BaCu$_2$M$^{IV}$Q$_4$ ($M^{IV}$ = Si, Ge, and Sn; Q = S, Se): synthesis, crystal structures, optical performances and theoretical calculations†

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Five non-centrosymmetric (NCS) quaternary metal chalcogenides, BaCu$_2$SiSe$_4$, BaCu$_2$GeS$_4$, BaCu$_2$GeSe$_4$, BaCu$_2$SnS$_4$, and BaCu$_2$SnSe$_4$, were successfully synthesized by solid-state reaction in vacuum-sealed silica tubes. They crystallized in the three different space groups: $Ama2$ for BaCu$_2$SnSe$_4$, $P3_121$ for BaCu$_2$GeS$_4$ and BaCu$_2$GeSe$_4$, and $P3_221$ for BaCu$_2$SiSe$_4$ and BaCu$_2$SnS$_4$. Note that BaCu$_2$GeS$_4$ and BaCu$_2$GeSe$_4$ show the mirror symmetrical structures to those of BaCu$_2$SiSe$_4$ and BaCu$_2$SnS$_4$. In comparison with their structures, it can be found that the [CuSe$_4$] units are connected together to form a two-dimensional (2D) layer structure in BaCu$_2$SnS$_4$, which is different from the 3D framework structure formed by the interlinked [CuQ$_4$] (Q = S and Se) units in other four title compounds. In addition, BaCu$_2$SnSe$_4$ exhibits only one type of tunnel structure with the isolated [BaSe$_4$] units existing in each tunnel, which is also different from the other title compounds (two types of tunnels with the isolated [BaSe$_4$] and [BaSe$_6$] 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 (~22 μm). Powder SHG measurement shows that BaCu$_2$SnS$_4$ possesses good SHG response about 1.6 times of that of benchmark AgGaS$_2$ (AGS) at the particle size 55–88 μm. All results indicate that BaCu$_2$SnS$_4$ 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.

Introduction

Frequency-conversion technology on nonlinear optical (NLO) materials was invented to extend the laser wavelength ranges and has been further developed for decades.1–4 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.5–14 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.20–31 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 chalcogen atoms to form the distorted [M$^{IV}$Q$_4$] tetrahedra.34–41 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$_2$Hg$_3$Ge$_3$S$_8$,36 Li$_2$CdGeS$_4$,42 Na$_2$BaSnS$_4$,43 Na$_2$Hg$_3$Ge$_3$S$_8$.44 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
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 $\text{MIV}_4^\circ$ 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 $\text{BaCu/MIV}/Q$ ($\text{MIV} = \text{Si}, \text{Ge}, \text{Sn}; Q = \text{S}, \text{Se}$) systems and successfully synthesized five metal chalcogenides, including $\text{BaCu}_2\text{SiSe}_4$, $\text{BaCu}_2\text{GeSe}_4$, $\text{BaCu}_2\text{GeSe}_4$, $\text{BaCu}_2\text{SnS}_4$, and $\text{BaCu}_2\text{SnSe}_4$. Among them, although the crystal structures of latter four compounds 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.

$\text{BaCu}_2\text{GeS}_4$ and $\text{BaCu}_2\text{SnS}_4$

The crystals of $\text{BaCu}_2\text{GeS}_4$ and $\text{BaCu}_2\text{SnS}_4$ 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$^{-1}$ 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 $\text{BaCu}_2\text{GeS}_4$ and red crystals of $\text{BaCu}_2\text{SnS}_4$ were obtained after drying in air. They are stable in air for several months.

$\text{BaCu}_2\text{SiSe}_4$, $\text{BaCu}_2\text{GeSe}_4$, and $\text{BaCu}_2\text{SnSe}_4$

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 $\text{BaCu}_2\text{SiSe}_4$, $\text{BaCu}_2\text{GeSe}_4$, and $\text{BaCu}_2\text{SnSe}_4$ 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 was data 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. All structure determinations were based on direct method and refined through the full-matrix least-squares on $F^2$ by SHELXTL crystallographic program package. The final structures were checked with PLATON program, 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.$^\dagger$ The bond angles and selected bond distances are shown in Table S2 in the ESI.$^\dagger$

**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 2θ 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,$^\dagger$ 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.$^\dagger\dagger$ 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$^{-1}$ 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
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, powder SHG responses of title compounds were investigated by a Q-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 light-tight 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 BaCu2MIVQ4 (MIV = Si, Ge, and Sn; Q = S, Se). The \textit{ab initio} DFT method calculations were performed by the plane wave pseudopotential implemented in the CASTEP package. The local density approximations (LDA) with CA–PZ functional, a 900 eV cutoff energy for the plane-wave basis set and norm-conserving pseudopotentials (NCP) were 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 \( 4 \times 4 \times 2 \) for BaCu2SnSe4. The configurations for discrete electron orbital generating pseudopotentials were Ba 5p6 6s2, Cu 3p6 3d10 4s1, Si 3s2 3p2, Ge 4s2 4p2, Sn 5s2 5p2, S 3s2 3p2 and Se 4s2 4p4 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). At a zero frequency, the formula of second-order NLO coefficients can be derived as

\[
\chi^{(2)} = \chi^{(2)}(VE) + \chi^{(2)}(VH)
\]

where,

\[
\chi^{(2)}(VH) = \frac{\epsilon^3}{2\hbar^2 m^2} \sum_{\alpha} \left\{ \frac{d^2k}{4\pi^2} P(\alpha\beta\gamma) \text{Im} \left[ P_{\alpha \alpha} P_{\beta \beta} P_{\gamma \gamma} \right] \right\} \times \left( \frac{1}{\omega_{\lambda \lambda}^2} + \frac{2}{\omega_{\lambda \gamma}^2} \right) \tag{2}
\]

\[
\chi^{(2)}(VE) = \frac{\epsilon^3}{2\hbar^2 m^2} \sum_{\alpha} \left\{ \frac{d^2k}{4\pi^2} P(\alpha\beta\gamma) \text{Im} \left[ P_{\alpha \alpha} P_{\beta \alpha} P_{\gamma \gamma} \right] \right\} \times \left( \frac{1}{\omega_{\lambda \lambda}^2} + \frac{2}{\omega_{\lambda \gamma}^2} \right) \tag{3}
\]

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

Results and discussion

Crystal structure

Although all title compounds have the similar formula BaCu2MIVQ4, they crystallize in the different polar space groups. Among them, BaCu2SnSe4 crystallizes in the \textit{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 BaCu2SnSe4, they show obvious structural transformation from orthorhombic to trigonal system. Note that BaCu2GeSe4 and BaCu2GeSn4 crystallize in the \textit{P3}21 space group, while BaCu2SiSe4 and BaCu2SnSe4 crystallize in the mirror symmetry \textit{P3}21 space group. The current crystal data is consistent with the previously reported phases.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Crystal data and structure refinement for title compounds</th>
</tr>
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<tbody>
<tr>
<td>Empirical formula</td>
<td>BaCu2GeS4</td>
</tr>
<tr>
<td>( f_w )</td>
<td>465.25</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Trigonal</td>
</tr>
<tr>
<td>Space group</td>
<td>( P3_121 )</td>
</tr>
<tr>
<td>( a ) (Å)</td>
<td>6.2092(8)</td>
</tr>
<tr>
<td>( b ) (Å)</td>
<td>6.2092(8)</td>
</tr>
<tr>
<td>( c ) (Å)</td>
<td>15.520(4)</td>
</tr>
<tr>
<td>( D_{\text{h}} ) (g cm(^{-3}))</td>
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</tr>
<tr>
<td>( \mu ) (mm(^{-1}))</td>
<td>17.089</td>
</tr>
<tr>
<td>GOF on ( S )</td>
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</tr>
<tr>
<td>( R_1, wR_2 ) (all data)%</td>
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<tr>
<td>Absolute structure parameter</td>
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</tr>
<tr>
<td>Largest diff. peak and hole (e Å(^{-3}))</td>
<td>1.306, −1.117</td>
</tr>
</tbody>
</table>

\( R_1 = F_a - F_c/F_a \) and \( wR_2 = [w(F_a^2 - F_c^2)^2/wF_a^4]^{1/2} \) for \( F_a^2 > 2 \sigma(F_a^2) \).
**BaCu$_2$SiSe$_4$**

It crystallizes in a polar trigonal space group $P3_121$ with $Z = 3$ and 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$_4$] tetrahedra and edge or corner-sharing linked [CuSe$_4$] ligands with charge-balanced Ba cations located at the framework tunnels (Fig. 1a). The isolated [SiSe$_4$] 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. The distorted [CuSe$_4$] 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$_4$] units are interestingly found, such as six-member ring (6-MR) and 4-MR (Fig. 2a). In addition, the [BaSe$_8$] 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$_8$]$_n$ 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$_8$] ligands in the different tunnels still interlink by sharing corners and edges to make up framework structure.

**BaCu$_2$GeSe$_4$**

It crystallizes in the trigonal $P3_121$ space group that shows the mirror symmetry compared with the structure of BaCu$_2$SiSe$_4$. 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$_2$SiSe$_4$. In addition, the existence patterns of [BaSe$_8$] polyhedras in BaCu$_2$GeSe$_4$ are in consistence with that in BaCu$_2$SiSe$_4$. Note that the arrangement direction of [GeSe$_4$] units in BaCu$_2$GeSe$_4$ is opposite with that in the BaCu$_2$SiSe$_4$, thus, it show mirror symmetry structure with that of BaCu$_2$SiSe$_4$.

**BaCu$_2$SnSe$_4$**

It crystallizes in a polar orthorhombic space group $Amma$ 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$_4$] 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. 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$_6$] polyhedra, which is close to those of other related compounds, including BaGa$_4$Se$_7$ (3.429–3.861 Å) and Ba$_7$Sn$_3$Se$_{13}$ (3.183–3.761 Å). Each [BaSe$_6$] unit is linked with six other [BaSe$_8$] units by sharing corners and edges in the $b$–$c$ plane. Note that the [BaSe$_6$] polyhedra exist isolated in the same tunnel (Fig. 3c), but the [BaSe$_8$] polyhedra in the different tunnels connect together by...
sharing corners and edges to make up framework structure (Fig. 3d).

**Structural comparison**

In view of their similar structures among the four compounds (BaCu$_2$SiSe$_4$, BaCu$_2$GeSe$_4$, BaCu$_2$GeS$_4$, BaCu$_2$SnS$_4$), we have chosen the BaCu$_2$SiSe$_4$ and BaCu$_2$SnSe$_4$ 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$_2$SiSe$_4$ and BaCu$_2$SnSe$_4$, they have some similarities: all of them have the [BaSe$_8$] octahedra and isolated [MIVSe$_4$] (MIV = Si and Sn) tetrahedra in their structures. However, they still have several obviously different features in their structures: (i) the asymmetric unit and those of BaCu$_2$SnSe$_4$ (6 and 8) and BaCu$_2$SiSe$_4$ (6 and 4); (ii) the [BaSe$_8$] units are more highly distorted in BaCu$_2$SnSe$_4$ than those in BaCu$_2$SiSe$_4$, owing to the largest difference ($\Delta d$) between Ba–Se that $\Delta d$ (Ba–Se) = 0.098 Å in BaCu$_2$SnSe$_4$ is larger than that (0.066 Å) in BaCu$_2$SiSe$_4$; (iii) the [CuSe$_6$] units link together to make up the tunnel structure in BaCu$_2$SiSe$_4$, whereas the [CuSe$_6$] units connect with each other to form layer structure in BaCu$_2$SnSe$_4$; (iv) note that the [BaSe$_8$] polyhedra exist in isolation in each tunnel of BaCu$_2$SnSe$_4$, but in BaCu$_2$SiSe$_4$, the [BaSe$_8$] polyhedra show two types of connection modes: isolation and chain; (v) each [BaSe$_8$] unit is linked with six other [BaSe$_8$] units in BaCu$_2$SnSe$_4$, which is different from that each [BaSe$_8$] polyhedron connects with eight other [BaSe$_8$] units in BaCu$_2$SiSe$_4$. Similarly, the main structural differences as mentioned above are also found between BaCu$_2$SnSe$_4$ and other compounds. Interestingly, previous researches show that the structures of metal chalco-genides can be changed with the difference in M or Q atoms in crystal structures. 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†) were measured, and the spectral results show that the experimental band gaps are 2.62 eV for BaCu$_2$SiSe$_4$, 2.47 eV for BaCu$_2$GeSe$_4$, 1.88 eV for BaCu$_2$GeS$_4$, 1.96 eV for BaCu$_2$SnS$_4$ and 1.72 eV for BaCu$_2$SnSe$_4$, respectively. Among them, BaCu$_2$SiSe$_4$ and BaCu$_2$GeS$_4$ 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$_2$ (1.65 eV) and AgGaSe$_2$ (1.75 eV). IR spectra of title compounds were also measured on the micro-crystal 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 μm, 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$_2$Se$_2$ (~18 μm), LiCdGeS$_4$ (~22 μm), AGS (~23 μm), SnGa$_2$S$_7$ (~25 μm), Li$_4$HgGe$_2$S$_7$ (~22 μm) and CsCd$_4$Ga$_5$S$_{12}$ (~25 μm). 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$^{-1}$ (10–22 μm). As for the selenides, the obvious absorption peaks include BaCu$_2$SiSe$_4$ (221.5 cm$^{-1}$), BaCu$_2$GeS$_4$ (275 cm$^{-1}$) and BaCu$_2$SnSe$_4$ (195 cm$^{-1}$), which can be assigned to the characteristic absorptions of the Si–Se, Ge–Se, and Sn–Se modes, respectively. For the sulfides, the absorption peaks for BaCu$_2$GeS$_4$ and BaCu$_2$SnS$_4$ are 367.5 and 337.5 cm$^{-1}$ that correspond to the Ge–S and Sn–S bonding interactions, respectively. The intensive peak positions for the family of BaCu$_2$MIVQ$_4$ are affected by the tetravalent (IV) metals, and the peak positions slightly shifted towards the short wavelength with the change of the M IV cations (from Si to Sn). By comparing the absorption peaks of sulphides (BaCu$_2$GeS$_4$ and BaCu$_2$SnS$_4$) and selenides (BaCu$_2$SiSe$_4$, BaCu$_2$GeSe$_4$ and BaCu$_2$SnSe$_4$), 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 μm Q-switch laser in different particle sizes at room temperature and commercial AGS crystal was used as a reference. Among them, BaCu$_2$SnS$_4$ has a good SHG response that is about
1.6 times that of benchmark AGS in the particle size range 55–88 μm (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 μm. 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), the highest point of the valence band (VB) and the lowest point of the conduction band (CB) locate at the different points for BaCu2SnSe4, 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 BaCu2GeS4, 1.31 eV for BaCu2GeSe4, 1.63 eV for BaCu2SiSe4, 1.09 eV for BaCu2SnS4 and 1.07 eV for BaCu2SnSe4 (Fig. 6a for BaCu2SnS4, Fig. S5 for other compounds, 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. Moreover, the PDOS of title compounds were also obtained (Fig. S6 in the ESI). From the PDOS of BaCu2SnS4 (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 TP/PDOS were also achieved and familiar with that of BaCu2SnSe4. Moreover, SHG coefficients ($d_{ij}$) for title compounds were similar to that of BaCu2SnS4 (Fig. S7 in the ESI), respectively. Therefore, we chose the occupied and unoccupied of VH to investigate the mainly origin of the SHG response for BaCu2SnS4. Fig. 6c and d plot the occupied and unoccupied states of VH and clearly showing that the SHG effect of BaCu2SnS4 was derived from the [CuS4] and [SnS4] tetrahedra. In addition, 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. As for BaCu2SnS4, the VE and VH contributions were 90.01% ($d_{11}$) and 9.99% ($d_{11}$), respectively. Thus, the four compounds only have one independent NLO tensor ($d_{11}$). The theoretical SHG coefficients ($d_{ij}$) are $d_{11} = 0.28$ pm V$^{-1}$ for BaCu2GeS4, $d_{11} = 5.62$ pm V$^{-1}$ for BaCu2GeSe4, $d_{11} = 4.18$ pm V$^{-1}$ for BaCu2SiSe4, and $d_{11} = 12.09$ pm V$^{-1}$ for BaCu2SnSe4, respectively. In addition, BaCu2SnSe4 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$^{-1}$. In comparison with their calculated SHG coefficients ($d_{ij}$) values, it can be found that BaCu2GeS4, BaCu2GeSe4, and BaCu2SiSe4 are smaller than that of BaCu2SnS4, which are also consistent with their experimental results. Unfortunately, the SHG experimental observation ($0.3\times$ AgGaS2) is smaller than that of commercial AGS (11 pm V$^{-1}$) to that of BaCu2SnS4, which may be by its narrow optical bandgap (1.72 eV) and long shortwave absorption edge (up to 1 μm). 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 BaCu2SnSe4. Note that BaCu2SnS4 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. As for BaCu2SnS4, the VH and VE contributions were 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 BaCu2SnS4. Fig. 6c and d plot the occupied and unoccupied states of VH and clearly showing that the SHG effect of BaCu2SnS4 was derived from the [CuS4] and [SnS4] tetrahedra.

**Conclusions**

In summary, a family of NCS quaternary BaCu2MIVQ4 (MIV = Si, Ge, and Sn; Q = S, Se) were successfully synthesized and characterized. Interestingly, title compounds crystallize in different space groups. Among them, BaCu2GeS4 and BaCu2GeSe4 crystallize in the trigonal space group P3$_1$21 that are mirror symmetric with BaCu2SiSe4 and BaCu2SnS4 (space group P3$_1$21), while BaCu2SnSe4 crystallizes in the orthorhombic space group Ama2. In BaCu2SnSe4, irregular [CuSe4] units are firstly linked with each other by sharing corners and edges to form a 2D layer structure in the ac plane, and then the isolated [SnSe4] tetrahedra as a bridge connect with these layers to form a 3D tunnel structure along the c-axis. Different from the structure that all the [BaSe8] units of BaCu2SnSe4 existed in the same tunnel structure in isolation in BaCu2SnSe4, other four title compounds exhibit two types of tunnel structure (I, 4-MR and II, 6-MR) with the isolated [BaSe8] units and [BaSe6]$_2$ 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

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**Fig. 6** (a) Calculated band gap of BaCu2SnSe4; (b) PDOS of BaCu2SnSe4; (c) SHG-density of BaCu2SnS4 at VH occupied; (d) SHG-density of BaCu2SnS4 at VH unoccupied.
critical atmospheric transparent windows (3–5 and 8–14 µm). Experimental band gaps of BaCu₂SiSe₄ and BaCu₂GeS₄ 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 BaCu₂SnS₄ has a good SHG response about 1.6 times of that AGS in the particle size range 55–88 µm. The overall research results indicate that BaCu₂SnS₄ has a promising application as a potential NLO material in the IR region.

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Notes and references