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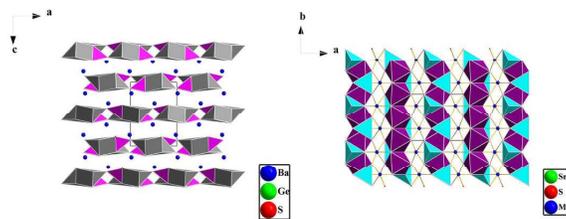
Structure of Ba_2GeS_4 on single crystal was firstly determined, and structure and properties of new compound Mg_2SnS_4 were reported.

Journal Name

ARTICLE

Ba₂GeS₄ and Mg₂SnS₄: synthesis, structures, optical properties and electronic structures

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Two ternary metal chalcogenides, Ba₂GeS₄ and Mg₂SnS₄, have been synthesized by high-temperature solid-state reaction. Single-crystal X-ray diffraction analysis reveals that they crystallize in the same space group *P*nma with the three-dimensional framework composed of discrete MS₄ (M=Ge, Sn) tetrahedra, but they are not isostructural. Since the arrangements of isolated MS₄ (M=Ge, Sn) units are obviously different in the Ba₂GeS₄ and Mg₂SnS₄ structures, which make their *a* and *c* axes be exchanged, thus leads to different structures for title compounds. The UV–Vis–IR diffuse reflectance spectra exhibit that the optical band gap is about 2.05 eV for Mg₂SnS₄. IR spectra of title compounds are also measured and shown wide IR transmission range. First-principle theoretical studies are also used to aid the understanding of electronic structures and linear optical properties.

Introduction

Metal chalcogenides have attracted attention for a few decades owing to their structural diversity, interesting physical properties and potential technological applications.[1–8] In recent years, extensive efforts in the synthesis and characterization have led to the discovery of many new important metal chalcogenides.[9–15] The MQ₄ (M=Si, Ge and Sn, Q=S, Se and Te) tetrahedra, as one of functional groups, have been frequently introduced into crystal struture, which can be bridged a variety of different metal centers into extended structures and applied in many important fields, such as NLO materials, thermoelectric materials, solar energy converters, and detector materials.[16–20] Ternary metal chalcogenides with the formula A₂MQ₄ (A= alkaline-earth or transition metal; M= Si, Ge, Sn; Q=S, Se, Te) have been discovered, especially the transition metal A₂MQ₄ compounds, most of them have been reported their stuctures and properties, which are proved to be potential magnetic materials, such as Mn₂SiS₄, Fe₂GeSe₄, Fe₂SiS₄, and Mn₂GeSe₄ et al.[21–25] However, compared with transition metal A₂MQ₄ compounds, alkaline-earth compounds have been not systemically studied and most of their structures and relative chemical-physical properties have been rarely reported. Therefore, in order to further examine the crystal structures and physical properties, we have extended the study in the alkaline-earth A₂MQ₄ compounds and obtained two crystals Ba₂GeS₄ and Mg₂SnS₄. So far, as for Ba₂GeS₄, only the crystal structure data based on powder samples were reported, there still have no reported data on single crystals, and only cell dimension was reported for Mg₂SnS₄ without any further research of its single structure and properties.[26,27] Herein, we report the synthsis, crystal structures, Raman spectroscopy and optical properties of the title compounds in detail. And the electronic structures and linear optical properties using the first-principle theoretical calculation are also reported.

Experimental

Synthesis and crystal growth

Chemicals in this work were used as obtained: Ba, Mg, Ge, Sn, and S were purchased from Beijing Founde Star Science &Technology Co. Ltd., with purities of 4 N. All of the above chemicals were used without further purification.

The binary starting materials BaS, MgS, GeS₂, and SnS₂ were synthesized by the stoichiometric reactions of elements at high temperatures in sealed silica tubes evacuated to 10^{-3} Pa. During the crystal growth and synthesis of the polycrystalline samples, all reactants were ground and loaded into 10-mm-i.d. fused-silica tubes, then moved to a high-vacuum line, and flame-sealed under a high vacuum of 10^{-3} Pa. The tubes were then placed in computer-controlled furnaces and heated according to the heating profiles detailed below.

Ba₂GeS₄. The mixtures of BaS (2 mmol) and GeS₂ (1 mmol) were heated to 1050 °C in 30 h, left for 72 h, cooled to 600 °C at a rate of 3 °C/h, and finally cooled to room temperature by switching off the furnace. Many block-shaped crystals with yellow color were found in the ampules and stable in air. The EDS elemental analyses on single crystals of Ba₂GeS₄ confirmed the Ba/Ge/S molar ratio of 2.14:1:3.96, which is in good agreement with the stoichiometric proportions from single-crystal X-ray structural analyses (Figure S1a and Table S1a in the Electronic Supplementary Information).

Mg₂SnS₄. The mixtures of MgS (2 mmol) and SnS₂ (1 mmol) were heated to 850 °C in 30 h, left for 72 h, cooled to 400 °C at a rate of 3 °C/h, and finally cooled to room temperature by switching off the furnace. Many block-shaped crystals with red color were found in the ampules and stable in air. The EDS elemental analyses on single crystals of Mg₂SnS₄ confirmed the Mg/Sn/S molar ratio of 1.9:1.15:3.81, which is also in good agreement with the stoichiometric proportions from single-crystal X-ray structural analyses (Figure S1b and Table S1b in the Electronic Supplementary Information).

Polycrystalline sample of Mg₂SnS₄ was synthesized by solid-state reaction techniques. The mixtures of MgS and SnS₂ in the molar ratio of 2:1 were heated to 700 °C in 20 h and kept

at that temperature for 72 h, and then the furnace was turned off. On the contrary, we failed to obtain the pure powder samples of Ba_2GeS_4 after many solid-state reactions at different temperatures.

The powder X-ray diffraction (XRD) data were carried out with a Bruker D2 PHASER diffractometer equipped with a diffracted beam monochromator set for Cu Kα radiation (λ = 1.5418 Å). The diffraction pattern was taken from 10° to 70° (2θ) with a scan step width of 0.02^o and a fixed counting time of 1 s/step (Fig. 1). The experimental powder XRD pattern was found to be in agreement with the calculated one on the basis of the single crystal crystallographic data of Mg_2SnS_4.
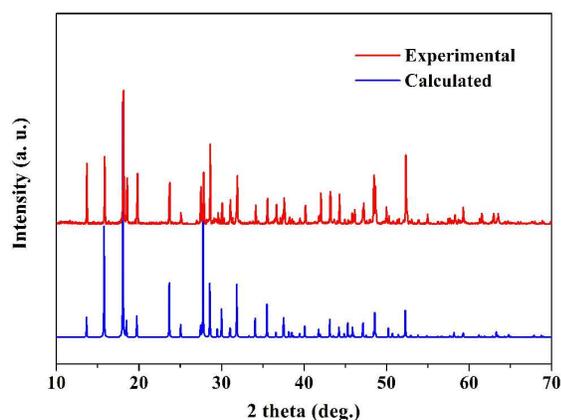

Figure 1. Experimental and calculated XRD patterns of Mg_2SnS_4. The blue curve is calculated pattern; the red one is experimental one.

Table 1 Crystal data and structure refinement for Ba_2GeS_4 and Mg_2SnS_4.

Empirical formula	Ba_2GeS_4	Mg_2SnS_4
Formula weight	475.51	295.55
Temperature	296 (2) K	296 (2) K
Crystal system	Orthorhombic	Orthorhombic
Space group	Pnma (No.62)	Pnma (No.62)
Unit cell dimensions	a = 8.983(11) Å	a = 12.967(9) Å
	b = 6.875(9) Å	b = 7.511(5) Å
	c = 12.221(16) Å	c = 6.226(4) Å
Z , V	4, 754.7(17) Å^3	4, 606.4(7) Å^3
Density (calculated)	4.185 g/cm^3	3.237 g/cm^3
Absorption coefficient	15.269 mm^{-1}	5.652 mm^{-1}
F (000)	832	552
Crystal size	0.096×0.121× 0.132 mm^3	0.076×0.199× 0.203 mm^3
Limiting indices	$-7 \leq h \leq 11$, $-8 \leq k \leq 7$, $-15 \leq l \leq 15$	$-8 \leq h \leq 16$, $-9 \leq k \leq 7$, $-8 \leq l \leq 4$
Completeness to theta = 27.28	99.2 %	99.2 %
Goodness-of-fit on F^2	1.099	1.17
Final R indices [F_o^2> $2σ(F_o^2)$][a]	R_1=0.0227 wR_2 = 0.0460	R_1= 0.0175 wR_2 = 0.0467
R indices (all data) [a]	R_1=0.0276 wR_2 = 0.0472	R_1= 0.0184 wR_2 = 0.047
Extinction coefficient	0.00047(12)	0.0100(7)
Largest diff. peak and hole	0.910 and -0.992 e Å^{-3}	0.585 and -0.968 e Å^{-3}

[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 $F_o^2 > 2σ (F_o^2)$

Single-crystal X-ray crystallography

All data were collected by SMART APEX II Single-Crystal Diffractometer using monochromatic Mo Kα radiation (λ = 0.71073 Å) at 296(2) K and integrated with the SAINT program.[28] All calculations were used with programs from the SHELXTL-97 crystallographic software package.[29] The structure was solved by direct method. All atoms were refined using full matrix least squares techniques with anisotropic thermal parameters, final least-squares refinement is on F_o^2 with data having $F_o^2 \geq 2σ (F_o^2)$. The structure was checked for missing symmetry elements by the program PLATON.[30] Crystal data and structure refinement information are presented in Table 1. Final atomic coordinates and equivalent isotropic displacement parameters of the title compounds are listed in Tables S2 (a) and (b) in the Supporting Information. Selected interatomic distances and angles are given in Tables S3 (a) and (b) in the Supporting Information.

UV–Vis-IR diffuse reflectance spectrum

Optical diffuse reflectance spectra were measured at room temperature with Shimadzu SolidSpec-3700DUV spectrophotometer. Data were collected in the wavelength range 190–2600 nm.

Infrared spectroscopy

The infrared spectrum was recorded on a Shimadzu IRAffinity-1 Fourier transform infrared spectrometer in the 400–4000 cm^{-1} range, the picked single-crystals of title compounds were mixed thoroughly with dried KBr.

Raman spectroscopy

The Raman spectrum of Mg_2SnS_4 was collected on a LABRAM HR Evolution spectrometer equipped with a CCD detector using 633 nm radiations from a diode laser. The sample was simply placed on a small glass slide and a 50 × objective lens was used to choose the area of the crystal specimens to be measured. The maximum power of 60 mW and beam diameter of 35 μm were used. The spectrum was collected using an integration time of 15 s.

Computational descriptions

To investigate a deep structure-property relationship, the electronic structures were obtained using density functional theory (DFT) based *ab initio* calculations implemented in the CASTEP package.[31] The exchange-correlation potential was calculated using Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) with the scheme.[32] The following orbital electrons were treated as valence electrons, Ba: $5s^2 5p^6 6s^2$, Mg: $2s^2 2p^6 3s^2$, Ge: $4s^2 4p^2$, Sn: $5s^2 5p^2$, S: $3s^2 3p^4$. For the purpose of achieving energy convergence, a plane-wave basis set energy cutoff was 700.0 eV within normal-conserving pseudo-potential (NCP),[33] and the Monkhorst-Pack schemewas 4 × 3 × 2 in the Brillouin Zone (BZ) of the primitive cell are chosen.[34] The refractive indices of title compounds were also calculated.[35]

Results and discussion

Crystal structure

Ba_2GeS_4. Ba_2GeS_4 crystallizes in the centrosymmetric space group Pnma of the orthorhombic system, with unit cell parameters of a =

8.983(11) Å, b = 6.875(9) Å, c =12.221(1) Å, and Z = 4. There are two crystallographically unique Ba atoms, one Ge atom, and three S atoms in the asymmetric unit. The Ba atoms have two different coordination environments. The Ba1 atom is in the nine coordination environments, which are bonded to S atoms to make up the $Ba1S_9$ polyhedra, with Ba1–S bond distances ranging from 3.120 (4) to 3.575 (4) Å, while the Ba2 atom is in the eight coordination environments, which are bonded to S atoms to make up the BaS_8 polyhedra, with Ba2–S bond distances ranging from 3.209 (4) to 3.618 (4) Å. The Ge atoms are tetrahedrally coordinated to four sulfur atoms forming isolated GeS_4 units and Ge–S bond distances range from 2.178 (2) to 2.198 (3) Å.
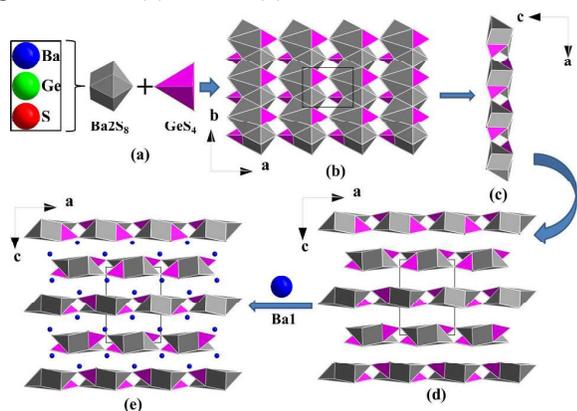

Figure 2. (a) The coordinations of $Ba2S_8$ and GeS_4; (b) a layer with corner or edges-shared $Ba2S_8$ and GeS_4 groups in the ab plane; (c) a layer with $Ba2S_8$ and GeS_4 groups in the ac plane; (d) the $Ba2S_8$ and GeS_4 layers stack along the c-axis; (e) three-dimensional framework of Ba_2GeS_4 (all the Ba1-S bonds are removed).
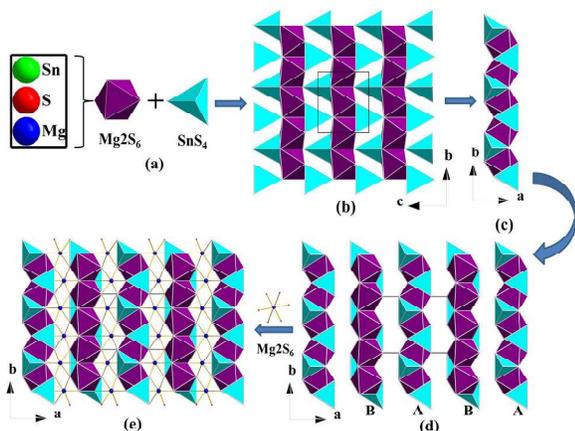

Figure 3. (a) The coordinations of $Mg2S_6$ and SnS_4; (b) a layer with corner or edges-shared $Mg2S_6$ and SnS_4 groups in the bc plane; (c) a layer with $Mg2S_6$ and SnS_4 groups in the ab plane; (d) the $Mg2S_6$ and SnS_4 layers stack along the a-axis; (e) three-dimensional framework of Mg_2SnS_4.

The crystal structure of Ba_2GeS_4 is illustrated in Figure 2. In the structure, $Ba2S_8$ polyhedra and isolated GeS_4 tetrahedra (Fig. 2a) are connected to each other by corner or edges sharing S atoms to form the layered structures which stack along the c-axis (Fig. 2d). The Ba1 cations fill in the space of these layers to balance charge and hold the layers together through coordination with S atoms, giving rise to a 3D framework (Fig. 2e). As we know, for A_2MQ_4 (A= alkali

earth metal; M= Si, Ge, Sn; Q=S, Se, Te) compounds, their structures are mainly related to the radii of A and M atoms. However, there still exist some exceptions, such as Ba_2GeQ_4 (Q= S, Se).[36] They crystallize in different space groups ($Pnma$ vs $P2_1/m$) with the same stoichiometry. As seen from their structures, there have some similarities; (i) isolated GeQ_4 (Q=S, Se) tetrahedra exist in their structures; (ii) the Ba atoms exhibit same coordination numbers of nine (Ba1) and eight (Ba2) in both compounds. However, the $Ba1Q_9$ and $Ba2Q_8$ polyhedra are a bit more distorted in Ba_2GeSe_4 than that in Ba_2GeS_4, because the largest difference between the Ba–Q bond lengths between $Ba1Se_9$ and $Ba2Se_8$ polyhedra are about 0.269 Å for Ba_2GeSe_4 and 0.041 Å for Ba_2GeS_4, thus induces a change in structure. This phenomenon is also found in other compounds, such as Ba_2SiS_4 ($Pnma$) and Ba_2SiSe_4 ($P2_1/m$).[37,38] Therefore, although the structures of A_2MQ_4 (A= alkali earth metal; M= Si, Ge, Sn; Q=S, Se, Te) compounds are mainly related to the radii of A and M atoms, the different chalcogen atoms cannot be ignored in such structure predictions. In addition, it should be noted that this phenomenon has not yet been expanded to include selenides and tellurides that Ba_2SiSe_4 was reported to be isotypic with Ba_2SiTe_4.[37]

Mg_2SnS_4. Mg_2SnS_4 crystallizes in the space group $Pnma$ of the orthorhombic system with $a = 12.967(9)$ Å, $b = 7.511(5)$ Å, and $c = 6.226(4)$ Å. There are two crystallographically unique Mg atoms, one Sn atom, and three S atoms in the asymmetric unit. Unlike Ba_2GeS_4, the Mg atoms only have one coordination environment. The Mg1 and Mg2 atoms have the six coordination environments and Mg1–S and Mg2–S bond lengths range from 2.545 (0) to 2.654 (2) and 2.552 (2) to 2.730 (1) Å, respectively. The Sn–S bond lengths range from 2.350 (6) to 2.402 (3) Å.

The crystal structure of Mg_2SnS_4 is illustrated in Fig. 3. In the structure, the $Mg2S_6$ polyhedra and isolated SnS_4 tetrahedra (Fig. 3a) are connected to each other by corner or edges sharing S atoms to form the layered structures which stack along the a-axis (Fig. 3d). There should be noted that the adjacent layers are shown inverse arrangement and these layers are stacked in ABAB··· modes. The Mg1 cations fill in the space of these layers to balance charge and hold the layers together through coordination with S atoms, giving rise to a 3D framework (Fig. 3e). Compared with the structures of Ba_2GeS_4 and Mg_2SnS_4, it can be seen that although they possess the similar isolated MS_4 (M=Ge, Sn) units, stoichiometry and 3D framework, they are not isostructural. The main reasons are as follow: (i) the arrangements of isolated MS_4 (M=Ge, Sn) units are obviously different in Ba_2GeS_4 and Mg_2SnS_4 structures, which make their a and c axes exchanged; (ii) The coordination environments of the Ba atoms and Mg atoms are also different due to their different atomic radius. Both of the above reasons are resulting in different structures.
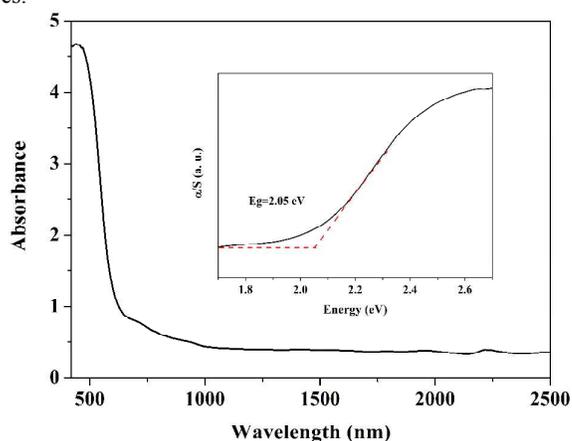

Figure 4. The diffuse reflectance spectrum for Mg_2SnS_4.

UV–Vis–NIR diffuse reflectance spectrum

The UV–Vis–NIR diffuse reflectance spectrum of Mg_2SnS_4 in the region 190–2600 nm is shown in Figure 4. Absorption (K/S) data are calculated from the Kubelkae–Munk function:[39, 40]

$$F=(1–R)^2/2R=K/S$$

where R is the reflectance, K is the absorption, and S is the scattering. Kubelka–Munk function is taken as the maxima of the absorption bands. It can be seen that its optical band gap is about 2.05 eV, respectively, consistent with red color of crystal.

Raman and IR spectra

Raman spectrum of Mg_2SnS_4 is shown in Figure 5. From the figure, it can be seen that the strong absorptions at 400, 356, 311, and 242 cm^{-1} are due to asymmetric and symmetric stretching vibrations of the Sn−S−Sn modes, in SnS_4 tetrahedral units. In addition, the absorptions below 200 cm^{-1} are probably due to Mg−S vibrations. The IR transmission spectra of Ba_2GeS_4 and Mg_2SnS_4 are shown in Figure S2 in the Electronic Supplementary Information. From the figure, we can see that there are no obvious
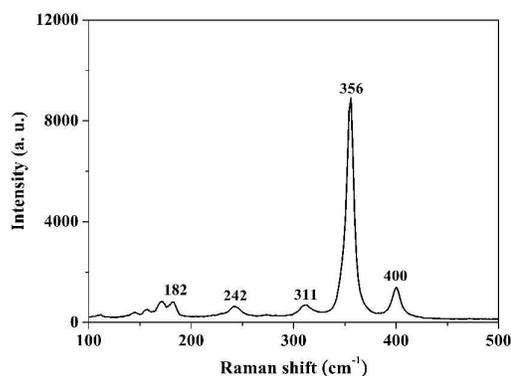

Figure 5. Raman spectrum of Mg_2SnS_4.

optical absorption peaks and the compounds exhibit a wide IR transmission range from the wavenumber 4000 cm^{-1} to 500 cm^{-1}, namely, from the near-IR up to 20 μm, which covers the important band ranges of 3−5 and 8−14 μm of the atmosphere transparent windows. The result indicates that title compounds have potential application as optical materials in the IR range.
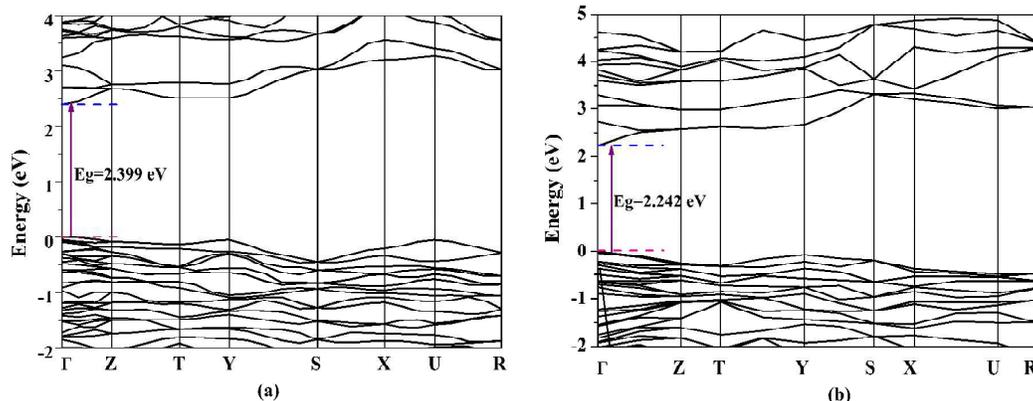

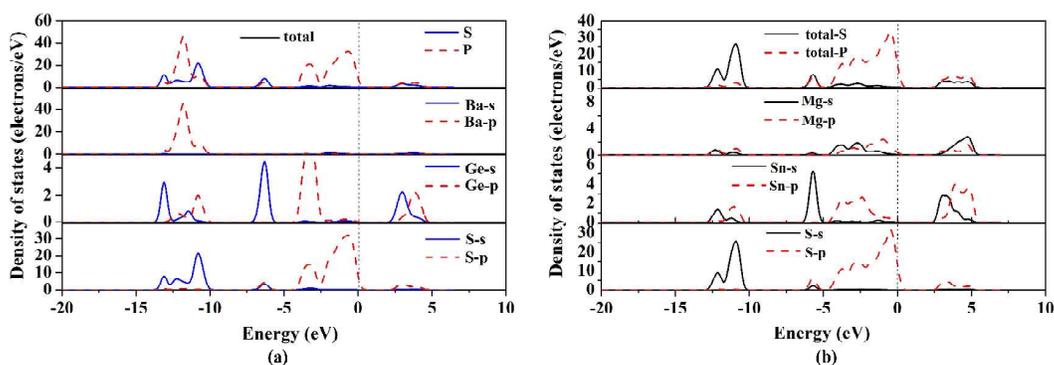Figure 6. Calculated band structures of Ba_2GeS_4 (a) and Mg_2SnS_4 (b).

Figure 7. The total and partial densities of states of Ba_2GeS_4 (a) and Mg_2SnS_4 (b).

Theoretical calculations

To gain further insights on the electronic structures and optical properties of the title compound, theoretical calculations based on DFT methods were used. The band structures of titled compounds are shown in Fig. 6. It can be seen that the top of valence band

(VB) and the bottom of conduction band (CB) are located at the same k-point (Γ), describing the direct band gaps of 2.399 eV for Ba_2GeS_4 and 2.242 eV for Mg_2SnS_4, respectively. The latter value is slightly larger than the experimental observations (2.05 eV for Mg_2SnS_4). In generally, the experimental gaps should be larger than the calculated band gap.[41,42] However, there still have some

reports giving the experimental values smaller than the calculated bandgaps owing to the inaccurately describing of the eigenvalues of the electronic states in GGA. For example, (i) the calculated bandgaps of $Ba_3AGa_5Se_{10}Cl_2$ (A = Cs, Rb, and K) are reported as 2.22, 2.21, and 2.23 eV, which are larger than the experimental values of (2.08, 2.05, and 2.04 eV);[43] (ii) as for Ba_2BiGaS_5 and Ba_2BiInS_5, their calculated band gaps are 2.41 and 1.61 eV, and also larger than the experimental values of 2.38 and 1.55 eV.[44] Therefore, we think that the calculated bandgaps are reasonable and can be accepted in this paper.

The total and partial densities of states (DOS and PDOS) are shown in Fig. 7. For Ba_2GeS_4, the VB from −15 to −10 eV are mainly composed of the Ba 5p and S 3s orbitals, which have some contribution to the Ba-S bonding. The upper of the valence states from −7 eV show a large hybridization between Ge 4s (and 4p) and S 3p orbitals, indicating very strong chemical bonds between the Ge and S atoms, but the valence band maximum is dominated by S 3p orbitals. The bottom of CB is mainly composed of the orbitals of S and Ge atoms. Accordingly, the GeS_4 units determine the energy band gap of Ba_2GeS_4. In addition, as for Mg_2SnS_4, near the top of the VB (from −5.0 to FL), there shows some obvious hybridizations between Mg 2p, Sn 5p and S 3p orbitals with a little mixture of Mg 3s and Sn 5s orbitals, revealing a few of chemical bonds between the Mg−S and Sn−S. For the CB bottom (2.242 to 10 eV), it is dominated with the orbitals of all atoms, and the S 3p and Sn 5s orbitals determine the CB minimum. Thus, as similar with Ba_2GeS_4, it can be found that the SnS_4 units determine the energy band gap of Mg_2SnS_4.

On the basis of the electronic structures, the imaginary part of dielectric function ε_2 can be calculated, and its real part is determined by the Kramers−Kronig transform, from which the refractive indices (and the birefringence Δn) were obtained.[45] Figure 8 shows the theoretical birefringences of the Ba_2GeS_4 and Mg_2SnS_4 crystals. It can be seen that both of them have relatively large birefringences (Δn) and their birefringences are about 0.08 and 0.15 as the wavelength is longer than 1 μm, respectively. As for Mg_2SnS_4, the coplanar arrangement of MgS_6 and SnS_4 units at b-c plane leads to the larger birefringence. Therefore, the Ba_2GeS_4 and Mg_2SnS_4 crystals may have good potential to be applied in optical isolator as efficient birefringent crystals, especially the Mg_2SnS_4 crystal.
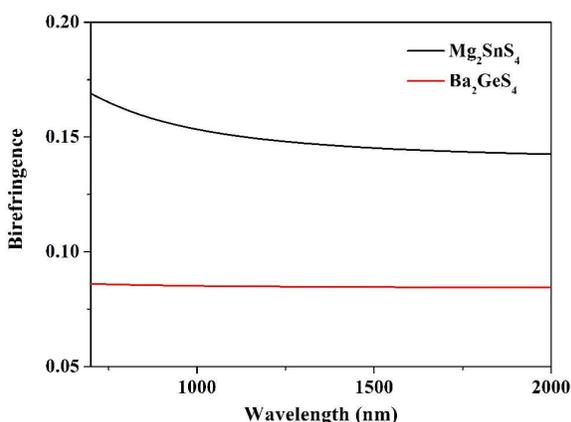

Figure 8. The birefringence curves of Ba_2GeS_4 and Mg_2SnS_4.

Conclusions

In summary, the synthesis, crystal structures, and properties of two compounds, Ba_2GeS_4 and Mg_2SnS_4, have been reported.

They crystallize in the orthorhombic space group Pnma (Z=4) with the three-dimensional framework composed of discrete MS_4 (M=Ge, Sn) tetrahedra. However, although the Ba_2GeS_4 and Mg_2SnS_4 compounds possess the same stoichiometry and similar isolated MS_4 (M=Ge, Sn) units, they are not isostructural and the main reasons as follows: (i) the arrangements of isolated MS_4 (M=Ge, Sn) units are obviously different in the Ba_2GeS_4 and Mg_2SnS_4 structures, which make their a and c axes exchanged; (ii) The coordination environments of the Ba and Mg atoms are also different due to their different atomic radius. In addition, compared with the Ba_2GeQ_4 (Q=S, Se) compounds, they crystallize in different space groups (Pnma vs $P2_1$/m), which is also found in other ternary compounds and indicates that the different chalcogen atoms cannot be ignored in structure predictions. The UV–Vis–NIR diffuse reflectance spectrum of Mg_2SnS_4 and Raman spectra of title compounds are systemically reported and shown that title compounds have wide IR transmission range. The calculated band structures and the density of states of the two compounds suggest that their indirect gaps are 2.399 eV (Ba_2GeS_4) and 2.242 eV (Mg_2SnS_4), respectively. Their birefringences simulated by the DFT method are about 0.08 and 0.15, respectively, as the wavelength is longer than 1 μm. We think that Ba_2GeS_4 and Mg_2SnS_4 may have good potential to be applied in optical isolator as efficient birefringent crystals due to their large birefringences, especially Mg_2SnS_4.

Acknowledgements

Notes and references

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† Electronic Supplementary Information (ESI) available: CCDC-number 1040642 for Ba_2GeS_4 and CCDC-number 1040643 for Mg_2SnS_4; CIF file; The EDX spectra and data, and IR spectra of Ba_2GeS_4 and Mg_2SnS_4, atomic coordinates and equivalent isotropic displacement parameters, and selected bond distances and angles tables for Ba_2GeS_4 and Mg_2SnS_4.

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