



Syntheses, crystal and electronic structure of a series of quaternary rare-earth sulfides $MgRE_6Si_2S_{14}$ ($RE = Y, Ce, Pr, Nd$ and Sm)



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ABSTRACT

Five isostructural quaternary rare-earth sulfide $MgRE_6Si_2S_{14}$ ($RE = Y, Ce, Pr, Nd$ and Sm) have been successfully synthesized via high-temperature solid-state method. They crystallize in the hexagonal space group $P6_3$ and belong to the $MnLa_6Si_2S_{14}$ structure type. Their 3-D structures are constructed by the connection between infinite 1-D $[(RE_6S_6)^{6+}]_{\infty}$ tubular and $(SiS_4)^{4-}$ tetrahedron, and Mg^{2+} ions occupy the octahedral interspaces in the $[(RE_6S_6)^{6+}]_{\infty}$ tubular. The lanthanide contraction phenomenon among these compounds is also discussed. Electronic structure calculation indicates that $MgY_6Si_2S_{14}$ has an indirect optical energy gap of 2.26 eV, and its optical absorption is mainly ascribed to the charge transition from S-3p to Y-4d states.

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1. Introduction

Recently, metal chalcogenides (*MCh*) are being investigated extensively because they have wide applications in the fields of photocatalysis [1–3] solar cells [4,5], lithium ion batteries [6–8], second-order (SO) nonlinear optics (NLO) [9–11], γ -ray detection [12] and thermoelectrics [13]. For compounds with non-centrosymmetric (NCS) structures, they are potential SO NLO [9–11] and ferroelectric materials [14]. *MCh* with NCS structures are extensively studied as SO NLO materials because of their wide transparent window in the middle- and far-infrared (IR) region, which is one of the hottest topics on photoelectric materials because of the lack of available IR SO NLO materials. Until now, there are many *MCh* have been reported with good SO NLO behaviors, either possessing high second-harmonic generation (SHG) intensities or high anti-laser damage thresholds, such as $ZnY_6Si_2S_{14}$ [10], Li_2CdGeS_4 [15], $BaGa_4S_7$ [16], $Na_2In_2MS_6$ ($M = Si, Ge$) [17], $BaGeOSe_2$ [18], $La_3Ga_{0.5}(Ge_{0.5}/Ga_{0.5})S_7$ [11], $ACsP_2Se_8$ ($A = K, Rb, Cs$) [19], $Ba_{23}Ga_8Sb_2S_{38}$ [20], $AX^{II}_4X^{III}_5Se_{12}$ ($A = K^+ - Cs^+$; $X^{II} = Mn^{2+}, Cd^{2+}$; $X^{III} = Ga^{3+}, In^{3+}$) [21] and $K_{1-x}Cs_xPSe_6$ [22]. Among these NCS *MCh*, $ZnY_6Si_2S_{14}$ [10] and $La_3Ga_{0.5}(Ge_{0.5}/Ga_{0.5})S_7$ [11] are isostructural with the $MnLa_6Si_2S_{14}$ structure type and have high SHG

intensities. Chen et al. concluded that half-occupation of A site or fully-occupation of B site should have strong SHG intensities, and all the reported ARE_3EQ_7 or $BRE_6E_2Q_{14}$ (A : coin- or alkali-metal; B : divalent main- or transition-metal; RE : rare-earth metal; E : Si, Ge and Sn; Q : S and Se) compounds being SHG-active with strong SHG intensities supports this conclusion [11].

Until now, there are more than one hundred of $MnLa_6Si_2S_{14}$ structure type *MCh* have been reported with the formula ARE_3EQ_7 or $BRE_6E_2Q_{14}$, which shows versatile chemical compositions and rich physical properties. Combining their rich structure chemistry and potentially being SO NLO materials, it is interesting to synthesize more $BRE_6E_2Q_{14}$ (or $B_{0.5}RE_3EQ_7$) compounds and explore their SO NLO properties.

Recently, our work has been devoted to discover *MCh* with novel crystal structures and potential applications in the fields of optical, magnetic and electric properties, such as SO NLO [9–11], photocatalytic [1–3] and magnetic properties [23], and voltage-dependent effect [10]. The discovery of SHG-active $ZnY_6Si_2S_{14}$ [10], $La_3Ga_{0.5}(Ge_{0.5}/Ga_{0.5})S_7$ and $La_3In_{0.5}(Ge_{0.5}/In_{0.5})S_7$ [11] push us to look for more $BRE_6E_2Q_{14}$ compounds. Luckily, a series of such compounds with the formula $MgRE_6Si_2S_{14}$ ($RE = Y, Ce, Pr, Nd$ and Sm) was obtained by us recently. Herein, we report the syntheses and crystal structures of $MgY_6Si_2S_{14}$ (1), $MgCe_6Si_2S_{14}$ (2), $MgPr_6Si_2S_{14}$ (3), $MgNd_6Si_2S_{14}$ (4) and $MgSm_6Si_2S_{14}$ (5). The lanthanide contraction among these compounds and electronic structure of 1 are also discussed.

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2. Experimental section

2.1. Synthesis and analyses

All starting materials were used as received without further purification. Single crystals of the title compounds (except for **3**) were obtained by solid-state reaction with KI as flux. The starting materials are RE_2O_3 ($RE = Y, Nd$ and $Sm, 99.9\%$), CeO_2 (99.9%), S (99.999%), Mg (99%), Si (99.99%) and boron powder (99%). Each sample has a total mass of 500 mg and 400 mg KI (99%) additional, and the molar ratios of elements $RE: S: Mg: Si$ are 6: 14: 1: 2. The mixtures of starting materials were ground into fine powders in an agate mortar and pressed into pellets, followed by being loaded into quartz tubes. The tubes were evacuated to be 1×10^{-4} torr and flame-sealed. The samples were placed into a muffle furnace, heated from the room temperature to 573 K in 5 h and equilibrated for 10 h, followed by heating to 923 K in 5 h and equilibrated for 10 h, then heated to 1223 K in 5 h and maintained for 7 days, finally cooled down to 573 K in 5 days and powered off. The single crystals of **1, 2, 4** and **5** stable in moisture and air were obtained. Using the same synthetic method, only powder sample of **3** can be obtained. Semiquantitative microscope element analysis on the as-prepared samples was performed on a field-emission scanning electron microscope (FESEM, Zeiss Supra55) equipped with an energy dispersive X-ray spectroscope (EDS, Bruker, Quantax), which confirmed the presence of $RE, S, Si,$ and Mg with the approximate composition of $MgRE_6Si_2S_{14}$, and no other elements were detected. The exact compositions were established from the X-ray structure determinations.

2.2. Structure determination

The intensity data of **1, 2, 4** and **5** were collected on Bruker D8 QUEST X-ray diffractometer with graphite-monochromated $Mo-K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Their structures were solved by Direct Method and refined by full-matrix least-squares techniques on F^2 with anisotropic thermal parameters for all atoms. All the calculations were performed with SHELXTL-97 package of crystallographic software [24]. The final refinement included anisotropic displacement parameters for all atoms and a secondary extinction correction. The crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, and bond lengths are listed in Tables 1–3, respectively. The powder sample of **3** was characterized

Table 1

Crystal data and structure refinement parameters of the $MgRE_6Si_2S_{14}$ ($RE = Y, Ce, Nd$ and Sm) compounds.

Chemical formula	$MgY_6Si_2S_{14}$ (1)	$MgCe_6Si_2S_{14}$ (2)	$MgNd_6Si_2S_{14}$ (4)	$MgSm_6Si_2S_{14}$ (5)
Fw	1062.79	1370.05	1394.77	1431.43
T (K)	296			
Crystal system	Hexagonal			
Space group	$P6_3$			
Z	1			
a (Å)	9.840(5)	10.287(3)	10.120(1)	10.035(1)
c (Å)	5.619(3)	5.698(4)	5.675(1)	5.647(1)
V (Å ³)	471.2(4)	522.2(4)	503.3(1)	492.5(1)
D_{calcd} (g cm ⁻³)	3.745	4.356	4.602	4.826
μ (mm ⁻¹)	19.955	14.330	16.776	19.215
$F(000)$	498	612	624	636
θ range (°)	4.14 to 25.49	3.96 to 25.44	2.32 to 25.48	2.34 to 27.44
Measd. reflns	2157	1981	3770	4357
Indep. reflns/ R_{int}	528/0.0391	651/0.0216	628/0.0271	750/0.0398
$R1, wR2$ ($I > 2\sigma(I)$) ^a	0.0189/0.0396	0.0144/0.0355	0.0092/0.0198	0.0135, 0.0313
$R1, wR2$ (all data) ^a	0.0198/0.0398	0.0144/0.0355	0.0092/0.0198	0.0140, 0.0314
GOF on F^2	0.901	1.135	0.949	1.145
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$, e/Å ³	0.441/−0.426	0.573/−0.729	0.391/−0.400	0.808/−1.107

^a $R1 = \|F_o\| - \|F_c\|/\|F_o\|$; $wR2 = [w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]^{1/2}$.

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (U_{eq} , Å² $\times 10^3$) of the $MgRE_6Si_2S_{14}$ ($RE = Y, Ce, Nd$ and Sm) compounds.

Atom	x	y	z	$U_{\text{eq}}/\text{Å}^2$
MgY₆Si₂S₁₄ (1)				
Y(1)	3583(1)	1285(1)	4045(1)	7(1)
Si(1)	3333	−3333	3175(4)	6(1)
Mg(1)	0	0	6793(12)	6(1)
S(1)	4156(1)	−1061(1)	1687(2)	7(1)
S(2)	913(1)	−1600(1)	4304(2)	8(1)
S(3)	6667	3333	1891(4)	7(1)
MgCe₆Si₂S₁₄ (2)				
Ce(1)	1229(1)	3579(1)	6863(1)	8(1)
Si(1)	3333	6667	12710(4)	7(1)
Mg(1)	0	0	4250(16)	9(2)
S(1)	3333	6667	9052(4)	11(1)
S(2)	4095(1)	5239(1)	14123(2)	9(1)
S(3)	−1626(1)	833(1)	6741(2)	10(1)
MgNd₆Si₂S₁₄ (4)				
Nd(1)	6423(1)	8760(1)	7621(1)	8(1)
Si(1)	3333	6667	3475(3)	7(1)
Mg(1)	10000	10000	10003(13)	7(1)
S(1)	4770(1)	5888(1)	4914(1)	8(1)
S(2)	7525(1)	9150(1)	12477(2)	9(1)
S(3)	3333	6667	−199(3)	9(1)
MgSm₆Si₂S₁₄ (5)				
Sm(1)	8750(1)	6421(1)	3139(1)	7(1)
Si(1)	6667	3333	−2722(3)	6(1)
Mg(1)	10000	10000	5777(16)	8(1)
S(1)	6667	3333	968(3)	8(1)
S(2)	5878(1)	4777(1)	−4171(2)	7(1)
S(3)	11624(1)	9134(1)	3302(2)	8(1)

^a U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

using powder X-ray diffraction (Fig. 1), and the data was then used to determine its unit cell parameters using Jade 5.0 software. The CIF documents of **1, 2, 4** and **5** have also been deposited with Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany [fax: (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de] with depository number CSD-431156 for **1**, CSD-431159 for **2**, CSD-431157 for **4** and CSD-431158 for **5**.

2.3. Calculation details

The calculation model was built directly from the single-crystal structure data of **1**. The electronic structure calculation including band structure and density of states based on density functional

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