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A Series of Mixed-metal Germanium lodates as Second-Order NLO Materials

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ABSTRACT: A series of new compounds in A/Ae-Ge⁴⁺-IO₃ system, namely, $A_2Ge(IO_3)_6(A = Li, Na, Rb, Cs)$ and $BaGe(IO_3)_6(H_2O)$ have been obtained by introducing GeO₆ octahedra into ternary metal iodate system. The structures of all five new compounds feature zero-dimensional [Ge(IO₃)₆]²⁻ anion composed of a GeO₆ octahedron connecting with six IO₃ groups, the alkali or alkali-earth cations acting as spacers between these anions and keeping charge balance. Interestingly, the isomeric Li₂Ge(IO₃)₆ and Na₂Ge(IO₃)₆ are noncentrosymmetric (NCS), whereas the isostructural Rb₂Ge(IO₃)₆ and Cs₂Ge(IO₃)₆ are centrosymmetric (CS). BaGe(IO₃)₆(H₂O) is the first NCS alkali-earth germanium iodate reported. Powder second harmonic generation (SHG) measurements show that Li₂Ge(IO₃)₆, Na₂Ge(IO₃)₆, and BaGe(IO₃)₆(H₂O) crystals are phase-matchable and display very large SHG signals of about 32, 15 and 12 times that of KH₂PO₄ (KDP) under 1064 nm radiation, respectively, and 2, 0.8 and 0.8 times that of KTiOPO₄ (KTP) under 2.05 mm laser radiation. The compounds show high thermal stability and large laser damage threshold (LDT), indicating their potential applications as NLO materials in visible and IR spectral regions. Optical properties measurement, thermal analysis, as well as theoretical calculations on SHG origin have been performed. Our studies indicate that introducing non second-order Jahn-Teller(SOJT) distortive MO₆ octahedra into metal iodate systems can also lead to good mixed-metal iodates NLO materials.

INTRODUCTION

Noncentrosymmetric (NCS) materials have attracted extensive academic interest due to their potential application as nonlinear optical (NLO) materials as well as functional materials with ferroelectric, pyroelectric, and piezoelectric properties.¹⁻³ Due to their frequency conversion function, NLO materials have been widely applied in photoelectric and laser technologies.⁴⁻⁷ It is commonly recognized that ideal second order NLO materials should better feature large second harmonic generation (SHG) efficiency, eligible phase matching angle and birefringence, high laser damage threshold (LDT), wide transparency window, good thermal stability, nonhygroscopicity and a facile synthetic route.⁸⁻¹²

During the past decades, metal iodate systems have been extensively investigated since the stereochemically active lonepair electrons on IO₃ unit can induce the formation of NCS or polar materials with excellent SHG properties when the lonepairs are properly aligned.¹³⁻¹⁶ A number of iodates with large SHG signals have been reported, exemplified by α -LiIO₃,^{17, 18} NaI₃O₈,¹⁹BiO(IO₃),²⁰ and Bi(IO₃)F₂.²¹ During the past decades, great efforts have been made in the syntheses of metal iodates containing octahedrally coordinated d⁰ transition metal(TM) cations.²²⁻³⁹ It is based on the idea of forming NLO materials by the synergistic effect of the second-order Jahn-Teller (SOJT) distortion of both the lone-pair electrons on iodate groups and d⁰ TM cations. A large number of mixed-metal iodates containing d⁰ TM cations with large SHG responses have been successfully obtained, such as $A_2Ti(IO_3)_6(A = Li, Na)^{22}$ NaVO₂(IO₃)₂(H₂O),²⁴ A(VO)₂O₂(IO₃)₃(A = K, Rb, Cs, NH₄),²⁵, ²⁶ Zn₂(VO₄)(IO₃),²⁷ BaNbO(IO₃)₅,²⁸ AMoO₃(IO₃)(A = Li, K, Rb, Cs),^{29,30} *etc.* It is interesting to find that, among these compounds, $A_2Ti(IO_3)_6(A = Li, Na)$ exhibit very strong SHG effect though the out-of-center distortion of TiO₆ octahedron is very small.²² The well alignment of the iodate groups leads to the "addition" of the polarization of lone pairs, which results in the large SHG signals. Even for the other compounds with much more notable distortion of the MO₆ octahedra, the lone pairs on iodate groups seem to make major contributions to the SHG efficiency. Thus controlling the proper alignment of the iodate groups to enhance the net polarization is the key point in synthesize NLO iodate material. Introducing MO₆ octahedra into iodates can be a good way to "guide" the alignment of the iodate and thus strong SHG effect.

Later the phases of $A_2Sn(IO_3)_6(A = Li, Na)$ were isolated by replacing the Ti⁴⁺ with Sn^{4+,40} Even though the second-order Jahn Teller (SOJT) distortive TiO₆ octahedron is replaced by the non SOJT-distortive SnO₆ octahedron, their structures stay unchanged. Results of SHG measurements show that the SHG intensities of $A_2Sn(IO_3)_6(A = Li, Na)(\sim 15, 12 \times KDP)$ are only slightly weaker than those of $A_2Ti(IO_3)_6(A = Li, Na)$ (~17, 14×KDP). This may be due to the larger ionic radius of Sn^{4+} than that of Ti⁴⁺, which elongates the M-O bonds and give a rise to the unit cell volumes of $A_2Sn(IO_3)_6(A = Li, Na)$, leading to lower density of polar IO₃ units and thus slightly weakened SHG intensity. Among the post-transitional main group cations (In³⁺, Ga³⁺, Ge⁴⁺, Sn⁴⁺, Sb⁵⁺) that tend to adopt octahedral geometry, Ge⁴⁺ have the smallest ionic radius. The small ionic radius of Ge4+ can lead to more compact unit cell and higher density of the polar units in the resultant compounds and thus higher SHG intensity. The introduction of GeO₆ octahedra into metal iodates may also lead to other interesting physical properties of the materials. Up to date, only K₂Ge(IO₃)₆ was reported in the mixed-metal germanium iodate system.⁴¹ As K₂Ge(IO₃)₆ crystallizes in the space group of $R\bar{3}$, it is centrosymmetric (CS) and SHG-inert. Herein, our explorations of new compounds in the A/Ae-Ge⁴⁺-IO₃ systems led to five new germanium iodates, namely, A₂Ge(IO₃)₆(A = Li, Na, Rb, Cs) and BaGe(IO₃)₆(H₂O), among which, Li₂Ge(IO₃)₆, Na₂Ge(IO₃)₆ and BaGe(IO₃)₆(H₂O) are noncentrosymmetric and display very large SHG signals of about 32, 15 and 12 times that of KDP. Herein we report their syntheses, crystal structures, optical properties, SHG effects, LDT values as well as theoretical calculations.

EXPERIMENTAL SECTION

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Materials and Methods. Li₂CO₃ (99+%), Na₂CO₃ (99+%), Rb₂CO₃ (99+%), Ba(IO₃)₂·H₂O (99+%), Cs₂CO₃ (99+%), GeO₂ (99+%), I₂O₅ (99.0%), were used as purchased from Shanghai Reagent Factory. Powder X-ray diffraction (XRD) patterns were recorded on Rigaku MiniFlex II diffractometer with graphite-monochromated Cu–K α radiation in the 2 θ range of 5– 65°. Microprobe elemental analyses were performed on a field emission scanning electron microscope (FESEM, JSM6700F) with energy dispersive X-ray spectroscope (EDS, Oxford INCA). Infrared (IR) spectra were recorded on Magna 750 FT-IR spectrometer in the form of KBr pellets in 4000–400 cm⁻¹. UV-vis-NIR spectra in 200-2500 nm were collected on PerkinElmer Lambda 900 UV-Vis-NIR spectrophotometer. By using Kubelka-Munk function,42 reflectance spectra were converted into absorption spectrum. Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) were performed with NETZCH STA 449F3 unit under N₂ atmosphere, at a heating rate of 10 °C/min. Powder SHG measurements were carried out with Q-switch Nd:YAG laser generating radiations at 1064 nm according to Kurtz and Perry method.⁴³ A₂M(IO₃)₆(A=Li, Na; M=Ti, Sn) crystals were obtained hydrothermally according to the references.^{22, 40} Crystalline A₂M(IO₃)₆(A=Li, Na; M=Ge, Ti, Sn) and BaGe(IO₃)₆(H₂O) samples were sieved into distinct particlesize ranges (25-45, 45-53, 53-75, 75-105, 105-150, 150-210 μ m). Sieved KH₂PO₄ (KDP) and KTiOPO₄ (KTP) samples in the same particle-size ranges were taken as references for SHG measurement under 1064 nm and 2.05 µm laser radiation. Crystalline samples in the particle-size range of 150-210 μ m were used for SHG measurements. The laser-induced damage threshold (LDT) measurements were performed on crystalline samples of A₂M(IO₃)₆(A=Li, Na; M=Ge, Ti, Sn), BaGe(IO₃)₆(H₂O) and α -LiIO₃ in the particle-size range of 150- $210 \,\mu\text{m}$ with AgGaS₂ sample in the same particle-size range as the reference, under 1064 nm laser source (10 ns, 1Hz). The laser spot has a diameter of 3.6mm. The energy of the laser emission was gradually increased until the samples turned black in color. It should be noted that the LDT measurement using powder samples is feasible since each crystallite has a diameter much larger than the wavelength of the incident laser. Thus, each crystallite behaves as a macroscopic bulk material with the similar multiphoton absorption (a main process for LDT as the laser pulse width is shorter than 50 ps).44

Syntheses. Single crystals of $A_2Ge(IO_3)_6$ (A = Li, Na, Cs) were obtained hydrothermally from a mixture of A_2CO_3 (A =

Li, Na, Cs) (0.8 mmol), GeO₂ (0.3 mmol), I₂O₅ (1.2 mmol), and H₂O (2 mL) in 23 mL Teflon-lined autoclave. Single crystals of Rb₂Ge(IO₃)₆ were prepared from a mixture of Rb₂CO₃ (0.8 mmol), GeO₂ (0.3 mmol), I_2O_5 (2.5 mmol), and H_2O (2 mL) in 23 mL Teflon-lined autoclave. Single crystals of BaGe(IO₃)₆(H₂O) were prepared from a mixture of Ba(IO₃)₂·H₂O (0.5 mmol), GeO₂ (0.3 mmol), I₂O₅ (1.2 mmol), and H₂O (2 mL) in 23 mL Teflon-lined autoclave. The autoclaves were heated to 230 °C in 6 h and held for 4 days, and then cooled to 30 °C at a rate of 3 °C/h. Colorless prismatic crystals of Li₂Ge(IO₃)₆ and Na₂Ge(IO₃)₆, and block-shaped crystals of Rb₂Ge(IO₃)₆, Cs₂Ge(IO₃)₆ and BaGe(IO₃)₆(H₂O) were collected in high yields of ca. 85% (based on Ge). Powder XRD analyses confirmed the purities of the products (Figure S1). EDS elemental analyses gave average A/Ge/I molar ratios of 2.1: 1.0: 5.9, 2.0: 1.0: 5.8, 2.0: 1.0: 5.9, respectively for Na, Rb and Cs compounds, and Ba/Ge/I molar ratio of 1.1: 1.0: 5.9 for $BaGe(IO_3)_6(H_2O)$, which are in good agreement with those determined from single crystal X-ray diffraction studies (Figure S2).

Single Crystal Structure Determination. Single-crystal X-ray diffraction data were collected on an Agilent Technologies SuperNova dual-wavelength CCD diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å) at 293 K. Data reduction was performed with the program CrysAlisPro, and absorption correction based on the multi-scan method was applied.⁴⁵ The structures were solved by direct method and refined by fullmatrix least-squares fitting on F^2 using SHELXL-97.⁴⁶ All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The H atom associated with the water molecule in $BaGe(IO_3)_6(H_2O)$ is located at geometrically calculated position and refined with isotropic thermal parameters. The structures were checked for missing symmetry elements using PLATON and none was found.⁴⁷ The Flack parameters were refined to 0.22(14), 0.03(7) and 0.43(3) for NCS $Li_2Ge(IO_3)_6$, $Na_2Ge(IO_3)_6$ and $BaGe(IO_3)_6(H_2O)$, respectively, indicating the existence of racemic twinning in Na₂Ge(IO₃)₆ and BaGe(IO₃)₆(H₂O).^{48,49} Crystallographic data and structure refinements of the five compounds are given in Table 1, and selected bond distances are listed in Table S1.

Computational Descriptions. Single-crystal structural data of Li₂Ge(IO₃)₆, Na₂Ge(IO₃)₆ and BaGe(IO₃)₆(H₂O) were used for the theoretical calculations. The electronic structures and optical properties were performed using a plane-wave basis set and pseudo-potentials within density functional theory (DFT) implemented in the total-energy code CASTEP.^{50,51} For the exchange and correlation functional, we chose Perdew-Burke-Ernzerhof (PBE) in the generalized gradient approximation (GGA).⁵² The interactions between the ionic cores and the electrons were described by the norm-conserving pseudopotential.53 The following valence-electron configurations were considered in the computation: Li-2s¹, Na-2p⁶3s¹, Ba-5s²5p⁶6s², Ge-4s²4p², I-5s²5p⁵, and O-2s²2p⁴. The numbers of plane waves included in the basis sets were determined by a cutoff energy of 750eV. Monkhorst-Pack kpoint sampling of $3 \times 3 \times 4$ and $3 \times 3 \times 2$ was used to perform numerical integration of Brillouin zone for $A_2Ge(IO_3)_6(A = Li, A)$ Na), and $BaGe(IO_3)_6(H_2O)$, respectively. Other parameters and convergent criteria were set as the default values of CASTEP code. During the optical property calculations, approximately

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Table 1. Crystallographic Data and for A₂Ge(IO₃)₆(A=Li, Na, Rb, Cs) and BaGe(IO₃)₆(H₂O).

formula	LigGe(IO2)	Na ₂ Ge(IO ₂)	RhaGe(IOa)	$C_{10}G_{2}(IO_{2})$	BaGa(IOa) (Ha	
	1125.07	11(7.07	1202.02	1207.01	1077.25	
FW	1135.87	1167.97	1292.93	1387.81	12/7.35	
crystal system	hexagonal	hexagonal	trigonal	trigonal	trigonal	
space group	<i>P</i> 6 ₃ (No. 173)	<i>P</i> 6 ₃ (No. 173)	R3 (No. 148)	<i>R</i> 3 (No. 148)	<i>R</i> 3(No. 146)	
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)	
a (Å)	9.1900(6)	9.4604(4)	11.3256(10)	11.5185(10)	11.3707(4)	
b (Å)	9.1900(6)	9.4604(4)	11.3256(10)	11.5185(10)	11.3707(4)	
<i>c</i> (Å)	5.2393(5)	5.3260(3)	11.4380(14)	11.6063(14)	11.3223(7)	
γ (°)	120.000	120.000	120.000	120.000	120.000	
$V(Å^3)$	383.21(5)	412.81(3)	1270.6(2)	1333.6(2)	1267.77(10)	
Ζ	1	1	9	9	3	
λ (Mo-Ka) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	
$Dc (g/cm^{-3})$	4.922	4.698	5.069	5.184	5.019	
	14.183	13.221	18.545		15.152	
$\mu (\text{mm}^{-1})$				16.266		
GOF on F^2	1.302	1.128	1.071	0.921	1.009	
Flack factor	0.22(14)	0.03(7)			0.43(3)	
$R_1, wR_2[I > 2\sigma(I)]$	0.0401, 0.1472	0.0296, 0.0683	0.0314, 0.0697	0.0309, 0.0779	0.0225, 0.0482	
R_1 , wR_2 (all data)	0.0403, 0.1472	0.0324, 0.0700	0.0357, 0.0741	0.0338, 0.0803	0.0230, 0.0485	
$R_1 = \Sigma \mathbf{F}_0 - \mathbf{F}_c / \Sigma$	$ \mathbf{F}_0 , wR_2 = \{\Sigma w[($	$(F_{o})^{2} - (F_{c})^{2} \frac{1}{2} \sum w [(F_{o})^{2}]^{2}$	$[2]^{2}]^{1/2}$.			
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150 ~170 and 490 empty bands were involved to ensure the convergence of linear optical properties and SHG coefficients for $A_2Ge(IO_3)_6(A = Li, Na)$, and $BaGe(IO_3)_6(H_2O)$, respectively. The other parameters and convergent criteria were the default values of CASTEP code. The calculations of second-order NLO properties were based on length-gauge formalism within the independent-particle approximation.⁵⁴ We adopted the Chen's static formula, which was derived by Rashkeev et al.⁵⁵ and later improved by Chen's group.56 The static second-order NLO susceptibility can be expressed as

 $\chi^{\alpha\beta\gamma} = \chi^{\alpha\beta\gamma}(VE) + \chi^{\alpha\beta\gamma}(VH) + \chi^{\alpha\beta\gamma}(two bands)$

where $\chi^{\alpha\beta\gamma}$ (VE) and $\chi^{\alpha\beta\gamma}$ (VH) give the contributions to $\chi^{\alpha\beta\gamma}$ from virtual-electron processes and virtual-hole processes, respectively; $\chi^{\alpha\beta\gamma}$ (two bands) is the contribution to $\chi^{\alpha\beta\gamma}$ from the two-band processes. The formulas for calculating $\gamma^{\alpha\beta\gamma}(VE)$, $\chi^{\alpha\beta\gamma}$ (VH), and $\chi^{\alpha\beta\gamma}$ (two bands) are given in Ref. 56.

RESULTS AND DISCUSSION

A series of alkali and alkaline earth metal germanium iodates, namely, $A_2Ge(IO_3)_6$ (A = Li, Na, Rb, Cs) and $BaGe(IO_3)_6(H_2O)$, have been isolated through hydrothermal reactions. It is interesting to note that, for the sythesis of RbGe(IO₃)₆, more excess amount of I₂O₅ is needed compared with those for $A_2Ge(IO_3)_6$ (A = Li, Na, Cs). Otherwise, only RbIO₃ crystals can be obtained. The structures of the five new compounds all feature a 0D [Ge(IO₃)₆]²⁻ anion composed of GeO₆ octahedron corner-sharing with six IO₃ groups, with alkali or alkali-earth cations as the spacers and keeping charge balance. Remarkably, Li₂Ge(IO₃)₆, Na₂Ge(IO₃)₆, and $BaGe(IO_3)_6(H_2O)$ crystals are phase-matchable and display very large SHG signals of about 32, 15 and 12 times that of KH₂PO₄ (KDP) under 1064 nm radiation, and they also exhibit high thermal stability and LDT values.

Structural Description.

Among these five compounds, $Li_2Ge(IO_3)_6$ and Na₂Ge(IO₃)₆ crystalize in polar space group P6₃ (No. 173) and BaGe(IO₃)₆(H₂O) in polar R3 (No. 146), whereas $Rb_2Ge(IO_3)_6$

and $Cs_2Ge(IO_3)_6$ crystalize in centrosymmetric space group $R\overline{3}$ (No. 148). It is interesting that the four stoichiometrically identical compounds display two different structure types. The structures of A2Ge(IO3)6 (A=Li, Na, Rb, Cs) and $BaGe(IO_3)_6(H_2O)$ all feature a zero-dimensional $[Ge(IO_3)_6]^{2-1}$ anion composed of a GeO_6 octahedron connecting with six IO_3 groups, with alkali or alkali-earth cations filling in the inter anionic spaces and keeping charge balance (Figures 1 and 2).

The acentric phases $A_2Ge(IO_3)_6$ (A = Li, Na) are isostructural with $A_2M(IO_3)_6$ (M = Ti, Sn) $A_2Ti(IO_3)_6$ (M = Ti, Sn).^{22, 40} Their asymmetric units contain one alkali metal, one Ge, one I, and six O atoms. The alkali metal and Ge atoms are lying on the threefold axis, while other atoms occupy the general sites. The alkali metal atom is in pseudo-octahedral coordination environment with six O atoms, with the bond distances in the ranges of 2.06(2)-2.27(7) Å for Li-O and 2.371(7)-2.335(7) Å for Na-O bond, respectively. The Ge atom is octahedrally coordinated by six oxygen atoms from six iodate groups in a unidentate fashion (Figure 1a). The Ge-O distances range from 1.995(11) to 2.033(12) Å, which is slightly longer than those reported in centrosymmetric K₂Ge(IO₃)₆.⁴¹ Comparing the Ge-O bonds in $A_2Ge(IO_3)_6$ (A = Li, Na) with M-O bonds in $A_2M(IO_3)_6$ (M = Ti, Sn), we can see that Ge-O bonds (1.995 to 2.033 Å) are slightly shorter than Ti-O (2.028 to 2.056 Å) and Sn-O bonds (2.07 to 2.14 Å) due to the smallest ionic radius of Ge^{4+} (Table S2). The I⁵⁺ atoms are coordinated by three oxygen atoms in a IO3 trigonal pyramidal geometry, which is very common in metal iodates.²³⁻²⁸ The I-O bond lengths are in the range of 1.766(11) to 1.879(6) Å. Bond valence calculations gave values of 0.94 (Li), 1.35 (Na), and 5.09-4.91 (I), respectively, revealing that alkali metal and I are in oxidation states of 1+ and 5+, respectively.^{57,58} Likewise, the centrosymmetric phases $A_2Ge(IO_3)_6$ (A = Rb, Cs) are isostructural with $A_2Ti(IO_3)_6$ (A = Rb, Cs),²² and $A_2Sn(IO_3)_6$ (A = Rb, Cs),⁴⁰ K₂Ge(IO₃)₆.⁴¹ Their asymmetric units contain one alkali metal, one Ge, one I, and six O atoms. The alkali metal cation lies on the threefold axis, Ge atom occupying sites with $\overline{3}$ symmetry, and the remaining atoms located at the general

sites. The Rb⁺ or Cs⁺ ion is ten-coordinated by ten O atom, with the bond distances in the ranges of 2.897(5)-3.056(4) Å for Rb-O and 3.038(5)-3.162(4) Å for Cs-O bond, respectively. Each Ge atom also coordinates with six oxygen atoms from six iodate



Figure 1. Views of (c) the coordination geometry around Ge^{4+} in Li₂Ge(IO₃)₆, (b) the structure of Li₂Ge(IO₃)₆ along *c*-axis, (c) he coordination geometry around Ge⁴⁺ in Rb₂Ge(IO₃), and (d) the structure of Rb₂Ge(IO₃)₆ along *c*-axis.

groups in a unidentate fashion into a GeO₆ octahedron (Figure 1c). The Ge–O distances are in the range of 1.886(4)-1.875(4) Å, which is close to the Ge-O distance (1.901 Å) in the reported K₂Ge(IO₃)₆.⁴¹ The Ge-O distances (1.886-1.875 Å) in A₂Ge(IO₃)₆ (A = Rb, Cs) are also shorter than the Ti-O distances reported in A₂Ti(IO₃)₆ (A = Rb, Cs) (1.949-1.943 Å) and Sn-O distances in A₂Sn(IO₃)₆ (A = Rb, Cs) (2.038-2.037 Å) (Table S2). The I-O bond lengths are in the range of 1.784(4) to 1.886(4) Å. Bond valence calculations gave values of 1.26 (Rb), 1.24(Cs), 4.91-5.02 (I), and 4.13-4.25 (Ge), respectively, revealing that Rb (or Cs), I and Ge are in oxidation states of 1+, 5+ and 4+.^{57, 58}

For the polar BaGe(IO₃)₆(H₂O), its asymmetric unit contains one Ba, one Ge, two I, and seven O atoms. Ba, Ge and O(1W) atoms are lying on the $\bar{3}$ axis, while the remaining atoms occupy the general sites. The Ba atom is ten-coordinated by nine iodate oxygen atoms and an aqua ligand with Ba-O bond distances in the range of 2.635(10)-3.024(5) Å (Figure 2a). The Ge atom is octahedrally coordinated by six iodate groups in a unidentate fashion (Figure 2b). The Ge–O distances fall in the range from 1.855(5) to 1.896(5) Å. The I-O bond lengths are in the range of 1.781(5) to 1.880(5) Å. Bond valence calculations gave values of 2.11, 4.98-5.01, and 4.26 for Ba, I and Ge, respectively, revealing that Ba, I and Ge are in oxidation states of 2+, 5+ and 4+.^{57,58}

Comparing the NCS phases with the CS ones, it is notable that the structures of the $[Ge(IO_3)_6]^{2+}$ units are different to some extent, deciding the polarity of the structure of the compounds. In the structure of Li₂Ge(IO₃)₆ and Na₂Ge(IO₃)₆, the six IO₃ groups in a $[Ge(IO_3)_6]^{2+}$ unit lie in a parallel manner towards *c*axis thus the lone pairs are in a perfect parallel alignment which leads to the favorable "addition" of the polarizations of the IO₃ groups. In the structure of BaGe(IO₃)₆(H₂O), the polarizations of six IO₃ groups in a $[Ge(IO_3)_6]^{2+}$ unit compensate each other along *a* and *b*-axis but constructively add along *c*-axis. Thus, macroscopic dipole moments along *c*-axis, are favorable for the formation of polar structure and SHG response. This polarity shift from polar to non-polar with the increase of the alkali metal cation size can be explained referring to the previous study.²² In order to maintain the octahedral environment around Li⁺ and Na⁺ cations in the noncentrosymmetric structure, the IO₃ groups connecting with Ge⁴⁺ have to align in a parallel fashion. For Rb⁺ and Cs⁺ cations with larger size, higher coordination environment is preferred, thus, leading to the antiparallel alignment of the IO₃ groups.

Thermal Analyses. Thermogravimetric analyses (TGA) indicate that A2Ge(IO3)6 (A=Li, Na, Rb, Cs) show good thermal stability and exhibit similar thermal behavior. Samples of A₂Ge(IO₃)₆ (A=Li, Na, Rb, Cs) display two steps of weight losses in the temperature region of 30 ~ 800 °C and are thermally stable up to 416, 410, 460, and 414°C, respectively (Figure S3). The thermal stability of $A_2Ge(IO_3)_6$ (A = Li, Na, Rb, Cs) seems at the same level with that of $A_2M(IO_3)_6$ (A = Li, Na, Rb, Cs; $M = Ti^{4+}$, Sn⁴⁺) (stable up to ~400 °C). For $Li_2Ge(IO_3)_6$, the sample quickly lost weight in the temperature region of 416 ~ 497 °C and then showed one small step of weight loss in the temperature region of 497 ~ 615 °C. Endothermic peaks were observed at 474 and 562°C in the DSC curve. For Na₂Ge(IO₃)₆, the sample showed one sharp step of weight loss in the temperature region of 410 ~ 490 °C, followed by one mild step of weight loss in the temperature region of 490 ~ 604 °C. Endothermic peaks were observed at 443 and 543°C in the DSC curve. For Rb₂Ge(IO₃)₆, the sample exhibited a large weight loss in the temperature region of 460 ~ 525 °C and then a small step of weight loss in the temperature region of 525 ~



Figure 2. Views of (a) the coordination geometry around Ba^{2+} in BaGe(IO₃)₆(H₂O) (b) he coordination geometry around Ge⁴⁺ in BaGe(IO₃)₆(H₂O), (c) he structure of BaGe(IO₃)₆(H₂O) along *c*-axis.



Figure 3. UV-vis-IR spectra of A_2 Ge(IO₃)₆ (A = Li, Na, Rb, Cs) and BaGe(IO₃)₆(H₂O).

624 °C. Endothermic peaks were observed at 499 and 607°C in the DSC curve. For Cs₂Ge(IO₃)₆, the sample quickly lost weight in the temperature region of 414 ~ 492 °C and then slowly lost one small step of weight loss in the temperature region of 492 ~ 607 °C. Endothermic peaks were observed at 483 and 602°C in the DSC curve. Sample of BaGe(IO₃)₆(H₂O) is thermally stable up to 396 °C and displays three steps of weight losses in the temperature region of 30 ~ 800 °C. After dehydration at around 396 ~ 404 °C, the sample quickly lost weight in the temperature region of 404 ~ 464 °C and then slowly lost weight in the temperature region of 464 ~ 653 °C. Endothermic peaks were observed at 397, 444 and 639°C in the DSC curve. The residuals at 500°C are amorphous and at 800°C should be Ba₅(IO₆)₂ and GeO₂ based on PXRD studies (Figure S4). The weight losses correspond to the release of H₂O, I₂ and O₂, and the experimental and calculated values are given in Figure S3.

Optical Measurements. IR spectra reveal that A_2 Ge(IO₃)₆ (A=Li, Na, Rb, Cs) and BaGe(IO₃)₆(H₂O) are transparent in the region of 2.5 – 10.8 μ m (4000 – 922 cm⁻¹), 2.5 – 10.8 μ m (4000 – 923 cm⁻¹), 2.5 – 11.7 μ m (4000 – 843 cm⁻¹), 2.5 – 12.1 μ m (4000 – 828 cm⁻¹), and 2.5 – 2.7 μ m (4000 – 3650 cm⁻¹), respectively (Figure S5). Absorption bands observed in the range of 3000 - 3650 cm⁻¹ and 1380-1650 cm⁻¹ can be attributed to O – H vibration for BaGe(IO₃)₆(H₂O). Absorption bands observed at 878 and 782 cm⁻¹, 872 and 797 cm⁻¹, 814 and 797 cm⁻¹, 818 and 801 cm⁻¹ and 881 and 765 cm⁻¹can be assigned to Ge – O vibration for A₂Ge(IO₃)₆ (A=Li, Na, Rb, Cs) and BaGe(IO₃)₆(H₂O), respectively.^{59, 60} Other bands observed at 756, 737, 688, 515 and 431 cm⁻¹, 755, 739, 688, 508 and 429 cm⁻¹, 768, 704 and 466 cm⁻¹, 777, 762 and 460 cm⁻¹, and 760, 737 and 495 cm⁻¹can be assigned to the I – O vibration.¹⁷⁻²⁰

UV-vis absorption spectra reveal absorption edges of 321, 267, 305, 300 and 304 nm for $A_2Ge(IO_3)_6$ (A = Li, Na, Rb, Cs) and BaGe(IO₃)₆(H₂O), respectively (Figure 3). Thus, $A_2Ge(IO_3)_6$ (A = Li, Na, Rb, Cs) and BaGe(IO₃)₆(H₂O) are

transparent in the region of 0.32 - 10.8, 0.26 - 10.8, 0.30 - 11.7, 0.30 - 12.1, and $0.30 - 2.7 \ \mu$ m, respectively. Optical diffuse-reflectance spectra indicate a wide band gap of 3.86, 4.60, 4.06, 4.12, and 4.06 eV for A₂Ge(IO₃)₆ (A=Li, Na, Rb, Cs) and BaGe(IO₃)₆(H₂O), respectively, confirming their wide-band-gap semiconductor nature.

SHG Measurements. As Li₂Ge(IO₃)₆, Na₂Ge(IO₃)₆ and BaGe(IO₃)₆(H₂O) crystallize in noncentrosymmetric space groups, powder SHG measurements were conducted using both KDP and KTP samples as references. In the visible and near-IR region, powder SHG measurements revealed that Li₂Ge(IO₃)₆, Na₂Ge(IO₃)₆ and BaGe(IO₃)₆(H₂O) samples are phasematchable and display very large SHG signals of about 32, 15, and 12 times that of KDP sample under 1064 nm laser radiation, respectively, and 2, 0.8 and 0.8 times that of KTP sample under 2.05 mm laser radiation (Figure 4). Their SHG responses are much higher than most of metal iodates reported, *eg.* BiO(IO₃) (12.5×KDP),²⁰ Bi(IO₃)F₂(11.5×KDP),²¹ NaVO₂(IO₃)₂(H₂O) (20×KDP),²⁴ BaNbO(IO₃)₅(14×KDP),²⁸ α-AgI₃O₈(9×KDP) and β-AgI₃O₈(8×KDP).⁶¹

It is meaningful to discuss the SHG intensity shift among the isostructural $A_2M(IO_3)_6$ (A = Li, Na; M = Ge, Ti, Sn). Taking $Li_2M(IO_3)_6$ (M = Ge, Ti, Sn) for example, with the decrease of the M⁴⁺ cation size from Sn⁴⁺ to Ge⁴⁺(Sn⁴⁺>Ti⁴⁺>Ge⁴⁺), the M-O bond distances shortened consequently, which leads to the shrink of the unit cell volume from $Li_2Sn(IO_3)_6$ to $Li_2Ge(IO_3)_6$ ($Li_2Sn(IO_3)_6 > Li_2Ti(IO_3)_6 > Li_2Ge(IO_3)_6$) (Table S2). Since the numbers of IO₃ units per unit cell are identical for $Li_2M(IO_3)_6$ (M = Ge, Ti, Sn), the density of the polar IO₃ unit increases from $Li_2Sn(IO_3)_6$ to $Li_2Ge(IO_3)_6$ ($Li_2Ge(IO_3)_6 > Li_2Ti(IO_3)_6 > Li_2Sn(IO_3)_6$). This tendency are in accordance with the SHG intensities observed ($Li_2Ge(IO_3)_6 > Li_2Ti(IO_3)_6 > Li_2Sn(IO_3)_6$). Similar phenomenon was also observed in the series of Na₂M(IO₃)₆ (M = Ge, Ti, Sn). As the M⁴⁺ cation size downgrades, the unit cell volume reduces, leading to a upgrade

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Figure 4. Oscilloscope traces of the SHG signals (150 - 210 mm) of Li₂Ge(IO₃)₆, Na₂Ge(IO₃)₆ and BaGe(IO₃)₆(H₂O) at 1064 nm (a) and 2.05 μ m (c). Plots of measured SHG intensity versus particle sizes of Li₂Ge(IO₃)₆, Na₂Ge(IO₃)₆ and BaGe(IO₃)₆(H₂O) under laser radiation at $\lambda = 1064$ nm (b) and 2.05 μ m (d). KDP and KTP samples serve as the references for $\lambda = 1064$ nm and 2.05 μ m laser radiation, respectively.

in the density of polar unit and thus enhanced SHG intensity. Likewise, when the M^{4+} cation is set, $Li_2M(IO_3)_6$ exhibits larger SHG response than $Na_2M(IO_3)_6$, which can as well be explained by the smaller cation size of Li^+ than that of Na^+ .

To estimate the direction and magnitude of the dipole moments, calculations of the dipole moments based on the geometric structure were performed on A2Ge(IO3)6 (A=Li, Na, Rb, Cs) and BaGe(IO₃)₆(H₂O) and the titanium iodates and tin iodates using the method reported earlier (Table S3). 7, 22, 62-67 For the phases crystalizing in the space group $R\overline{3}$, the MO₆ (M=Ge, Ti, Sn) octahedra are non-distortive and the polarization of the iodate groups cancel out each other due to the centrosymmetric space group, leading to a net dipole moment of 0 D for a unit cell. For the noncentrosymmetric phases, the calculated dipole moments for MO₆ (M=Ge, Ti, Sn) octahedra are very small and can be neglected. Since Li₂Ge(IO₃)₆ and Na₂Ge(IO₃)₆ crystalize in P6₃ space group and BaGe(IO₃)₆(H₂O) in R3 space group, the *a*-, and *b*-component of the polarizations from IO₃ units within one unit cell are cancelled out completely, while the c-component is positive and adds up to a net dipole moment. For $Li_2Ge(IO_3)_6$, the ccomponent of the local dipole moment of $I(1)O_3$ is calculated to be 16.92 D, which compares favorably to that of the IO₃ groups in $Li_2Ti(IO_3)_6$ (15.13 D) and $Li_2Sn(IO_3)_6$ (15.02 D). For

 $Na_2Ge(IO_3)_6$, the *c*-component of local dipole moment of I(1)O₃ is calculated to be 15.43 D, which compares well to that of the IO₃ groups in Na₂Ti(IO₃)₆ (15.05 D) and Na₂Sn(IO₃)₆ (15.28 D). Each unit cell contains six $I(1)O_3$ and the *c*-component adds up to a net dipole moment of 101.5 and 92.6 D for Li₂Ge(IO₃)₆ and Na₂Ge(IO₃)₆, respectively, significantly larger than the isomeric titanium and tin iodates with the calculated values of 90.2 - 92.6 D. For $BaGe(IO_3)_6(H_2O)$ in the polar space group of R3, the local dipole moments of $I(1)O_3$ and $I(2)O_3$ were calculated to be 1.65 and 9.94 D, respectively. Each unit cell contains 18 $I(1)O_3$ and 18 $I(2)O_3$, and the *c*-component adds up to a net dipole moment of 208.6 D. Taking into consideration the similar unit-cell volumes, the dipole moments per unit volume of Li₂Ge(IO₃)₆, Na₂Ge(IO₃)₆ and BaGe(IO₃)₆(H₂O) are 0.265, 0.224 and 0.165 $D \cdot Å^{-3}$, respectively, which is considerably larger than those of the reported polar iodates with strong SHG effect, e.g. Bi(IO₃)F₂ (0.135 D·Å⁻³)⁸ and K₂Au(IO₃)₅ (0.114 $D \cdot A^{-3}$).⁶⁸ Dipole moments calculation reveals that the proper alignment of IO₃ units leads to the strong SHG responses of the compounds. The largest SHG effect of $Li_2Ge(IO_3)_6$ can be attribute to the more polarizable IO3 units, as well as the smallest unit cell volume leading to largest density of IO₃ units. It is expected that the SHG efficiencies of Li₂Ge(IO₃)₆ and $BaGe(IO_3)_6(H_2O)$ would be even stronger without the racemic twinning problem.

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LDT Measurements. As $A_2Ge(IO_3)_6$ (A = Li, Na) and $BaGe(IO_3)_6(H_2O)$ possess large band gaps, LDT measurements were performed using AgGaS₂ as the reference. Results reveal large LDT values of 76.63, 68.77, and 81.54 MW/cm², which are about 42, 38, 39, 25 and 45 times higher than that of AgGaS₂ (1.81 MW/cm²). The LDT values of the three mixed-metal germanium iodates are at the same level with those of $A_2M(IO_3)_6(A=Li, Na; M=Ti, Sn)(Table S4)$, and are comparable to α -LiIO₃ with a large SHG response (~300× α -SiO₂) and high LDT value of 104.53 MW/cm² (54×AgGaS₂). Hence, $A_2Ge(IO_3)_6$ (A = Li, Na) and BaGe(IO₃)_6(H₂O) are a promising candidate for high-power NLO applications in the visible to IR window.



Figure 5. The SHG density for $Li_2Ge(IO_3)_6$ (a: VB, b: CB), $Na_2Ge(IO_3)_6$ (c: VB, d: CB) and $BaGe(IO_3)_6(H_2O)$ (e: VB, f: CB).

Theoretical Studies. To reveal the SHG effect origins of the title compounds, theoretical calculations have been performed employing DFT methods. The calculated results on band structures (Figure S6) indicate that due to the structural similarity, the band structures of Li₂Ge(IO₃)₆ and Na₂Ge(IO₃)₆ are very similar to each other: the bands in both VB and CB are very flat, but the bands in CB are looser than those in VB. We also find that $BaGe(IO_3)_6(H_2O)$ is an indirect band gap compound with the valence band maximum (VBM) and the conduction band minimum (CBM) at G and A points, respectively. The band structures calculations also give the band gaps of 3.176 eV, 3.312 eV and 3.047 eV for $\text{Li}_2\text{Ge}(\text{IO}_3)_6$, Na₂Ge(IO₃)₆ and BaGe(IO₃)₆(H₂O), respectively, which are smaller than the experimental values $[Li_2Ge(IO_3)_6: 3.86 \text{ eV};$ Na2Ge(IO3)6: 4.6 eV; BaGe(IO3)6(H2O): 4.06 eV]. The band gap underestimation by theoretical calculations should be attributed to the limitation of the exchange and correlation function of GGA-PBE. Hence, to accurately describe the optical properties, the scissors of 0.684 eV, 1.288 eV and 1.013 eV have been adopted to match the experimental gaps in the following analyses for Li₂Ge(IO₃)₆, Na₂Ge(IO₃)₆ and $BaGe(IO_3)_6(H_2O)$, respectively.

The partial density of states is a powerful technique to assign the band structure and understand the bonding interactions in the crystal. As shown in Figure S7, the PDOS diagrams of the three compounds behave very similar, so we take Li₂Ge(IO₃)₆ as an example to describe them in detail. We can see that the electronic states of I and Ge atoms are fully overlapped with those of O atoms in the whole energy region, showing the strong bonding interactions of I-O and Ge-O bonds in the compound. The peaks below -9.0 eV in the VB region are mainly originated from the O-2s and I-5s5p states; the VB region near Fermi level (-8.0 eV ~ 0 eV) is contributed by O-2p and I-5s5p, mixed by a little amount of Ge-4s4p and Li-2s states. In CB, the electronic states are comprised of the unoccupied I-5s5p, O-2p, Ge-4s4p and Li-2s orbitals. For Li₂Ge(IO₃)₆, the highest VB is dominated by the 2p nonbonding states of O atoms, while the lowest CB is the empty I-5p, O-2p and some Ge-4s orbitals, so the band gap of $Li_2Ge(IO_3)_6$ is determined by I, O and Ge atoms.

The SHG coefficients of three polar crystals were also calculated. The calculated largest SHG tensors d_{31} are 1.90×10^{-8} esu, 1.09×10^{-8} esu and 1.02×10^{-8} esu for Li₂Ge(IO₃)₆, Na₂Ge(IO₃)₆ and BaGe(IO₃)₆(H₂O), respectively, which are somewhat smaller than the corresponding measured values (32, 15 and 12 times that of KDP for Li₂Ge(IO₃)₆, Na₂Ge(IO₃)₆ and BaGe(IO₃)₆(H₂O), respectively).

Li₂Ge(IO₃)₆ and Na₂Ge(IO₃)₆ are isostructural and have the same anionic groups, but what causes such a difference in SHG responses between them? Naturally, we examined whether the band gap effect controls the SHG difference. As described above, the experimental band gaps of Li₂Ge(IO₃)₆ and Na₂Ge(IO₃)₆ are 3.86 and 4.6 eV, respectively. If Li₂Ge(IO₃)₆ had a gap of 4.6 eV, the calculated *d*₃₁ would be sharply decreased from 1.897 × 10⁻⁸ to 1.235 × 10⁻⁸ esu; and if Na₂Ge(IO₃)₆ had a gap of 3.86 eV, the calculated *d*₃₁ would be largely increased from 1.090 × 10⁻⁸ to 1.633 × 10⁻⁸ esu; obviously, the re-evaluated SHG coefficients are very close to those of the other compounds. Therefore, we can believe that

the large SHG difference between $Li_2Ge(IO_3)_6$ and $Na_2Ge(IO_3)_6$ is mainly caused by their difference in band gaps.

To investigate the origin of such strong SHG effects, it is desirable to show clearly which energy levels of electronic states contribute to the SHG effect, so we perform the spectral decomposition of the largest tensor d_{31} for Li₂Ge(IO₃)₆, Na₂Ge(IO₃)₆ and BaGe(IO₃)₆(H₂O), as plotted in the bottommost panels of Figure S7. For the isostructural $Li_2Ge(IO_3)_6$ and $Na_2Ge(IO_3)_6$, the most contributed regions are just in the upper part of VB (-5.0 ~0 eV) and the bottommost CB (< 7.5 eV), the corresponding electronic states are mainly the O-2p and I-5p states in VB and the unoccupied I-5p, Ge-4s and O-2p states in CB. While for BaGe(IO₃)₆(H₂O), the SHGcontributed energy region is from -3.0 eV to 7.0 eV, which also corresponds to O-2p, I-5p and Ge-4s states. Furthermore, SHG density analyses have been performed to accurately and intuitively show which orbitals give contributions to SHG for these compounds. As indicated in Figure 5, for the three compounds, the main contributions in VB comes from the O-2p nonbonding states, especially the terminal O atoms, while the SHG contributions in CB are mainly at the unoccupied O-2p and I-5p states.

Integral of SHG density over VB and CB shows that the strong SHG responses of Li₂Ge(IO₃)₆, Na₂Ge(IO₃)₆ and BaGe(IO₃)₆(H₂O) originate from IO₃ groups dominantly, and the calculated contribution percentages of Li⁺/Na⁺/Ba²⁺, GeO₆ and IO₃ groups are <0.01%, 8.68% and 91.25% for Li₂Ge(IO₃)₆, 0.14%, 8.10% and 91.67% Na₂Ge(IO₃)₆, and 0.83%, 7.59% and 90.59% for BaGe(IO₃)₆(H₂O). The results imply that in the three compounds, except for IO₃ groups, GeO₆ groups play an insignificant part in SHG process, while the alkali metal and alkali-earth metal cations give tiny contributions that are negligible.

CONCLUSIONS

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In summary, by introducing GeO₆ octahedra into metal iodates, five new mixed-metal iodates in the A/Ae-Ge⁴⁺-IO₃ system, namely, A₂Ge(IO₃)₆(A = Li, Na, Rb, Cs) and BaGe(IO₃)₆(H₂O), have been obtained. The NCS A₂Ge(IO₃)₆(A = Li, Na) exhibit large SHG responses and LDT values, wide transmittance window, and high thermal stabilities, which make them promising new NLO crystals in visible and IR spectral regions. BaGe(IO₃)₆(H₂O) cystals are potential NLO material in the visible window. Results of our work indicate that introducing non-SOJT-distortive MO₆ octahedra can also be a facile strategy to design NCS mixed-metal iodates with large SHG effect and potential application.

ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic files in CIF format, check reports, simulated and experimental XRD patterns, TGA and DSC curves, IR and UV spectra, crystallographic data and structure refinements, selected bond distances, calculated state energy of the L-CB and H-VB, calculated band structure, DOS and PDOS. This material is available free of charge via the Internet at http://pubs.acs.org.

Accession Codes

CCDC 1819449–1819453 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, or by

emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest

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REFERENCES

1. Chen, C.; Liu, G. Recent Advances in Nonlinear Optical and Electrooptical Materials. Annu. Rev. Mater. Res. 1986, 16, 203-243.

2. Becker, P. Borate Materials in Nonlinear Optics. Adv. Mater. 1998, 10, 979-992.

3. Ok, K. M.; Chi, E. O.; Halasyamani, P. S. Bulk Characterization Methods for Non-Centrosymmetric Materials: Second-Harmonic Generation, Piezoelectricity, Pyroelectricity and Ferroelectricity. *Chem. Soc. Rev.* **2006**, *35*, 710-717.

4. Halasyamani, P. S.; Poeppelmeier, K. R. Noncentrosymmetric Oxides. *Chem. Mater.* **1998**, *10*, 2753-2769.

5. Yao, W.; He, R.; Wang, X.; Lin, Z.; Chen, C. Analysis of Deep-UV Nonlinear Optical Borates: Approaching the End. *Adv. Opt. Mater.* **2014**, *2*, 411-417.

6. Rondinelli, J. M.; Kioupakis, E. Predicting and Designing Optical Properties of Inorganic Materials. *Annu. Rev. Mater. Res.* **2014**, *45*, 491-518.

7. Ok, K. M. Toward the Rational Design of Novel Noncentrosymmetric Materials: Factors Influencing the Framework Structures. *Acc. Chem. Res.* **2016**, *49*, 2774-2785.

8. Kang, L.; Zhou, M.; Yao, J.; Lin, Z.; Wu, Y.; Chen, C. Metal Thiophosphates with Good Mid-infrared Nonlinear Optical Performances: A First-Principles Prediction and Analysis. *J. Am. Chem. Soc.* **2015**, *137*, 13049-13059.

9. Li, C.; Yin, W. L.; Gong, P. F.; Li, X. S.; Zhou, M. L.; Mar, A.; Lin, Z. S.; Yao, J. Y.; Wu, Y. C.; Chen, C. T. Trigonal Planar $[HgSe_3]^{4^-}$ Unit: A New Kind of Basic Functional Group in IR Nonlinear Optical Materials with Large Susceptibility and Physicochemical Stability. *J. Am. Chem. Soc.* **2016**, *47*, 6135-6138.

10. Zhou, M. L.; Yang, Y.; Guo, Y. W.; Lin, Z. S.; Yao, J. Y.; Wu, Y. C.; Chen, C. T. Hg-Based Infrared Nonlinear Optical Material KHg₄Ga₅Se₁₂ Exhibits Good Phase-Matchability and Exceptional Second Harmonic Generation Response. *Chem. Mater.* **2017**, *29*, 7993-8002.

11. Zhang, M.; Su, X.; Mutailipu, M.; Yang, Z. H.; Pan, S. L. $Bi_3OF_3(IO_3)_4$: Metal Oxyiodate Fluoride Featuring a Carbon-Nanotube-like Topological Structure with Large Second Harmonic Generation Response. *Chem. Mater.* **2017**, *29*, 945-949.

12. Zhang, M.; Hu, C.; Abudouwufu, T.; Yang, Z. H.; Pan, S. L. Functional Materials Design via Structural Regulation Originated from Ions Introduction: A Study Case in Cesium Iodate System. *Chem. Mater.* **2018**, *30*, 1136-1145.

13. Wickleder, M. S. Inorganic Lanthanide Compounds with Complex Anions. *Chem. Rev.* **2002**, *102*, 2011-2088.

14. Sun, C. F.; Yang, B. P.; Mao, J. G. Structures and Properties of Functional Metal Iodates. *Sci China* **2011**, *54*, 911-922.

15. Kong, F.; Sun, C. F.; Yang, B. P.; Mao, J. G. Second-Order Nonlinear Optical Materials Based on Metal Iodates, Selenites, and Tellurites. *J. G. Struct. Bonding* **2012**, *144*, 43-103.

16. Hu, C. L.; Mao, J. G. Recent Advances on Second-order NLO Materials based on Metal Iodates. *Coordin. Chem. Rev.* **2015**, 288, 1-17.

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60

17. Jerphagnon, J. Optical Nonlinear Susceptibilities of Lithium Iodate. *Appl. Phys. Lett.* **1970**, *16*, 298-299.

18. Otaguro, W. S.; Wiener - Avnear, E.; Porto, S. P. S. Determination of the Second Harmonic Generation Coeffecient and the Linear Electrooptic Coeffecient in LiIO₃ through Oblique Raman Phonon Measurements. *Appl. Phys. Lett.* **1971**, *18*, 499-501.

19. Phanon, D.; Gautier-Luneau, I. Promising Material for Infrared Nonlinear Optics: NaI_3O_8 Salt Containing an Octaoxotriiodate(V) Anion Formed from Condensation of $[IO_3]$ ⁻ Ions. *Angew. Chem. Int. Ed.* **2007**, *46*, 8488-8491.

20. Nguyen, S. D.; Yeon, J.; Kim, S. H.; Halasyamani, P. S. BiO(IO₃): A New Polar Iodate that Exhibits an Aurivillius-type (Bi₂O₂)²⁺ Layer and a Large SHG Response. *J. Am. Chem. Soc.* **2011**, *133*, 12422-12425.

21. Mao, F. F.; Hu, C. L.; Xu, X.; Yan, D.; Yang, B. P.; Mao, J. G. Bi(IO₃)F₂: The First Metal Iodate Fluoride with a Very Strong Second Harmonic Generation Effect. *Angew. Chem., Int, Ed*, **2017**, *56*, 2151-2155.

22. Chang, H. Y.; Kim, S. H.; Ok, K. M.; Halasyamana, P. S. Polar or Nonpolar? A⁺ Cation Polarity Control in A_2 Ti(IO₃)₆(A = Li, Na, K, Rb, Cs, Tl). *J. Am. Chem. Soc.* **2009**, *131*, 6865-6873.

23. Chang, H. Y.; Kim, S. H.; Halasyamani, P. S.; Ok, K. M. Alignment of Lone Pairs in a New Polar Material: Synthesis, Characterization, and Functional Properties of Li₂Ti(IO₃)₆. *J. Am. Chem. Soc.* **2009**, *131*, 2426-2427.

24. Yang, B. P.; Hu, C. L.; Xu, X.; Sun, C. F.; Zhang, J. H.; Mao, J. G. NaVO₂(IO₃)₂(H₂O): A Unique Layered Material Produces a Very Strong SHG Response. *Chem. Mater.* **2010**, *22*, 1545-1550.

25. Sykora, R. E.; Ok, K. M.; Halasyamani, P. S.; Well, D. M.; Albrecht-Schmitt, T. E. New One-Dimensional Vanadyl Iodates: Hydrothermal Preparation, Structures, and NLO Properties of A[VO₂(IO₃)₂] (A = K, Rb) and A[(VO)₂(IO₃)₃O₂] (A = NH₄, Rb, Cs). *Chem. Mater.* **2002**, *14*, 2741-2749.

26. Sun, C. F.; Hu, C. L.; Xu, X.; Yang, B. P.; Mao, J. G. Explorations of New Second-order Nonlinear Optical Materials in the Potassium Vanadyl Iodate System. *J. Am. Chem. Soc.* **2011**, *133*, 5561-5572.

27. Yang, B. P.; Hu, C. L.; Xu, X.; Huang, C.; Mao, J. G. Zn₂(VO₄)(IO₃): A Novel Polar Zinc(II) Vanadium(V) Iodate with a Large SHG Response. *Inorg. Chem.* **2013**, *52*, 5378-5384.

 Sun, C. F.; Hu, C. L.; Xu, X.; Ling, J. B.; Hu, T.; Kong, F.; Long, X.
 F.; Mao, J. G. BaNbO(IO₃)₅: A New Polar Material with A Very Large SHG Response. *J. Am. Chem. Soc.* **2009**, *131*, 9486-9487.

Sykora, R. E.; Ok, K. M.; Halasyamani, P. S.; Albrecht-Schmitt, T. E. Structural Modulation of Molybdenyl Iodate Architectures by Alkali Metal Cations in AMoO₃(IO₃)(A=K, Rb, Cs): A Facile Route to New Polar Materials with Large SHG Responses. *J. Am. Chem. Soc.* 2002, *124*, 1951-1957.

30. Chen, X. A.; Zhang, L.; Chang, X. A.; Xue, H. P.; Zang, H. G.; Xiao, W. Q.; Song, X. M.; Yan, H. LiMoO₃(IO₃): A new molybdenyl iodate based on WO₃-type sheets with large SHG response. *J. Alloys Compd.* **2007**, *428*, 54-58.

31. Chen, X. A.; Chang, X. A.; Zang, H. G.; Wang, Q.; Xiao, W. Q. Hydrothermal Synthesis and Structural Characterization of a Novel NLO Compound, La(MoO₂)(OH)(IO₃)₄. *J. Alloys Compd.* **2005**, *36*, 255-259.

32. Suffren, Y.; Gautier-Luneau, I. Titanyl Iodate - A Promising Material for Infrared Nonlinear Optics Showing Structural Similarities with KTP. *Eur. J, Inorg. Chem.* **2012**, *2012*, 4264-4267.

33.Yang, B. P.; Xu, X.; Huang, C.; Mao, J. G. $K_4TM_4(V_2O_{7/2}(IO_3)_4(H_2O))$ (TM = Zn, Ni, Co): A Series of Quinary Mixed Metal–vanadium(v)–iodates. *CrystEngComm* **2013**, *15*, 10464-10469.

34. Eaton, T.; Lin, J.; Cross, J. N.; Stritzinger, J. T.; Albrecht-Schmitt, T.
E. Th(VO₃)₂(SeO₃) and Ln(VO₃)₂(IO₃) (Ln = Ce, Pr, Nd, Sm, and Eu): Unusual Cases of Aliovalent Substitution. *Chem. Commun.* 2014, *50*, 3668-3670.

35. Sun, C. F.; Hu, T.; Xu, X.; Mao, J. G. Syntheses, Crystal Structures, and Properties of Three New Lanthanum(III) Vanadium Iodates. *Dalton Trans* **2010**, *39*, 7960-7967.

36. Sykora, R. E.; Wells, D. M.; Albrecht-Schmitt, T. E. New Molybdenyl Iodates: Hydrothermal Preparation and Structures of Molecular $K_2MoO_2(IO_3)_4$ and Two-Dimensional β -KMoO₃(IO₃). *J. Solid. State. Chem.* **2002**, *166*, 442-448.

37. Shehee, T. C.; Sykora, R. E.; Ok, K. M.; Halasyamani, P. S.; Albrecht-Schmitt, T. E. Hydrothermal Preparation, Structures, and NLO Properties of the Rare Earth Molybdenyl Iodates, RE(MoO₂)(IO₃)₄(OH) [RE=Nd, Sm, Eu]. *Inorg. Chem.* **2003**, *42*, 457-462.

38. Sykora, R. E.; Wells, D. M.; Albrecht-Schmitt, T. E. Further Evidence for the Tetraoxoiodate (V) Anion, IO_4^{3-} : Hydrothermal Syntheses and Structures of Ba[$(MoO_2)_6(IO_4)_2O_4$]·H₂O and Ba₃[$(MoO_2)_2(IO_6)_2$]·2H₂O. *Inorg. Chem.* **2002**, *41*, 2697-2703.

39. (a) Sun, C. F.; Hu, C. L.; Kong, F.; Yang, B. P.; Mao, J. G. Syntheses and Crystal Structures of Four NewSilver(I) Iodates with d⁰-transition Metal Cations. *Dalton Trans* **2010**, *39*, 1473-1479.(b) Ok, K. M.; Halasyamani, P. S. New d⁰ Transition Metal Iodates: Synthesis, Structure, and Characterization of BaTi(IO₃)₆, LaTiO(IO₃)₅, Ba₂VO₂(IO₃)₄· (IO₃), K₂MoO₂ (IO₃)₄, and BaMoO₂ (IO₃)₄· H₂O. *Inorg. Chem.* **2005**, *44*, 2263-2271.

40. Kim, Y. H.; Tran, T. T.; Halasyamani, P. S.; Ok, K. M. Macroscopic Polarity Control with Alkali Metal Cation Size and Coordination Environment in a Series of Tin Iodates. *Inorg. Chem. Front.* **2015**, *2*, 361-368.

41. Schellhaas, F.; Hartl, H.; Frydrych, R. Die Kristallstruktur von Kaliumhexajodatogermanat(IV). *Acta Crystallogr. B* **1972**, *28*, 2834-2838.

42. Kubelka, P.; Munk, F. An Article on Optics of Paint Layers. Z. Tech. Physical **1931**, *12*, 886-892.

43. Kutz, S. K.; Perry, T. T. A Powder Technique for the Evaluation of Nonlinear Optical Materials. *J. Appl. Phys.* **1968**, *39*, 3798-3813.

44. Zhang, M. J.; Li, B. X.; Liu, B. W.; Fan, Y. H.; Li, X. G.; Zeng, H. Y.; Guo, G. C. Ln_3GaS_6 (Ln = Dy, Y): New Infrared Nonlinear Optical Materials with High Laser Induced Damage Thresholds. *Dalton Trans* **2013**, *42*, 14223-14229.

45. Blessing, R. H. An Empirical Correction for Absorption Anisotropy. *Acta Crystallogr. Sect. A* **1995**, *51*, 33-38.

46. Sheldrick, G. M. SHELXTL, Version 5.1, Crystallographic Software Package; Bruker-AXS: Madison, WI. **1998**.

47. Spek, A. L. Single-crystal Structure Validation with the Program PLATON. J. Appl. Crystallogr 2003, 36, 7-13.

48.Flack, H. D. On Enantiomorph-polarity Estimation. Acta Crystallogr. Sect. A 1983, 39, 876-881.

49. Flack, H. D.; Bernardinelli, G. The Use of X-ray Crystallography to Determine Absolute Configuration. *Chirality* **2008**, *20*, 681-690.

50. Milman, V.; Winkler, B.; White, J. A.; Pickard, C. J.; Payne, M. C.; Akhmatskaya, E. V.; Nobes, R. H. Electronic Structure, Properties, and Phase Stability of Inorganic Crystals: A Pseudopotential Plane-wave Study. *Int. J. Quantum Chem.* **2000**, *77*, 895-910.

51. Lindan, P. J. D. First-Principles Simulation: Ideas, Illustrations and the CASTEP Code. J. Phys.: Condens. Matter 2002, 14, 2717-2744.

52. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.

53. Lin, J. S.; Qteish, A.; Payne, M. C.; Heine, V. V. Optimized and Transferable Nonlocal Separable *ab Initio* Pseudopotentials. *Phys. Rev. B* **1993**, *47*, 4174-4180.

54. Aversa, C.; Sipe, J. E. Nonlinear Optical susceptibilities of Semiconductors: Results with a Length-gauge Analysis. *Phys. Rev. B* **1995**, *52*, 14636-14645.

55. Rashkeev, S. N. Efficient ab initio Method for the Calculation of Frequency-dependent Second-order Optical Response in Semiconductors. *Phys. Rev. B* **1998**, *57*, 3905-3919.

56. Lin, J.; Lee, M. H.; Liu, Z. P.; Chen, C. T.; Pickard, C. J. Mechanism of the Linear and Nonlinear Optical Effects in β -BaB₂O₄ Crystal. *Phys. Rev. B* **1999**, *60*, 13380-13389.

57. Brese, N. E.; O'Keeffe, M. Bond-valence Parameters for Solids. *Acta Crystallogr. Sect. B* **1991**, *47*, 192-197.

58. Brown, I. D.; Altermatt, D. Acta Crystallographica. Acta Crystallogr. Sect. B 1985, 41, 244-247.

59. Paques-Ledent, M. T. Vibrational Studies of Olivine-type Compounds—III. Orthosilicates and Germanates A¹B¹¹¹X^{1V}O₄. *Spectrochimica Acta Part A Molecular Spectroscopy* **1976**, *32*, 383-395.

60. Xu, X.; Hu, C. L.; Kong, F.; Zhang, J. H.; Mao, J. G.; Sun, J. Cs2GeB4O9: a New Second-Order Nonlinear-Optical Crystal. *Inorg. Chem.* **2013**, *52*, 5831-5837.

61. Xu, X.; Hu, C. L.; Li, B. X.; Yang, B. P.; Mao, J. G. α-AgI₃O₈ and β-AgI₃O₈ with Large SHG Responses: Polymerization of IO₃ Groups into the I₃O₈ Polyiodate Anion. *Chem. Mater.* **2014**, *26*, 3219-3230.

62. Sun, C. F.; Hu, C. L.; Mao, J. G. PbPt(IO₃)₆(H₂O): A New Polar Material with two Types of Stereoactive Lone-pairs and a Very Large SHG Response. *Chem Commun (Camb)* **2012**, *48*, 4220-4222.

63. Sun, C. F.; Hu, C. L.; Xu, X.; Mao, J. G. Polar or Non-polar? Syntheses, Crystal Structures, and Optical Properties of Three New Palladium(II) Iodates. *Inorg Chem* **2010**, *49*, 9581-9589.

64. Maggard, P. A.; Nault, T. S.; Stern, C. L.; Poeppelmeier, K. R. Alignment of Acentric $MoO_3F_3^{3-}$ Anions in a Polar Material: $(Ag_3MoO_3F_3)(Ag_3MoO_4)Cl.$ J. Solid. State. Chem. **2003**, 175, 27-33.

65. Izumi, H. K.; Kirsch, J. E.; Charlotte, L. S.; Poeppelmeier, K. R. Examining the Out-of-Center Distortion in the [NbOF₅]² Anion. *Inorg. Chem.* **2005**, *44*, 884-895.

66. Sivakumar, T.; Hong, Y. C.; Baek, J. w.; Halasyamani, P. S. Two New Noncentrosymmetric Polar Oxides: Synthesis, Characterization, Second-Harmonic Generating, and Pyroelectric Measurements on TISeVO₅ and TITeVO₅. *Chem. Mater.* **2007**, *38*, 4710-4715.

67. Hong, Y. C.; Kim, S. H.; Ok, K. M.; Halasyamani, P. S. New Polar Oxides: Synthesis, Characterization, Calculations, and Structure–Property Relationships in $RbSe_2V_3O_{12}$ and $TlSe_2V_3O_{12}$. *Chem. Mater.* **2009**, *21*, 1654-1662.

68. Xu, X.; Hu, C. L.; Li, B. X.; Mao, J. G. K₂Au(IO₃)₅ and β -KAu(IO₃)₄: Polar Materials with Strong SHG Responses Originating from Synergistic Effect of AuO₄ and IO₃ Units. *Chem. Eur.J* **2016**, *22*, 1750–1759.

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