Syntheses, characterization and calculations of $\text{Li}_m\text{A}_n\text{M}_6\text{O}_{15}$ (A=Rb, Cs; M=Si, Ge; $m+n=6$)

Jingjing Xu, Hongping Wu, Hongwei Yu*, Zhanggui Hu, Jiyang Wang and Yicheng Wu

ABSTRACT Alike phosphates, silicates and germanates exclusively containing tetrahedral basic building units (BBUs) can also exhibit ultraviolet (UV) even deep-UV transitions. They are important for the design of new UV or deep-UV nonlinear optical (NLO) materials. In this paper, four new alkali metal silicates and germanates, $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$, $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$, $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ were successfully synthesized by a high temperature solid state reaction. They obey the general formula of $\text{Li}_m\text{A}_n\text{M}_6\text{O}_{15}$ (A=Rb, Cs; M=Si, Ge; $m+n=6$) and all exhibit the $\text{Sr}_2\text{Be}_2\text{B}_2\text{O}_7$ (SBBO)-like structures. More importantly, $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ crystallize in the noncentrosymmetric (NCS) structures and exhibit remarkable phase-matched second harmonic generation (SHG) effect, $0.8\times\text{KH}_2\text{PO}_4$ (KDP) and $1\times\text{KDP}$, respectively. These indicate that they are potential as UV or deep-UV NLO materials. Furthermore, their optical and NLO properties as well as thermal properties were measured. The structure-property relationships were studied by the dipole moment calculations and the first-principles calculations.

Keywords: NLO material, silicate, germanate, UV region, SHG effect, structure-property relationship

INTRODUCTION

Nonlinear optical (NLO) materials capable of efficiently expanding the wavelengths of solid-state laser from the deep ultraviolet (deep-UV) (< 200 nm) to the infrared (IR) region (~ 20 μm) play a crucial role in modern laser science and technology [1–10]. It is well-known that the NLO materials can be divided into deep-UV, UV and IR NLO materials according to the transmittance range [10–15]. Up to now, in UV and deep-UV region, the research interests are dominantly focused on borates, which results in the discoveries of a number of high-performance NLO crystals, such as commercialized $\beta\text{-BaB}_2\text{O}_4$ ($\beta\text{-BBO}$) [16], LiB_3O_5 (LBO) [17], CsB_3O_5 (CBO) [18], $\text{KBe}_2\text{BO}_3\text{F}_2$

(KBBF) [19], and some recently reported beryllium borates, e.g., NaBeB_3O_6 [20], $\text{Na}_2\text{CsBe}_6\text{B}_5\text{O}_{15}$ [21], $\text{LiNa}_5\text{Be}_{12}\text{B}_{12}\text{O}_{33}$ [22], and halogen-containing borates, e.g., $\text{M}_2\text{B}_{10}\text{O}_{14}\text{F}_6$ (M=Ca, Sr) [23], $\text{NH}_4\text{Be}_2\text{BO}_3\text{F}_2$ [24], $\text{CsB}_4\text{O}_6\text{F}$ [25], $\text{Ba}_3\text{B}_6\text{O}_{11}\text{F}_2$ [26]. Among them, the KBBF and $\text{Sr}_2\text{Be}_2\text{B}_2\text{O}_7$ (SBBO) [27] family of compounds have been widely considered as the most promising deep-UV NLO materials.

Beyond borates, the materials with tetrahedral basic building units (BBUs), i.e., phosphates, silicates and germanates can also be seen as the potential candidates for the design of new UV or deep-UV NLO materials because the tetrahedral BBUs are beneficial to the short UV cut-off edges. However, a main problem hindering the practical application of the materials with tetrahedral BBUs is their small second harmonic generation (SHG) responses. According to the anion group theory [28], the microscopic SHG effect generated by the rigid PO_4 , SiO_4 and GeO_4 groups are one order smaller than the planar B–O groups. Therefore, enhancing SHG responses of these materials is crucial for their possible applications as NLO materials. Recently, considerable research interests have been focused on the phosphates, and a series of new strategies have been put forward to enhance the SHG response of phosphates, for example, condensing P–O groups that may help to increase the distortion of PO_4 tetrahedra, which has led to a series of deep-UV polyphosphate NLO crystals with excellent properties, e.g., $\text{Ba}_5\text{P}_6\text{O}_{20}$ ($0.8\times\text{KH}_2\text{PO}_4$ (KDP)) [29], $\text{RbBa}_2(\text{PO}_3)_5$ ($1.4\times\text{KDP}$) [30], $\text{RbNaMgP}_2\text{O}_7$ ($1.5\times\text{KDP}$) [31], $\text{K}_4\text{Mg}_4(\text{P}_2\text{O}_7)_3$ ($1.3\times\text{KDP}$) and $\text{Rb}_4\text{Mg}_4(\text{P}_2\text{O}_7)_3$ ($1.4\times\text{KDP}$) [32]. In addition, the SHG effects were also further increased from polyphosphate to orthophosphate, such as LiCs_2PO_4 ($2.6\times\text{KDP}$) [33]. However remarkably, the silicates and germanates with the similar structure features with phosphates are still rarely reported as the viable NLO

Tianjin Key Laboratory of Functional Crystal Materials, Institute of Functional Crystal, Tianjin University of Technology, Tianjin 300384, China

* Corresponding author (email: hwuy15@gmail.com)

crystals except $\text{Li}_3\text{AlSiO}_5$ [34], $\text{Rb}_2\text{ZnSi}_3\text{O}_8$ [35], $\text{M}_2\text{TiO-Si}_2\text{O}_7$ ($\text{M}=\text{Ba}, \text{Sr}$) [36,37], $\text{Li}_2\text{A}_4\text{TiOM}_4\text{O}_{12}$ ($\text{A}=\text{K}, \text{Rb}, \text{M}=\text{Si}, \text{Ge}$) [38–40], $\text{Ae}_2\text{MGe}_2\text{O}_7$ ($\text{Ae}=\text{Ba}, \text{Sr}; \text{M}=\text{Zn}, \text{Mg}$) [41,42], PbTeGeO_6 [43], $\text{Cs}_2\text{Bi}_2\text{O}(\text{Ge}_2\text{O}_7)$ [44] owing to their weak SHG responses.

We are interested in exploring new silicates and germanates as new NLO materials, because silicates have the most abundant constitute in the earth's crust, and $\alpha\text{-SiO}_2$ is also the first NLO crystal observed by the frequency doubling effect. In our previous research, by combining the $d^0 \text{Ti}^{4+}$ with germanate groups, we have successfully synthesized a new NLO material, $\text{Li}_2\text{K}_4\text{TiOGe}_4\text{O}_{12}$ with excellent NLO properties, including the transmission range covering 0.28 to 5.8 μm , a moderate phase-matched SHG response ($2\times\text{KDP}$), high laser damage threshold (LDT) (910 MW cm^{-2} , $40\times\text{AgGaS}_2$), small anisotropic thermal expansion and desirable specific heat and thermal conductivity [40]. But for this material, owing to the d-d electron transition, it cannot be UV-transparent. In this paper, we expect to synthesize some UV-transparent silicate and germanate NLO crystals, so we exclusively used the alkaline cations because the alkaline cations have no d-d or f-f electron transitions and are favorable for the wide UV transparent regions. Our study has resulted in the discoveries of four new mixed alkali metal silicates and germanates, including two centrosymmetric (CS) isomorphous $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$ and $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$, and two non-centrosymmetric (NCS) isomorphous $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$. Obviously, the above four materials obey the general formula of $\text{Li}_m\text{A}_n\text{M}_6\text{O}_{15}$ ($\text{A}=\text{Rb}, \text{Cs}; \text{M}=\text{Si}, \text{Ge}; m+n=6$), but crystallize in completely different space groups. It indicates that the cation substitution in the same group has a great effect on the crystal structures in these materials. More interestingly, for the NCS $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$, they can exhibit remarkable SHG effects, $0.8\times\text{KDP}$ and $1\times\text{KDP}$, respectively, and both of them are phase-matchable. In addition, some other interesting structural features are also observed in the CS $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$ and $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$, e.g., (i) the Li^+ cations are coordinated in planar LiO_3 triangles, which are rather rare for Li^+ cations. They are generally coordinated in LiO_4 tetrahedra or LiO_6 octahedra. (ii) $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$ and $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$ display the SBBO-like structures with the BeO_4 tetrahedra substituted by the SiO_4 tetrahedra and the BO_3 triangle substituted by the LiO_3 triangle, which will be helpful to develop the SBBO-like silicates. Herein, we will systematically report their syntheses, structures, and the effect of cation substitution on the structures as well as their NLO properties and the origin of the remarkable SHG responses.

EXPERIMENTAL SECTION

Reagents

Li_2CO_3 (Tianjin Fuchen Chemical Reagents Factory, 97%), Rb_2CO_3 (Aladdin Chemical Co. Ltd, 99%), Cs_2CO_3 (Tianjin Hengshan Chemical, 99.9%), SiO_2 (Aladdin Chemical Co. Ltd., 99%), GeO_2 (Tianjin Hengshan Chemical, 99.9%) were used as received.

Syntheses

Polycrystalline samples of the title compounds were synthesized by a conventional solid-state method. Stoichiometric reagents: Li_2CO_3 (0.247 g, 0.003 mol), Rb_2CO_3 (1.546 g, 0.007 mol), SiO_2 (1.207 g, 0.020 mol) for $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$; Li_2CO_3 (0.204 g, 0.003 mol), Cs_2CO_3 (1.800 g, 0.006 mol), SiO_2 (0.996 g, 0.017 mol) for $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$; Li_2CO_3 (0.306 g, 0.004 mol), Rb_2CO_3 (0.958 g, 0.004 mol), GeO_2 (1.736 g, 0.017 mol) for $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$; Li_2CO_3 (0.271 g, 0.004 mol), Cs_2CO_3 (1.195 g, 0.004 mol), GeO_2 (1.535 g, 0.0147 mol) for $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$, which were thoroughly ground and preheated at 300°C for 10 h. The temperature was raised to 850°C for $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$ and $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$, 700°C for $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$, and held for 3 days with several intermittent grindings to get their single phases. The purity was confirmed by powder X-ray diffraction (XRD) patterns. There are some extra small peaks in $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$, which may come from the decomposition and volatilization of the samples (Fig. S1).

Single crystals of the title compounds were grown by spontaneous crystallization through the high temperature solution method. Polycrystalline samples of the title compounds were thoroughly ground and packed into platinum crucibles, and gradually heated to 1100°C for $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$ and $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$, 1000°C for $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ and held for 5 h to ensure the mixtures completely melted, then cooled to 500°C at a rate of 5°C h^{-1} , subsequently cooled to room temperature by switching off the furnace. Thus, colorless small crystals of the title compounds were obtained.

Powder XRD

Powder XRD patterns were carried out using the SmartLab9KW X-ray diffractometer at room temperature ($\text{Cu K}\alpha$ radiation) ($\lambda=1.5418 \text{ \AA}$). Data were collected in the 2θ range of $10^\circ\text{--}70^\circ$ with a step size of 0.01° and a step time of 2 s.

Single-crystal XRD

The crystal data of the title compounds were collected on

the Bruker SMART APEX II 4K CCD diffractometer with Mo K α radiation ($\lambda=0.71073$ Å) at 293(2) K, and the data were integrated with SAINT program [45]. The structures were solved by using the SHELXTL system through the direct method [46]. Crystal parameters and structure refinements are given in Table 1. Other structural data including the refined atomic positions, the equivalent isotropic displacement parameters, and the selected bond distances (Å) and angles (°) are given in Tables S1 and S2.

Thermal stability

Thermal gravimetric (TG) analysis and differential scanning calorimetry (DSC) of the title compounds were carried out on a STA4495 TG/DTA analyzer (NETZSCH Instruments). The samples were enclosed in platinum crucibles and heated to 1300°C for Li₂Rb₄Si₆O₁₅ and Li₂Cs₄Si₆O₁₅, 900°C for Li₃Rb₃Ge₆O₁₅, 880°C for Li₃Cs₃Ge₆O₁₅ with heating and cooling rates of 5°C min⁻¹ under an atmosphere of flowing nitrogen.

UV-vis-NIR diffuse reflectance spectroscopy

The ultraviolet vis near-infrared (UV-vis-NIR) diffuse reflectance spectra of the title compounds were measured under nitrogen atmosphere at room temperature with a Hitachi UV-vis-NIR spectrophotometer equipped with an integrating sphere over the spectral range of 190–2600 nm. Teflon was used as the reference material.

IR spectroscopy

The IR spectra of the title compounds were recorded on a

Nicolet iS50 FT-IR spectrometer in the range of 400–4000 cm⁻¹.

Powder SHG measurement

The SHG responses were measured at room temperature according to the method proposed by Kurtz and Perry [47] with a diode-pumped Nd:YAG laser operating at an optical wavelength of 1064 nm. For the reason that the SHG efficiency depends strongly on particle size, the samples were graded into the following several different particle size ranges: 25–53, 54–75, 76–106, 107–120, 121–150, 151–180 and 181–212 μm. The KDP samples with the same particle size ranges serve as the references.

Calculation method

The electronic structures of the title compounds were calculated by the plane wave pseudopotential method based on density function theory (DFT) with CASTEP program [48]. Norm-conserving pseudopotential (NCP) was chosen to characterize the core-electron interactions. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) function was chosen to describe the exchange-correlation effects [49–51]. The following electrons were treated as valence states: Li 1s²2s¹, Rb 4s²4p⁶5s¹, Cs 5s²5p⁶6s¹, Si 3s²3p², Ge 4s²4p² and O 2s²2p⁴. In addition, the plane-wave cutoff energy was set at 830 eV. Monkhorst-pack *k*-points used in sampling were 2×2×1 for Li₂Rb₄Si₆O₁₅ and Li₂Cs₄Si₆O₁₅, and 1×2×3 for Li₃Rb₃Ge₆O₁₅ and Li₃Cs₃Ge₆O₁₅.

Table 1 Crystallographic data and structure refinements for Li_mA_nM₆O₁₅ (A=Rb, Cs; M=Si, Ge; *m*+*n*=6)

Empirical formula	Li ₃ Rb ₃ Ge ₆ O ₁₅	Li ₃ Cs ₃ Ge ₆ O ₁₅	Li ₂ Rb ₄ Si ₆ O ₁₅	Li ₂ Cs ₄ Si ₆ O ₁₅
Formula weight	317.59	365.03	764.32	954.06
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Pca</i> 2 ₁	<i>Pca</i> 2 ₁	<i>C</i> 2/ <i>m</i>	<i>C</i> 2/ <i>m</i>
Unit cell (Å)	<i>a</i> =17.021(2)	<i>a</i> =17.1747(15)	<i>a</i> =18.556(3)	<i>a</i> =19.0824(10)
	<i>b</i> =6.2304(8)	<i>b</i> =6.3710(6)	<i>b</i> =8.3879(13)	<i>b</i> =8.4878(4)
	<i>c</i> =5.0747(7)	<i>c</i> =5.1198(4)	<i>c</i> =10.6839(16)	<i>c</i> =11.0070(5)
	β =90°	β =90°	β =90°	β =90°
Z, Volume (Å ³)	4, 538.14(12)	4, 560.21(8)	4, 1662.9(5)	4, 1782.77(15)
Density (g cm ⁻³)	3.920	4.328	3.053	3.555
Absorption coefficient (mm ⁻¹)	20.087	17.068	12.208	8.587
Goodness-of-fit on <i>F</i> ²	1.226	1.275	1.158	1.344
Final <i>R</i> indices [<i>F</i> _o ² >2s(<i>F</i> _o ²)] ^a	<i>R</i> ₁ =0.0496, <i>wR</i> ₂ =0.1441	<i>R</i> ₁ =0.0340, <i>wR</i> ₂ =0.1078	<i>R</i> ₁ =0.0780, <i>wR</i> ₂ =0.1933	<i>R</i> ₁ =0.0213, <i>wR</i> ₂ =0.0717
<i>R</i> indices (all data)	<i>R</i> ₁ =0.0643, <i>wR</i> ₂ =0.2018	<i>R</i> ₁ =0.0406, <i>wR</i> ₂ =0.1317	<i>R</i> ₁ =0.0934, <i>wR</i> ₂ =0.2039	<i>R</i> ₁ =0.0255, <i>wR</i> ₂ =0.0827

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

RESULTS AND DISCUSSION

Structures of $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$ and $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$

The crystal structures of $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$ and $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$ were determined by single crystal XRD, which indicates $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$ and $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$ are isomorphic and crystallize in the space group $C2/m$, thus we only depict the structure of $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$. Its asymmetric unit is composed of 17 crystallographically independent atoms: one Li, four Cs, three Si and nine O atoms (Table S1). It is clear that $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$ exhibits a SBBO-like structure. The fundamental building units (FBUs) are planar LiO_3 triangles and SiO_4 tetrahedra. Firstly, the SiO_4 tetrahedra and LiO_3 triangles connect with each other to form a $[\text{LiSi}_3\text{O}_9]_\infty$ layer similar with the $[\text{BeBO}_4]_\infty$ layer in SBBO. However, different from SBBO where the $[\text{BeBO}_4]_\infty$ layers are connected to form $[\text{Be}_2\text{B}_2\text{O}_7]_\infty$ double layers, these $[\text{LiSi}_3\text{O}_9]_\infty$ layers in $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$ are further connected *via* sharing O atoms to form the three-dimensional (3D) $[\text{Li}_2\text{Si}_6\text{O}_{15}]$ framework and the Cs^+ cations are filled in the space to balance the residual charges (Fig. 1a and b). In connectivity terms, the structure of $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$ can also be written as $\{2[\text{LiO}_{3/2}]^{2-} 6[\text{SiO}_{4/2}]\}^{4-}$ with the charge balanced by four Cs^+ cations. In addition, the Li^+ cations in $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$ are coordinated in planar LiO_3 triangles with the sum of three O–Li–O bond angles to be 360°

(Fig. S2). The LiO_3 triangle coordination is rather rare for Li^+ cations, which are generally coordinated in LiO_4 tetrahedra or LiO_6 octahedra. Owing to the low coordination numbers, the Li–O bond distances in $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$ are also shorter than other Li–O bonds. They range from 1.835(8) to 1.852(8) Å. For SiO_4 tetrahedra, the Si–O bond lengths in Si–O–Si linkage range from 1.620(3) to 1.6463(17) Å, the Si–O bond lengths for Si–O–Li linkage range from 1.560(3) to 1.563(3) Å, and the Cs–O bond lengths range from 3.141(4) to 3.757(3) Å (Table S2). The bond valence sum (BVS) analyses for each atom result in values of 1.08 for Li^+ , 0.81–1.03 for Cs^+ , 4.11–4.14 for Si^{4+} and 1.86–2.25 for O^{2-} (Table S1). They are all consistent with expected oxidation states.

Structures of $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$

$\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ are also isomorphic, so only the crystal structure of $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ is described in detail as a representation. The single crystal XRD shows it crystallizes in orthorhombic NCS and polar space group $Pca2_1$. The asymmetric unit contains one Li, one Cs, two Ge and five O atoms (Table S1). The FBUs are LiO_4 and GeO_4 tetrahedra. Clearly, the $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ also exhibits the SBBO-like structure. Firstly, the GeO_4 tetrahedra connect with each other by corner-sharing forming the $[\text{Ge}_6\text{O}_{15}]_\infty$ layers. These $[\text{Ge}_6\text{O}_{15}]_\infty$ layers stack along the *b*

Figure 1 (a) The $[\text{BeBO}_4]_\infty$ layer in SBBO and the 3D crystal structure for SBBO with the bonds of Sr–O being removed; (b) the $[\text{LiSi}_3\text{O}_9]_\infty$ layer in $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$ and the 3D crystal structure for $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$ with the bonds of Cs–O being removed; (c) the $[\text{Ge}_6\text{O}_{15}]_\infty$ layer in $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ and the 3D crystal structure for $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ with the bonds of Cs–O being removed.

axis and are connected with LiO_4 tetrahedra to form the 3D $[\text{Li}_3\text{Ge}_6\text{O}_{15}]$ framework with the Cs^+ cations residing in the cavities to balance the residual charges (Fig. 1c). In connectivity terms, the structure of $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ can be written as $\{3[\text{LiO}_{3/3}\text{O}_{1/2}]^{2-} 3\{[\text{GeO}_{3/3}\text{O}_{1/2}]^{1+} [\text{GeO}_{4/2}]\}^{1+}\}^{3-}$ with three Cs^+ cations to balance the residual charges. The Li–O bond lengths are 1.92(2)–2.12(3) Å, the Ge–O bond lengths are 1.687(9)–1.823(11) Å, and the Cs–O bond lengths are 2.968(13)–3.562(11) Å (Table S2). The BVS analyses for each atom in $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ result in values of 0.97 for Li^+ , 1.12 for Cs^+ , 3.94–3.97 for Ge^{4+} and 1.81–2.12 for O^{2-} (Table S1). Those are consistent with expected oxidation states.

As discussed above, $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$, $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$, $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ obey the general formula of $\text{Li}_m\text{A}_n\text{M}_6\text{O}_{15}$ ($\text{A}=\text{Rb}, \text{Cs}$; $\text{M}=\text{Si}, \text{Ge}$; $m+n=6$) and all exhibit SBBO-like structures, i.e., the FBUs firstly form a framework with the cavities in the structure which are further filled by the alkaline-earth or alkaline cations. Remarkably, from SBBO to $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$, the FBUs are becoming larger, e.g., the BeO_4 and BO_3 for SBBO, SiO_4 and LiO_3 for $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$, and GeO_4 and LiO_4 for $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$. That makes the cavities of their frameworks for cations are also becoming larger from SBBO to $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$. Therefore, for SBBO, the small Sr^{2+} cations are big enough to fill the relative small cavities, whereas for

$\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$, the larger Cs^+ cations are necessary owing to their larger cavities. Especially for $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$, the cavities formed by the GeO_4 and LiO_4 tetrahedra are so large that the $[\text{Li}_3\text{Ge}_6\text{O}_{15}]$ framework is pulled to generate a large distortion even when large size Cs^+ or Rb^+ cations are filled in it. The large distortion also results in the generation of a microscopic polarity in $[\text{Li}_3\text{Ge}_6\text{O}_{15}]$ framework, which leads to the polar structures of $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$.

Thermal stability

The thermal behaviors of the title compounds were studied by the TG/DSC measurements (Fig. 2). Clearly, all of these materials have good thermal stability. There is only one endothermic peak on their respective heating DSC curves. For $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$, $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$, there is one exothermic peak observed on their respective cooling DSC curves as well. While for $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$, owing to the higher melt viscosity, there is no exothermic peak on its cooling DSC curve. The above results all suggest that the title materials melt congruently. The melting behaviors are also further confirmed through comparing the powder XRD patterns of their recrystallized samples with the ones of pure phases (Fig. S1).

Optical properties

The UV-vis-NIR diffuse reflectance spectra of the title

Figure 2 The TG/DSC curves for (a) $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$, (b) $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$, (c) $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$, (d) $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$. All data indicate that the title compounds melt congruently.

compounds in the region of 190–2600 nm are shown in Fig. S3. Obviously, $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ own relatively short UV absorption edges (~ 220 nm). For $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$ and $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$, they should have exhibited the shorter UV cut-off edges than $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$. But owing to the special fluorescence effect, the diffuse reflectance spectra are upward drift in deep-UV region (< 300 nm). Notably, there are no obvious absorption in these regions. Therefore, these indicate $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$ and $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$ will exhibit deep-UV cut-off edges (< 190 nm).

In addition, the IR spectra of the title compounds are shown in Fig. S4. The peaks at $957\text{--}632\text{ cm}^{-1}$ can be attributed to the symmetric stretching vibrations of SiO_4 groups. The peaks at 468 and 436 cm^{-1} can be assigned to the symmetric bending vibrations of SiO_4 groups. The peaks at $832\text{--}757\text{ cm}^{-1}$ can be attributed to the symmetric stretching vibrations of GeO_4 groups, and the peaks at 470 , 452 and 440 cm^{-1} can be assigned to the symmetric bending vibrations of GeO_4 groups. The assignments are consistent with those previously reported [52–54].

Powder SHG measurements

Furthermore, as $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ crystal-

lize in the NCS and polar structures, the powder SHG responses were measured based on the Kurtz and Perry method [47] with a diode-pumped Nd:YAG laser operating at an optical wavelength of 1064 nm. Clearly, $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ can exhibit remarkable SHG effects, $0.8\times\text{KDP}$ and $1\times\text{KDP}$, respectively, and both of them are phase-matchable (Fig. 3). The SHG responses of $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ are also comparable to those of the SHG-enhanced phosphates, e.g., $\text{Ba}_3\text{P}_3\text{O}_{10}\text{Cl}$ ($0.6\times\text{KDP}$) and $\text{Ba}_3\text{P}_3\text{O}_{10}\text{Br}$ ($0.5\times\text{KDP}$) [55], $\text{RbBa}_2(\text{PO}_3)_5$ ($1.4\times\text{KDP}$) [30], $\text{K}_4\text{Mg}_4(\text{P}_2\text{O}_7)_3$ ($1.3\times\text{KDP}$) and $\text{Rb}_4\text{Mg}_4(\text{P}_2\text{O}_7)_3$ ($1.4\times\text{KDP}$) [32], and LiCs_2PO_4 ($2.6\times\text{KDP}$) [33].

In order to better understand the origin of the SHG responses of $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$, we quantified the contributions of LiO_4 and GeO_4 groups for SHG response based on the dipole moment calculation. In $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$, the dipole moments from the LiO_4 units and GeO_4 units are 1.24 and 1.32 Debye (D), respectively. And both of them are directed along the polar c axis. Those show the polarization of $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ mainly originates from the interaction of LiO_4 and GeO_4 groups. In $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$, the similar results have been obtained, the dipole moments for LiO_4 units and GeO_4 units are

Figure 3 Phase-matching curves for KDP, $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ at 1064 nm, the solid curves are a guide for the eyes and not a fit to the data (a). The SHG signals for KDP, $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ in the same particle sizes (b), $0.8\times\text{KDP}$ for $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $1\times\text{KDP}$ for $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$.

2.99 and 1.04 D, respectively, and both of them are also directed along the polar c axis. Those indicate the remarkable SHG responses of $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ will mainly arise from the synergistic effect of the LiO_4 and GeO_4 groups (Table 2).

Electronic structure calculations

To further investigate the relationship between electronic structures and optical properties of the title compounds, DFT method was chosen to complete the relative calculations as shown in Fig. 4. For $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$ and $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$, the valence band (VB) maximum and the conduction band (CB) minimum are located at the G point, thus they are direct band gap compounds with the band gaps of 4.33 and 4.47 eV, respectively. Similarly, for $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$, the VB maximum and the CB minimum are located at the Y point and they

exhibit the similar band structures with direct band gaps of 3.20 and 3.23 eV, respectively.

The total and partial densities of states (DOS) can be observed in Fig. 5. For $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$ and $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$, the top of VBs ranging from -10 to 0 eV are mainly composed of the O 2p, Rb 4p, Si 3p states and O 2p, Cs 5p, Si 3p states. The CBs from 0 to 10.0 eV are derived from the Rb 4p, Si 3p states and Cs 5p, Si 3p states. For $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$, the top of VBs extend in a wide range from -10 to 0 eV. It is worth noting that strong hybridizations occur among the O 2p, Rb 4p, Ge 4s4p states and O 2p, Cs 5p, Ge 4s4p states, while the bottom of CBs are mostly composed of the hybridizations of Rb 4p, Ge 4s4p states and Cs 5p, Ge 4s4p states. Accordingly, these indicate that the observed absorptions on their diffuse reflectance spectra of all the title compounds mainly originate from the O 2p, Si 3p and Ge 4p states.

Table 2 Direction and magnitude of dipole moments in LiO_4 tetrahedra and GeO_4 tetrahedra in the unit cell

Species		a -axis (D)	b -axis (D)	c -axis (D)	Total (D)
$\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$	LiO_4	0	0	−1.24	1.24
	GeO_4	0	0	−1.32	1.32
	Unit cell	0	0	−2.56	2.56
$\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$	LiO_4	−0.38	0.04	2.96	2.99
	GeO_4	0	0	1.04	1.04
	Unit cell	−0.38	0.04	4.01	4.02

Figure 4 Calculated band gaps for (a) $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$, (b) $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$, (c) $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$, (d) $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$. They are all direct band gap compounds with the band gaps of 4.33, 4.47, 3.20 and 3.23 eV, respectively.

Figure 5 The densities of states for (a) $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$, (b) $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$, (c) $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$, (d) $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$. These indicate that the observed absorptions on their diffuse reflectance spectra mainly originate from the O 2p and Si 3p and Ge 4p states.

In addition, the SHG coefficients of $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ were also calculated. They exhibit $mm2$ point symmetry and thus have three independent non-vanishing second-order NLO susceptibility tensor d_{31} , d_{32} , and d_{33} under the restriction of Kleinman symmetry. The calculated values: $d_{31} = -0.60 \text{ pm V}^{-1}$, $d_{32} = 0.59 \text{ pm V}^{-1}$, $d_{33} = 1.08 \text{ pm V}^{-1}$ for $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$, $d_{31} = 0.85 \text{ pm V}^{-1}$, $d_{32} = -0.58 \text{ pm V}^{-1}$, $d_{33} = -0.83 \text{ pm V}^{-1}$ for $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$. Among them, the SHG coefficients of $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ are approximately $1.5 \times \text{KDP}$ and $2.2 \times \text{KDP}$ ($d_{36}^{\text{KDP}} = 0.39 \text{ pm V}^{-1}$) [56], respectively, which are consistent with the experimental SHG intensities.

CONCLUSION

Four new alkali metal silicates and germanates, including two CS $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$ and $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$, and two NCS $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ were successfully synthesized by a high temperature solid state reaction. Structurally, they obey the general formula of $\text{Li}_m\text{A}_n\text{M}_6\text{O}_{15}$ ($\text{A} = \text{Rb}, \text{Cs}$; $\text{M} = \text{Si}, \text{Ge}$; $m+n=6$) and exhibit SBBO-like structures. And it is very interesting that the Li^+ cations in $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$ and $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$ are coordinated in the LiO_3 triangles. They are very rare for the coordination of Li^+ cations. The physical property measurements indicate that all of these materials melt congruently and they

possess wide UV even deep-UV transparent windows. The absorption edges for $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ are $\sim 220 \text{ nm}$ and the absorption edges for $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$ and $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$ are less than 190 nm . More importantly, the NCS $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ and $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ can exhibit the remarkable phase-matchable SHG effects, $0.8 \times \text{KDP}$ and $1 \times \text{KDP}$, respectively. These indicate the alkaline silicates and germanates are potential as UV or deep-UV NLO materials. Furthermore, our discovery demonstrates that the silicates and germanates with tetrahedral BBUs can indeed be used to design UV or deep-UV NLO materials. How to further improve their overall performances as UV or deep-UV NLO materials will be the direction in our follow-up study.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information The supporting data are available in the online version of the paper. Accession Codes: CCDC 1983008, 1983009, 1983010 and 1983011 contains 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: +441223 336033.

Jingjing Xu received her BSc degree in applied physics from Tianjin University of Commerce in 2018. She is currently a master student in Professor Hongwei Yu's research group at Tianjin University of Technology. Her research focuses on the syntheses, crystal growth, and evaluation of new optical electronic functional materials.

Hongwei Yu received his PhD degree in material physics and chemistry from the University of Chinese Academy of Sciences. He did post-doctoral research at Houston University and Northwestern University in USA from 2014 to 2017. From 2018, he has been working as a full professor at Tianjin University of Technology. His current research interests include the design, syntheses, crystal growth, and evaluation of new optical electronic functional materials.

$\text{Li}_m\text{A}_n\text{M}_6\text{O}_{15}$ ($\text{A}=\text{Rb}, \text{Cs}$; $\text{M}=\text{Si}, \text{Ge}$; $m+n=6$)的合成、表征以及计算

徐晶晶, 吴红萍, 俞洪伟*, 胡章贵, 王继扬, 吴以成

摘要 与磷酸盐类似, 含四面体基本结构单元的硅酸盐和锆酸盐也能表现出紫外甚至深紫外的透过, 因此, 它们对新型紫外或深紫外非线性光学材料的研究具有十分重要的意义. 本文采用高温固相法成功合成了4种新型碱金属硅酸盐和锆酸盐, 即 $\text{Li}_2\text{Rb}_4\text{Si}_6\text{O}_{15}$, $\text{Li}_2\text{Cs}_4\text{Si}_6\text{O}_{15}$, $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ 和 $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$. 它们具有相同的结构通式 $\text{Li}_m\text{A}_n\text{M}_6\text{O}_{15}$ ($\text{A}=\text{Rb}, \text{Cs}$; $\text{M}=\text{Si}, \text{Ge}$; $m+n=6$), 且都表现出 $\text{Sr}_2\text{Be}_2\text{B}_2\text{O}_7$ (SBBO)类型的结构. 更重要的是, $\text{Li}_3\text{Rb}_3\text{Ge}_6\text{O}_{15}$ 和 $\text{Li}_3\text{Cs}_3\text{Ge}_6\text{O}_{15}$ 结晶于非中心对称(NCS)空间群, 表现出相对较大的二次谐波(SHG)效应(分别为 $0.8\times\text{KDP}$ 和 $1\times\text{KDP}$), 并且可以实现相位匹配. 这表明它们是潜在的紫外/深紫外非线性光学晶体材料. 此外, 我们也研究了它们的光学性能、非线性光学性质以及热学性质. 通过偶极矩和第一性原理计算, 我们还详细分析了它们的结构-性能关系.