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Solid-state synthesis, structural variants and transformation of three-dimensional sulfides, $AGaSnS_4$ (A = Na, K, Rb, Cs, Tl) and $Na_{1.263}Ga_{1.263}Sn_{0.737}S_4$

Asmita Kumari, Kanamaluru Vidyasagar*

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India

Abstract

New cubic-$AGaSnS_4$ (A = Na, K, Rb, Cs, Tl) and orthorhombic-$NaGaSnS_4$ compounds were synthesized by solid-state reactions and characterized by X-ray diffraction and diffuse reflectance spectroscopy. Single crystals of orthorhombic-$Na_{1.263}Ga_{1.263}Sn_{0.737}S_4$ were obtained in the crystal growth attempts of sodium compound. All six new compounds have orthorhombic $AgGaGeS_4$ and cubic $BaGa_2S_4$ structures, as determined from single crystal X-ray structures of $Na_{1.263}Ga_{1.263}Sn_{0.737}S_4$ and cubic-$AGaSnS_4$ (A = Na, K, Rb). Orthorhombic-$NaGaSnS_4$ and known layered-$KGaSnS_4$ undergo structural transformation to thermodynamically stable cubic form.
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Keywords: Quaternary sulfides; Solid state synthesis; X-ray diffraction; Crystal structure; Crystal growth; Structural transformation

1. Introduction

The reactive molten flux method [1], employing alkali-metal polysulfides, is widely used for synthesizing, at relatively low temperatures, a number of novel phases, mostly in the form of single crystals that enable unambiguous characterization by single crystal X-ray diffraction. The new phases, generally metastable in nature, are the mixed-metal polysulfides and simple ternary and quaternary sulfides [2,3]. Simple sulfides have been reported [4–6] in large number in the quaternary $A/M/M'/S$ system, where A is an alkali-metal and M and M' represent transition, post-transition and main group metals in the oxidation states I, II, IV and VI. They possess diverse structure types ranging from linear to three-dimensional and could be broadly categorized into three types, namely, metal-rich compounds [4], sulfur-rich ones [5] and those having a 1:1 ratio of metal to sulfur [6]. Previously we reported [7] the utility of this technique in the exploratory synthetic investigation of quaternary $A/Cd/Sn/S$ (A = Li, Na) systems for isolation of three sulfides, three-dimensional

Na_2CdSnS_4 and layered $Na_6CdSn_4S_{12}$ and Li_2CdSnS_4. Apart from compositional and structural diversity of these sulfides, it is interesting that Cd^{2+} and Sn^{4+} ions have tetrahedral coordination in A_2CdSnS_4 compounds and octahedral coordination in sulfur-rich $Na_6CdSn_4S_{12}$.

$KGaGeS_4$, $KInGeS_4$ and $KGaSnS_4$, synthesized by solid state reactions, are the only three compounds known [8] in largely unexplored $A/M/M'/S$ (A = alkali metal; M = Al, Ga, In; M' = Si, Ge, Sn) quaternary systems. We have initiated a similar synthetic study of $A/Ga/Sn/S$ (A = alkali metal) system for new sulfides with coordinatively versatile Ga^{3+} and Sn^{4+} ions and, in one such attempt by flux method, isolated single crystals of $KGaSnS_4$ in another structural modification. This new three-dimensional structure, distinctly different from its known layered version [8], is found to be same as thermodynamically stable cubic(γ) form [9,10] of $AGaSnSe_4$ (A = K, Rb) and $KInSnSe_4$. Structural variants of $AMSnSe_4$ (A = alkali metal; M = Ga, In) selenides and the effect of rate of cooling of melt on obtaining γ-form were reported in the recent past. The only known isomorphous sulfide analogue of $KGaSnS_4$ is $CuGaSnS_4$ realized by Garbato et al. [11], who reported the powder X-ray pattern without any further crystallographic information. We have thus become interested

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*Corresponding author. Fax: +91 44 22570509/4202.
E-mail address: kvsagar@iitm.ac.in (K. Vidyasagar).

to synthesize and structurally characterize AGaSnS$_4$ (A = alkali metal, Tl, Cu, Ag) compounds and examine structural transformations, if any. In this paper, we report the synthesis and characterization of new AGaSnS$_4$ (A = Na($\mathbf{1}$), K($\mathbf{2}$), Rb($\mathbf{3}$), Cs($\mathbf{4}$) and Tl($\mathbf{5}$)) and Na$_{1.263}$Ga$_{1.263}$Sn$_{0.737}$S$_4$ ($\mathbf{6}$) compounds, having two types of three-dimensional structures and structural transformation of sodium compound.

2. Experimental

2.1. Synthesis and crystal growth

Chemicals, S, Ga, Sn, SnS, Na, K$_2$S$_2$, Tl$_2$S, AGaS$_2$ (A = Na, Rb, Cs), NaI and I$_2$, were employed for the solid-state synthesis and crystal growth of AGaSnS$_4$ (A = Na($\mathbf{1}$), K($\mathbf{2}$), Rb($\mathbf{3}$), Cs($\mathbf{4}$) and Tl($\mathbf{5}$)) compounds in evacuated sealed quartz tubes of 12 cm length and 1.2 cm diameter. AGaS$_2$ compounds were prepared by known procedures [12] and all other chemicals (>99.9% purity) were purchased from CERAC Inc. and Alfa Aesar.

Polycrystalline samples of compounds $\mathbf{1}$–$\mathbf{5}$ were prepared, on a scale of about 2 g, by heating stoichiometric mixtures of appropriate reactants at 850 °C for 4 days and then cooling to room temperature at the rate of 2 °C/h. Cubic modification of sodium compound ($\mathbf{1}$-c) was synthesized from a reactant mixture of NaGaS$_2$, SnS and S, whereas its orthorhombic modification ($\mathbf{1}$-o) was obtained from Na, Ga, SnS and S. Only cubic modification was isolated for compounds $\mathbf{2}$–$\mathbf{5}$.

Single crystals of $\mathbf{1}$-c and $\mathbf{3}$–$\mathbf{5}$ were grown by chemical vapor transport (CVT) technique, using I$_2$ as the transporting agent. About 0.2 g of polycrystalline samples of $\mathbf{1}$-c and $\mathbf{3}$–$\mathbf{5}$ were sealed, along with a spec of solid iodine, in evacuated quartz tubes. These quartz tubes were heated in a tubular furnace such that the sample was at 750 °C and the other end of the tube was at a colder zone, which was about 100 °C less. Block shaped reddish brown crystals of $\mathbf{3}$ and $\mathbf{4}$ and very thin plate-like orange crystals of $\mathbf{1}$-c and $\mathbf{5}$ grew at the colder end of the quartz tube after 7 d of heating. Crystals of $\mathbf{2}$ were obtained from molten flux of potassium polysulfide. A mixture of Ga (0.035 g; 0.502 mmol), Sn (0.060 g; 0.50 mmol), S (0.320 g; 9.9 mmol) and K$_2$S$_2$ (0.710 g; 4.98 mmol) was heated at 450 °C for 4 days and then cooled to room temperature over a period of 1 day. The entire product-contents of the reaction were washed thoroughly with water to isolate the water-insoluble, homogeneous phases of $\mathbf{2}$ in the form of reddish-brown, block shaped crystals (0.14 g; 78.4% yield).

Crystals of $\mathbf{6}$ were formed inadvertently in crystal growth attempts for compound $\mathbf{1}$-o. A mixture of 0.20 g of $\mathbf{1}$-o and 2.0 g of NaI was heated at 700 °C for 1 day and then cooled to 600 °C over a period of 3 days, followed by further cooling to room temperature for 1 day. The entire contents were then washed thoroughly with water to isolate the water-insoluble plate-like yellow-orange crystals of $\mathbf{6}$ and

small quantity of gray powder of presumably SnS. The crystals were manually separated from the powder.

Single crystal X-ray data collection was successful for sodium ($\mathbf{1}$-c and $\mathbf{6}$), potassium ($\mathbf{2}$) and rubidium ($\mathbf{3}$) compounds. The quality of single crystals of cesium ($\mathbf{4}$) and thallium ($\mathbf{5}$) compounds was not good. However, cubic unit cell parameter could be determined for compound $\mathbf{4}$.

2.2. X-ray diffraction and crystal structure

The powder X-ray diffraction (XRD) patterns of compounds $\mathbf{1}$–$\mathbf{5}$ were recorded on a Shimadzu XD-D1 powder diffractometer, using CuKα ($\lambda = 1.5406$ Å) radiation. The monophasic nature of $\mathbf{1}$–$\mathbf{5}$ was verified by comparing their powder XRD patterns with those simulated, using the LAZY-PULVERIX program [13], on the basis of the single crystal X-ray structures.

Single crystals of $\mathbf{1}$–$\mathbf{3}$ and $\mathbf{6}$, suitable for X-ray diffraction, were selected and mounted on thin glass fibers with epoxy glue. Data sets were gathered from the crystals at 25 °C, using MoKα radiation ($\lambda = 0.7103$ Å). Single crystals of $\mathbf{1}$-c and $\mathbf{6}$ were optically aligned on a Bruker APEX II charge-coupled device X-ray diffractometer using a digital camera. APEX II software (v 1.0–22, Bruker AXS) was used for preliminary determination of the cell constants and data collection control. The determination of integral intensities and global refinement were performed using SAINT+ (v 7.09, Bruker AXS) with a narrow-frame integration algorithm. A semiempirical absorption correction [14] was subsequently applied using SADABS. Data sets from the crystals of $\mathbf{2}$ and $\mathbf{3}$ were gathered on an Enraf–Nonius CAD4 automated four-circle diffractometer, by standard procedures involving ω–2θ scan techniques. These data sets were reduced by routine computational procedures. Absorption corrections based on azimuthal scans of reflections with angle $\chi \approx 90°$ were applied. The structure solution and refinements were carried out, respectively, by using the programs [15,16] SIR 92 and SHELXL 97 and the graphic program [17] DIAMOND was used to draw the structures.

The centrosymmetric $Pa\bar{3}$ and noncentrosymmetric $Fdd2$ space groups were determined for compounds $\mathbf{2}$ and $\mathbf{6}$ respectively, from the systematic absences of reflections. For both compounds, the crystallographic sites occupied randomly by gallium and tin atoms were located by direct methods. These positions were refined and Fourier difference maps led to location of alkali metal and sulfur atoms of the asymmetric unit. For compound $\mathbf{2}$, their site occupancy factors were refined to be ~50% each and, therefore, fixed at 50% in the subsequent refinements. In view of large thermal parameter of sodium in compound $\mathbf{6}$, its site occupancy was also refined along with the disordered site occupancies of gallium and tin. The asymmetric unit content was found to be Na$_{0.943}$Ga$_{0.954}$Sn$_{0.546}$S$_3$ with almost equal content of sodium and gallium. The site occupancies of sodium and

gallium were, therefore, constrained to be equal in the subsequent refinements and the final asymmetric unit content was found to be $Na_{0.947}Ga_{0.947}Sn_{0.553}S_3$. The occupancies of gallium and tin were, respectively, 0.546(4) and 0.453(4) in the $M(1)$ (16b position) and 0.401(2) and 0.099(3) in the $M(2)$ (8a position) sites. Thus $Na_{1.263}Ga_{1.263}Sn_{0.737}S_4$ compound (6) has 12 formula units in the unit cell. Structures of compounds 1-c and 3 were modeled by starting with the refined positional parameters of 2 and potassium was appropriately replaced by sodium and rubidium. All atoms of the four crystal structures were refined anisotropically and the final Fourier difference maps did not show any chemically significant feature. For only sodium compound 1-c, the final Fourier difference map contained three peaks with electron density of $> 1 e/A^3$, located close to sodium 1 or 2. Pertinent crystallographic data, positional and thermal parameters and bond lengths are presented in Tables 1–3. Some of Na–S bonds in 1-c are a bit longer as reported [18] for $Na_{0.5}Pb_{1.75}GeS_4$ and the values of all other bond lengths in the four compounds are in the normal range and comparable to those reported [8,12b] in the literature. The CIF files, containing the supplementary crystallographic data, for these four compounds are deposited in the Fachinformationszentrum Kalsruhe, Germany and given the deposition numbers, CSD-417380 (1-c), CSD-417381 (2), CSD-417382 (3) and CSD-417383 (6).

2.3. Spectroscopic data

Optical diffuse reflectance measurements were made at room temperature with a CARY |5E| UV–VIS–NIR spectrophotometer to measure the band gap. $BaSO_4$ powder was used as reference (100% reflectance). Absorption data were calculated from the reflectance data using the Kubelka–Munk [19] function: $\alpha/S = (1-R)^2/2R$, where R is the reflectance at a given wavelength, α is the absorption coefficient and S is the scattering coefficient. The scattering coefficient is known to be practically wavelength independent for particles larger than 5 μm, which is smaller than the particle size of the sample used here.

3. Results and discussion

The powder XRD patterns (Fig. 1) of four AGaSnS$_4$ (A = K(2), Rb(3), Cs(4) and Tl(5)) compounds are similar to one another and indexed on cubic unit cells with similar parameters. They compare well with those simulated on the basis of single crystal X-ray structures of 2 and 3, revealing that these four compounds have same structure. The cubic unit cell parameters of 4 and 5, as determined from single crystal and powder XRD data, are 13.357(7) and 13.24(1) Å respectively. Compounds 2–5 are isostructutral with known [10,20] phases, BaGa$_2$S$_4$ and cubic(γ)-KInSnSe$_4$. In BaGa$_2$S$_4$, gallium is tetrahedrally coordinated to sulfur atoms and each GaS$_4$ tetrahedron is corner-connected to four such tetrahedra, to give rise to three-dimensional anionic framework of $[Ga_2S_4]^{2-}$, with voids filled by Ba^{2+} ions. Similarly, compounds 2–5 have three-dimensional, tetrahedral anionic framework of $[GaSnS_4]^-$, wherein gallium and tin are disordered equally over the tetrahedral sites (Fig. 2). This type of disorder is reported [10] to be present in structurally characterized

Table 1
Pertinent crystallographic data for AGaSnS$_4$ (A = Na(1-c), K(2), Rb(3)) and $Na_{1.263}Ga_{1.263}Sn_{0.737}S_4$ (6) compounds

Compound	1-c	2	3	6
Formula	NaGaSnS$_4$	KGaSnS$_4$	RbGaSnS$_4$	Na$_{1.263}$Ga$_{1.263}$Sn$_{0.737}$S$_4$
Formula weight	339.64	355.75	402.12	332.82
Crystal system	Cubic	Cubic	Cubic	Orthorhombic
a (Å)	13.0161(1)	13.050(5)	13.174(5)	12.7262(5)
b (Å)	–	–	–	23.1145(9)
c (Å)	–	–	–	7.2585(3)
V (Å^3)	2205.17(3)	2222.4(2)	2286.4(2)	2135.2(2)
Space group (no.)	$Pa\bar{3}$ (205)	$Pa\bar{3}$ (205)	$Pa\bar{3}$ (205)	$Fdd2$ (43)
Z	12	12	12	12
ρ_{calcd} (g/cm^3)	3.069	3.190	3.505	3.170
λ (Å)	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	8.14	8.58	14.14	8.40
Total reflections	3880	656	676	1224
Independent reflections	2968	619	570	1222
Parameters refined	34	34	34	55
$R_{(int)}$	0.0451	0.0972	0.1094	0.0331
R^a	0.0391	0.0345	0.0330	0.0167
R_w^b	0.1229	0.0874	0.0749	0.0449
GooF	1.149	1.197	1.055	1.200
Largest diff. peak/hole	6.367/−1.279	0.859/−0.684	0.768/−0.921	0.528/−0.571

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

Table 2
Positional parameters and equivalent isotropic thermal parameters for $A\mathrm{GaSnS_4}$ (A = Na(**1-c**), K(**2**), Rb(**3**)) and $\mathrm{Na_{1.263}Ga_{1.263}Sn_{0.737}S_4}$ (**6**) compounds

Compound	Atom	x	y	z	$U_{(eq)}$[a]
1-c	Na(1)	0.37470(7)	0.37470(7)	0.37470(7)	0.0164(3)
	Na(2)	0.00000	0.50000	0.50000	0.0461(1)
	$M(1)$[b]	0.14129(1)	0.62807(1)	0.19702(1)	0.01405(5)
	S(1)	−0.02760(6)	0.57783(6)	0.22844(7)	0.0248(1)
	S(2)	0.20655(6)	0.62827(7)	0.36383(5)	0.0205(2)
2	K(1)	0.3743(1)	0.3743(1)	0.3743(1)	0.0431(7)
	K(2)	0.0000	0.5000	0.5000	0.084(2)
	$M(1)$[b]	0.14163(3)	0.62783(4)	0.19702(4)	0.0183(3)
	S(1)	−0.0275(1)	0.5777(1)	0.2282(1)	0.0289(4)
	S(2)	0.2067(1)	0.6278(1)	0.3633(1)	0.0246(4)
3	Rb(1)	0.37230(5)	0.37230(5)	0.37230(5)	0.0385(4)
	Rb(2)	0.00000	0.50000	0.50000	0.0538(5)
	$M(1)$[b]	0.14706(4)	0.62297(4)	0.19478(3)	0.0172(3)
	S(1)	−0.0201(1)	0.5773(1)	0.2296(1)	0.0289(4)
	S(2)	0.2160(1)	0.6218(1)	0.3579(1)	0.0223(4)
6	Na(1)[c]	0.17047(2)	0.0474(1)	0.9023(3)	0.0651(9)
	$M(1)$[d]	0.13239(2)	0.13556(1)	0.37356(3)	0.0161(1)
	$M(2)$[e]	0.0000	0.0000	0.40240(6)	0.0159(2)
	S(1)	0.04470(6)	0.07714(3)	0.5834(1)	0.0212(2)
	S(2)	0.10593(6)	0.22990(3)	0.4740(1)	0.0219(2)
	S(3)	0.05799(6)	0.13657(3)	0.0793(1)	0.0223(2)

[a] $U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.
[b] Occupancy of Sn/Ga is 0.5/0.5.
[c] Occupancy of Na is 0.947(4).
[d] Occupancy of Sn/Ga is 0.454(4)/0.546(4).
[e] Occupancy of Sn/Ga is 0.099(3)/0.401(3).

Table 3
Bond lengths (Å) for $A\mathrm{GaSnS_4}$ (A = Na(**1-c**), K(**2**), Rb(**3**)) and $\mathrm{Na_{1.263}Ga_{1.263}Sn_{0.737}S_4}$ (**6**)

	1-c	**2**	**3**	**6**
$A(1)$–S(1)	3.226(1) × 3	3.237(2) × 3	3.333(2) × 3	3.340(3)
$A(1)$–S(2)	3.380(1) × 3	3.390(3) × 3	3.504(2) × 3	2.765(2)
$A(1)$–S(2)′				2.829(2)
$A(1)$–S(3)				2.819(2)
$A(2)$–S(1)	3.6948(7) × 6	3.706(2) × 6	3.714(2) × 6	
$A(2)$–S(2)	3.6272(6) × 6	3.639(2) × 6	3.764(2) × 6	
$M(1)$–S(1)	2.3296(8)	2.337(2)	2.323(2)	2.3213(8)
$M(1)$–S(2)	2.3314(7)	2.331(2)	2.332(2)	2.3238(8)
$M(1)$–S(1)′	2.3246(8)	2.327(2)	2.327(2)	
$M(1)$–S(2)′	2.3321(7)	2.342(2)	2.331(2)	
$M(1)$–S(3)				2.3365(9)
$M(1)$–S(3)′				2.3149(8)
$M(2)$–S(1)				2.2867(8) × 2
$M(2)$–S(2)				2.2923(8) × 2

cubic(γ)-KInSnSe$_4$. A^+ ions fill voids of the framework and have six and twelve coordinations. Previously KGaSnS$_4$ with layered structure [8], distinctly different from the present cubic one (**2**), is reported to contain eight-coordinated K$^+$ ions and two-dimensional, tetrahedral anionic framework of [GaSnS$_4$]$^-$, built from both corner- and edge-sharing of tetrahedra. We have found that it transforms to cubic modification, upon quenching of its melt at 900 °C or during vapor transport by iodine. This structural transformation involves a major change in the tetrahedral [GaSnS$_4$]$^-$ framework, with concomitant change of coordination number of potassium. Thus the isolation of these two forms of KGaSnS$_4$ by conventional solid-state reactions seems to depend on the rate of cooling.

Two structural modifications, orthorhombic and cubic, have been isolated for NaGaSnS$_4$ (**1**) by solid-state reactions of different reactants. The apparent difference in the reactivities of NaGaS$_2$ and elemental mixture of Na, Ga and S could be the reason for isolation of two modifications. The cubic modification (**1-c**) is ascertained to be isostructural with **2**–**5** by single crystal XRD study. However, the observed relative intensities of some reflections in its powder XRD pattern (Fig. 3) are different from those calculated, probably due to preferential orientation of the crystallites. The values of unit cell volumes of these five cubic $A\mathrm{GaSnS_4}$ compounds (**1**–**5**) vary in accordance with the size of A^+ ion.

Orthorhombic NaGaSnS$_4$ (**1-o**) has, as deduced from its powder XRD pattern (Fig. 3), the following unit cell parameters: $a = 12.529(2)$, $b = 23.360(4)$ and $c = 7.029(3)$ Å. It transforms to cubic form (**1-c**), upon quenching of its melt at 850 °C or during vapor transport by iodine. However, it decomposes in molten NaI flux into single crystals of Na$_{1.263}$Ga$_{1.263}$Sn$_{0.737}$S$_4$ (**6**) that has similar orthorhombic unit cell parameters (Table 1). Identification of structure of **6** as that of known [21] AgGaGeS$_4$ led to the deduction that **1-o** also has the same structure. The observed (Fig. 3) and simulated XRD powder patterns of
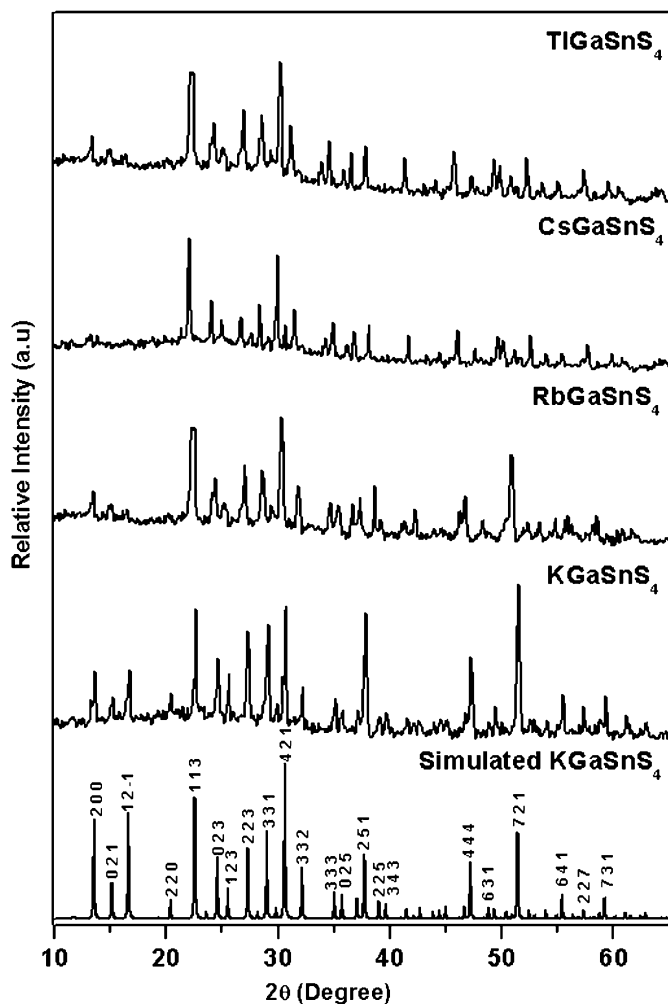
Fig. 1. Powder X-ray diffraction patterns of AGaSnS$_4$ (A = K, Rb, Cs and Tl) compounds.
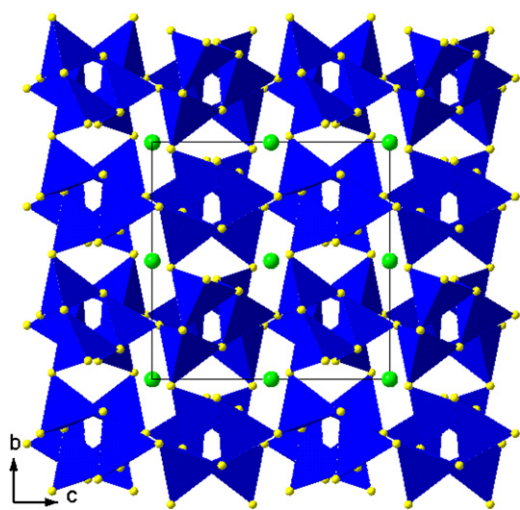

Fig. 3. Powder X-ray diffraction patterns of cubic- and orthorhombic-NaGaSnS$_4$.

Fig. 2. Polyhedral representation of unit cell of cubic KGaSnS$_4$ compound, viewed along [100] (S— yellow; K— green).

1-o indeed agree well. AgGaGeS$_4$ is considered to be 1:1 solid solution of AgGaS$_2$ and GeS$_2$ and reported [21] to crystallize in noncentrosymmetric orthorhombic
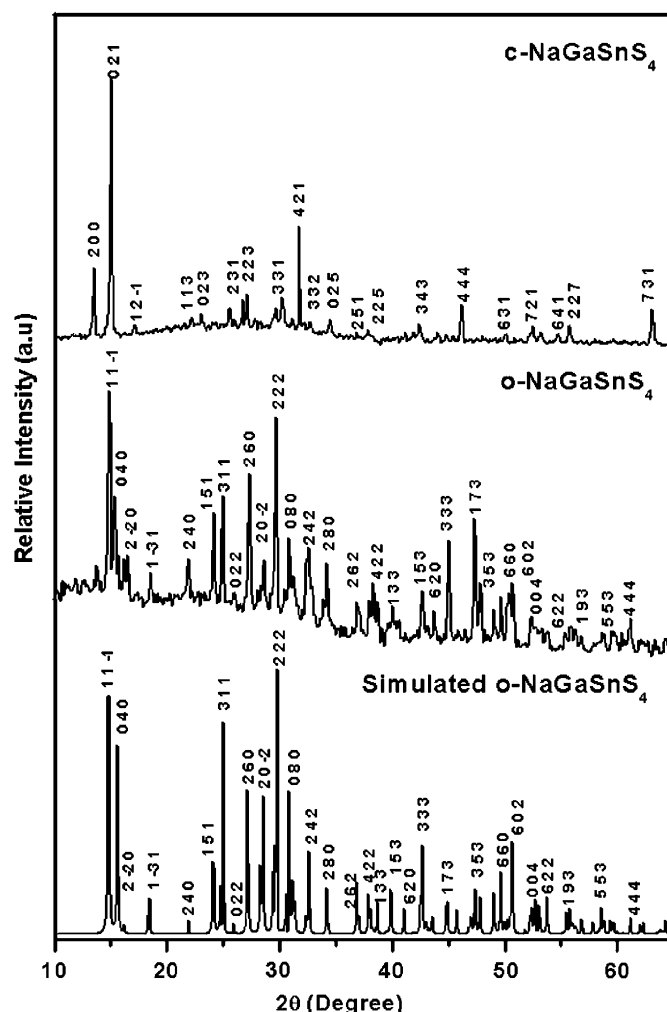
space group *Fdd*2 with asymmetric unit content of Ag$_{\sim0.75}$Ga$_{0.75}$Ge$_{0.75}$S$_3$.

Though compositionally not similar, Na$_{1.263}$Ga$_{1.263}$-Sn$_{0.737}$S$_4$ (**6**) has the structure of AgGaGeS$_4$ and asymmetric unit content of Na$_{0.947}$Ga$_{0.947}$Sn$_{0.553}$S$_3$. Three-dimensional anionic [Ga$_{1.263}$Sn$_{0.737}$S$_4$]$^{1.263-}$ framework is built from corner connected M(1)S$_4$ and M(2)S$_4$ tetrahedra, where M(1) and M(2) represent tetrahedral sites occupied randomly by gallium and tin atoms. M(1)S$_4$ tetrahedra form M(1)S$_3$ chains parallel to 101 and 10$\bar{1}$. M(2) site atoms are coordinated to unshared sulfur atoms of M(1)S$_4$ tetrahedra of two such chains along *b*-axis (Fig. 4a). This anionic framework contains, along *c*-axis, channels of 12-membered rings in which Na$^+$ ions reside (Fig. 4b). Na$^+$ ions have distorted tetrahedral coordination, with the wide 86.6(1)–144.8(2)° range of values of S–Na–S bond angles. A selenide analogue of **6** is Na$_{0.92}$Ga$_{0.90}$Sn$_{0.597}$Se$_3$ that was reported [9] to crystallize in noncentrosymmetric monoclinic space group *C*2.

Thus the isostructural orthorhombic NaGaSnS$_4$ (**1-o**) would have asymmetric unit content of Na$_{0.75}$-Ga$_{0.75}$Sn$_{0.75}$S$_3$ and similar anionic tetrahedral [GaSnS$_4$]$^-$
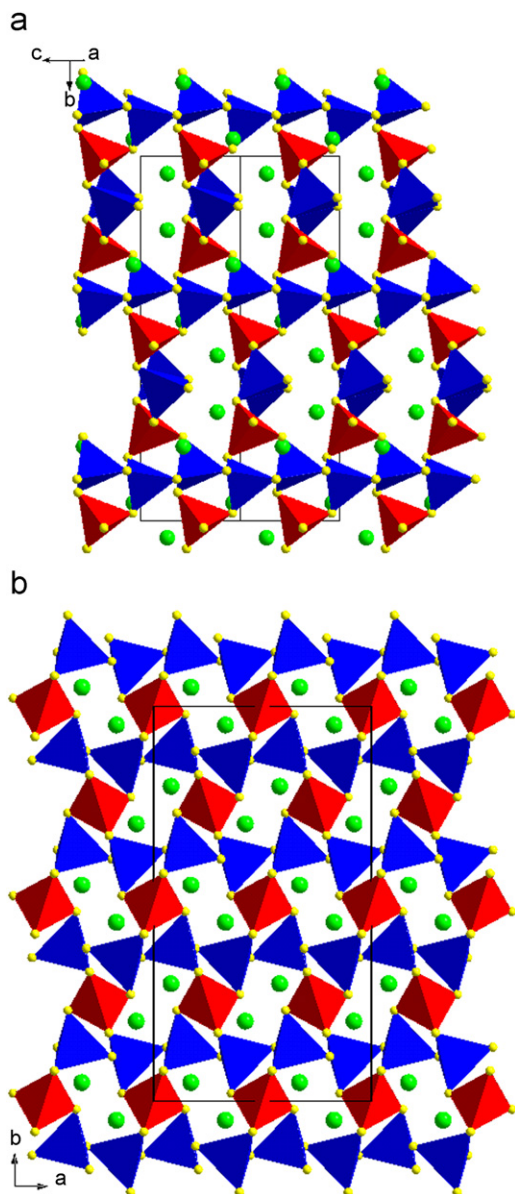
Fig. 4. $Na_{1.263}Ga_{1.263}Sn_{0.737}S_4$ compound: Polyhedral representation of unit cell viewed along (top) [101] and (bottom) [001] (S—◯; Na—◯; Gray and black tetrahedral (online: blue and red tetrahedra) represent $M(1)S_4$ and $M(2)S_4$, respectively).

are obtained in the present study. However, unlike those selenides, the cubic AGaSnS$_4$ compounds could be obtained by simple solid-state reactions.

Optical absorption spectra indicate that all compounds are wide band gap semiconductors. The values of band gap were estimated to be 1.75, 2.10, 2.70, 2.75 and 1.90 eV for **1**, **2**, **3**, **4** and **5** respectively. The band gap value is same for both structural modifications (**1-o** and **1-c**) of sodium compound.

4. Concluding remarks

New three-dimensional AGaSnS$_4$ (A = Na, K, Rb, Cs and Tl) were synthesized by solid-state reactions and single crystals of orthorhombic-Na$_{1.263}$Ga$_{1.263}$Sn$_{0.737}$S$_4$ were obtained in the crystal growth attempts. All of them were structurally characterized, by X-ray diffraction, to be similar to cubic BaGa$_2$S$_4$ and orthorhombic AgGaGeS$_4$. NaGaSnS$_4$ is isolated in both cubic and orthorhombic modifications and its orthorhombic form transforms to cubic one. Na$_{1.263}$Ga$_{1.263}$Sn$_{0.737}$S$_4$ has orthorhombic structure and the other four are obtained in only cubic form. Synthesis and crystal growth of CuGaSnS$_4$ and AgGaSnS$_4$ compounds are in progress.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc. 2007.04.017.

framework with Na$^+$ ions in the void space. Therefore, the structural transformation of **1-o** to **1-c** seems to involve only little change in the corner-shared tetrahedral [GaSnS$_4$]$^-$ framework, with simultaneous change of coordination number of sodium from 4 to 6 and 12.

Two modifications of KInSnSe$_4$, namely one-dimensional α-form and two-dimensional β-form are known [10] to be kinetically stable phases that undergo, on heating or annealing, irreversible transformation to thermodynamically stable cubic (γ) modification. Synthesis and single crystal X-ray structures of similar gallium selenides, α-KGaSnSe$_4$, β-KGaSnSe$_4$, β-RbGaSnSe$_4$ and β-CsGaSnSe$_4$ and transformations of α and β to γ-modifications for potassium and rubidium compounds have been reported [9]. Similar results

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