# Alkali-Metal Thiogermanates: Sodium Channels and Variations on the La<sub>3</sub>CuSiS<sub>7</sub> Structure Type

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**Supporting Information** 

**ABSTRACT:** Five new isotypic quaternary chalcogenides containing rareearth metal atoms crystallizing in the hexagonal noncentrosymmetric space group  $P6_3$  (No. 173) with the La<sub>3</sub>CuSiS<sub>7</sub> structure type have been synthesized by reacting the appropriate anhydrous rare-earth trichloride with sodium thiogermanate, Na<sub>2</sub>GeS<sub>3</sub>. The reaction between LnCl<sub>3</sub> and Na<sub>2</sub>GeS<sub>3</sub> in an evacuated fused-silica ampule produced high yields of goodquality crystals of NaLn<sub>3</sub>GeS<sub>7</sub> [Ln = Ce (I), Nd (II), Sm (III), Gd (IV), and Yb (V)], while a similar reaction between EuCl<sub>3</sub> and Na<sub>2</sub>GeS<sub>3</sub> yielded a quinary chloride thiogermanate, Na<sub>1.2</sub>Eu<sub>3.4</sub>Cl<sub>2</sub>Ge<sub>3</sub>S<sub>9</sub> (VI), incorporating a cyclic trimeric Ge<sub>3</sub>S<sub>9</sub> building unit and adopting a structure related to La<sub>3</sub>CuSiS<sub>7</sub>. The crystal structure of the compounds comprises a complex network of bicapped trigonal-prismatic LnS<sub>8</sub> and GeS<sub>4</sub> tetrahedra, which creates channels along the [001] direction. The Na<sup>+</sup> cations reside in these channels within trigonally distorted octahedral coordination environments,



surrounded by six S atoms. For compounds III–V, the temperature dependence of the magnetic susceptibility indicates that these compounds are paramagnetic with  $\mu_{\text{eff.}} = 1.86$ , 8.01, and 3.87  $\mu_{\text{B}}$ , for III–V, respectively. The experimental  $\mu_{\text{eff}}$  for IV is close to the theoretical value of 7.94 for free Gd<sup>3+</sup> ions, while  $\mu_{\text{eff}}$  values for III and V deviate from their theoretical values of 0.86 and 4.54  $\mu_{\text{B}}$  for Sm<sup>3+</sup> and Yb<sup>3+</sup> ions, respectively. These compounds are semiconductors with optical band gaps of around 1.3 eV for III and V. Extended Hückel calculations suggest that the valence band comprises primarily S 3p and the bottom of the conduction band is dominated by empty rare-earth 5d orbitals. Compound VI exhibits a sharp optical absorption of around 2.18 eV, which is attributed to the f  $\rightarrow$  d transition of Eu<sup>II</sup>. The effective magnetic moment of 7.94  $\mu_{\text{B}}$ /Eu is in excellent agreement with the theoretical value of 7.94  $\mu_{\text{B}}$  for the free Eu<sup>2+</sup> ion.

## INTRODUCTION

The multicomponent system involving a rare-earth chalcogenide in combination with several other main-group elements has attracted a great deal of attention not only because they can form a large number of structure types but also because of their ability to be flexible in composition over a wide range within one structure type.<sup>1-7</sup> In general, in the solid-state chemistry of rare earths, the gradually changing size of the rare-earth metal becomes the only determining factor as to whether an isostructural member within a particular structure type will form or not. Such a variation of components within one structure type has practical implications on the fundamental properties of the materials, for example, in the case of rare-earth metals, spectroscopic and magnetic properties resulting from the f electrons. However, it becomes even more interesting in terms of tuning the properties when one is able to vary multiple components of the system while keeping the structure type intact. One such group of quaternary chalcogenides belongs to the hexagonal crystal system space group P63, first reported in 1968 as the cell parameters calculated from powder X-ray diffraction data, and has proven to be a remarkably robust structure type.8 Single-crystal structure investigations revealed that these compounds belong to the Ce<sub>6</sub>Al<sub>3.33</sub>S<sub>14</sub><sup>9</sup> or La<sub>3</sub>CuSiS<sub>7</sub>

structure type.<sup>10</sup> Today, a large number of compounds are known with this structure type with the general formula  $A_6B_2C_2Q_{14}$  or  $A_3BCQ_7$ , while some have vacancies within the [A-B] metal network.<sup>11-49</sup> In all of these compounds, A is a trivalent rare-earth metal and Q is chalcogen, S, or Se. The B sites are localized on the hexagonal axis and occupy all of the positions from the center of an octahedron (for example, Mg, Mn, Fe, Co, Ni, and Zn<sup>12,15,23,28</sup>) to the trigonal side faces of octahedra (as in Cu and Ag<sup>13,17,27,32</sup>) having coordination numbers ranging from 6 to 3, in an environment of Q atoms. A great variety of atoms having different charges (such as 1+, 2+, and 3+)<sup>18</sup> occupy the B sites, and often they are only partially occupied. The C sites are localized on the ternary axis and are found in a tetrahedral coordination environment of Q atoms. They are occupied by tetravalent Si, Ge, and Sn, <sup>18,35,39,41,42</sup> trivalent Al, Ga, In, and Fe,<sup>18,24</sup> and divalent Be<sup>18</sup> or Fe.<sup>23,34</sup> Light alkali-metal cations occupying the B sites were unknown until the first report by the Schleid group in rare-earth thiosilicates, NaY<sub>3</sub>SiS<sub>7</sub>.<sup>33,47</sup> In this paper, we report the

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### Table 1. Crystal Data and Structural Refinement Parameters for Compounds I-VI

compound	I	Ш	III	IV	v	
chemical formula	NaCe <sub>3</sub> GeS <sub>7</sub>	NaNd <sub>3</sub> GeS <sub>7</sub>	NaSm <sub>3</sub> GeS <sub>7</sub>	NaGd <sub>3</sub> GeS <sub>7</sub>	NaYb <sub>3</sub> GeS <sub>7</sub>	
fw	740.36	752.72	771.05	791.75	839.12	
cryst syst	hexagonal	hexagonal	hexagonal	hexagonal	hexagonal	
space group	<i>P</i> 6 <sub>3</sub> (No. 173)	<i>P</i> 6 <sub>3</sub> (No. 173)	<i>P</i> 6 <sub>3</sub> (No. 173)	<i>P</i> 6 <sub>3</sub> (No. 173)	P6 <sub>3</sub> (No. 173)	
T/K	293(2)	293(2)	100(2)	293(2)	293(2)	
wavelength /Å	0.71073	0.71073	0.71073	0.71073	0.71073	
a/Å	10.2248(3)	10.0820(4)	9.9366(7)	9.8646(4)	9.5421(6)	
c/Å	5.8035(4)	5.7897(5)	5.8018(8)	5.8007(5)	5.8833(7)	
volume/Å <sup>3</sup>	525.45(4)	509.66(5)	496.10(8)	488.84(5)	463.92(7)	
Ζ	2	2	2	2	2	
$ ho_{ m calc}$ /Mg m $^{-3}$	4.679	4.905	5.162	5.379	6.007	
$\mu/\mathrm{mm}^{-1}$	16.946	19.354	21.939	24.597	34.713	
Flack parameterx	0.046(8)	0.04(3)	0.00(4)	0.03(2)	0.02(3)	
GOF(S)	1.214	1.303	1.097	1.188	1.093	
R1 $[I > 2\sigma(I)]^a$	0.015	0.027	0.032	0.019	0.034	
wR2(F <sup>2</sup> ) (all data) <sup>b</sup>	0.0395	0.0756	0.0886	0.0546	0.0857	
$\delta F/\mathrm{e}~\mathrm{\AA}^{-3}$	0.890, -0.758	0.944, -2.553	1.265, -2.289	0.809, -2.087	1.357, -1.232	
	compound		VI			
	chemical form	nula	Na <sub>1.2</sub> Eu <sub>3.4</sub>	Cl <sub>2</sub> Ge <sub>3</sub> S <sub>9</sub>		
	fw		1121.46			
	cryst syst		hexagonal			
	space group		<i>P</i> 6 <sub>3</sub> (No.	173)		
	T/K		293(2)			
	wavelength/Å	L	0.71073			
	a/Å		9.5388(3)			
	c/Å		11.7178(9	)		
	volume/Å <sup>3</sup>		923.35(8)			
	Ζ		2			
	$ ho_{ m calc}/ m Mg~m^{-3}$		4.034			
	$\mu/\mathrm{mm}^{-1}$		17.498			
	Flack parame	ter x	0.00(2)			
	GOF(S)		1.072			
	R1 $[I > 2\sigma(I)]$	$]^{a}$	0.0322			
	wR2 $(F^2)$ (all	data) <sup>b</sup>	0.0733			
	$\delta F/e$ Å <sup>-3</sup>		1.337, -1.	.035		
$1 - \sum    E   -  E   / \sum  E  ^{k}$	$b_{\rm uv} \mathbf{P} 2 = \int \mathbf{\nabla} [u (\mathbf{E}^2 - \mathbf{E}^2)]$	$(\Sigma^{2})^{2}/\Sigma^{2}$	$-1/[\sigma^2(E)^2 + (aD)^2 + 1]$	$D$ where $D = \begin{bmatrix} T^2 \\ T \end{bmatrix}$	$\frac{21}{2} = 0.0172$	

<sup>*a*</sup>R1 =  $\sum |||F_0| - |F_c|| / \sum |F_0|$ . <sup>*b*</sup>wR2 = { $\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2]$ }<sup>*i*/2</sup>,  $w = 1/[\sigma^2(F_0)^2 + (aP)^2 + bP]$ , where  $P = [F_0^2 + 2F_c^2]/3$ ; a = 0.0172 and b = 0.2723 for I; a = 0.0424 and b = 1.1100 for II; a = 0.0610 and b = 5.4309 for III; a = 0.0282 and b = 1.7229 for IV; a = 0.0583 and b = 1.2194 for V; a = 0.0467, b = 0.

structures and some properties of the first few members of Nacontaining thiogermanates in the  $La_3CuSiS_7$  structure type, NaLn<sub>3</sub>GeS<sub>7</sub> (Ln = Ce, Nd, Sm, Gd, and Yb), as well as a new quinary compound Na<sub>1.2</sub>Eu<sub>3.4</sub>Cl<sub>2</sub>Ge<sub>3</sub>S<sub>9</sub> related to the La<sub>3</sub>CuSiS<sub>7</sub> structure type, synthesized from anhydrous rare-earth chloride (LnCl<sub>3</sub>) and ternary thiogermanate (Na<sub>2</sub>GeS<sub>3</sub>).

### EXPERIMENTAL SECTION

**Synthesis.** Good-quality single crystals of the family of compounds  $NaLn_3GeS_7$  [Ln = Ce (I), Nd (II), Sm (III), Gd (IV), and Yb (V)] and  $Na_{1,2}Eu_{3,4}Cl_2Ge_3S_9$  (VI) were obtained from the reaction of the appropriate anhydrous rare-earth chloride (LnCl<sub>3</sub>) and the ternary sodium thiogermanate,  $Na_2GeS_3$ .  $Na_2GeS_3$  was prepared by heating a stoichiometric mixture of  $Na_2S_2$ , Ge, and S in a sealed fused-silica ampule at 725 °C for 3 h.  $Na_2S_2$  was prepared from the stoichiometric combination of the elements in liquid ammonia as described previously for several alkali polychalcogenides.<sup>50,51</sup> CeCl<sub>3</sub>, NdCl<sub>3</sub>, SmCl<sub>3</sub>, EuCl<sub>3</sub>, GdCl<sub>3</sub>, and YbCl<sub>3</sub> (Sigma-Aldrich, 99.99% anhydrous powder) were used as received. Typically, 0.36 mmol of LnCl<sub>3</sub> (Ln = Ce, Nd) and 0.28 mmol of  $Na_2GeS_3$  (9:7 LnCl<sub>3</sub>/Na<sub>2</sub>GeS<sub>3</sub>) were mixed and ground in an agate mortar inside a  $N_2$ -filled glovebox. The mixture was then transferred to a graphite crucible, which was then placed inside a fused-silica tube, evacuated, flame-sealed, placed vertically in a

temperature-controlled furnace, and heated at 825 °C for 96 h. The details of the reactions are given in ref 52. For the reactions with CeCl<sub>3</sub> and NdCl<sub>3</sub>, only a few high-quality crystals of NaCe<sub>3</sub>GeS<sub>7</sub> and NaNd<sub>3</sub>GeS<sub>7</sub>, respectively, were obtained. The major phase for these two reactions was Ln<sub>4</sub>(GeS<sub>4</sub>)<sub>3</sub> (Ln = Ce and Nd).<sup>52</sup> Similar reactions with SmCl<sub>3</sub>, GdCl<sub>3</sub>, and YbCl<sub>3</sub> yielded only the NaLn<sub>3</sub>GeS<sub>7</sub> (Ln = Sm, Gd, and Yb) phase as the major product, and no Ln<sub>4</sub>(GeS<sub>4</sub>)<sub>3</sub> could be detected in our analyses. The reaction between EuCl<sub>3</sub> and Na<sub>2</sub>GeS<sub>3</sub> yielded red crystals of Na<sub>1,2</sub>Eu<sup>II</sup><sub>3,4</sub>Cl<sub>2</sub>Ge<sub>3</sub>S<sub>9</sub> as the major product. The reduction of Eu from Eu<sup>3+</sup> in starting EuCl<sub>3</sub> to Eu<sup>2+</sup> in **VI** could be explained by either oxidation of S<sup>2-</sup> to S or oxidation of some of Cl<sup>-</sup> to Cl<sub>2</sub> gas. The presence of elemental S was not evident in the final product; however, the formation of Cl<sub>2</sub> could not be ruled out. In all of the as-synthesized products, the presence of traces of GeS<sub>2</sub> (cold end of the ampule) and NaCl could be detected.

It is important to comment on the chosen synthesis method. The initial aim was to substitute trivalent rare earths in the  $Na_2GeS_3$  structure through a metathesis route:

$$LnCl_3 + 2Na_2GeS_3 = NaLn(GeS_3)_2 + 3NaCl$$
(1)

The structure of  $Na_2GeS_3$  comprises infinite anionic chains of corner-shared  $GeS_4$  tetrahedra, where the  $Na^+$  cations reside in the interchain spaces. Our hypothesis has been to incorporate rare-earth ions in place of Na ions and retain the integrity of the corner-shared

<b>Fable 2. Selected Interatomic Distances</b>	(Å	) and Angles	(deg)	for tl	he Coord	lination Po	lyhedra of	I-V
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	Ce (I)	Nd (II)	Sm (III)	Gd (IV)	Yb (V)
		Ln-S			
Ln1-S1	3.0442(9)	3.0012(15)	2.9532(16)	2.9276(12)	2.812(2)
Ln1-S2 <sup>#1</sup>	2.8377(10)	2.7976(18)	2.763(2)	2.7337(17)	2.722(4)
Ln1-S2 <sup>#2</sup>	2.8385(10)	2.8112(18)	2.788(2)	2.7703(17)	2.653(4)
Ln1-S3#3	2.9023(11)	2.8705(19)	2.840(2)	2.8240(18)	2.780(3)
Ln1-S2 <sup>#4</sup>	2.9732(15)	2.919(3)	2.860(3)	2.832(2)	2.694(4)
Ln1-S3#5	2.9998(11)	2.959(2)	2.924(2)	2.9057(19)	2.826(3)
Ln1-S3#6	3.0414(11)	3.0169(19)	3.003(2)	3.0081(17)	3.031(4)
Ln1-S2 <sup>#7</sup>	3.1642(15)	3.172(3)	3.212(3)	3.248(2)	3.465(4)
		Na-S			
Na1-S2 <sup>#1</sup>	2.629(3)	2.630(6)	2.622(10)	2.616(5)	2.573(8)
Na1-S2 <sup>#2</sup>	2.629(3)	2.630(6)	2.622(10)	2.616(5)	2.573(8)
Na1-S2 <sup>#7</sup>	2.646(3)	2.647(6)	2.670(10)	2.610(5)	2.536(8)
Na1-S2 <sup>#8</sup>	2.629(3)	2.630(6)	2.622(10)	2.610(5)	2.573(8)
Na1-S2 <sup>#9</sup>	2.646(3)	2.647(6)	2.670(10)	2.610(5)	2.536(8)
Na1-S2 <sup>#10</sup>	2.646(3)	2.647(6)	2.670(10)	2.616(5)	2.536(8)
		Ge-S			
Ge1-S3	2.2249(11)	2.226(2)	2.227(2)	2.2246(18)	2.214(4)
Ge1-S3 <sup>#3</sup>	2.2249(11)	2.226(2)	2.227(2)	2.2246(18)	2.214(4)
Ge1-S3 <sup>#5</sup>	2.2249(11)	2.226(2)	2.227(2)	2.2246(18)	2.214(4)
Ge1-S1 <sup>#11</sup>	2.1710(19)	2.172(3)	2.177(4)	2.177(3)	2.195(6)
		S-Ge-	S		
S1 <sup>#11</sup> -Ge1-S3	112.96(4)	113.40(6)	114.02(7)	114.11(5)	115.26(11)
S1 <sup>#11</sup> -Ge1-S3 <sup>#3</sup>	112.96(4)	113.40(6)	114.02(7)	114.11(5)	115.26(11)
S1 <sup>#11</sup> -Ge1-S3 <sup>#5</sup>	112.96(4)	113.40(6)	114.02(7)	114.11(5)	115.26(11)
S3-Ge1-S3 <sup>#3</sup>	105.76(4)	105.27(7)	104.57(8)	104.45(6)	103.12(13)
S3-Ge1-S3 <sup>#5</sup>	105.76(4)	105.27(7)	104.57(8)	104.45(6)	103.12(13)
S3 <sup>#3</sup> -Ge1-S3 <sup>#5</sup>	105.76(4)	105.27(7)	104.57(8)	104.45(6)	103.12(13)

<sup>a</sup>Symmetry transformations used to generate equivalent atoms: #1, -x + y + 1, -x + 1, z; #2, x - 1, y, z; #3, -y + 1, x - y + 1, z; #4, y, -x + y + 1,  $z + \frac{1}{2}$ ; #5, -x + y, -x + 1, z; #6, y - 1, -x + y,  $z + \frac{1}{2}$ ; #7, y, -x + y + 1,  $z - \frac{1}{2}$ ; #8, -y, x - y - 1, z; #9, x - y - 1, z - 1,  $z - \frac{1}{2}$ ; #10, -x + 1, -y,  $z - \frac{1}{2}$ ; #11, x, y, z - 1.

 $\rm GeS_4$  chains. When we did not get our intended product, we modified the ratios of rare-earth chloride and  $\rm Na_2GeS_3$  and found that the reaction of LnCl<sub>3</sub> and Na<sub>2</sub>GeS<sub>3</sub> with a 9:7 ratio gave the best yield of NaLn<sub>3</sub>GeS<sub>7</sub> in the case of SmCl<sub>3</sub>. Consequently, we carried out similar reactions for the other rare-earth metals, and the reactions are listed below in the form of unbalanced equations:

$$9\text{CeCl}_{3} + 7\text{Na}_{2}\text{GeS}_{3}$$

$$\rightarrow \text{NaCe}_{3}\text{GeS}_{7} (\mathbf{I}; \text{minor}) + \text{Ce}_{4}(\text{GeS}_{4})_{3} (\text{major}) + \text{GeS}_{2}$$

$$+ \text{NaCl} (2)$$

 $9NdCl_3 + 7Na_2GeS_3$ 

$$\rightarrow \text{NaNd}_3\text{GeS}_7 (\mathbf{II}; \text{minor}) + \text{Nd}_4(\text{GeS}_4)_3 (\text{major}) + \text{GeS}_2 + \text{NaCl} (3)$$

9SmCl<sub>3</sub> + 7Na<sub>2</sub>GeS<sub>3</sub>

$$\rightarrow \text{NaSm}_3\text{GeS}_7 (\text{III}; \text{major}) + \text{GeS}_2 + \text{NaCl}$$
(4)

9GdCl<sub>3</sub> + 7Na<sub>2</sub>GeS<sub>3</sub>

$$\rightarrow \text{NaGd}_3\text{GeS}_7 (\mathbf{IV}; \text{major}) + \text{GeS}_2 + \text{NaCl}$$
(5)

 $9YbCl_3 + 7Na_2GeS_3 \rightarrow NaYb_3GeS_7 (\mathbf{V}; major) + GeS_2 + NaCl$ (6)

 $9\text{EuCl}_{3} + 7\text{Na}_{2}\text{GeS}_{3}$  $\rightarrow \text{Na}_{1,2}\text{Eu}_{3,4}\text{Cl}_{2}\text{Ge}_{3}\text{S}_{9} (\textbf{VI}) + \text{GeS}_{2} + \text{NaCl}$ (7) However, the same reactions with  $LaCl_3$  yielded a completely different product:  $La_3Cl(GeS_4)_2$ . We did not succeed in preparing phase pure  $NaLn_3GeS_7$  by heating a stoichiometric combination of pure elements and the binaries  $Na_2S$  and  $GeS_2$  under similar conditions, suggesting that the metathesis route may be the only way to prepare phase-pure materials.

X-ray Structure Determination. Intensity data sets for compounds I-V were collected on a Bruker Smart CCD diffractometer. These data were integrated with SAINT,<sup>53</sup> the program SADABS was used for the absorption correction for compounds  $\tilde{I}-IV,^{54}$  and the HABITUS was used for the numerical absorption correction of compounds V and VI.55 The structures were solved by direct methods using SHELXS-97<sup>56</sup> and difference Fourier syntheses. Full-matrix least-squares refinement against |F<sup>2</sup>| was carried out using the SHELXTL-PLUS<sup>55</sup> suite of programs. On the basis of systematic absences, the space group P63 was chosen for all of the compounds, which immediately revealed that I-V are isostructural to  $La_3 CuSiS_7$ .<sup>10</sup> The rare-earth metal cation was easily located on the 6c sites, while subsequent refinement identified Ge on the 2b sites, three S atoms on the 2b and 6c sites, respectively, and Na on the 2a site approximately 2.6 Å away from one of the S atoms. The last cycles of refinement for I-V included anisotropic thermal parameter refinement for all of the atoms. The refinement of compound V did not merge to a good R factor (R1 = 20%), indicating that the crystal might be merohedrally twinned. So, a twin law, TWIN 0 -1 0 -1 0 0 0 0 1, was used,<sup>58</sup> which immediately improved R1 from 20% to 2%, and BASF was refined to 0.49(3). The crystal was also checked for the simultaneous presence of racemic twinning using TWIN 0 -1 0 -1 0 0 0 0 1 -4 with three BASF variables, but the negligible value of the last two BASFs (0.05 and 0.06) indicated the absence of racemic twinning. The structure was finally refined with one BASF variable, with the -4 term removed

from the TWIN law. For compound VI, the rare-earth atoms (Eu1 and Eu2) and one Ge and five S atoms were easily located and refined isotropically. At this point, another atom at 2.915 Å away from one of the S atoms was assigned as Na and refined. The refinement resulted into a high thermal parameter for Na ( $U_{11} = 0.05336$ ), indicating that Na may be partially occupied. So, the in the subsequent refinement, the occupancy of Na was varied and refined at 0.593(2). However, elemental analysis employing energy-dispersive spectrometry (EDS) indicated the presence of Cl in the crystal with the following ratio: Na:Eu:Cl:Ge:S = 1.3:3.5:2:3:9. To account for the presence of Cl atoms in the structure and to balance the charge of the compound, we simply assigned two S atoms that were not bonded to a Ge atom to Cl atoms and refined. Because there is hardly any difference between the scattering factor of the S and Cl atoms, it was not possible to locate Cl crystallographically. At this point, to balance the charge and to satisfy elemental analysis, more Na and less Eu were required, which obviously indicated that the Eu sites may have mixed occupancy of Eu and Na. The introduction of Na into both Eu sites by varying the occupancy and keeping the coordinates fixed clearly indicated that Eu2 has 20% of Na in its site. The mixed-occupancy model of Eu and Na in the 6c site also brought down the weighted R factor from 20% to 18%. Finally, anisotropic refinement was carried out for all of the atoms, and the refinement merged to a very good R factor. On the basis of the occupancy of Eu2/Na2 (80/20%) and Na1 (60%) in the final round of refinement, we came to the formula Na12Eu34Cl2Ge3S9 for compound VI. Details of the final refinements and cell parameters for I-VI are given in Table 1. The final atomic coordinates for compounds I-V and VI are supplied as Supporting Information (SI; Tables S1 and S2), and the important interatomic distances and angles for I-V and VI are given in Tables 2 and 3, respectively. Further details of the crystal

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for the Coordination Polyhedra of  $VI^a$ 

moiety	distance (Å)	moiety	angle (deg)
Eu1-S2#1	3.024(2)	S3-Ge1-S2	114.82(8)
Eu1-S2#2	3.024(2)	S3-Ge1-S1 <sup>#8</sup>	115.40(8)
Eu1-S2	3.024(2)	S2-Ge1-S1 <sup>#8</sup>	99.90(8)
Eu1-Cl1	3.032(3)	S3-Ge1-S1	110.32(9)
Eu1-S3#3	3.037(2)	S2-Ge1-S1	105.34(8)
Eu1-S3#4	3.037(2)	S1 <sup>#8</sup> -Ge1-S1	110.25(9)
Eu1-S3 <sup>#5</sup>	3.037(2)		
Eu2-Cl2	2.898(2)	Eu2 <sup>#2</sup> -Cl1-Na2 <sup>#1</sup>	114.06(5)
Eu2-Cl1	2.933(3)	Eu2#2-Cl1-Eu2#1	114.06(5)
Eu2-S2#6	3.105(2)	Eu2#2-Cl1-Eu2	114.06(5)
Eu2-S3#2	3.184(2)	Eu2#1-Cl1-Eu2	114.06(5)
Eu2-S1	3.214(2)	Eu2#2-Cl1-Eu1	104.36(6)
Eu2-S3	3.315(2)	Eu2 <sup>#1</sup> -Cl1-Eu1	104.36(6)
Eu2-S2#2	3.460(2)		
Ge1-S3	2.154(2)		
Ge1-S2	2.165(2)		
Ge1-S1 <sup>#8</sup>	2.243(4)		
Ge1-S1	2.244(2)		

<sup>a</sup>Symmetry transformations used to generate equivalent atoms: #1, -y + 1, x - y + 1, z; #2, -x + y, -x + 1, z; #3, x - y, x,  $z - \frac{1}{2}$ ; #4, y, -x + y + 1,  $z - \frac{1}{2}$ ; #5, -x + 1, -y + 1,  $z - \frac{1}{2}$ ; #6, -x + 1, -y + 1,  $z + \frac{1}{2}$ ; #7, -x, -y,  $z + \frac{1}{2}$ ; #8, -x + y + 1, -x + 1, z.

structure investigations may be obtained from Fachinformationszentrum Karlsruhe, Eggenstein-Leopoldshafen, Germany [fax (49) 7247-808-666; e-mail crysdata@fiz.karlsruhe.de] on quoting the depository numbers CSD 421445 (I), 421443 (II), 421442 (III), 421444 (IV), 421441 (V), and 421446 (VI).

*Physical Property Measurements.* Diffuse-reflectance spectrometry (DRS) measurements for the compounds were performed on a Varian Cary 500 UV-vis-near-IR spectrophotometer equipped with a Praying Mantis accessory. A poly-Teflon standard was used as the

reference. The Kubelka–Munk function was applied to obtain bandgap information.<sup>59</sup> Magnetic susceptibilities of **III–VI** were measured at 1 T over the temperature range 1.8-300 K, and the isothermal magnetization at 1.8 K up to a field of 5 T was measured with a Quantum Design SQUID magnetometer.

## RESULTS AND DISCUSSION

Compounds I-V belong to the same structure type, namely, the La<sub>3</sub>CuSiS<sub>7</sub> family, and are analogous to the Na-containing



**Figure 1.** Perspective view of the crystal structure of I along the *c* axis showing the complex networks of rare-earth polyhedra and  $GeS_4$  tetrahedra. Na<sup>+</sup> ions are located in the one-dimensional channel made by S atoms.



**Figure 2.** (a) Coordination environment around the rare-earth cation. (b) Coordination environment around the Na<sup>+</sup> cation. The thermal ellipsoids are given at 90% probability. The numbers in parentheses are symmetry codes given in Table 2

thiosilicate structure NaY<sub>3</sub>SiS<sub>7</sub>.<sup>33,47</sup> Structures I–V contain six atoms in their asymmetric unit: the crystallographically unique Ln, Na, and Ge atoms are located on the 6c, 2a, and 2b Wyckoff positions, respectively, while three crystallographically distinct S atoms are located on a special position (S1 on the 2b Wyckoff position) related by 3-fold symmetry and on general positions (S2 and S3 on the 6c Wyckoff position), respectively. The structure of NaLn<sub>3</sub>GeS<sub>7</sub> (Ln = Ce, Nd, Sm, Gd, and Yb) is built up from an intricate connectivity of GeS<sub>4</sub> tetrahedra, NaS<sub>6</sub> octahedra, and LnS<sub>8</sub> bicapped trigonal prisms (Figure 1). The rare-earth cations (Ln<sup>3+</sup>) are in a distorted trigonal-prismatic environment capped by two S atoms, one at roughly 3.0 Å (S3#6) and the other at a longer distance, roughly 3.2–3.4 Å (S2#7), as seen in Figure2a. The LnS<sub>8</sub> bicapped trigonal prisms are connected to neighboring LnS<sub>8</sub> polyhedra through common



**Figure 3.** Perspective view of the structure of VI along the *c* axis showing the presence of a cyclic trimer of corner-shared  $\text{GeS}_4$  tetrahedra (in green) and rare-earth atoms. Na<sup>+</sup> ions and Cl atoms are also located in the  $6_3$  channel.

face, edge, and corner sharing to create a three-dimensional network. Such connectivity creates a tunnel of octahedral holes along the  $6_3$  axis and creates tetrahedral holes in the lattice. The Na<sup>+</sup> and Ge<sup>4+</sup> cations fill the octahedral holes in the tunnel and the tetrahedral holes in the lattice, respectively. The average interatomic distances between the Ln<sup>3+</sup> cations and S<sup>2-</sup> anions  $[d(Ce-S)_{ave} = 2.975(1) \text{ Å}, d(Nd-S)_{ave} = 2.943(2) \text{ Å}, d(Sm-S)_{ave} = 2.918(3) \text{ Å}, d(Gd-S)_{ave} = 2.906(2) \text{ Å}, and <math>d(Yb-S)_{ave} = 2.873(3) \text{ Å}]$  are within the comparable range of those reported for Ce<sup>3+</sup>-, Nd<sup>3+</sup>-, Sm<sup>3+</sup>-, Gd<sup>3+</sup>-, <sup>42</sup> and Yb<sup>3+</sup>-containing sulfides.<sup>60</sup> Moreover, they show the trend in lanthanide contraction. It is to be noted here that one of the longer capping Ln-S distances gets increasingly longer with decreasing size of the lanthanides and becomes quite long for Yb<sup>3+</sup> [3.465(4) Å].

The alkali cation position  $(Na^+)$  is fully occupied and surrounded by six S atoms in an octahedral environment (Figure 2b). The NaS<sub>6</sub> octahedra share opposite faces and form a chain that runs along the 6<sub>3</sub> axis. Apart from the face sharing within themselves, NaS<sub>6</sub> octahedra share common faces with neighboring rare-earth polyhedra through Ln–S–Na linkages. The absence of Ge–S–Na linkages indicates that channel building S atoms do not belong to the GeS<sub>4</sub> tetrahedra. The average interatomic distances between the Na<sup>+</sup> cations and S<sup>2–</sup> anions  $[d(Na–S)_{ave} = 2.637(2), 2.638(3), 2.646(1), 2.613(2),$ and 2.554(4) Å, respectively, for I–V] do not show any particular trend with decreasing size of the lanthanides, and the distances are comparable to the Na–S distances in related



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Figure 4. Coordination environment around the two crystallographically distinct Eu atoms in VI.

compounds<sup>33,47</sup> but are definitely shorter than many Na–Scontaining compounds.<sup>60</sup> Moreover, these NaS<sub>6</sub> octahedra are trigonally distorted wherein Na<sup>+</sup> ions are slightly displaced along the shared face, creating three short bonds and three long bonds, reminiscent of the chains found in the polar hexagonal ternary chlorides of AMX<sub>3</sub> (A = alkali metal, M = transition metal, and X = halogen).<sup>61</sup> The trigonal distortion also explains the lack of any center of inversion at the Na1 site.

The GeS<sub>4</sub> tetrahedra are isolated from each other and share common edges and corners with the neighboring LnS<sub>8</sub> polyhedra. The GeS<sub>4</sub> tetrahedra also surround the columns of NaS<sub>6</sub> octahedra, but they do not share Ge-S-Na linkages. These GeS<sub>4</sub> tetrahedra all point in one direction along the 3fold axis, again displaying the noncentrosymmetric nature of the structure. The GeS<sub>4</sub> tetrahedra are distorted, with S-Ge-S angles varying between ~103 and 114°, while the average Ge-S distances range between 2.209(2) and 2.214(4) Å in all five structures (see Table 3). The GeS<sub>4</sub> tetrahedra are trigonally distorted with one short and three long Ge-S bonds, and this trigonal distortion increases as the size of the rare earth decreases from I through V, as reflected by the S-Ge-S angles (Table 3). Out of three crystallographically distinct S atoms, two (S1 and S3) belong to the  $GeS_4$  unit and participate in forming Ge-S-Ln linkages, while the other S one (S2) only forms Na-S-Na, Ln-S-Na, or Ln-S-Ln linkages. For this reason, some authors prefer a different structural formula for this family of compounds, for example,  $NaY_3S_3[SiS_4]$ .<sup>33</sup>

The S2 atom has shown unique structural and substitutional chemistry. For example, if  $S^{2-}$  is partially substituted by a mononegative anion like chloride (Cl<sup>-</sup>), no alkali-metal cation may be required in the channel to balance the charge. So, essentially an empty channel structure can be created and it has already been found in Sm<sub>3</sub>S<sub>2</sub>Cl[SiS<sub>4</sub>] by the Schleid group.<sup>47</sup>



				VI							I		
atom	Wy	site	occ	x	у	z	atom	Wy	occ	site	x	у	z
Eu1	2b	3	1	<sup>1</sup> / <sub>3</sub>	<sup>2</sup> / <sub>3</sub>	<sup>1</sup> / <sub>3</sub> *	Ge1	2b	1	3	<sup>1</sup> / <sub>3</sub>	<sup>2</sup> / <sub>3</sub>	<sup>1</sup> / <sub>3</sub> *
Eu2	6c	1	0.8	0.2522(2)	0.3366(2)	0.6542(3)	Ce1	6c	1	1	0.1273(2)	0.3566(2)	0.7513(1)
Na2	6c	1	0.2	0.2522(6)	0.3366(6)	0.6542(3)							
Ge1	6c	1	1	0.6631(3)	0.5529(2)	0.4926(5)							
Cl1	2b	3	1	<sup>1</sup> / <sub>3</sub>	<sup>2</sup> / <sub>3</sub>	0.5921(3)	S1	2b	1	3	<sup>1</sup> / <sub>3</sub>	<sup>2</sup> / <sub>3</sub>	0.9592(2)
Cl2	2a	3	1	0	0	0.6404(4)							
S1	6c	1	1	0.4420(2)	0.3297(2)	0.4296(3)							
S2	6c	1	1	0.6748(2)	0.7503(2)	0.3939(2)	S2	6c	1	1	0.8421(1)	0.0875(1)	0.7339(3)
\$3	6c	1	1	0.6497(3)	0.5760(2)	0.6746(9)	S3	6c	1	1	0.4792(2)	0.8951(2)	0.4829(2)
Na1	2a	3	0.6	0	0	0.3951(2)	Na1	2a	1	3	0	0	0.4866(8)

\*The z coordinate has been fixed to 1/3; occ = occupancy, Wy = Wyckoff.

0.008

0.007

0.006

0.005

0.004



( cm<sup>3</sup>/mol of Sm) 0.003 0.000 × 0.002 200 H/Tesla *vs* T at 1 Tesla 100 0.001  $\chi_{_{M}}$ vs T at 1 Tesla 0.000 .= 0 150 250 300 0 50 100 200 T/K

**Figure 5.** Plots showing the magnetic susceptibility ( $\chi$ ) and inverse susceptibility ( $\chi^{-1}$ ) of compound III as a function of the temperature. The inset shows the isothermal magnetization at 1.8 K.



**Figure 6.** Plots showing the magnetic susceptibility ( $\chi$ ) and inverse susceptibility ( $\chi^{-1}$ ) of compound IV as a function of the temperature. The inset shows the isothermal magnetization at 1.8 K.

One can also think of a hypothetical composition; for example,  $S^{2-}$  can be replaced by a different chalcogen,  $Se^{2-}$  or  $Te^{2-}$ , creating a mixed chalcogen phase of this structure type,  $NaLn_3Q_3GeS_4$  (Q = Se or Te). Such a substitution can potentially tune the band gap of the material.

The structure of VI, on the other hand, is new and related to the La<sub>3</sub>CuSiS<sub>7</sub> structure type (Figure 3). There are nine atoms in the asymmetric unit, in which one site has a mixed occupancy of Eu and Na (Eu2/Na2). The similarity between the La<sub>3</sub>CuSiS<sub>7</sub> structure type and VI becomes evident once the coordinates and the atoms are compared between VI and I (Table 4). Clearly, the cations Eu1 and Eu2/Na2 in VI are located at the 2a and 6c sites, which were occupied by Ge1 and Ln1, respectively, in I-V, while the anions Cl1, S2, and S3 in VI, which are located at the 2b and 6c sites, were occupied by the anions S1, S2, and S3, respectively, in I-V. Along the 63 axis, the Na<sup>+</sup> and Cl<sup>-</sup> ions alternate in the channel and the *c* axis is doubled in VI, compared to I-V, and in addition there is one more anionic site in VI occupied by S (S1) located at the 6c

general site. The structure of VI is a complex network of cyclic trimers of corner-shared GeS<sub>4</sub> tetrahedra, Eu–S/Cl polyhedra, and NaS<sub>3</sub>Cl<sub>2</sub> trigonal bipyramids. Eu1 adopts a Cl-capped trigonally distorted octahedral coordination with six S atoms; Eu2, on the other hand, forms a very distorted S-capped trigonal prism with two Cl and four S atoms (Figure 4). The capping S atom forms a very high Eu2-S interatomic distance [3.4599(2) Å]. Eu1-centered polyhedra are isolated from their symmetrically generated Eu1 polyhedra but share edges with Eu2-centered polyhedra. Eu2-centered polyhedra, on the other hand, are edge-shared in a plane perpendicular to the *c* axis and form a layer, while such layers are again fused to the next layer along the *c* axis, through corner and edge sharing between the Eu2 and Eu1 polyhedra, respectively, to form an infinite threedimensional Eu-S/Cl-Eu network. The GeS4 tetrahedra, on the other hand, are not isolated but connected through the corner to form a cyclic Ge<sub>3</sub>S<sub>9</sub> trimeric unit. These Ge atoms are placed in the tetrahedral voids created by the S atoms. Out of the two Cl atoms, one (Cl1) adopts a trigonally distorted

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**Figure 7.** Plots showing the magnetic susceptibility ( $\chi$ ) and inverse susceptibility ( $\chi^{-1}$ ) of compound **V** as a function of the temperature. The inset shows the isothermal magnetization at 1.8 K.



**Figure 8.** Plots showing the magnetic susceptibility ( $\chi$ ) and inverse susceptibility ( $\chi^{-1}$ ) of compound VI as a function of the temperature. The inset shows the isothermal magnetization at 1.8 K.



Figure 9. Optical absorption spectra (taken on the crushed single crystals) of III and V, transformed from the DRS data.



Figure 10. Optical absorption spectra (taken on the crushed single crystals) of VI, transformed from the DRS data.

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-				. 2		
symbol	$\chi_i$	$H_{ii}$ (eV)	$\zeta_1$	coeff 1	$\zeta_2$	coeff 2
Sm	6s	-5.860000	1.750000	0.562300	1.000000	0.553000
	6р	-2.850000	1.390000	1.000000	0.000000	0.000000
	5d	-6.400000	2.650000	0.520000	1.200000	0.640000
	4f	-8.080000	9.900000	0.429300	4.900000	0.715900
Ge	4s	-16.000000	2.160000	1.000000		
	4p	-9.000000	1.850000	1.000000		
S	3s	-20.000000	2.122000	1.000000		
	3p	-13.300000	1.827000	1.000000		
Na	3s	-5.100000	0.733000	1.000000		
	3p	-3.000000	0.733000	1.000000		
	Density of States	1.00 - - 0.69 - 0.38 - 0.07 -			tal n e (s and p) (s and p) (s) m (d)	

Table 5. Exponents $\zeta_i$	and Valence-Shell	Ionization Potential	s H <sub>ii</sub> of Slater-Type	e Orbitals χ <sub>ι</sub> U	sed for EHTB Calculations
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-17.75

-12.75

Energy (eV)

-7.75

tetrahedral coordination surrounded by four Eu atoms, while Cl2 is located in the 63 channel and adopts a five-coordinate trigonal-bipyramidal geometry. The Eu-Cl distances are in the range 2.898(2)-3.032(3) Å, which is well within the comparable range of Eu-Cl distances in Eu<sup>2+</sup>-containing compounds.<sup>62</sup> The 2+ oxidation state of Eu is also confirmed by magnetic measurement (vide infra). Na1, which is also located in the 63 axis has five-coordinate trigonal-bipyramidal geometry, with the three S atoms in the trigonal plane and two Cl atoms occupying the axial positions. The Na–S distances are 2.812(2) Å, certainly longer than the NaLn<sub>3</sub>GeS<sub>7</sub> (I–V) series of compounds but similar to the values reported in NaLnS<sub>2</sub>.<sup>6</sup> The most remarkable features of this structure are the presence of a Ge<sub>3</sub>S<sub>9</sub> cyclic trimeric unit and the alternating presence of Na and Cl along the 63 channel. The chalcogenides of the main-group elements are always interesting because of their ability to form various building units. These building units in the chalcogermanate family include the most common tetrahedral  $\text{GeQ}_4$ ,<sup>63</sup> edge- and corner-shared tetrahedra ( $\text{Ge}_2\text{Q}_6$  and  $\text{Ge}_2\text{Q}_7$ ),<sup>64,65</sup> a supertetrahedron ( $\text{Ge}_4\text{Q}_{10}$ ),<sup>66</sup> an ethane-like dimer ( $\text{Ge}_2\text{Q}_6$ ),<sup>67</sup> and chairlike and five-membered ring  $\text{Ge}_4 \text{Q}_{10}^{67}$  units besides some more complex units. However, to our knowledge, such a corner-shared cyclic trimeric unit of GeS<sub>4</sub> tetrahedra was not known thus far. On the other hand, the presence of  $Na^+$  or  $Cu^+$  along the  $6_3$ channel was a signature of the La<sub>3</sub>CuSiS<sub>7</sub> structure type, while

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the presence of Cl in the  $6_3$  channel of VI makes it a unique structure type. The only other example of a quinary sulfide/ chloride containing a rare-eath metal and a main-group element is LaCa<sub>2</sub>GeS<sub>4</sub>Cl<sub>3</sub>.<sup>68</sup>

.2.75

Magnetic Measurements. The plots of the temperature dependence of the magnetic susceptibility  $(\chi)$  and inverse susceptibility  $(\chi^{-1})$  of III–V in the range 1.8–300 K are given in Figures 5–7, respectively. The asymptotic nature of the  $\chi(T)$ plots at 1 T for III-V respectively under field-cooled and zerofield-cooled (FC and ZFC) conditions confirms the paramagnetic behavior of the compounds, and no magnetic transitions were observed under these conditions. The absence of any transition in III-V was also confirmed by the FC and ZFC  $\chi(T)$  measurements under low applied field (10 Oe, data not shown). The plot of  $\chi^{-1}(T)$  for the Sm compound (III) at high field (1 T) does not show linear behavior at any temperature range and could not be fitted to the Curie-Weiss law (Figure 5). The curved nature of the  $\chi^{-1}(T)$  plot is typical of Sm<sup>3+</sup> (4f<sup>5</sup>), known as van Vleck paramagnetism,<sup>69</sup> and occurs as a result of the competing nature of the thermal energy  $(k_{\rm B}T)$ and energy difference between the ground and first excited states arising from the splitting of the <sup>6</sup>H ground term of Sm<sup>3+</sup> due to spin-orbit coupling. At higher temperatures, the thermal energy term exceeds the energy gap and the excited states may be sufficiently populated. Similar magnetic behavior of Sm<sup>3+</sup> has been observed in many other chalcogenides.<sup>70-72</sup>

The room temperature magnetic moment of Sm in III is calculated to be 1.86  $\mu_{\rm B}$ , which is greater than the calculated value according to  $\mu_{\rm eff} = g[J(J+1)]^{1/2}$  for free Sm<sup>3+</sup> ions (0.85)  $\mu_{\rm B}$ ) but close to the room temperature paramagnetic moment calculated by using the van Vleck formula  $(1.55 \ \mu_{\rm B})$ .<sup>69</sup> Such high moments are often observed in many Sm<sup>3+</sup>-containing compounds.<sup>72</sup> The isothermal magnetization (M) measured at 1.8 K for III exhibits a linear increase with increasing applied field (inset in Figure 5). This behavior is indicative of antiferromagnetic behavior, and the value of the saturation moment at 5 T is about 0.025  $\mu_{\rm B}/{\rm Sm}$ , which is significantly less than that expected for a fully ordered Sm<sup>3+</sup> moment ( $gJ = 5 \mu_B/$ Sm). The  $\chi^{-1}(T)$  plot of **IV** at 1 T, on the other hand, is linear in the entire temperature range (1.8–300 K), and fitting of the data in 100–300 K range according to the Curie–Weiss law  $\chi$  =  $C/(T-\theta)$  yields the value of the effective moment  $\mu_{\rm eff} = 8.01$  $\mu_{\rm B}$  and the paramagnetic Curie temperature ( $\theta_{\rm p}$ ) = -8.27 K (Figure 4). The effective paramagnetic moment of **IV** is in good agreement with the theoretical magnetic moment of 7.94  $\mu_{\rm B}$ expected for Gd3+ with a 4f7 configuration, and the negative sign and small magnitude of  $\theta_p$  indicated a very weak antiferromagnetic coupling between the Gd<sup>3+</sup> ions. The isothermal magnetization (M) of **IV** measured at 1.8 K exhibits a steady increase in magnetization with increasing field; the saturation moment at 5 T is about 5.94  $\mu_{\rm B}/{\rm Gd}$  (see inset of Figure 6). The saturation moment of ~6  $\mu_{\rm B}$ /Gd for IV at 5 T and 1.8 K is slightly less than that expected for a fully ordered Gd<sup>3+</sup> moment of 7  $\mu_{\rm B}$ /Gd. The  $\chi^{-1}(T)$  plot of V at 1 T is linear in the temperature range (150–300 K), and fitting of the data in the 150-300 K range according to the Curie-Weiss law yields the value of the effective moment  $\mu_{\text{eff}} = 3.87 \ \mu_{\text{B}}$  and the paramagnetic Curie temperature ( $\theta_p$ ) = +2.12 K (Figure 7). The effective paramagnetic moment of V is slightly less than the theoretical magnetic moment of 4.54  $\mu_{\rm B}$  expected for Yb<sup>3+</sup> having a 4f<sup>13</sup> configuration, and the positive sign and small magnitude of  $\theta_p$  indicate a very weak ferromagnetic coupling between the Yb<sup>3+</sup> ions. The lower than expected magnetic moment for Yb3+ may indicate the presence of Yb2+ in the material. However, we did not observe any occupancies of less than 1 on S sites (mainly on S2, 6c Wyckoff position) or the presence of both Cl1- and S2- in the non-Ge-bonded S sites (S2). The absence of Cl was also evident in EDS analysis. The isothermal magnetization (M) of V measured at 1.8 K exhibits a steady increase in magnetization with increasing field. The saturation moment at 5 T is about 1.57  $\mu_{\rm B}$ /Yb (inset in Figure 7), which is substantially less than that expected for a fully ordered Yb<sup>3+</sup> ( $gJ = 4 \mu_B$ /Yb) moment. The plot of the temperature dependence of the magnetic susceptibility ( $\chi$ ) and inverse susceptibility  $(\chi^{-1})$  of **VI** in the range 2–300 K is given in Figure 8. The asymptotic nature of the  $\chi(T)$  plots at 5000 Oe (1 T = 10 000 Oe) under FC and ZFC conditions indicates paramagnetic behavior of the compounds, and no magnetic transitions are observed under these conditions (at an applied field of 0.5 T). The absence of any transition in VI is also established by the FC and ZFC  $\chi(T)$  measurements under low applied field (10 Oe), which are again asymptotic. The plots of  $\chi^{-1}(T)$  at 5000 Oe show linear behavior between 2 and 300 K, and the data in the range 100-300 K could be fitted to the Curie–Weiss law,  $\chi = C/(T - \theta)$ , thus yielding the values of the effective moment ( $\mu_{\rm eff})$  of 7.94  $\mu_{\rm B}$  and the paramagnetic Curie temperature ( $\theta_p$ ) = -3.88. The effective paramagnetic moment is the same as the theoretical magnetic moment of 7.94  $\mu_{\rm B}$  expected for Eu in the 2+ oxidation state with seven f

electrons, and the negative sign and small magnitude of  $\theta_p$ indicate a very weak antiferromagnetic correlation in the paramagnetic region. The isothermal magnetization (*M*) measured at 1.8 K for VI does not seem to saturate even at 5 T, and the value of the saturation moment at 5 T is about 6.65  $\mu_B$ /Eu (inset in Figure 8). The saturation moment of 6.65  $\mu_B$ /Eu is close to the theoretical saturation moment of 7  $\mu_B$ /Eu, indicating that at low temperature and high field (5 T) an almost parallel spin of the electrons of Eu in VI can be reached. The paramagnetic moment and magnetization behavior of VI are similar to those of several Eu<sup>2+</sup>-containing main-group chalcogenides, Eu<sub>2</sub>GeSe<sub>4</sub>, Eu<sub>2</sub>Ge<sub>2</sub>Se<sub>5</sub>,<sup>73</sup> Eu<sub>2</sub>GeS<sub>4</sub>,<sup>74</sup> Eu<sub>2</sub>SnS<sub>4</sub>,<sup>75</sup> and Na<sub>2</sub>EuGeSe<sub>4</sub>.<sup>76</sup>

**Optical Properties.** The absorption data calculated from DRS using the Kubelka–Munk function for two compounds, **III** and **V**, are shown in Figure 9. The absorption spectra of the compounds show steep absorptions, from which the optical gaps are calculated. These were calculated to be around 1.33 and 1.30 eV, for **III** and **V**, respectively. Such energy gaps are within the range of semiconductors and are consistent with the dark color of the materials. The characteristic  $f \rightarrow f$  transition at low energies below the band-gap transition would indicate that the f states should be found in the midgap. On the other hand, the optical band gap of 2.18 eV in the case of **VI** can be tentatively assigned to the  $f \rightarrow d$  transition of Eu<sup>II</sup> and is consistent with the red color of the compound (Figure 10).

To develop further insight into the nature of the electronic band gap and other transitions, we calculated the total and partial densities of states (DOSs), employing the extended Hückel method within the framework of the tight-binding approximation (EHTB).<sup>77</sup> The DOSs were calculated based on the crystal structure for 396 k points. The parameters of the atomic orbitals employed in the calculation are default values from the CAESAR program,<sup>78</sup> which are given in Table 5. For compounds III and V, calculations indicate that the valence band maximum near the Fermi level is mostly made up of S 3p states admixed with a small amount of rare earth 5d and Ge 3p states (Figure 11). The states at the Fermi level comprise the empty rare earth 5d states. There is almost a negligible contribution of Na 3s near the Fermi level. The EHTB method has some limitations, does not provide reliable band gaps, and also does not reliably localize the f states of the rare-earth element. However, it is possible to qualitatively relate the optical gaps to the charge-transfer transition from predominantly S 3p orbitals to empty rare earth 5d orbitals.

## CONCLUSIONS

We have extended the family of the La<sub>3</sub>CuSiS<sub>7</sub> (A<sub>3</sub>BCQ<sub>7</sub>) structure type by incorporating Na in the Cu (B) sites. Though the metathesis-type reaction between LnCl<sub>3</sub> and Na<sub>2</sub>GeS<sub>3</sub> favors the formation of NaLn<sub>3</sub>GeS<sub>7</sub> for Ln = Ce, Nd, Sm, Gd, and Yb, the same reaction condition leads to stabilization of a rare cyclic trimeric Ge<sub>3</sub>S<sub>9</sub> unit for Eu. This was probably possible because of the presence of infinite corner-shared chains of GeS<sub>4</sub> tetrahedra in Na<sub>2</sub>GeS<sub>3</sub>. Thus, this kind of metathesis synthetic approach can play an important role in the discovery of new structure types containing unusual building blocks. The scope of such reactions is very high because there are large numbers of ternary chalcogenides of main-group elements with alkali metals containing various building units.

ASSOCIATED CONTENT

#### Supporting Information

Final atomic coordinates for compounds **I–VI** (Tables S1 and S2), along with X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http:// pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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