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Syntheses and single-crystal structures of La_3AgSnS_7, $Ln_3M_xMS_7$ (Ln = La, Ho, Er; M = Ge, Sn; $1/4 \leq x \leq 1/2$)

Hui-Yi Zeng *, Fa-Kun Zheng, Guo-Cong Guo *, Jin-Shun Huang

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

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Abstract

In our investigation of non-centrosymmetric rare earth sulfides in the La_3AgSnS_7/KBr, $LaAlGeS_5$/NaBr, $HoAlGeS_5$/KBr, $ErAlGeS_5$/NaBr, Er_3AgGeS_7/KBr and La_3NaSnS_7/NaBr systems, five compounds belonging to the $R_6B_2C_2Q_{14}$ family have been obtained. These compounds crystallize in the $P6_3$ space group, and the crystal data are as follows—La_3AgSnS_7: $a = 10.3780(15)$ Å, $c = 5.9900(12)$ Å, $Z = 2$; $La_3Ge_{0.25}GeS_7$: $a = 10.2970(15)$ Å, $c = 5.8120(12)$ Å, $Z = 2$; $Ho_3Ge_{0.272(10)}GeS_7$: $a = 9.6480(14)$ Å, $c = 5.7920(12)$ Å, $Z = 2$; $Er_3Ge_{0.330(10)}GeS_7$: $a = 9.5930(14)$ Å, $c = 5.8490(12)$ Å, $Z = 2$; $La_3Sn_{0.25}SnS_7$: $a = 10.2770(15)$ Å, $c = 6.0030(12)$ Å, $Z = 2$. Single-crystal analysis indicated that the crystal structures consist of three types of building block: LnS_n, MS_4, and AgS_3 (for La_3AgSnS_7) or MS_6 units (for $Ln_3M_xMS_7$, Ln = La, Ho, Er; M = Ge, Sn; $1/4 \leq x \leq 1/2$), as any other compounds belonging to the $R_6B_2C_2Q_{14}$ family. $Ln_3M_xMS_7$ (Ln = La, Ho, Er; M = Ge, Sn; $1/4 \leq x \leq 1/2$) are deficient compounds with the B sites occupied partly by M(II), and/or M(IV).

Keywords: Non-centrosymmetric; Rare earth; Sulfide; Crystal structure; Deficient

1. Introduction

Second-order nonlinear optical (NLO) materials have played a key role in areas such as laser frequency conversion and optical parameter oscillators [1,2]. Acentric chalcogenides are particularly interesting, as they are potential second-order NLO materials for use in the IR region. A number of chalcogenides adopting a non-centrosymmetric space group have been synthesized, and some IR NLO chalcogenide materials, such as $AgGaS_2$ [2,3], $LiInS_2$ [4], $LiGaQ_2$ (Q = S, Se, Te) [5] have been recognized.

A large family of rare earth chalcogenides with the general formula $R_6B_2C_2Q_{14}$ (R = rare earth, B = 6-coordinated element, C = 4-coordinated element, Q = S, Se) [6–28] crystallize in the hexagonal system with space group $P6_3$, which are of great interest and deserve further investigation in the search for new non-centrosymmetric compounds as potential IR NLO materials [15–17]. In many cases, the B sites in the saturated formulas $R_6B(I)_2C(IV)_2Q_{14}$, $R_6B(II)_2C(III)_2Q_{14}$ are occupied partly by elements of a higher oxidation state, the charge/occupancy balance leads to the deficient compositions $R_6(B_{2m}\square_{2-2m})C_2Q_{14}$ ($\square$ = vacancy) with 2m = 1/2, 2/3, 1 and 4/3 [6]. $Nd_6Ge_3S_{14}$, $La_6MnSi_2S_{14}$, $Ln_6In_{2/3}Si_2S_{14}$, $La_6Sn_{1/2}Si_2S_{14}$ and $Dy_6Ge_{2.5}S_{14}$ are typical deficient compounds [6].

In our investigation of non-centrosymmetric rare earth sulfides La_3AgSnS_7, La_3NaSnS_7 (presumed compound), Er_3AgGeS_7 (presumed compound) [29], and $LnAlGeS_5$ (presumed compounds) (Ln = La, Ho, Er) ($LnAlGeS_5$, analogues of the acentric $LaBGeO_5$ [30]), five compounds belonging to the $R_6B_2C_2Q_{14}$ family have been obtained. Here, we report the syntheses, and the systematic structure investigation of La_3AgSnS_7 (=$La_6Ag_2Sn_2S_{14}$) and four deficient compounds: $Ln_3M_xMS_7$ (=$Ln_6(M_{2x}\square_{2-2x})M_2S_{14}$) (Ln = La, Ho, Er; M = Ge, Sn; $1/4 \leq x \leq 1/2$; $\square$ = vacancy).

2. Synthesis

All starting materials were used as received: Al (99.999%), Ge (99.999%), Ho (99.9%), S (99.999%), Ag_2S (99.9%), Er_2S_3

* Corresponding authors. Tel.: +86 591 83705054; fax: +86 591 83714946.
E-mail addresses: zhy@fjirsm.ac.cn (H.-Y. Zeng), gcguo@fjirsm.ac.cn (G.-C. Guo).

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Table 1
Reaction condition and unit cell (in the hexagonal system) for La_3AgSnS_7, $Ln_3M_xMS_7$ (Ln = La, Ho, Er; M = Ge, Sn; $1/4 \leq x \leq 1/2$)

Starting materials (mmol)	Heating profile (precursor preparation)	Precursor	Flux	Heating profile (crystal growth)	Crystal	Unit cell		Compound
						a (Å)	*c* (Å)	
La_2S_3:Ag_2S:SnS_2 0.360:0.121:0.241	30–750 °C/72 h 750–750 °C/24 h 750–1000 °C/10 h 1000–1000 °C/240 h Power switched off	La_3AgSnS_7	0.80 g KBr	40–850 °C/54 h 850–850 °C/360 h 850–600 °C/166.67 h Power switched off	**1**	10.3780(15)	5.9900(12)	La_3AgSnS_7
La_2S_3:Al:Ge:S 0.278:0.556:0.556:1.946	30–700 °C/37.22 h 700–700 °C/24 h 700–1000 °C/15 h 1000–1000 °C/240 h 1000–640 °C/180 h Power switched off	$LaAlGeS_5$	0.80 g NaBr	40–850 °C/54 h 850–850 °C/240 h 850–700 °C/100 h Power switched off	**2**	10.2970(15)	5.8120(12)	$La_3Ge_xGeS_7$
Ho:Ge:Al:S 0.556:0.556:0.556:2.780	40–360 °C/8 h 360–500 °C/9.33 h 500–500 °C/50 h 500–850 °C/23.33 h 850–850 °C/240 h 850–450 °C/133.33 h Power switched off	$HoAlGeS_5$	0.70 g KBr	30–900 °C/14.5 h 900–900 °C/240 h 900–650 °C/166.67 h Power switched off	**3**	9.6480(14)	5.7920(12)	$Ho_3Ge_xGeS_7$
Er_2S_3:Al:Ge:S 0.278:0.556:0.556:1.946	30–700 °C/37.22 h 700–700 °C/24 h 700–1000 °C/15 h 1000–1000 °C/240 h 1000–640 °C/180 h Power switched off	$ErAlGeS_5$	0.80 g NaBr	40–850 °C/54 h 850–850 °C/240 h 850–700 °C/100 h Power switched off	**4**	9.5970(14)	5.8220(12)	$Er_3Ge_xGeS_7$
Er_2S_3:Ag:Ge:S 0.374:0.249:0.249:0.624	20–500 °C/25 h 500–500 °C/24 h 500–700 °C/10 h 700–700 °C/30 h 700–800 °C/25 h 800–800 °C/120 h Power switched off	Er_3AgGeS_7	0.80 g KBr	40– 850 °C/13.5 h 850–850 °C/240 h 850–650 °C/133.33 h Power switched off	**5**	9.5930(14)	5.8490(12)	$Er_3Ge_xGeS_7$
La_2S_3:Na_2S:SnS_2 0.768:0.256:0.512	30–750 °C/144 h 750–750 °C/80 h 750–1000 °C/250 h 1000–1000 °C/144 h 1000–380 °C/216 h Power switched off	La_3NaSnS_7	0.80 g NaBr	30–830 °C/64 h 830–830 °C/212 h 830–700 °C/65 h Power switched off	**6**	10.2770(15)	6.0030(12)	$La_3Sn_xSnS_7$