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# New quaternary sulfides in the AE-RE-Sn-S system (AE = alkaline-earth, RE = rare earth)

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ABSTRACT

In our investigation of rare earth sulfides in the AE-RE-Sn-S (AE = alkaline-earth, RE = rare earth) system, three isostructural quaternary sulfides have been obtained. These compounds adopt the $Eu_5Zr_3S_{12}$ structure type and crystallize in the *P*-62*m* space group (no. 189); the crystal data are as follows: $Sr_2Y_{2.67}Sn_3S_{12}$, $a = 11.600(7)$ Å, $c = 3.948(3)$ Å, $Z = 1$; $Ca_3La_2Sn_3S_{12}$, $a = 11.5997(6)$ Å, $c = 3.9407(4)$ Å, $Z = 1$; $Ca_3Er_2Sn_3S_{12}$, $a = 11.448(3)$ Å, $c = 3.8780(11)$ Å, $Z = 1$. Single-crystal analysis indicated that the crystal structures consist of three types of building block: $RES_7$, $AES_6$, and $SnS_6$ units. The structure of $Sr_2Y_{2.67}Sn_3S_{12}$ is characterized by the $^1_\infty[Y_3S(1)_{12/2}S(2)_3S(3)_3]$ trimer-chains along the *c* direction, which are connected into a 3-dimensional framework by the Sn atoms via S(1), S(2), and S(3), with Sr atoms filling in the channels along the *c* direction. The optical band gap of 1.45 eV for $Ca_3La_2Sn_3S_{12}$ was deduced from the diffuse reflectance spectrum.

## 1. Introduction

Research on rare earth chalcogenides has been an active area of solid state chemistry due to their rich structural chemistry and various interesting physical properties [1–5]. Although many alkaline-earth rare earth ternary chalcogenides [6–32] and a few rare earth tin ternary ones [33–40] have been reported, nothing is known so far about the AE-RE-Sn-Q (AE = alkaline-earth, RE = rare earth; Q = S, Se, Te) system. In our investigation of non-centrosymmetric rare earth sulfides in the AE-RE-Sn-S (AE = alkaline-earth, RE = rare earth) system, three quaternary sulfides have been obtained. Here we present the synthesis, crystal structure of $Sr_2Y_{2.67}Sn_3S_{12}$ and $AE_2(RE_{3-x}AE_x)Sn_3S_{12}$ (AE = Ca/La, RE = Ca/La, $x = 0$; AE = Ca, RE = Er, $x = 1$), and the experimental band gap of $Ca_3La_2Sn_3S_{12}$.

## 2. Experimental

### 2.1. Synthesis

All starting materials were used as received: CaS (99.5%, Alfa), SrS (99.9%, Alfa), $La_2S_3$ (99.5%, Alfa), $Er_2S_3$ (99.5%, Alfa), $SnS_2$ (99.5%, Alfa), Sn (99.999%, Sinopharm Chemical Reagent Co., SCRC), S (99.999%, SCRC), Y (99.5%, Jin-Rui Rare Earth Co.), La (99.5%, Jin-Rui Rare Earth Co.), and KBr (99.9%, SCRC).

Single crystals were obtained via a precursors/flux method. Appropriate starting materials were mixed together and ground thoroughly within a nitrogen-filled glovebox, pressed into pellets, and then sealed in evacuated fused silica ampoules. The ampoules were then put in resistance furnaces and heated slowly to 950–1000 °C, kept at this temperature for 100–316 h (for details, see Table 1) with one intermediate grinding and re-pressing of the materials. The products obtained from this procedure were mixed with fluxes (for details, see Table 2). Upon regrinding, and resealing, the precursor/flux mixtures were heated at 850–900 °C for 200–240 h, then slowly cooled to 550–600 °C, and finally to room temperature by switching off the furnace powers. Black crystals of $Sr_2Y_{2.67}Sn_3S_{12}$ and $Ca_3Er_2Sn_3S_{12}$ as minor phases and $Ca_3La_2Sn_3S_{12}$ as major product were isolated manually from the residues after the fluxes were removed by washing with distilled water. These compounds are stable in air.

### 2.2. X-ray crystallography

#### 2.2.1. Single crystal diffraction

Single crystals were mounted on glass fibers for X-ray diffraction analysis. All measurements were performed on diffractometers equipped with a graphite-monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å) at 293 K. For measurements performed on a Rigaku Scxmini CCD or a Rigaku Mercury2 CCD diffractometer, intensity data were collected in the range of $2.00 < \theta < 30.00°$ with an $\omega$ scan mode and reduced by software CrystalClear [41]. For measurements performed on a Rigaku AFC7R diffractometer, intensity data were collected in the range of $2.00 < \theta < 30.00°$ with an $\omega$-2$\theta$ scan mode and corrected for Lorentz-polarization as well as for empirical absorption by the $\psi$-scan technique, the collected intensity data were reduced by CrystalStructure [42].

The structures were solved by direct methods with program SHELXS-97 [43] and refined by full-matrix least-squares techniques using program SHELXL-97 [44] in the WinGX system [45]. The final structures were examined for additional symmetry with ADDSYM/PLATON [46]. No change of space group was suggested.

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**Table 1**
Reaction conditions for targets.

| Starting materials (mmol) | Reaction temperature × time (precursor preparation) | Target |
|---|---|---|
| Y:SrS:Sn:S<br>0.200:0.300:0.300:0.901 | 1000 °C × 120 h | “$Ca_3Y_2Sn_3S_{12}$” (a) |
| La:CaS:Sn:S<br>0.100:0.150:0.150:0.452 | 1000 °C × 120 h | “$Ca_3La_2Sn_3S_{12}$” (b) |
| $La_2S_3$:CaS:Sn:S<br>0.100:0.200:0.300:0.605 | 1000 °C × 110 h | “$Ca_3La_2Sn_3S_{12}$” (c) |
| $Er_2S_3$:CaS:$SnS_2$<br>0.354:0.531:0.708 | 1000 °C × 316 h | “$Ca_3Er_4Sn_4S_{17}$” (d) |
| $Er_2S_3$:CaS:Sn:S<br>0.710:1.070:1.420:2.844 | 950 °C × 120 h | “$Ca_3Er_4Sn_4S_{17}$” (e) |

Additional crystallographic details are given in Table 3, the positional coordinates and isotropic equivalent thermal parameters are listed in Table 4, and the bond distances are given in Table 5 .

Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-423505 for $Sr_2Y_{2.67}Sn_3S_{12}$, CSD-423506 for $Ca_3La_2Sn_3S_{12}$, CSD-423507 for $Ca_3Er_2Sn_3S_{12}$.

### 2.2.2. X-ray powder diffraction

The powder diffraction pattern $Ca_3La_2Sn_3S_{12}$ was recorded on a PANalytical X'Pert Pro diffractometer at 40 kV and 40 mA, using germanium-monochromatized Cu-Kα radiation (λ = 1.54057 Å). The observed powder pattern was in good agreement with that simulated pattern based on the single-crystal structure refinement (Fig. 1).

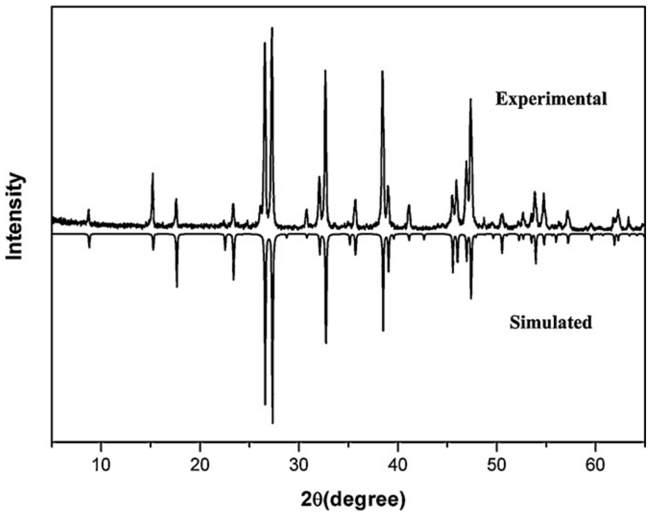

**Fig. 1.** X-ray diffraction pattern of $Ca_3La_2Sn_3S_{12}$.

### 2.3. EDX analyses

Semi-quantitative energy dispersive analysis by X-ray (EDX) were performed with an EDX-equipped Hitachi S-3500 SEM spectrometer on many selected crystals, as well as some crystals which had been measured by X-ray single diffraction. The measurements confirmed the presence of AE (AE = Ca, Sr), RE (RE = La, Er, Y), Sn, and S.

**Table 2**
Crystal growth conditions and unit cells (in the hexagonal system) for $Sr_2Y_{2.67}Sn_3S_{12}$, $Ca_3La_2Sn_3S_{12}$, and $Ca_3Er_2Sn_3S_{12}$.

| Precursor | Flux | Heating profile | Crystal | Unit cell | | Compound |
|---|---|---|---|---|---|---|
| | | | | a (Å) | c (Å) | |
| “$Ca_3Y_2Sn_3S_{12}$”<br>(a)<br>0.336 g | KBr<br>2.460 g | 30–600 °C/9 h<br>600–600 °C/15 h<br>600–850 °C/4.5 h<br>850–850 °C/120 h<br>850–700 °C/50 h<br>700–860 °C/3 h<br>860–560 °C/150 h<br>Power switched off | **1** | 11.6001(67) | 3.9480(30) | $Sr_2Y_{2.67}Sn_3S_{12}$ |
| “$Ca_3La_2Sn_3S_{12}$”<br>(b)<br>0.298 g | KBr<br>2.920 g | 60–900 °C/60 h<br>900–900 °C/240 h<br>900–630 °C/90 h<br>630–360 °C/90 h<br>Power switched off | **2** | 11.6060(16) | 3.9474(8) | $Ca_3La_2Sn_3S_{12}$ |
| | | | **3** | 11.5988(7) | 3.9414(4) | $Ca_3La_2Sn_3S_{12}$ |
| | | | **4** | 11.5997(6) | 3.9407(4) | $Ca_3La_2Sn_3S_{12}$ |
| “$Ca_3La_2Sn_3S_{12}$”<br>(c)<br>0.880 g | KBr<br>2.148 g | 30–600 °C/9 h<br>600–600 °C/15 h<br>600–850 °C/4.5 h<br>850–850 °C/120 h<br>850–700 °C/50 h<br>700–860 °C/3 h<br>860–560 °C/150 h<br>Power switched off | **5** | 11.5878(8) | 3.9487(6) | $Ca_3La_2Sn_3S_{12}$ |
| | | | **6** | 11.5954(19) | 3.9480(8) | $Ca_3La_2Sn_3S_{12}$ |
| | | | **7** | 11.5905(7) | 3.9354(4) | $Ca_3La_2Sn_3S_{12}$ |
| “$Ca_3Er_4Sn_4S_{17}$”<br>(d)<br>0.256 g | CaS<br>0.004 g + KBr<br>2.208 g | 30–850 °C/20 h<br>850–850 °C/216 h<br>850–700 °C/45 h<br>700–860 °C/0.5 h<br>860–600 °C/144 h<br>600–600 °C/15 h<br>Power switched off | **8** | 11.4651(11) | 3.8675(8) | $Ca_3Er_2Sn_3S_{12}$ |
| “$Ca_3Er_4Sn_4S_{17}$”<br>(e)<br>0.324 g | CaS<br>0.007 g + KBr<br>1.872 g | 30–600 °C/20 h<br>600–600 °C/15 h<br>600–850 °C/4.5 h<br>850–850 °C/240 h<br>850–700 °C/50 h<br>700–860 °C/3 h<br>860–560 °C/150 h<br>Power switched off | **9** | 11.448(3) | 3.8780(11) | $Ca_3Er_2Sn_3S_{12}$ |

**Table 3**
Experimental details for $Sr_2Y_{2.67}Sn_3S_{12}$ **1**, $Ca_3La_2Sn_3S_{12}$ **4**, and $Ca_3Er_2Sn_3S_{12}$ **9**.

| Empirical formula | $Sr_2Y_{2.67}Sn_3S_{12}$ **1** | $Ca_3La_2Sn_3S_{12}$ **4** | $Ca_3Er_2Sn_3S_{12}$ **9** |
|---|---|---|---|
| $F_w$ | 1153.42 | 1138.85 | 1205.26 |
| Crystal color and shape | Black, column | Black, column | Black, needle |
| Crystal size (mm) | 0.2 × 0.2 × 0.2 | 0.2 × 0.2 × 0.2 | 0.30 × 0.05 × 0.04 |
| Diffractometer | Rigaku Scxmini CCD | Rigaku Mercury2 CCD | Rigaku AFC7R |
| Crystal system/space group | Hexagonal/$P$-62$m$ | Hexagonal/$P$-62$m$ | Hexagonal/$P$-62$m$ |
| $a$ (Å) | 11.600(7) | 11.5997(6) | 11.448(3) |
| $c$ (Å) | 3.948(3) | 3.9407(4) | 3.8780(11) |
| $V$ (Å$^3$), $Z$ | 460.1(5), 1 | 459.20(6), 1 | 440.2(2), 1 |
| $D_c$ (g/cm$^3$) | 4.163 | 4.118 | 4.510 |
| $\mu$ (Mo-K$\alpha$) (mm$^{-1}$) | 19.409 | 10.754 | 15.900 |
| $\theta$ range (°) | 2.03–27.46 | 3.51–27.47 | 2.05–29.98 |
| Reflections collected/unique/$R_{int}$ | 3667/435/0.0405 | 3426/431/0.0410 | 796/518/0.0928 |
| Data/restraints/parameters | 435/0/26 | 431/2/30 | 518/0/26 |
| $GOOF$ on $F^2$ | 1.162 | 1.126 | 1.042 |
| Final $R$ indices[a] ($I > 2\sigma(I)$) | $R_1 = 0.0341$, $wR_2 = 0.0802$ | $R_1 = 0.0367$, $wR_2 = 0.0984$ | $R_1 = 0.0402$, wR2 = 0.0990 |
| $R$ indices (all data) | $R_1 = 0.0388$, $wR_2 = 0.0865$ | $R_1 = 0.0378$, $wR_2 = 0.0992$ | $R_1 = 0.0444$, $wR_2 = 0.1012$ |
| Extinction efficient | 0.0113(15) | 0.0017(10) | 0.0057(11) |
| Flack $x$ | 0.01(3) | 0.00(9) | −0.02(4) |
| Largest diff. peak/hole (e/Å$^3$) | 2.617/−0.852 | 2.473/−1.360 | 1.727/−1.925 |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = (\Sigma(w(F_o{}^2| - F_c{}^2)^2)/\Sigma(w(F_o{}^2)^2))^{1/2}$.

**Table 4**
Positional and thermal parameters with ESD for $Sr_2Y_{2.67}Sn_3S_{12}$ **1**, $Ca_3La_2Sn_3S_{12}$ **4**, and $Ca_3Er_2Sn_3S_{12}$ **9**.

| Atom | Wyckoff site | Site occupancy | $x$ | $y$ | $z$ | Ueq (Å$^2$) |
|---|---|---|---|---|---|---|
| $Sr_2Y_{2.67}Sn_3S_{12}$ **1** | | | | | | |
| Y | 3$f$ | 0.89[a] | 0.2767(2) | 0 | 0 | 0.020(1) |
| Sr | 2$c$ | 1 | 1/3 | 2/3 | 0 | 0.019(1) |
| Sn | 3$g$ | 1 | 0.6695(2) | 0 | 1/2 | 0.018(1) |
| S(1) | 6$k$ | 1 | 0.5611(3) | 0.7504(3) | 1/2 | 0.019(1) |
| S(2) | 3$f$ | 1 | 0.5274(4) | 0 | 0 | 0.019(1) |
| S(3) | 3$f$ | 1 | 0.8234(6) | 0 | 0 | 0.039(2) |
| $Ca_3La_2Sn_3S_{12}$ **4** | | | | | | |
| Ca(1)/La(1) | 3$f$ | 0.71(1)/0.29(1) | 0.2752(2) | 0 | 0 | 0.026(1) |
| Ca(2)/La(2) | 2$c$ | 0.16(2)/0.84(2) | 1/3 | 2/3 | 0 | 0.015(1) |
| Sn | 3$g$ | 1 | 0.6691(1) | 0 | 1/2 | 0.020(1) |
| S(1) | 6$k$ | 1 | 0.5504(3) | 0.7483(3) | 1/2 | 0.014(1) |
| S(2) | 3$f$ | 1 | 0.5275(4) | 0 | 0 | 0.023(1) |
| S(3) | 3$f$ | 1 | 0.8194(6) | 0 | 0 | 0.038(1) |
| $Ca_3Er_2Sn_3S_{12}$ **9** | | | | | | |
| Er/Ca(1) | 3$f$ | 0.67/0.33[a] | 0.2841(1) | 0 | 0 | 0.013(1) |
| Ca(2) | 2$c$ | 1 | 1/3 | 2/3 | 0 | 0.012(1) |
| Sn | 3 g | 1 | 0. 6709(1) | 0 | 1/2 | 0.015(1) |
| S(1) | 6$k$ | 1 | 0. 5568(4) | 0.7474(4) | 1/2 | 0.013(1) |
| S(2) | 3$f$ | 1 | 0. 5271(5) | 0 | 0 | 0.022(1) |
| S(3) | 3$f$ | 1 | 0. 8252(5) | 0 | 0 | 0.023(1) |

[a] Fixed.

### 2.4. UV–vis diffuse reflectance spectroscopy

The optical diffuse reflectance spectrum of powdered $Ca_3La_2Sn_3S_{12}$ sample was measured at room temperature using a Perkin-Elmer Lambda 900 UV–vis spectrophotometer equipped with an integrating sphere attachment and $BaSO_4$ as reference. The absorption spectrum was calculated from the reflection spectrum via the Kubelka–Munk function: $\alpha/S = (1-R)^2/2R$, in which $\alpha$ is the absorption coefficient, $S$ is the scattering coefficient, and $R$ is the reflectance [47].

## 3. Results and discussion

### 3.1. Structure determination

The structures of $Sr_2Y_{2.67}Sn_3S_{12}$, $(Ca/La)_2(Ca/La)_3Sn_3S_{12}$, and $Ca_2(Er_2Ca)Sn_3S_{12}$ were solved by direct methods and difference Fourier synthesis. The structure refinements showed that the Y

**Table 5**
Bond lengths (Å) for $Sr_2Y_{2.67}Sn_3S_{12}$ **1**, $Ca_3La_2Sn_3S_{12}$ **4**, and $Ca_3Er_2Sn_3S_{12}$ **9**.

| Polyhedron | Bond | $Sr_2Y_{2.67}Sn_3S_{12}$ **1** | $Ca_3La_2Sn_3S_{12}$ **4** | $Ca_3Er_2Sn_3S_{12}$ **9** |
|---|---|---|---|---|
| $RES_7$ | RE-S(3) (×2) | 2.815(3) | 2.809(2) | 2.8414(14) |
| | RE-S(1) (×4) | 2.851(3) | 2.932(2) | 2.804(3) |
| | RE-S(2) (×1) | 2.908(6) | 2.927(5) | 2.782(6) |
| $SnS_6$ | Sn-S(1) (×2) | 2.515(3) | 2.530(3) | 2.508(4) |
| | Sn-S(2) (×2) | 2.572(4) | 2.565(3) | 2.544(4) |
| | Sn-S(3) (×2) | 2.662(5) | 2.631(4) | 2.623(4) |
| $AES_{6+3}$ | AE-S(1) (×6) | 3.042(3) | 2.956(2) | 2.965(3) |
| | AE-S(2) (×3) | 3.364(2) | 3.3638(5) | 3.3193(10) |

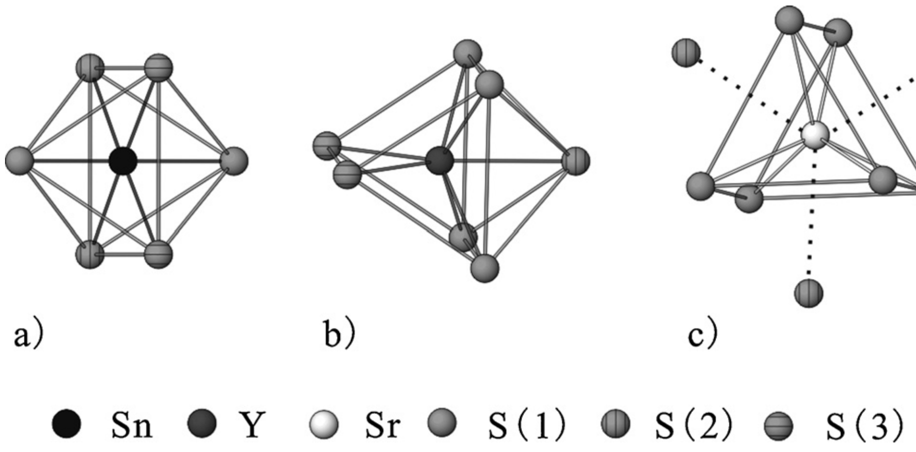

**Fig. 2.** Coordination geometry of $SnS_6$, $YS_7$, and $SrS_{6+3}$.

atom occupies the 3*f* sites only, the Sr atom the 2*c* sites for crystal **1**. The refined occupancy of Y at the 3*f* site indicated the $Sr_2Y_{2.87(27)}Sn_3S_{12}$ formula for crystal **1**, the site occupancy was then fixed at 0.89 for the charge/occupancy balance. The structure refinements showed mixed Ca/La occupations on both the 3*f* and 2*c* positions for crystal **2**, **3**, **4**, **5**, **6**, and **7**, because of the size similarity of $Ca^{2+}$ to $La^{3+}$ [48]. The formula $(Ca/La)_2{}^{2c}(Ca/La)_3{}^{3f}Sn_3S_{12}$ can be rounded off as $Ca_3La_2Sn_3S_{12}$ according to charge neutrality. For crystal **8** and **9**, the structure refinements showed that the 2*c* positions were occupied by the Ca atoms only, while the 3*f* sites by both Er and Ca atoms. The formula $Ca_2{}^{2c}(Er_2Ca)^{3f}Sn_3S_{12}$ (=$Ca_3Er_2Sn_3S_{12}$) can be deduced for the charge/occupancy balance for crystals **8** and **9**.

### 3.2. Structure description

$Sr_2Y_{2.67}Sn_3S_{12}$ **1**, $Ca_3La_2Sn_3S_{12}$ **4**, and $Ca_3Er_2Sn_3S_{12}$ **9** are isotypic with $Eu_5Zr_3S_{12}$ [49]. $Sr_2Y_{2.67}Sn_3S_{12}$ **1**, $Ca_3La_2Sn_3S_{12}$ **4**, and $Ca_3Er_2Sn_3S_{12}$ **9** each contains three types of building blocks in their structures: octahedral $SnS_6$, mono-capped trigonal prismatic $RES_7$ (RE = Y, Ca/La, Er/Ca), and trigonal prismatic $AES_6$ (AE = Sr, Ca/La, Ca). The Sn atom is coordinated by 2 × S(1), 2 × S(2) and 2 × S(3) atoms in a octahedral geometry (Fig. 2a); the Y atom is surrounded by 7 S (4 × S(1), 1 × S(2), and 2 × S(3)) atoms forming a mono-capped trigonal prism (Fig. 2b). The Sr atom is coordinated to form a trigonal prism by 6 × S(1) atoms, or is in a three-capped prismatic geometry if three distant S(2) atoms (at 3.364(2) Å) are included (Fig. 2c). The $SnS_6$ octahedra are condensed into a edge-sharing $^{1}_{\infty}[SnS(1)_2S(2)_{2/2}S(3)_{2/2}]$ chain along the *c* axis (Fig. 3a), while the $YS_7$ prisms each share opposite [S(1)-S(1)] edges along the *c* direction forming $^{1}_{\infty}[YS(1)_{4/2}S(2)S(3)_2]$ chains (Fig. 3b). Every three neighboring $^{1}_{\infty}[YS(1)_{4/2}S(2)S(3)_2]$ chains are inter-connected by edge-sharing (S(3)-S(3)-S(3)-S(3)) forming one $^{1}_{\infty}[Y_3S(1)_{12/2}S(2)_3S(3)_3]$ trimer-chain; these trimer-chains are further connected into a 3-dimensional framework by the Sn atoms via S(1), S(2), and S(3), with Sr atoms filling in the channels along the *c* direction (Fig. 4).

For octahedrally coordinated Sn atoms, all the Sn-S distances in $Sr_2Y_{2.67}Sn_3S_{12}$ **1** [2.515(3) – 2.662(5) Å], $Ca_3La_2Sn_3S_{12}$ **4** [2.530(3) – 2.631(4) Å], and $Ca_3Er_2Sn_3S_{12}$ **9** [2.508(4) – 2.623(4) Å] are in good agreement with those (2.510–2.720 Å) in $Na_2SnS_3$ [50]. For 7-coordinated Y, (Ca/La), and (Er/Ca) atoms, the Y-S distances varying from 2.676(3) to 2.813(5) Å, are consistent with those (2.655–2.894 Å) in $Pb_3Y_2Sn_3S_{12}$ [51]; the (Ca/La)-S distances range from 2.809(2) to 2.932(2) Å, comparable with those La-S distances in $LaTmS_3$ (2.885–3.051 Å) [52] and in $LaYbS_3$ (2.892–3.062 Å) [52]; the (Er/Ca)-S distances (2.782(6) – 2.8414(14) Å) fall in the range of 2.664(2) – 3.010(2) Å in $Er_3Ge_{0.330(10)}GeS_7$ [53]. For 6-coordinated Sr, (Ca/La), and Ca atoms, the Sr-S contact of 3.042(3) Å in $Sr_2Y_{2.67}Sn_3S_{12}$ **1** is very near the sum of ionic radii (3.02 Å) [48]; the (Ca/La)-S distance of 2.956(2) Å in $Ca_3La_2Sn_3S_{12}$ **4** and the Ca-S distance of 2.965(3) Å in $Ca_3Er_2Sn_3S_{12}$ **9**, are slightly longer than that (Ca/Eu)-S (2.92 Å) in $CaEuS_2$ [11,12].

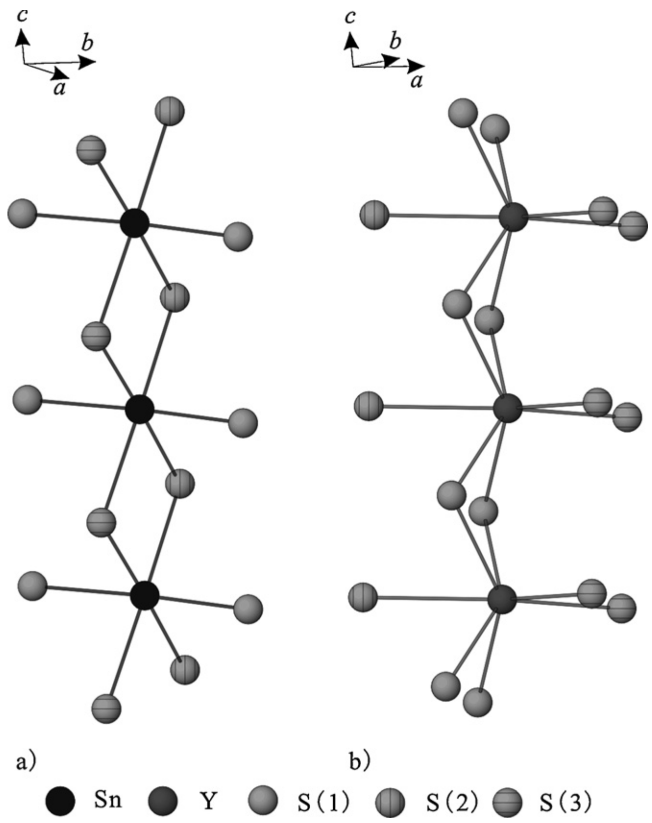

**Fig. 3.** The $^{1}_{\infty}[SnS(1)_2S(2)_{2/2}S(3)_{2/2}]$ chain, and the $^{1}_{\infty}[YS(1)_{4/2}S(2)S(3)_2]$ chain.

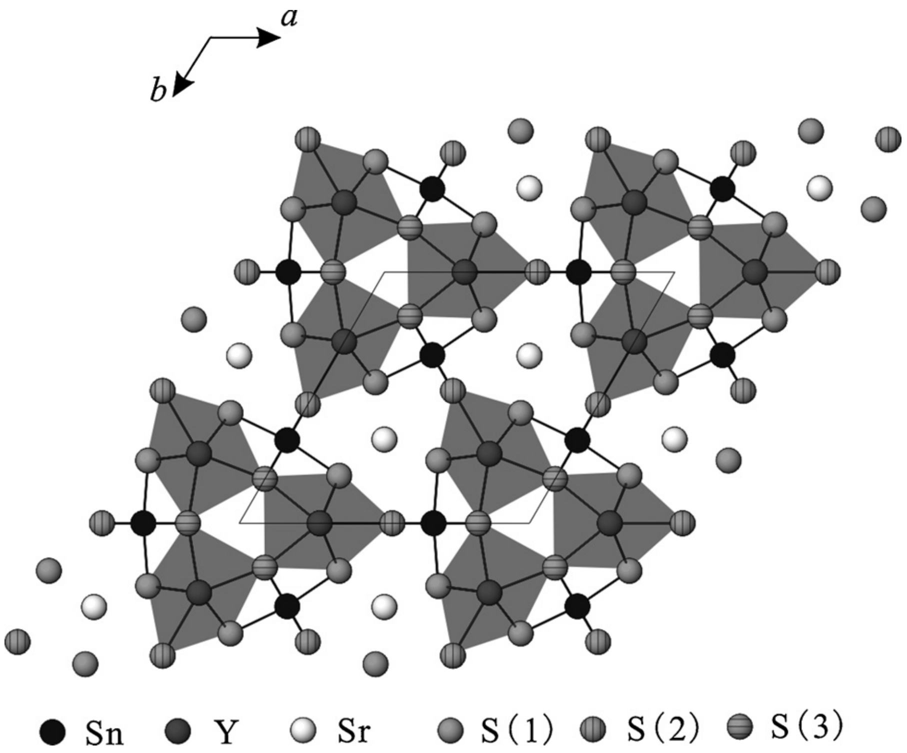

**Fig. 4.** View of $Sr_2Y_{2.67}Sn_3S_{12}$ along the *c* direction.

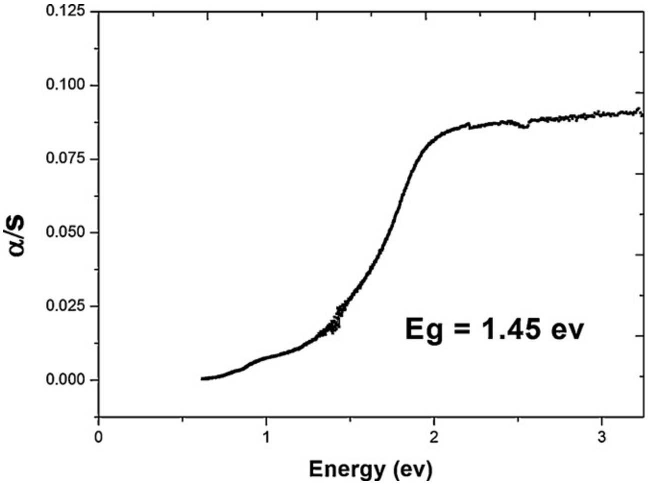

**Fig. 5.** Optical absorption spectrum of $Ca_3La_2Sn_3S_{12}$ transformed from diffuse reflectance data.

### 3.3. *Experimental band gap of $Ca_3La_2Sn_3S_{12}$*

A band gap of 1.45 eV was deduced from the diffuse reflectance spectrum of $Ca_3La_2Sn_3S_{12}$ (Fig. 5).

## 4. Conclusions

Three new quaternary sulfides, $Sr_2Y_{2.67}Sn_3S_{12}$, $Ca_3La_2Sn_3S_{12}$, and $Ca_3Er_2Sn_3S_{12}$, have been synthesized in the AE-RE-Sn-S (AE = alkaline-earth, RE = rare earth) system for the first time. They crystallize in the *P*-62*m* space group (no. 189) and are isostructural with $Eu_5Zr_3S_{12}$. The optical band gap was determined to be 1.45 eV for $Ca_3La_2Sn_3S_{12}$ with the use of the diffuse reflectance spectrum measurement.

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