second-harmonic generation (SHG) response that is about 1.5 times that of KDP (KH₂PO₄), whereas the SHG signal of K₂B₂Ge₃O₁₀ is very weak. Both compounds are insulators and transparent in the range of 300–5000 nm. The electronic structure calculations for both compounds also have been performed.

Introduction

The search for new second-order nonlinear optical (NLO) materials is of current interest and of great importance owing to their applications in photonic technologies.¹ Currently, the most widely used materials are inorganic crystals of borates such as β-BaB₂O₄ (BBO) and LiB₃O₅ (LBO) and phosphates such as KH₂PO₄ (KDP) and KTiOPO₄ (KTP).^{2,3} Metal borophosphates containing both borate and phosphate groups are also promising NLO materials.⁴ Recently, we found that the combination of B–O bonds and a lone pair-containing Se(IV) cation that is susceptible to second-order Jahn–Teller (SOJT) distortion can also afford a new type of second-order NLO compound.⁵ It is reported that the combination of transition metal ions with *d*⁰ electronic configurations, such

as W⁶⁺ and Mo⁶⁺, and lone pair-containing Se(IV) and Te(IV) cations, which are both susceptible to SOJT distortions, also can form inorganic solids with excellent second-harmonic generation (SHG) properties.⁶ Though reports on metal borogermanates are still limited, but it is clear they are able to form various noncentrosymmetric (NCS) structures with possible SHG properties as well as zeolite-type open frameworks.^{7–10} Most borogermanates were synthesized under hydrothermal conditions; hence, their structures usually incorporate water molecules or organic templates, which is not desirable for their practical uses.^{7,8} Therefore,

* To whom correspondence should be addressed. E-mail: mjg@fjirsm.ac.cn. Fax: (+86)591-8371-4946.

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we started a research program to explore systematically new second-order NLO materials within the borogermanate systems by applying the high-temperature solid-state synthetic technique. Our research efforts have led to two novel alkali borogermanates with NCS structures and high thermal stabilities, namely, CsB₃GeO₇ with a SHG response that is about 1.5 times that of KDP and K₂B₂Ge₃O₁₀. Herein, we report their syntheses, crystal structures, and optical properties.

Experimental Section

Materials and Methods. All of the chemicals were analytically pure from commercial sources and used without further purification. IR spectra were recorded on a Magna 750 FT-IR spectrometer as KBr pellets in the range of 4000–400 cm⁻¹. Microprobe elemental analyses were performed on 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 θ - 2θ diffractometer using graphite-monochromated Cu K α radiation in the angular range of $2\theta = 5$ – 85° with a step size of 0.05° . Optical diffuse reflectance spectra were measured at room temperature with a PE Lambda 900 UV–visible spectrophotometer. A BaSO₄ plate was used as a standard (100% reflectance). The absorption spectrum was calculated from reflectance spectra using the Kubelka–Munk function: $\alpha/S = (1 - R)^2/2R$,¹¹ where α is the absorption coefficient, S is the scattering coefficient that is practically wavelength independent when the particle size is larger than $5 \mu\text{m}$, and R is the reflectance. Thermogravimetric analyses were carried out with a NETZSCH STA 449C unit at a heating rate of $5^\circ\text{C}/\text{min}$ under a static air atmosphere. Differential thermal analysis (DTA) was performed under N₂ on a NETZSCH DTA 404PC. The sample and reference (Al₂O₃) were enclosed in Pt crucibles, heated from room temperature to 830°C (950°C for K₂B₂Ge₃O₁₀), and then cooled to 150°C at a rate of $5^\circ\text{C}/\text{min}$ for CsB₃GeO₇. The measurement of the powder frequency-doubling effect was carried out on the sieved (80–100 mesh) powder sample of CsB₃GeO₇ by means of the modified method of Kurtz and Perry.¹² The fundamental wavelength is 1064 nm generated by a Q-switched Nd:YAG laser. The SHG wavelength is 532 nm. Sieved KDP powder (80–100 mesh) was used as a reference.

Preparation of CsB₃GeO₇. Prism-shaped single crystals of CsB₃GeO₇ were initially obtained by standard solid-state reactions of a mixture of Cs₂CO₃ (1 mmol, 0.336 g), GeO₂ (3 mmol, 0.314 g), and H₃BO₃ (12 mmol, 0.742 g) at 640°C for 7 days. The atomic ratio of Cs:Ge determined by energy dispersive spectrometry (EDS) is 1.1:1.0, which is in good agreement with the atomic ratio determined from single-crystal X-ray structural analysis. After proper structural analysis, a pure powder sample of CsB₃GeO₇ was obtained quantitatively by the solid-state reaction of a Cs₂CO₃/GeO₂/H₃BO₃ mixture in a molar ratio of 1:2:6 at 600°C for 6 days. Its purity was confirmed by XRD powder diffraction studies (Supporting Information).

Preparation of K₂B₂Ge₃O₁₀. Single crystals of K₂B₂Ge₃O₁₀ were initially prepared by heating a mixture of K₂CO₃ (0.5 mmol, 0.069 g), GeO₂ (1 mmol, 0.105 g), and H₃BO₃ (2 mmol, 0.124 g) at 700°C for 7 days. The atomic ratio of K:Ge determined by EDS is 2.0:2.9, which is in good agreement with the atomic ratio

Table 1. Crystal Data and Structure Refinements for CsB₃GeO₇ and K₂B₂Ge₃O₁₀

formula	CsB ₃ GeO ₇	K ₂ B ₂ Ge ₃ O ₁₀
fw	349.93	477.59
cryst syst	orthorhombic	monoclinic
space group	<i>Pna</i> 2 ₁	<i>I</i> 2
<i>a</i> , Å	9.542(3)	11.860(6)
<i>b</i> , Å	9.823(3)	6.160(2)
<i>c</i> , Å	7.009(2)	12.000(9)
α , deg	90	90
β , deg	90	96.696(6)
γ , deg	90	90
<i>V</i> , Å ³	657.0(3)	870.7(8)
<i>Z</i>	4	4
<i>D</i> _{calcd} , g cm ⁻³	3.538	3.643
μ (Mo K α), mm ⁻¹	10.111	11.292
GOF on <i>F</i> ²	1.085	1.043
R1, wR2 (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0151, 0.0342	0.0222, 0.0577
R1, wR2 (all data)	0.0157, 0.0344	0.0243, 0.0581

$$^a R1 = \sum |F_o| - |F_c| / \sum |F_o|, wR2 = \{\sum w[(F_o)^2 - (F_c)^2]^2 / \sum w(F_o)^2\}^{1/2}.$$

Table 2. Important Bond Lengths (Å) for CsB₃GeO₇ and K₂B₂Ge₃O₁₀^a

CsB ₃ GeO ₇			
Ge(1)–O(6)	1.724(2)	Ge(1)–O(1)	1.730(2)
Ge(1)–O(4)	1.758(3)	Ge(1)–O(7)	1.763(2)
B(2)–O(2) #1	1.346(4)	B(2)–O(7)	1.372(5)
B(2)–O(5)	1.377(5)	B(3)–O(3) #2	1.346(5)
B(3)–O(4)	1.370(5)	B(3)–O(5) #3	1.395(5)
B(1)–O(2)	1.459(4)	B(1)–O(6) #4	1.470(4)
B(1)–O(1)	1.474(4)	B(1)–O(3)	1.494(4)
K ₂ B ₂ Ge ₃ O ₁₀			
Ge(1)–O(1)	1.715(4)	Ge(1)–O(1) #1	1.715(4)
Ge(1)–O(2)	1.758(4)	Ge(1)–O(2) #1	1.758(4)
Ge(2)–O(5)	1.731(4)	Ge(2)–O(4)	1.736(3)
Ge(2)–O(3)	1.748(4)	Ge(2)–O(2)	1.765(4)
Ge(3)–O(7)	1.726(4)	Ge(3)–O(9)	1.728(4)
Ge(3)–O(8)	1.737(4)	Ge(3)–O(10)	1.753(4)
Ge(4)–O(6) #2	1.717(4)	Ge(4)–O(6) #3	1.717(4)
Ge(4)–O(10)	1.742(4)	Ge(4)–O(10) #4	1.742(4)
B(1)–O(1)	1.478(7)	B(1)–O(9) #5	1.482(6)
B(1)–O(3) #2	1.483(7)	B(1)–O(4) #6	1.484(6)
B(2)–O(6)	1.448(7)	B(2)–O(7)	1.483(6)
B(2)–O(8) #4	1.496(7)	B(2)–O(5)	1.532(7)

^a Following are symmetry transformations used to generate equivalent atoms. For CsB₃GeO₇: #1, $-x + 1/2, y - 1/2, z - 1/2$; #2, $-x + 1/2, y - 1/2, z + 1/2$; #3, $x, y, z + 1$; and #4, $x - 1/2, -y + 3/2, z$. For K₂B₂Ge₃O₁₀: #1, $-x + 2, y, -z + 2$; #2, $x, y - 1, z$; #3, $-x + 1, y - 1, -z + 2$; #4, $-x + 1, y, -z + 2$; #5, $x + 1/2, y - 1/2, z + 1/2$; and #6, $-x + 2, y - 1, -z + 2$.

determined from single-crystal X-ray structural analysis. After structural analysis, the monophasic powder samples of K₂B₂Ge₃O₁₀ were prepared quantitatively by the solid-state reactions of a K₂CO₃/GeO₂/H₃BO₃ mixture in a molar ratio of 1:3:2 at 600°C for 6 days. Its purity was confirmed by XRD powder diffraction studies (Supporting Information).

X-ray Crystallography. Data collections for both compounds were performed on a Rigaku Mercury CCD diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The data sets were corrected for Lorentz and polarization factors as well as for absorption by the multiscan method.¹³ Both structures were solved by the direct methods and refined by full-matrix least-squares fitting on *F*² by SHELXL-97.^{13b} Crystallographic data and structural refinements for both compounds are summarized in Table 1. Important bond distances are listed in Table 2. More details on the crystallographic studies as well as atomic displacement parameters are given in the Supporting Information.

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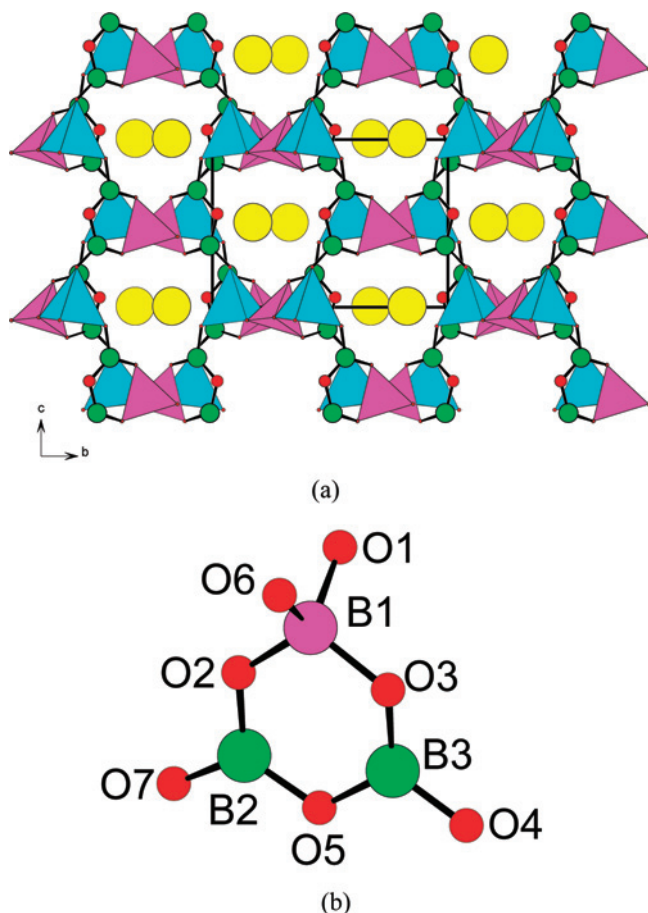


Figure 1. (a) View of the structure of CsB₃GeO₇ down the *a*-axis. The GeO₄ and BO₄ tetrahedra are shaded in cyan and pink, respectively. Three-coordinated B, Cs, and O atoms are drawn as green, yellow, and red circles, respectively. (b) B₃O₇⁵⁻ cluster unit.

Computational Descriptions. Single-crystal structural data of the two compounds were used for the theoretical calculations. Band structures and density of states (DOS) were performed with the total energy code, CASTEP.¹⁴ The total energy is calculated with the density functional theory (DFT) using the Perdew–Burke–Ernzerhof generalized gradient approximation (GGA).¹⁵ The interactions among the ionic cores and the electrons are described by the ultrasoft pseudopotential.¹⁶ The following orbital electrons are treated as valence electrons: Cs-5p⁶s¹, K-3p⁶s¹, Ge-4s²4p², B-2s²2p¹, and O-2s²2p⁴. The number of plane waves included in the basis is determined by a cutoff energy of 500 eV, and the numerical integration of the Brillouin zone is performed using a 3 × 3 × 4 Monkhorst–Pack *k*-point sampling for CsB₃GeO₇ (5 × 5 × 3 for K₂B₂Ge₃O₁₀). The other calculating parameters and convergent criteria were the default values of the CASTEP code.

Results and Discussion

The structure of CsB₃GeO₇ features a three-dimensional (3D) network composed of cyclic B₃O₇⁵⁻ anions bridged by Ge(IV) cations with one-dimensional (1D) tunnels along the

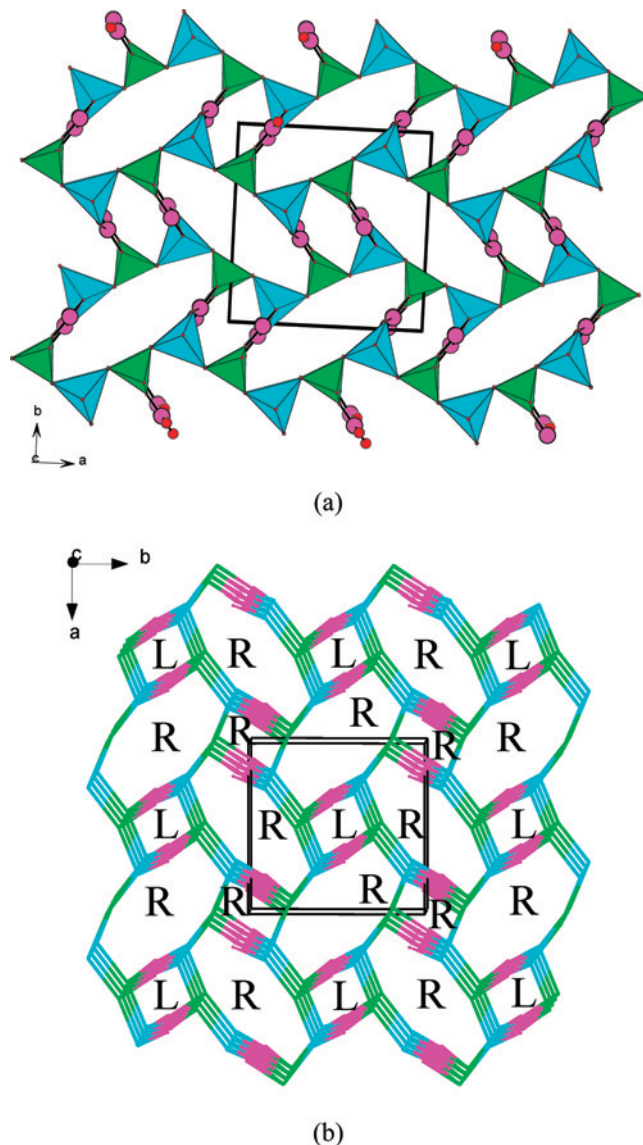


Figure 2. (a) View of the anionic structure of CsB₃GeO₇ down the *c*-axis. The GeO₄ and BO₄ tetrahedra are shaded in cyan and pink, respectively. Three-coordinated B, Cs, and O atoms are drawn as green, yellow, and red circles, respectively. (b) Wire representation of the 10-MR and 6-MR tunnels along the *c*-axis in CsB₃GeO₇.

a-axis that is occupied by the Cs⁺ cations (Figure 1a). The cyclic B₃O₇⁵⁻ anion is formed by one BO₄ tetrahedron, B(1), and two triangular BO₃ groups, B(2) and B(3), interconnected via corner sharing (Figure 1b). The anionic structure of B₃GeO₇⁵⁻ can be also considered as cluster units in KB₃O₃(OH)₄·H₂O, being fully deprotonated and interconnected by Ge(IV) atoms.¹⁷ The structure of CsB₃GeO₇ could also be viewed as the GeO_{4/2} tetrahedra being inserted between neighboring B₃O₇⁵⁻ anions in CsB₃O₅.¹⁸ The B–O bond distances of the three-coordinated boron atoms, B(2) and B(3), are significantly shorter [1.346(5)–1.395(5) Å] than that of the tetrahedrally coordinated boron atom [B(1), 1.459(4)–1.494(4) Å]. The O–B–O angles are in the range of 105.2(2)–111.2(2)° for the B(1)O₄ tetrahedron and in the

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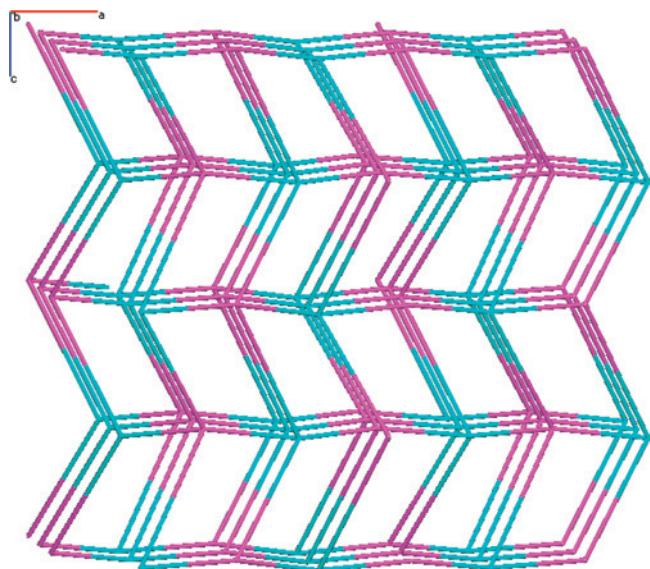


Figure 3. Topological view of the $4^2.6^3.8$ nets of CsB_3GeO_7 . The B_3O_7 groups and the Ge atoms were regarded as a four-connected node.

range of $113.6(3)$ – $125.1(4)^\circ$ for the triangular BO_3 groups. The Ge(IV) atom is tetrahedrally coordinated by four oxygen atoms with Ge–O distances ranging from $1.724(2)$ to $1.763(2)$ Å. The B–O–B bond angles of $118.7(3)$ – $124.7(3)^\circ$ and the B–O–Ge angles of $120.7(2)$ – $137.2(3)^\circ$ are comparable to those reported in other borogermanates.^{7–10} Each Cs^+ cation is 10-coordinated by 10 oxygen atoms with Cs–O bond distances in the range of $2.980(2)$ – $3.558(2)$ Å. Bond valence calculations indicate that the B atoms are in an oxidation state of +3, and the oxidation state of the Ge atom is +4. The calculated total bond valences for B(1), B(2), B(3), and Ge(1) are 3.03, 3.05, 3.01, and 4.05, respectively.¹⁹

The 3D anionic network of CsB_3GeO_7 exhibits two types of 1D helical tunnels along the c -axis (Figure 2a) The small tunnels are based on six-member rings composed of two GeO_4 , two BO_4 , and two BO_3 groups, whereas the large tunnels are composed of 10-member rings composed of four GeO_4 , four BO_4 , and two BO_3 groups. The large tunnels are right-handed, whereas the small tunnels are equally right- and left-handed (Figure 2b). Each small tunnel is surrounded by four large tunnels, whereas each large tunnel has four large and four small tunnels as its neighbors. In connectivity terms, the structure of CsB_3GeO_7 may also be written as $[(\text{GeO}_{4/2})^0(\text{BO}_{4/2})^{-2}(\text{BO}_{3/2})^0]^-$ with the charge balanced by the Cs^+ cation. Because both Ge(IV) and the $\text{B}_3\text{O}_7^{5-}$ cluster act as four-connected nodes, the anionic structure of CsB_3GeO_7 can also be described as a 3D four-connected network in the topological view with the Schläfli symbol of $4^2.6^3.8$ and vertex symbols of $4.6.4.6.6.8_2$ (Figure 3).²⁰

$\text{K}_2\text{B}_2\text{Ge}_3\text{O}_{10}$ features a different 3D network. Its anionic structure is based on cap-shaped $\text{B}_2\text{Ge}_3\text{O}_{14}^{10-}$ clusters interconnected via sharing oxygen corners (Figure 4a). The novel $\text{B}_2\text{Ge}_3\text{O}_{14}^{10-}$ cluster is composed of three GeO_4 and two BO_4 tetrahedra interconnected via corner sharing (Figure 4b). The three GeO_4 groups form a semicircle cluster with

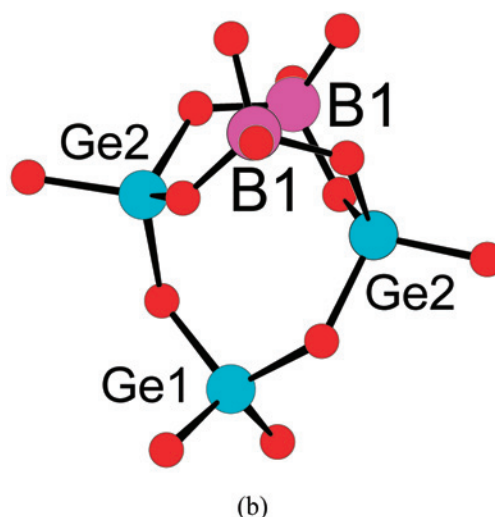
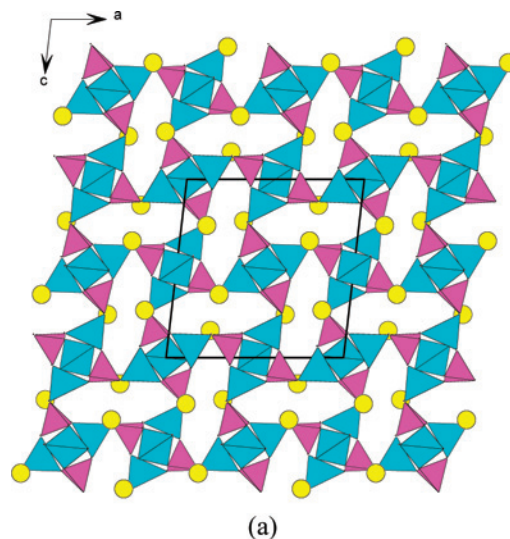


Figure 4. (a) View of the structure of $\text{K}_2\text{B}_2\text{Ge}_3\text{O}_{10}$ down the b -axis. The GeO_4 and BO_4 tetrahedra are shaded in cyan and pink, respectively. Cs atoms are drawn as yellow circles. (b) $[\text{B}_2\text{Ge}_3\text{O}_{14}]^{10-}$ cluster unit.

the head and tail Ge(IV) atoms further bridged by a pair of BO_4 tetrahedra, forming three Ge_3B four-member rings. Such a cluster resembles the organic cryptands, but this has not been observed in metal borogermanates. The B–O and Ge–O bonds are in the range of $1.448(7)$ – $1.532(7)$ and $1.715(4)$ – $1.765(4)$ Å, respectively, which are comparable to those in CsB_3GeO_7 . The O–B–O, O–Ge–O, and B–O–Ge angles are also in the expected ranges.^{7–10} Bond valence calculations indicate that the B atoms are in an oxidation state of +3, and the Ge atom is in an oxidation state of +4. The calculated total bond valences for B(1), B(2), Ge(1), Ge(2), Ge(3), and Ge(4) are 2.91, 2.97, 4.13, 4.04, 4.13, and 4.21, respectively.¹⁹

The $[\text{B}_2\text{Ge}_3\text{O}_{14}]^{10-}$ clusters are further interconnected via Ge–O–B bridges into a novel anionic 3D network with left- and right-handed 1D helical tunnels along the b -axis and potassium(I) cations located at the cavities of the structure (Figure 4a). These long, narrow-shaped, helical tunnels are based on eight-member rings composed of four GeO_4 and four BO_4 tetrahedra, and they are arranged in such a way that the right-handed tunnels are almost perpendicular to the

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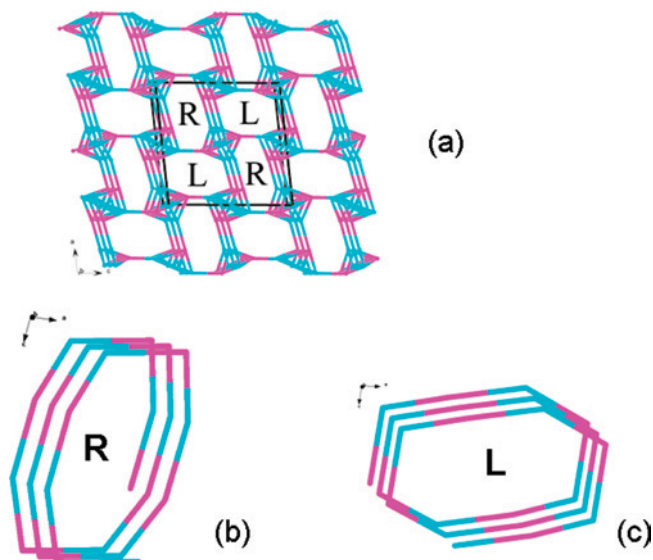


Figure 5. (a) Topological view of the anionic 3D network of K₂B₂Ge₃O₁₀ down the *b*-axis and wire representation of the (b) right-handed and (c) left-handed 8-MR tunnels along the *b*-axis.

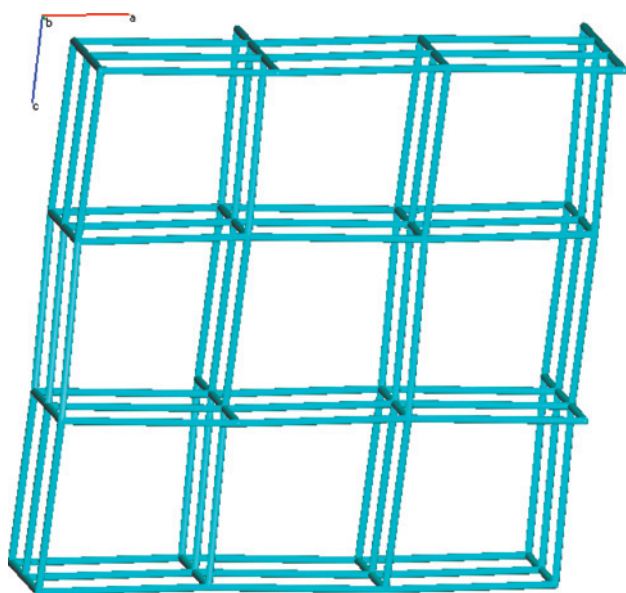


Figure 6. Topological view of the 4⁸.5⁴.6³ nets of K₂B₂Ge₃O₁₀. The B₂Ge₃O₁₄ groups were regarded as a six-connected node.

left-handed tunnels (Figure 5). The anionic structure of K₂B₂Ge₃O₁₀ also exhibits small 1D tunnels along the *a*- and *c*-axis which are based on severely twisted eight-member rings composed of three BO₄ and five GeO₄ tetrahedra. In connectivity terms, the structure of K₂B₂Ge₃O₁₀ also may be written as [3(GeO_{4/2})₂(BO_{4/2})²⁻]²⁻ with the charge balanced by two K⁺ cations. Because each B₂Ge₃O₁₄¹⁰⁻ cluster connects with six such neighbors, the anionic structure of K₂B₂Ge₃O₁₀ can be also viewed as a 3D six-connected network in the topological view with the Schläfli symbol of 4⁸.5⁴.6³, if the whole cluster is considered to be a six-connecting node (Figure 6).²⁰ Both potassium(I) ions [K(1) and K(2)] are 10-coordinated by 10 oxygen atoms with K–O distances ranging from 2.712(4) to 3.483(6) Å. It is interesting to compare the structure of K₂B₂Ge₃O₁₀ with those of the amine-templated borogermanates with the same B/Ge

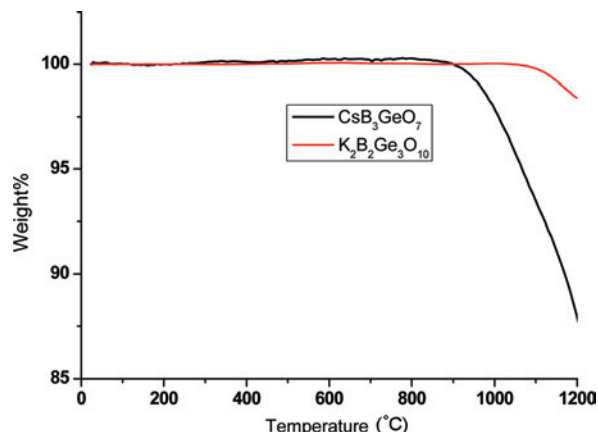


Figure 7. TGA curves for CsB₃GeO₇ (black) and K₂B₂Ge₃O₁₀ (red).

Table 3. State Energies (eV) of the L-CB and the H-VB of the Crystals CsB₃GeO₇ and K₂Ge₃B₂O₁₀

compound	k-point	L-CB	H-VB
CsB ₃ GeO ₇	G (0.000, 0.000, 0.000)	4.21327	0
	Z (0.000, 0.000, 0.500)	4.97752	−0.12395
	T (−0.500, 0.000, 0.500)	5.47271	−0.18482
	Y (−0.500, 0.000, 0.000)	4.93657	−0.09116
	S (−0.500, 0.500, 0.000)	5.21021	−0.11854
	X (0.000, 0.500, 0.000)	4.7479	−0.08748
	U (0.000, 0.500, 0.500)	5.07579	−0.1065
	R (−0.500, 0.500, 0.500)	5.48603	−0.10564
K ₂ Ge ₃ B ₂ O ₁₀	L (−0.500, 0.000, 0.500)	5.06016	0
	M (−0.500, −0.500, 0.500)	4.3534	−0.08985
	A (−0.500, 0.000, 0.000)	5.06065	−0.02438
	G (0.000, 0.000, 0.000)	3.52692	−0.02306
	Z (0.000, −0.500, 0.500)	5.06016	−1.08846E−6
	V (0.000, 0.000, 0.500)	4.30287	−0.05977

ratio such as [H₂en]₂B₂Ge₃O₁₁, [H₂DACH][B₂Ge₃O₉(OH)₂], and [H₂BAPPZ][B₂Ge₃O₉(OH)₂].^{7a,8c} The latter three compounds display a layered structure based on corner-sharing Ge₃B₂O₁₁ clusters. The Ge₃B₂O₁₁ cluster is formed by a corner-sharing Ge₃ tetrahedral ring with one GeO₄ tetrahedron further attached by two BO₄ tetrahedra. The interlayer distances and the degree of protonation on the borate groups are mainly controlled by the selection of the intercalated template cations.^{7a,8c}

Optical Properties. Optical diffuse reflectance spectrum studies indicate that both CsB₃GeO₇ and K₂B₂Ge₃O₁₀ are insulators with an optical band gap of 5.76 and 5.38 eV, respectively (Supporting Information). UV absorption spectra of CsB₃GeO₇ and K₂B₂Ge₃O₁₀ indicate that they are transparent in the range of 300–2500 nm (Supporting Information). IR studies indicate that they are transparent in the range of 4000–2000 cm^{−1} (2500–5000 nm). The IR spectrum of CsB₃GeO₇ displays strong absorption bands at 1334 and 1217 cm^{−1} for the BO₃ groups. The bands for the BO₄ groups for both compounds appear at 935–1023 cm^{−1}.²¹ The absorption peaks of 824–882 cm^{−1} can be assigned to the asymmetrical stretch of the GeO₄ groups. The absorption bands of the symmetrical stretch of the Ge–O bonds are shown in the region of 564–592 cm^{−1}, and bands from 440 to 472 cm^{−1}

(21) (a) Pan, S. L.; Watkins, B.; Smit, J. P.; Marvel, M. R.; Saratovsky, I.; Poeppelmeier, K. R. *Inorg. Chem.* **2007**, *46*, 3851. (b) Pan, C. Y.; Wang, G. M.; Zheng, S. T.; Yang, G. Y. *J. Solid State Chem.* **2007**, *180*, 1553.

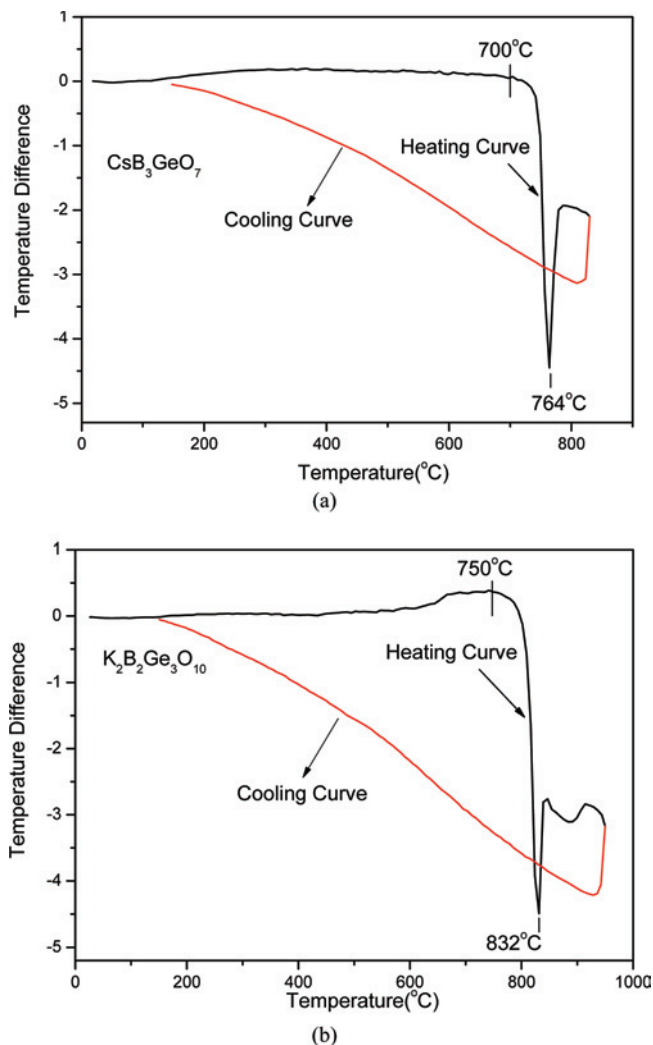


Figure 8. DTA curves for (a) CsB_3GeO_7 and (b) $\text{K}_2\text{B}_2\text{Ge}_3\text{O}_{10}$.

correspond to the bending vibrations of the Ge–O bonds (Supporting Information).^{8,21}

TGA and DTA Studies. TGA studies indicate no weight loss before 850 and 1000 °C, respectively, for CsB_3GeO_7 and $\text{K}_2\text{B}_2\text{Ge}_3\text{O}_{10}$ (Figure 7). Then they lost weight continuously, corresponding to the evaporation of some versatile components formed by decomposition. The total weight losses at 1200 °C are 87.8% for CsB_3GeO_7 and 98.5% for $\text{K}_2\text{B}_2\text{Ge}_3\text{O}_{10}$. DTA diagrams of CsB_3GeO_7 and $\text{K}_2\text{B}_2\text{Ge}_3\text{O}_{10}$ exhibit endothermic peaks at 764 and 832 °C, respectively, in the heating curves, but no exothermic peaks were found in the cooling curves for both compounds (Figure 8), indicating that CsB_3GeO_7 and $\text{K}_2\text{B}_2\text{Ge}_3\text{O}_{10}$ melt incongruently around 765 and 834 °C, respectively.^{21a} This point is also confirmed by the temperature-dependent XRD powder studies (Supporting Information). The XRD powder patterns measured below and above the melting point are different for both compounds, indicating that both compounds decomposed during melting, although no immediate weight losses were observed.

SHG Measurements. Both CsB_3GeO_7 and $\text{K}_2\text{B}_2\text{Ge}_3\text{O}_{10}$ display acentric structures; therefore, they may exhibit SHG properties. SHG measurements on a Q-switched Nd:YAG

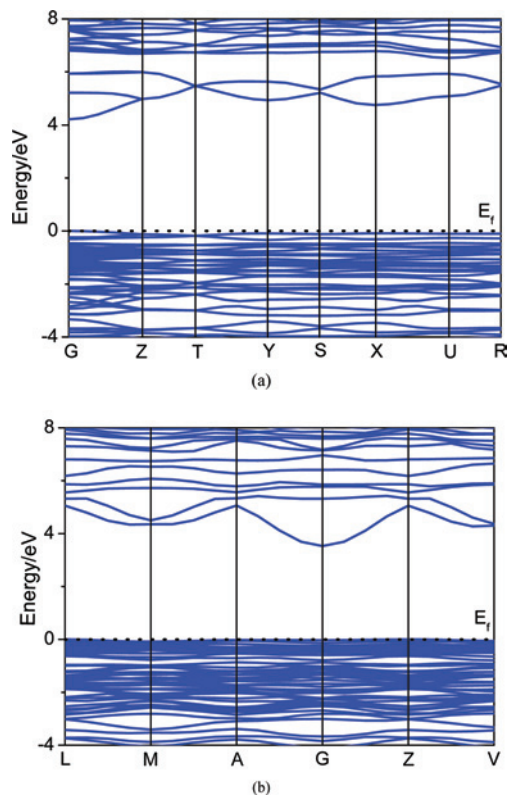


Figure 9. Band structures for the crystals (a) CsB_3GeO_7 and (b) $\text{K}_2\text{B}_2\text{Ge}_3\text{O}_{10}$. Bands are shown between -4 and 8 eV for clarity, and the Fermi level is set at 0 eV.

laser with the sieved powder samples (80–100 mesh) revealed that CsB_3GeO_7 displays a moderate–strong SHG response that is about 1.5 times that of KDP, whereas the SHG signal for $\text{K}_2\text{B}_2\text{Ge}_3\text{O}_{10}$ is very weak. The strong SHG response for CsB_3GeO_7 compared to that of $\text{K}_2\text{B}_2\text{Ge}_3\text{O}_{10}$ could be attributed to the presence of the triangular BO_3 groups in CsB_3GeO_7 .^{1–3,7a}

Theoretical Studies. The calculated band structures of CsB_3GeO_7 and $\text{K}_2\text{B}_2\text{Ge}_3\text{O}_{10}$ along high symmetry points of the first Brillouin zone are plotted in Figure 9. It is found that the top of the valence bands (VBs) is almost flat, whereas the bottom of the conduction bands (CBs) displays a small dispersion for both compounds. The state energies (eV) of the lowest conduction band (L-CB) and the highest valence band (H-VB) of both compounds are listed in Table 3. For CsB_3GeO_7 , the top of the VBs and the bottom of the CBs are located at the G point with a band gap of 4.21 eV. Therefore, it is a direct band gap insulator. For $\text{K}_2\text{B}_2\text{Ge}_3\text{O}_{10}$, the lowest of the CBs is localized at the G point and has an energy of 3.52692 eV, whereas the highest energy of the VBs (0.0 eV) is localized at the L point. Accordingly, $\text{K}_2\text{B}_2\text{Ge}_3\text{O}_{10}$ is an insulator with an indirect band gap of around 3.53 eV. The calculated band gaps of both compounds are somehow smaller than the experimental band gaps (5.76 eV for CsB_3GeO_7 and 5.38 eV for $\text{K}_2\text{B}_2\text{Ge}_3\text{O}_{10}$). This is not surprising as it is well-known that the GGA does not accurately describe the eigenvalues of the electronic states, which causes quantitative underestimation of band gaps, especially for insulators.²²

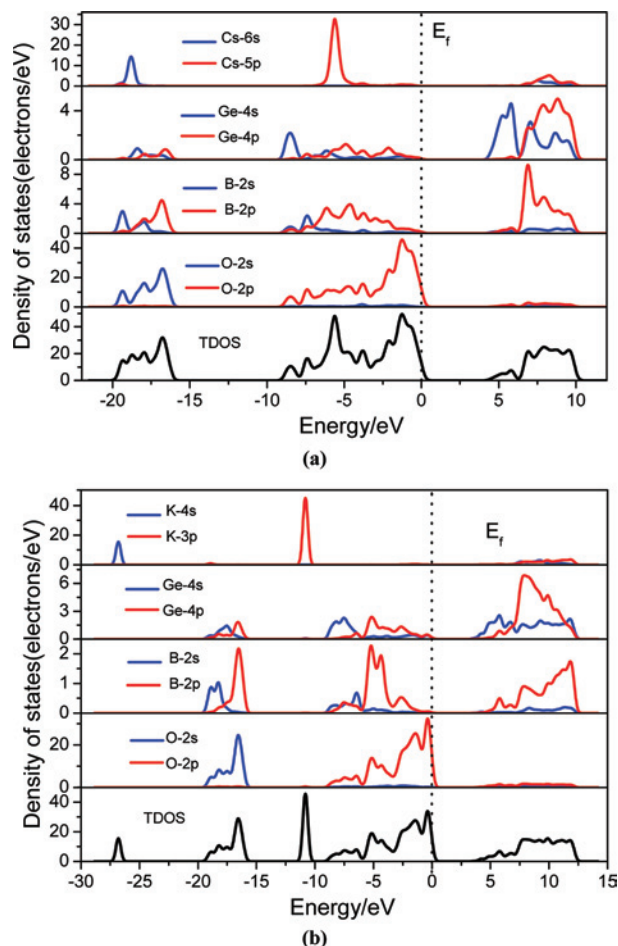


Figure 10. Total density of states and partial density of states of (a) CsB₃GeO₇ and (b) K₂B₂Ge₃O₁₀. The Fermi level is set at 0 eV.

The bands can be assigned according to the total and partial DOS as plotted in Figure 10. For CsB₃GeO₇, the bands above the Fermi level are mainly derived from B-2p, Ge-4s, and Ge-4p states. The VBs from -9.1 eV to the Fermi level are mainly composed of O-2p and Cs-5p states near -5.7 eV. The lowest VBs ranging from -19.7 to -16.3 eV

arise from mostly O-2s and Cs-6s states near -18.8 eV. For K₂B₂Ge₃O₁₀, the bands above the Fermi level are mainly derived from Ge-4s and Ge-4p states. The VBs from -9.0 eV to the Fermi level are mainly composed of O-2p states, while the O-2s states dominate the VBs ranging from -19.5 to -15.7 eV. In addition, the VBs near -10.8 and -26.8 eV are formed by K-3p and K-4s states, respectively.

Semiempirical population analyses allow for a more quantitative bond analysis. The calculated bond orders of Ge-O and B-O bonds are 0.57–0.90 and 0.49–0.62 e, respectively, for CsB₃GeO₇. It is obvious in observations that the overlap populations have the following order: three-coordinated boron > tetrahedrally coordinated boron (Supporting Information). For K₂B₂Ge₃O₁₀, the calculated bond orders of Ge-O and B-O bonds are 0.46–0.64 and 0.61–0.67 e, respectively (covalent single-bond order is generally 1.0 e). Accordingly, we can say that the covalent character of the B-O bond is larger than that of the Ge-O bond.

Conclusions

In summary, two novel alkali(I) borogermanates with new noncentrosymmetric structures, CsB₃GeO₇ and K₂B₂Ge₃O₁₀, have been synthesized by high-temperature solid-state reactions. CsB₃GeO₇ exhibits the SHG efficiency that is about 1.5 times that of KDP (KH₂PO₄). Both compounds are insulators with band gaps larger than 5.0 eV. Our future research efforts will be devoted to the preparation of other boron-rich borogermanates with good SHG properties by the inclusion of more triangular BO₃ groups.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (20731006, 20573113, and 20521101), Key Project of FJIRSM (No. SZD07001-2) and the Knowledge Innovation Program of the Chinese Academy of Sciences. We thank Professor Ding Li for his great help with the SHG measurements.

Supporting Information Available: Calculated bond orders, simulated and experimental XRD powder patterns, optical diffuse reflectance, and UV spectra as well as IR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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