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## PAPER



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# $BaCu_2M^{IV}Q_4$ ( $M^{IV} = Si$ , Ge, and Sn; Q = S, Se): synthesis, crystal structures, optical performances and theoretical calculations<sup>+</sup>

Leyan Nian,<sup>ab</sup> Junben Huang,<sup>b</sup> Kui Wu,<sup>\*b</sup> Zhi Su,<sup>\*a</sup> Zhihua Yang<sup>b</sup> and Shilie Pan<sup>\*ab</sup>

Five non-centrosymmetric (NCS) guaternary metal chalcogenides, BaCu<sub>2</sub>SiSe<sub>4</sub>, BaCu<sub>2</sub>GeS<sub>4</sub>, Ba BaCu<sub>2</sub>SnS<sub>4</sub>, and BaCu<sub>2</sub>SnSe<sub>4</sub>, were successfully synthesized by solid-state reaction in vacuum-sealed silica tubes. They crystallized in the three different space groups: Ama2 for BaCu<sub>2</sub>SnSe<sub>4</sub>, P3<sub>1</sub>21 for BaCu<sub>2</sub>GeS<sub>4</sub> and BaCu<sub>2</sub>GeSe<sub>4</sub>, and P3<sub>2</sub>21 for BaCu<sub>2</sub>SiSe<sub>4</sub> and BaCu<sub>2</sub>SnS<sub>4</sub>. Note that BaCu<sub>2</sub>GeS<sub>4</sub> and BaCu<sub>2</sub>GeSe<sub>4</sub> show the mirror symmetrical structures to those of BaCu<sub>2</sub>SiSe<sub>4</sub> and BaCu<sub>2</sub>SnS<sub>4</sub>. In comparison with their structures, it can be found that the [CuSe<sub>4</sub>] units are connected together to form a two-dimensional (2D) layer structure in BaCu<sub>2</sub>SnSe<sub>4</sub>, which is different from the 3D framework structure formed by the interlinked [CuQ<sub>4</sub>] (Q = S and Se) units in other four title compounds. In addition, BaCu<sub>2</sub>SnSe<sub>4</sub> exhibits only one type of tunnel structure with the isolated [BaSe<sub>8</sub>] units existing in each tunnel, which is also different from the other title compounds (two types of tunnels with the isolated [BaSe<sub>8</sub>] units and [BaSe<sub>6</sub>]<sub>n</sub> chains located). The interesting structural changes also indicate that slight change of cation size would result in different structure features, and future structure prediction should devote considerable attention to the different chalcogen atoms. Moreover, important optical properties (optical bandgap, infrared (IR) absorption edge, second harmonic generation (SHG) response) of the title compounds were systematically investigated. Among them, IR and Raman spectra indicate that all of them exhibit the wide IR absorption edges ( $\sim 22 \,\mu$ m). Powder SHG measurement shows that BaCu<sub>2</sub>SnS<sub>4</sub> possesses good SHG response about 1.6 times that of benchmark AgGaS<sub>2</sub> (AGS) at the particle size 55-88 µm. All results indicate that BaCu<sub>2</sub>SnS<sub>4</sub> can be expected as a potential IR nonlinear optical (NLO) candidate. Theoretical calculation was also used to analyze the structure-property relationship and their electronic structures and origin of NLO effect were studied in detail.

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## Introduction

Frequency-conversion technology on nonlinear optical (NLO) materials was invented to extend the laser wavelength ranges and has been further developed for decades.<sup>1-4</sup> Recently, a series of excellent nonlinear optical (NLO) materials have been

discovered and have basically satisfied the demand for the ultraviolet (UV < 400 nm) region.<sup>5-14</sup> However, commercially available IR NLO materials are limited in the IR region because of their inherent performance defects.15-19 Exploration of new IR NLO materials with outstanding performances is still a challenge to be resolved. During the last few decades, metal chalcogenides have become the preferred investigation system owing to their structural diversities and fascinating physicochemical properties.<sup>20-33</sup> Most of them contain the tetrahedral units, which have been verified as the "active units" to produce the main contribution for the NLO effect. Note that group 14 elements, such as Si, Ge, and Sn, are generally linked with chalcogens to form the distorted [M<sup>IV</sup>Q<sub>4</sub>] tetrahedra.<sup>34-41</sup> Up to now, a number of new metal chalcogenides with the  $[M^{IV}Q_4]$ tetrahedra and attractive NLO performances have been discovered, such as β-K<sub>2</sub>Hg<sub>3</sub>Ge<sub>2</sub>S<sub>8</sub>,<sup>36</sup> Li<sub>2</sub>CdGeS<sub>4</sub>,<sup>42</sup> Na<sub>2</sub>BaSnS<sub>4</sub>,<sup>43</sup> Na<sub>2</sub>-Hg<sub>3</sub>Ge<sub>2</sub>S<sub>8</sub>.<sup>44</sup> The investigation results also indicate that the coordination environments of the cations play a critical role in determining the structures of group 14 elements-containing compounds. Alkaline-earth metals (such as Ba), as high

<sup>&</sup>lt;sup>a</sup>College of Chemistry and Chemical Engineering, Xinjiang Normal University, Urumqi, Xinjiang 830054, China

<sup>&</sup>lt;sup>b</sup>Key Laboratory of Functional Materials and Devices for Special Environments of CAS, Xinjiang Key Laboratory of Electronic Information Materials and Devices, Xinjiang Technical Institute of Physics & Chemistry of CAS, 40-1 South Beijing Road, Urumqi 830011, China. E-mail: slpan@ms.xjb.ac.cn

<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: CIF file; checkcif; atomic coordinates, isotropic displacement parameters; selected bond lengths and angles; powder XRD patterns and IR spectra; particle size *versus* SHG intensity for BaCu<sub>2</sub>SnS<sub>4</sub> and AgGaS<sub>2</sub>; absorption spectra of title compounds; calculated electronic structures; projected density of states; calculated SHG density. CCDC 1540053, 1540054, 1540055, 1540056 and 1540057 for BaCu<sub>2</sub>SiSe<sub>4</sub>, BaCu<sub>2</sub>GeSe<sub>4</sub>, BaCu<sub>2</sub>SnS<sub>4</sub> and BaCu<sub>2</sub>SnSe<sub>4</sub>, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7ra05022d

#### Paper

electropositive elements, have the variable coordination environments with large cation size, so it can affect the structural features and optical properties. In addition, combination of distorted M<sup>IV</sup>Q<sub>4</sub> tetrahedral units and heavy metals into crystal structures may stand a chance to increase the odds of forming acentric structures. Guided by the above-mentioned ideas, we focused our research on the quaternary  $Ba/Cu/M^{IV}/Q$  ( $M^{IV} = Si$ , Ge, and Sn; Q = S, Se) systems and successfully synthesized five metal chalcogenides, including BaCu2SiSe4, BaCu2GeS4, BaCu2GeSe4, BaCu2SnS4 and BaCu2SnSe4. Among them, although the crystal structures of latter four compounds have been previously reported,45-48 their interesting structural changes and application potential as the IR NLO candidates have not been systematically investigated. Herein, we have studied the structural features and transformation of title compounds and their optical performances (such as optical bandgap, infrared (IR) absorption edge, second harmonic generation (SHG) response) have been reported for the first time. Moreover, theoretical calculation was also used to analyze the structure-property relationship and the origin of NLO effect for title compounds.

## Experimental

#### **Reagents and synthesis**

All the raw reagents with high purity (4 N) were commercially purchased by Shanghai Aladdin Biochemistry Technology Co., Ltd and used without any further purification. Since the Ba metal is easily oxidized in the air, an Ar-filled glove box was used to avoid the effects of oxygen and moisture in the preparation processes. Conventional high temperature solid-state method was used to synthesize the title compounds.

#### BaCu<sub>2</sub>GeS<sub>4</sub> and BaCu<sub>2</sub>SnS<sub>4</sub>

The crystals of BaCu<sub>2</sub>GeS<sub>4</sub> and BaCu<sub>2</sub>SnS<sub>4</sub> were synthesized by ratio of the reactants BaS, Cu, Ge/Sn and S in the ratio 1:2:1:3.5. First, the reaction mixture was loaded into the silica tubes (length 20 cm, diameter 10 mm) and sealed with a mixture of methane and oxygen flame under a high vacuum of  $10^{-3}$  Pa. Second, the furnace was programmed by the following steps: heated from room temperature to 600 °C in 30 h and kept at this temperature for 40 h; then, heated to 1050 °C in 20 h and left at this temperature for 100 h; finally, cooled to 400 °C at a rate of 5 °C h<sup>-1</sup> and then the furnace was shut down to room temperature. Third, the obtained products of title compounds were washed with *N*,*N*-dimethylformamide (DMF) to remove the unreacted sulfur and other byproducts. Finally, yellow crystals of BaCu<sub>2</sub>GeS<sub>4</sub> and red crystals of BaCu<sub>2</sub>SnS<sub>4</sub> were obtained after drying in air. They are stable in air for several months.

#### BaCu<sub>2</sub>SiSe<sub>4</sub>, BaCu<sub>2</sub>GeSe<sub>4</sub>, and BaCu<sub>2</sub>SnSe<sub>4</sub>

A stoichiometric mixture of Ba, Cu, M (M = Si, Ge and Sn), and Se in the molar ratio of 1:2:1:4 was loaded into the silica tubes. The increasing temperature-rise program of the three selenides were similar to that of the above two sulfides. The reaction temperature was set to be 1000 °C, which is different from that for sulfides. After the reaction, the products were also washed by DMF, and many red crystals of  $BaCu_2SiSe_4$ ,  $BaCu_2-GeSe_4$ , and  $BaCu_2SnSe_4$  were gained that can be stable in air for several months.

#### Structure determination

High-quality single crystals were selected by an optical microscope and mounted on glass fibers with epoxy, and then the crystal data was collected on a Bruker SMART APEX II 4K CCD diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 296 K. Lorentz and polarization factors were used to collect the date. and the absorption corrections were completed with multi-scan method.49 All structure determinations were based on direct method and refined through the full-matrix least-squares on  $F^2$ by SHELXTL crystallographic program package.<sup>50</sup> The final structures were checked with PLATON program,49 and no other higher symmetries elements were found. Crystallographic data and refinements of the title compounds were summarized in Table 1. The isotropic displacement parameters and atomic coordinates, as well as the results of the bond valence sum (BVS) calculations are given in Table S1 in the ESI.<sup>†</sup> The bond angles and selected bond distances are shown in Table S2 in the ESI.†

#### Powder X-ray diffraction

All the compounds were ground to micro-crystals for the powder XRD measurement. The PXRD data were collected on a Bruker D2 X-ray diffractometer equipped with a diffracted beam monochromator set for Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å) at room temperature. The  $2\theta$  range was 10–70° with a step size of 0.02° and a fixed counting time of 1 s per step. Seen from Fig. S1 in the ESI,† it can be found that no obvious byproducts was observed and the experimental powder XRD patterns of title compounds are in agreement with the calculated ones derived from the single-crystal data.

#### UV-vis-near IR diffuse-reflectance and IR spectroscopy

The diffuse-reflectance spectra of title compounds were collected by a Shimadzu SolidSpec-3700DUV spectrophotometer in the wavelength range of 190–2600 nm at room temperature. Then the reflectance spectra were converted to absorption spectra with the Kubelka–Munk function.<sup>51</sup> In addition, IR spectra were also measured with a Shimadzu IR Affinity-1 Fourier transform infrared spectrometer in wavenumber range from 450 to 4000 cm<sup>-1</sup> using picked single-crystals mixed with KBr pellets.

#### Raman spectroscopy

The Raman spectra of the crushed crystals of title compounds were collected on a LABRAM HR Evolution spectrometer equipped with a CCD detector using 532 nm radiation from a diode laser. For each sample, crystals were simply placed on a small glass slide and a  $50 \times$  objective lens was used to choose the area of the crystal specimens to be measured. The grating was set to be 600 gr per mm. The maximum power of 60 mW

Table 1 Crystal data and structure refinement for title compounds

Empirical formula	BaCu <sub>2</sub> GeS <sub>4</sub>	BaCu <sub>2</sub> GeSe <sub>4</sub>	BaCu <sub>2</sub> SiSe <sub>4</sub>	BaCu <sub>2</sub> SnS <sub>4</sub>	BaCu <sub>2</sub> SnSe <sub>4</sub>
fw	465.25	652.85	608.35	511.35	698.95
Crystal system	Trigonal	Trigonal	Trigonal	Trigonal	Orthorhombic
Space group	P3121	P3121	P3221	P3221	Ama2
<i>a</i> (Å)	6.2092(8)	6.5014(6)	6.4188(19)	6.353(3)	11.101(10)
<i>b</i> (Å)	6.2092(8)	6.5014(6)	6.4188(19)	6.353(3)	11.189(10)
<i>c</i> (Å)	15.520(4)	16.266(3)	16.083(10)	15.788(14)	6.728(6)
$Z, V(Å^3)$	3, 518.20(19)	3, 595.42(16)	3, 573.9(5)	3, 551.8(6)	4,835.7(13)
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	4.473	5.462	5.281	4.616	5.555
$\mu (\mathrm{mm}^{-1})$	17.089	32.160	29.673	15.358	29.945
GOF on $F^2$	1.031	1.054	0.920	0.876	1.018
$R_1$ , w $R_2 (I > 2\sigma(I))^a$	0.0185, 0.0366	0.0281, 0.0659	0.0264, 0.0437	0.0258, 0.0569	0.0251, 0.0527
$R_1$ , w $R_2$ (all data) <sup><i>a</i></sup>	0.0214, 0.0373	0.0287, 0.0663	0.0310, 0.0449	0.0317, 0.0594	0.0265, 0.0532
Absolute structure parameter	0.05(3)	0.09(4)	0.07(4)	-0.04(5)	0.06(3)
Largest diff. peak and hole (e $Å^{-3}$ )	1.306, -1.117	1.135, -1.207	0.846, -0.809	0.831, -0.945	1.041, -1.691
$^{a}R_{1} = F_{o} - F_{c}/F_{o}$ and $wR_{2} = [w(F_{o}^{2} - F_{c}^{2})^{2}/wF_{o}^{4}]^{1/2}$ for $F_{o}^{2} > 2\sigma(F_{o}^{2})$ .					

and beam diameter of 35 µm were used. The spectrum was collected using an integration time of 5 s.

#### Second-harmonic generation measurement

By the Kurtz and Perry method,<sup>52</sup> powder SHG responses of title compounds were investigated by a O-switch Ho:Tm:Cr:YAG laser (2.09 µm, 3 Hz, 50 ns). Polycrystalline samples of the title compounds were ground and sieved into distinct size ranges (0-38, 38-55, 55-88, 88-105, 105-155, 155-200, and 200-250 µm). Then, the samples were pressed between two glass slides in 1 mm thick and secured by a 1 mm thick silicone insole with an 8 mm diameter hole. In the end, they were placed into a lighttight box and irradiated by a pulsed infrared beam and measured with the detector. Oscilloscope was used to record the intensity of the frequency-doubled output emitted from the samples.

#### Theoretical calculation

Through density functional theory (DFT) calculations tests, we investigated the electronic structures, total and partial density of states (T/PDOS) and optical properties of BaCu<sub>2</sub> $M^{IV}Q_4$  ( $M^{IV} =$ Si, Ge, and Sn; Q = S, Se). The *ab initio* DFT method calculations were performed by the plane wave pseudopotential implemented in the CASTEP package.53 The local density approximations (LDA) with CA-PZ functional,54,55 a 900 eV cutoff energy for the plane-wave basis set and norm-conserving pseudopotentials (NCP)56 was employed in all computations. The Brillouin zone was integrated using Monkhorst-Pack-generated sets of k-points and we determined  $3 \times 3 \times 2$  k-point meshes for the former four target compounds and a  $4 \times 4 \times 2$  for BaCu<sub>2</sub>-SnSe<sub>4</sub>. The configurations for diverse electron orbital generating pseudopotentials were Ba 5p<sup>6</sup> 6s<sup>2</sup>, Cu 3p<sup>6</sup> 3d<sup>10</sup> 4s<sup>1</sup>, Si 3s<sup>2</sup>  $3p^2$ , Ge  $4s^2 4p^2$ , Sn  $5s^2 5p^2$ , S  $3s^2 3p^4$  and Se  $4s^2 4p^4$  and the other calculating parameters used in the calculations and convergent criteria were set by the default values of the CASTEP code. To explore the contributions from different structural units to the NLO coefficients, the SHG density method was performed by using the effective SHG: Virtual-Electron (VE) and Virtual-Hole

(VH).<sup>2</sup> At a zero frequency, the formula of second-order NLO coefficients can be derived as57

$$\chi^{\alpha\beta\gamma} = \chi^{\alpha\beta\gamma}(VE) + \chi^{\alpha\beta\gamma}(VH)$$
(1)

where,

$$\chi^{\alpha\beta\gamma}(\text{VH}) = \frac{e^3}{2\hbar^2 m^3} \sum_{\text{vv'c}} \int \frac{d^3k}{4\pi^3} P(\alpha\beta\gamma) \text{Im} \left[ p_{\text{vv'}}{}^{\alpha} p_{\text{v'c}}{}^{\beta} p_{\text{cv}}{}^{\gamma} \right] \\ \times \left( \frac{1}{\omega_{\text{cv}}{}^3 \omega_{\text{v'c}}{}^2} + \frac{2}{\omega_{\text{vc}}{}^4 \omega_{\text{cv'}}} \right)$$
(2)

$$\chi^{\alpha\beta\gamma}(\text{VE}) = \frac{e^3}{2\hbar^2 m^3} \sum_{\text{vcc'}} \int \frac{d^3k}{4\pi^3} P(\alpha\beta\gamma) \text{Im} \left[ p_{\text{vc}}{}^{\alpha} p_{\text{cc'}}{}^{\beta} p_{\text{c'v}}{}^{\gamma} \right] \\ \times \left( \frac{1}{\omega_{\text{cv}}{}^3 \omega_{\text{vc'}}{}^2} + \frac{2}{\omega_{\text{vc}}{}^4 \omega_{\text{c'v}}} \right)$$
(3)

here,  $\alpha$ ,  $\beta$ ,  $\gamma$  are Cartesian components, v and v' denote valence bands, c and c' denote conduction bands, and  $P(\alpha\beta\gamma)$  denotes full permutation. The band energy difference and momentum matrix elements are denoted as  $\hbar \omega_{ii}$  and  $P_{ii}^{\ \alpha}$ , respectively.

## Results and discussion

#### Crystal structure

Although all title compounds have the similar formula BaCu<sub>2</sub>-M<sup>IV</sup>Q<sub>4</sub>, they crystallize in the different polar space groups. Among them, BaCu<sub>2</sub>SnSe<sub>4</sub> crystallizes in the Ama2 space group of orthorhombic system, whereas other four compounds crystallize in the trigonal system. In other words, while through the simple element substitution (Sn to Ge, or Se to S) in BaCu<sub>2</sub>-SnSe<sub>4</sub>, they show obvious structural transformation from orthorhombic to trigonal system. Note that BaCu<sub>2</sub>GeS<sub>4</sub> and BaCu<sub>2</sub>GeSe<sub>4</sub> crystallize in the P3<sub>1</sub>21 space group, while BaCu<sub>2</sub>-SiSe<sub>4</sub> and BaCu<sub>2</sub>SnS<sub>4</sub> crystallize in the mirror symmetry P3<sub>2</sub>21 space group. The current crystal date is consistent with the previously reported phases.45-48

#### BaCu<sub>2</sub>SiSe<sub>4</sub>

It crystallizes in a polar trigonal space group  $P3_221$  with Z = 3and its asymmetric unit consists of one Ba, one Cu, one Si, two Se atoms. It exhibits a 3D framework structure built up of isolated [SiSe<sub>4</sub>] tetrahedra and edge or corner-sharing linked [CuSe<sub>4</sub>] ligands with charge-balanced Ba cations located at the framework tunnels (Fig. 1a). The isolated [SiSe<sub>4</sub>] ligands are approximately regular tetrahedra with d(Si-Se) = 2.263(2) to 2.269(2) Å, which is comparable to those of other known selenosilicates.<sup>58,59</sup> The distorted [CuSe<sub>4</sub>] units with d(Cu-Se) = 2.428(5) to 2.539(1) Å link together by sharing corners and edges to form the 3D tunnel structure. Note that two types (type I and type II) of tunnels that formed with the interconnection of the [CuSe<sub>4</sub>] units are interestingly found, such as six-member ring (6-MR) and 4-MR (Fig. 2a). In addition, the [BaSe<sub>8</sub>] polyhedra only locate within the 6-MR tunnels and show two types of connection modes: (i) exist in the isolation (Fig. 2b); (ii) link with each other by sharing Se corners to form the isolated  $[BaSe_6]_n$  chains (Fig. 2c). Each  $[BaSe_8]$  unit is linked with eight other  $[BaSe_8]$  units by sharing corners and edges in the *b*-*c* plane. Then, the [BaSe<sub>8</sub>] ligands in the different tunnels still interlink by sharing corners and edges to make up framework structure.

#### $BaCu_2GeSe_4$

It crystallizes in the trigonal *P*3<sub>1</sub>21 space group that shows the mirror symmetry compared with the structure of BaCu<sub>2</sub>SiSe<sub>4</sub>.



Fig. 1 (a) Crystal structure of  $BaCu_2SiSe_4$ ; (b) crystal structure of  $BaCu_2GeSe_4$ .



Fig. 2 (a) Two different types of tunnels (I and II) that formed with the interconnection of the  $[CuSe_4]$  units in  $BaCu_2SiSe_4$  and the Ba atoms only exist in the tunnel II; (b)  $[BaSe_8]$  polyhedra exist in the isolation in the tunnel II; (c) isolated  $[BaSe_6]_n$  chains in the tunnel II.

Seen from its structure, the  $[CuSe_4]$  units with d(Cu-Se) = 2.427(1) to 2.541(2) Å link with isolated  $[GeSe_4]$  units with d(Ge-Se) = 2.352(16) to 2.361(15) Å to form two types of 3D tunnel structure (6-MR and 4-MR), which is similar with the structural features in BaCu<sub>2</sub>SiSe<sub>4</sub>. In addition, the existence patterns of  $[BaSe_8]$  polyhedra in BaCu<sub>2</sub>GeSe<sub>4</sub> are in consistence with that in BaCu<sub>2</sub>SiSe<sub>4</sub>. Note that the arrangement direction of  $[GeSe_4]$  units in BaCu<sub>2</sub>GeSe<sub>4</sub> is opposite with that in the BaCu<sub>2</sub>SiSe<sub>4</sub>, thus, it show mirror symmetry structure with that of BaCu<sub>2</sub>SiSe<sub>4</sub>.

#### BaCu<sub>2</sub>SnSe<sub>4</sub>

It crystallizes in a polar orthorhombic space group Ama2 with Z = 4 and one crystallographically unique Ba, one Sn, one Cu, three Se atoms locate in its asymmetric unit. Seen from its structure (Fig. 3a), the irregular [CuSe<sub>4</sub>] with d(Cu-Se) = 2.431(3) to 2.546(2) Å are firstly linked with each other by sharing corners and edges to form the layer structure in the ac plane (Fig. 3b). Then, isolated  $[SnSe_4]$  tetrahedra with d(Sn-Se)= 2.509(3) - 2.545(2) Å as further bridge with these layers form the 3D tunnel structure along the c-axis, which may generate a wide range of applications for this compound, such as conductive material, heat-transfer material, ionic absorption, and photocatalysis.<sup>60-62</sup> The Ba atoms exist inside the tunnels and are linked with eight Se atoms showing d(Ba-Se) range from 3.311(2) to 3.409(2) Å to form distorted [BaSe<sub>8</sub>] polyhedra, which is close to those of other related compounds, including BaGa<sub>4</sub>Se<sub>7</sub> (3.429-3.861 Å)<sup>21</sup> and Ba<sub>7</sub>Sn<sub>3</sub>Se<sub>13</sub> (3.183-3.761 Å).<sup>63</sup> Each [BaSe<sub>8</sub>] unit is linked with six other [BaSe<sub>8</sub>] units by sharing corners and edges in the b-c plane. Note that the [BaSe<sub>8</sub>] polyhedra exist isolated in the same tunnel (Fig. 3c), but the [BaSe<sub>8</sub>] polyhedra in the different tunnels connect together by



**Fig. 3** (a) Crystal structure of BaCu<sub>2</sub>SnSe<sub>4</sub>; (b) regular [CuSe<sub>4</sub>] units are linked with each other to form the layer structure in the *ac* plane; (c) isolated [BaSe<sub>8</sub>] polyhedra exist in the same tunnel; (d) [BaSe<sub>8</sub>] polyhedra by sharing corners and edges to make up framework structure.

#### Structural comparison

In view of their similar structures among the four compounds (BaCu<sub>2</sub>SiSe<sub>4</sub>, BaCu<sub>2</sub>GeS<sub>4</sub>, BaCu<sub>2</sub>GeSe<sub>4</sub>, BaCu<sub>2</sub>SnS<sub>4</sub>), we have chosen the BaCu<sub>2</sub>SiSe<sub>4</sub> and BaCu<sub>2</sub>SnSe<sub>4</sub> as the representatives to discuss their structural comparison and the results can be extended to all of title compounds. In comparison with the structures of BaCu<sub>2</sub>SiSe<sub>4</sub> and BaCu<sub>2</sub>SnSe<sub>4</sub>, they have some similarities: all of them have the [BaSe<sub>8</sub>] octahedra and isolated  $[M^{IV}Se_4]$  ( $M^{IV} = Si$  and Sn) tetrahedra in their structures. However, they still have several obviously different features in their structures: (i) the asymmetric unit and Z (number of molecules in a unit cell) of BaCu<sub>2</sub>SiSe<sub>4</sub> have five crystallographically distinct sites and Z = 3, which are different from those of BaCu<sub>2</sub>SnSe<sub>4</sub> (6 and Z = 4); (ii) the [BaSe<sub>8</sub>] units are more highly distorted in BaCu<sub>2</sub>SnSe<sub>4</sub> than those in BaCu<sub>2</sub>SiSe<sub>4</sub>, owing to the largest difference ( $\Delta d$ ) between Ba–Se that  $\Delta d$  (Ba–Se) = 0.098 Å in BaCu<sub>2</sub>SnSe<sub>4</sub> is larger than that (0.066 Å) in BaCu<sub>2</sub>-SiSe<sub>4</sub>; (iii) the [CuSe<sub>4</sub>] units link together to make up the tunnel structure in BaCu<sub>2</sub>SiSe<sub>4</sub>, whereas the [CuSe<sub>4</sub>] units connect with each other to form layer structure in BaCu<sub>2</sub>SnSe<sub>4</sub>; (iv) note that the [BaSe<sub>8</sub>] polyhedra exist in isolation in each tunnel of BaCu<sub>2</sub>SnSe<sub>4</sub>, but in BaCu<sub>2</sub>SiSe<sub>4</sub>, the [BaSe<sub>8</sub>] polyhedra show two types of connection modes: isolation and chain; (v) each [BaSe<sub>8</sub>] unit is linked with six other [BaSe<sub>8</sub>] units in BaCu<sub>2</sub>SnSe<sub>4</sub>, which is different from that each [BaSe<sub>8</sub>] polyhedron connects with eight other [BaSe<sub>8</sub>] units in BaCu<sub>2</sub>SiSe<sub>4</sub>. Similarly, the main structural differences as mentioned above are also found between BaCu<sub>2</sub>SnSe<sub>4</sub> and other compounds. Interestingly, previous researches show that the structures of metal chalcogenides can be changed with the different M or Q atoms in crystal structures.44 Therefore, this observation indicates that the slight change of cation size would result in different structure features, and future structure prediction should be devoted considerable attentions to the different chalcogen atoms (Fig. 4).

#### **Optical properties**

The diffuse-reflectance UV-vis-NIR spectra of title compounds (Fig. S3 in the ESI<sup>†</sup>) were measured, and the spectral results show that the experimental band gaps are 2.62 eV for



Fig. 4 (a) Experimental band gap of BaCu<sub>2</sub>SnS<sub>4</sub>; (b) SHG intensities of BaCu<sub>2</sub>SnS<sub>4</sub> versus AgGaS<sub>2</sub> at the particle size of  $55-88 \mu m$ .

BaCu<sub>2</sub>SiSe<sub>4</sub>, 2.47 eV for BaCu<sub>2</sub>GeS<sub>4</sub>, 1.88 eV for BaCu<sub>2</sub>GeSe<sub>4</sub>, 1.96 eV for BaCu<sub>2</sub>SnS<sub>4</sub> and 1.72 eV for BaCu<sub>2</sub>SnSe<sub>4</sub>, respectively. Among them, BaCu<sub>2</sub>SiSe<sub>4</sub> and BaCu<sub>2</sub>GeS<sub>4</sub> have larger band gaps, which are comparable to those of commercial AGS (2.64 eV). The other three compounds have relatively narrow band gaps that are still comparable to those of other typical IR NLO crystals, such as ZnGeP<sub>2</sub> (1.65 eV) and AgGaSe<sub>2</sub> (1.75 eV). IR spectra of title compounds were also measured on the microcrystal powders, and the results (Fig. S2 in the ESI†) reveal that all of them have wide transmission regions from 4000-450  $cm^{-1}$ , namely, 2.5–22  $\mu m$ , that cover the two important atmospheric transparent windows of 3-5 and 8-12 µm, which are comparable to the IR absorption edges of other IR NLO powdered compounds such as BaGa<sub>4</sub>Se<sub>7</sub> (~18 μm),<sup>21</sup> LiCdGeS<sub>4</sub>  $(\sim 22 \ \mu m)^{35}$  AGS  $(\sim 23 \ \mu m)^{64}$  SnGa<sub>4</sub>S<sub>7</sub>  $(\sim 25 \ \mu m)^{65}$  Li<sub>4</sub>HgGe<sub>2</sub>S<sub>7</sub>  $(\sim 22 \ \mu m)^{66}$  and CsCd<sub>4</sub>Ga<sub>5</sub>S<sub>12</sub> ( $\sim 25 \ \mu m$ ).<sup>23</sup> Raman spectra (Fig. 5) also further verify that title compounds have the wide IR transmission region and no absorption peaks in the region of 450–1000 cm<sup>-1</sup> (10–22  $\mu$ m). As for the selenides, the obvious absorption peaks include BaCu<sub>2</sub>SiSe<sub>4</sub> (221.5 cm<sup>-1</sup>), BaCu<sub>2</sub>GeSe<sub>4</sub>  $(275 \text{ cm}^{-1})$  and BaCu<sub>2</sub>SnSe<sub>4</sub> (195 cm<sup>-1</sup>), which can be assigned to the characteristic absorptions of the Si-Se, Ge-Se, and Sn-Se modes, respectively. As for the sulfides, the absorption peaks for  $BaCu_2GeS_4$  and  $BaCu_2SnS_4$  are 367.5 and 337.5 cm<sup>-1</sup> that correspond to the Ge-S and Sn-S bonding interactions, respectively. The intensive peak positions for the family of  $BaCu_2M^{IV}Q_4$  are affected by the tetravalent (IV) metals, and the peak positions slightly shifted towards the short wavelength with the change of the M<sup>IV</sup> cations (from Si to Sn).<sup>44</sup> By comparing the absorption peaks of sulphides (BaCu2GeS4 and BaCu<sub>2</sub>SnS<sub>4</sub>) and selenides (BaCu<sub>2</sub>SiSe<sub>4</sub>, BaCu<sub>2</sub>GeSe<sub>4</sub> and BaCu<sub>2</sub>SnSe<sub>4</sub>), the peak positions shifted towards the short wavelength when the anion Q vary from S to Se. SHG responses for title compounds were also systemically measured with a 2.09 um O-switch laser in different particle sizes at room temperature and commercial AGS crystal was used as a reference. Among them, BaCu<sub>2</sub>SnS<sub>4</sub> has a good SHG response that is about



Fig. 5 Raman spectra of title compounds

1.6 times that of benchmark AGS in the particle size range 55–88  $\mu$ m (Fig. S4 in the ESI†) and the other four compounds show the weak SHG responses about 0.3 times of AGS in the particle size range 55–88  $\mu$ m. Note that SHG intensities were decreased with the increase of particle sizes for all of title compounds, which indicates that they exhibit the non-phase matching behavior.

#### Theoretical studies

First-principles computations were adopted to better understand the electronic structures of the title compounds. Based on the theoretical electronic structures (Fig. S5 in the ESI<sup>†</sup>), the highest point of the valence band (VB) and the lowest point of the conduction band (CB) locate at the different points for  $BaCu_2SnSe_4$ , which indicates that it is an indirect band gap compound, whereas the other four compounds are direct band gap semiconductors. Calculated results show that the theoretical band gaps are 1.53 eV for BaCu<sub>2</sub>GeS<sub>4</sub>, 1.31 eV for BaCu<sub>2</sub>-GeSe<sub>4</sub>, 1.63 eV for BaCu<sub>2</sub>SiSe<sub>4</sub>, 1.09 eV for BaCu<sub>2</sub>SnS<sub>4</sub> and 1.07 eV for BaCu<sub>2</sub>SnSe<sub>4</sub> (Fig. 6a for BaCu<sub>2</sub>SnS<sub>4</sub>, Fig. S5<sup>†</sup> for other compounds, respectively), respectively. The calculated band gaps are lower than the experimental values, which can be attributed to the discontinuity of exchange-correlation energy of the GGA functional.67,68 Moreover, the PDOS of title compounds were also obtained (Fig. S6 in the ESI<sup>†</sup>). From the PDOS of  $BaCu_2SnS_4$  (Fig. 6b), the region in the valence bands from -8 eV to Fermi level is mainly occupied by Cu-3d and S-3p states. Meanwhile, the bottom of conduction bands is derived from the S-3p and Sn-5s orbitals. As for the other four compounds, their T/PDOS were also achieved and familiar with that of BaCu<sub>2</sub>SnS<sub>4</sub>. Moreover, SHG coefficients  $(d_{ii})$  for title compounds were also calculated. Since BaCu<sub>2</sub>SiSe<sub>4</sub>, BaCu<sub>2</sub>GeS<sub>4</sub>, BaCu<sub>2</sub>GeSe<sub>4</sub> and BaCu<sub>2</sub>SnS<sub>4</sub> belong to 32 point group that allows for five nonzero coefficients in the SHG tensor and only two are independent:  $d_{11} = -d_{12} = -d_{26}$  and  $d_{14} = -d_{25}$ . However, the allowed coefficients from five to three were reduced by Kleinman symmetry,69 and results the condition that



Fig. 6 (a) Calculated band gap of  $BaCu_2SnS_4$ ; (b) PDOS of  $BaCu_2SnS_4$ ; (c) SHG-density of  $BaCu_2SnS_4$  at VH occupied; (d) SHG-density of  $BaCu_2SnS_4$  at VH unoccupied.

 $d_{14} = -d_{25} = 0$ , so the four compounds only have one independent NLO tensor  $(d_{11})$ . The theoretical SHG coefficients  $(d_{ij})$ are  $d_{11} = 0.28 \text{ pm V}^{-1}$  for BaCu<sub>2</sub>GeS<sub>4</sub>,  $d_{11} = 5.62 \text{ pm V}^{-1}$  for BaCu<sub>2</sub>GeSe<sub>4</sub>,  $d_{11} = 4.18$  pm V<sup>-1</sup> for BaCu<sub>2</sub>SiSe<sub>4</sub>, and  $d_{11} = 12.09$ pm  $V^{-1}$  for BaCu<sub>2</sub>SnS<sub>4</sub>, respectively. In addition, BaCu<sub>2</sub>SnSe<sub>4</sub> belongs to mm2 group that has three unequal NLO coefficients:  $d_{31} = 1.76, \ d_{32} = -12.65$  and  $d_{33} = -10.13$  pm V<sup>-1</sup>. In comparison with their calculated SHG coefficients  $(d_{ii})$  values, it can be found that BaCu2GeS4, BaCu2GeSe4, and BaCu2SiSe4 are smaller than that of BaCu<sub>2</sub>SnS<sub>4</sub>, which are also consistent with their experimental results. Unfortunately, the SHG experimental observation  $(0.3 \times \text{AgGaS}_2)$  is smaller than that  $(d_{32} =$ -12.65 pm V<sup>-1</sup>) of BaCu<sub>2</sub>SnSe<sub>4</sub>, which may be by its narrow optical bandgap (1.72 eV) and long shortwave absorption edge (up to 1  $\mu$ m). Thus, the SHG light (1045 nm) was likely to be weaken under the fundamental light (2090 nm), and then lead to the low SHG intensity. We believe that the precise SHG effect may be obtained by the long wavelength laser (e.g. carbon dioxide laser) for BaCu<sub>2</sub>SnSe<sub>4</sub>. Note that BaCu<sub>2</sub>SnS<sub>4</sub> exhibits a comparable SHG coefficient (12.09 pm  $V^{-1}$ ) to that of commercial AGS (11 pm  $V^{-1}$ ). Meanwhile, SHG density method was also used to investigate the origin of SHG responses for title compounds. The contributions of VE and VH to the total SHG coefficients were obtained using the band-resolved method, and the results were listed in Table S3 in the ESI.<sup>†</sup> As for BaCu<sub>2</sub>SnS<sub>4</sub>, the VH and VE contributions were about 90.01%  $(d_{11})$  and 9.99%  $(d_{11})$ , respectively. Therefore, we chose the occupied and unoccupied of VH to investigate the mainly origin of the SHG response for BaCu<sub>2</sub>SnS<sub>4</sub>. Fig. 6c and d plot the occupied and unoccupied states of VH and clearly showing that the SHG effect of BaCu<sub>2</sub>SnS<sub>4</sub> was derived from the [CuS<sub>4</sub>] and [SnS<sub>4</sub>] tetrahedra. In addition, the contributions of VE and VH for other four compounds were similar to that of BaCu<sub>2</sub>SnS<sub>4</sub> (Fig. S7 in the ESI†), which indicate that their origins of SHG effects are mainly derived from the cooperative contribution of the [CuO<sub>4</sub>] and [MQ<sub>4</sub>] units.

### Conclusions

In summary, a family of NCS quaternary  $BaCu_2M^{IV}Q_4$  ( $M^{IV} = Si$ , Ge, and Sn; Q = S, Se) were successfully synthesized and characterized. Interestingly, title compounds crystallize in different space groups. Among them, BaCu<sub>2</sub>GeS<sub>4</sub> and BaCu<sub>2</sub>GeSe<sub>4</sub> crystallize in the trigonal space group P3121 that are mirror symmetric with BaCu<sub>2</sub>SiSe<sub>4</sub> and BaCu<sub>2</sub>SnS<sub>4</sub> (space group P3<sub>2</sub>21), while BaCu<sub>2</sub>SnSe<sub>4</sub> crystallizes in the orthorhombic space group Ama2. In BaCu<sub>2</sub>SnSe<sub>4</sub>, irregular [CuSe<sub>4</sub>] units are firstly linked with each other by sharing corners and edges to form a 2D layer structure in the *ac* plane, and then the isolated [SnSe<sub>4</sub>] tetrahedra as a bridge connect with these layers to form a 3D tunnel structure along the *c*-axis. Different from the structure that all the [BaSe<sub>8</sub>] units of BaCu<sub>2</sub>SnSe<sub>4</sub> existed in the same tunnel structure in isolation in BaCu<sub>2</sub>SnSe<sub>4</sub>, other four title compounds exhibit two types of tunnel structure (I, 4-MR and II, 6-MR) with the isolated [BaSe<sub>8</sub>] units and [BaSe<sub>6</sub>], chains existed in the tunnel II. Raman and IR spectra indicate that their IR absorption edges can reach to 22 µm, which covers the two critical atmospheric transparent windows (3–5 and 8–14  $\mu$ m). Experimental band gaps of BaCu<sub>2</sub>SiSe<sub>4</sub> and BaCu<sub>2</sub>GeS<sub>4</sub> are 2.47 and 2.62 eV, respectively, and larger than those of other typical materials, which imply that they may exhibit the large LDTs and are applied in the high-power laser system. In addition, the results of SHG measurements indicate that BaCu<sub>2</sub>SnS<sub>4</sub> has a good SHG response about 1.6 times of that AGS in the particle size range 55–88  $\mu$ m. The overall research results indicate that BaCu<sub>2</sub>SnS<sub>4</sub> has a promising application as a potential NLO material in the IR region.

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