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Molten flux synthesis, single crystal X-ray structure and ion-exchange properties of the first polythiogallate, $CsGaS_3$ †

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A new polythiogallate, $CsGaS_3$, has been synthesized using molten flux of caesium polysulfide, and structurally characterized, by single crystal X-ray diffraction techniques, as possessing one-dimensional GaS_3^- chains, built from GaS_4 tetrahedra. Cs^+ ions undergo facile ion-exchange, at room temperature, with Rb^+, NH_4^+, Me_4N^+ and alkaline earth and a few divalent first row transition metal ions in aqueous solution. $AGaS_3$ (A = Cs, Rb, NH_4, Me_4N) compounds are, as determined from their diffuse reflectance spectra, insulators.

Introduction

Over the last fifteen years, the reactive molten flux method[1] employing alkali metal polysulfide, has become a powerful technique to synthesize, 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,[2,3] generally metastable in nature, are the intended polysulfides and, to a smaller extent, simple ternary and quaternary sulfides. Similar reactive molten flux methods have been developed for the synthesis of polyselenides[4] and ploytellurides.[5] In the ternary A/M/S systems, where A is alkali metal and M represents transition, post-transition and main group metals, a large number of polysulfides, such as $A_4Ti_3S_{14}$ (A = K, Rb, Cs), $Rb_4Hf_3S_{14}$, $A_2Sn_2S_8$ (A = K, Rb), $Cs_2Sn_2S_6$, Cs_2SnS_{14}, $Cs_2Sn_3S_7{\cdot}\frac{1}{2}S_8$, $Cs_2Sb_4S_8$, $CsSbS_6$, have been reported[1,4,6–8] to be realized by this synthetic method. These compounds, with varied and interesting formulations, have novel and mostly low-dimensional structures that are potentially conducive for so-called "soft-chemistry" like ion-exchange and intercalation/deintercalation reactions.

The ternary A/M/S (A = alkali metal; M = Sn, Sb) systems have been intensively investigated[6–8] for polysulfides, whereas the similar systems containing other main group metals, Al, Ga, In, Pb, and Bi are, to our knowledge, unexplored. For example, the phases, known to date, in the A/Ga/S systems are only a few simple sulfides,[9–13] $AGaS_2$ (A = Li, Na, K, Rb and Cs), $A_6Ga_2S_6$ (A = Na and K) and $Na_4Ga_2S_5$. These compounds, synthesized by conventional high temperature solid-state reactions, possess diverse structures ranging from molecular to three-dimensional frameworks with the tetrahedrally coordinated gallium. For example, $LiGaS_2$ and $CsGaS_2$ have three- and one-dimensional structures respectively, whereas other $AGaS_2$ (A = Na, K, Rb) compounds have two-dimensional structures. Such a structural diversity and low-dimensionality could be expected in polysulfides of A/Ga/S systems. We have thus become interested in the synthesis and characterization of new polysulfides of the A/Ga/S systems. It was during these exploratory synthetic attempts, by the alkali metal polysulfide flux method, that we isolated $CsGaS_3$ which represents the first example of polysulfide in these ternary systems. We report here, the synthesis, characterization and ion-exchange properties of this new one-dimensional polysulfide, $CsGaS_3$.

Experimental

All chemicals employed in the present study were of >99.5% purity and purchased from CERAC Inc. and Merck.

Synthesis

A mixture of Cs_2CO_3 (0.2 g; 0.06 mmol), Ga_2S_3 (0.032 g; 0.0135 mmol) and S (0.098 g; 0.30 mmol), in an evacuated sealed quartz tube of 13 cm length and 1.3 cm diameter, was heated in a furnace at 780 °C for four days and then cooled to room temperature over a period of four days. The entire product-contents of the quartz tube were then washed with water to dissolve away the caesium polysulfide flux, enabling the isolation of a single phase product, $CsGaS_3$, in the form of needle shaped, cream crystals (0.0608 g, 75% based on Ga_2S_3).

Ion exchange reactions

Ion exchange reactions were carried out by stirring, at room temperature for 6 h, the polycrystalline samples of $CsGaS_3$ with the aqueous solutions of NH_4Cl, Me_4NI, $FeSO_4$ and the metal chlorides, RbCl and ACl_2 (A = Ca, Sr, Ba, Mn, Co, Ni, Cu). For example, 0.2 g of $CsGaS_3$ was stirred with 15 mL of water containing 2 g of NH_4Cl and thus a 1 : 10 weight ratio of $CsGaS_3$ to metal salts was maintained in all other reactions as well. The solid products were washed several times with water and then air-dried. The ion-exchanged solid products and the filtrates were examined for the presence or absence of caesium and other mono- and di-valent ions. These ion-exchange reactions were ascertained to be quantitative, as for example, from the absence of caesium and the presence of ammonium ions in the ion-exchanged solid product, NH_4GaS_3. The amount of sulfur in the four $AGaS_3$ (A = Cs, Rb, NH_4 and Me_4N) compounds and a selected few other ion-exchanged AGa_2S_6 compounds was estimated by conventional quantitative analysis[14] and found to be in agreement with the theoretical values.

Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XD-D1 powder X-ray diffractometer using Cu-Kα (λ = 1.5405 Å) radiation. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer Delta series TG instrument

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† Electronic supplementary information (ESI) available: powder XRD patterns, thermogravimetric curves, IR spectra and optical absorption spectra for $AGaS_3$ (A = Cs, Rb, NH_4 and Me_4N). See http://www.rsc.org/suppdata/dt/b2/b207741h/

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and Dupond 2000 thermal analyser under a nitrogen flow with a heating rate of 20 °C min^{-1}. Infrared spectra were recorded on a Bruker 17S 66V FT-IR spectrometer. The samples were ground with dry KBr (4000–400 cm^{-1}) and pressed into transparent discs for recording infrared spectra. Optical diffuse reflectance measurements were made at room temperature, to measure the band gap, with a Shimadzu UV-VIS-NIR spectrophotometer, using $BaSO_4$ powder as a reference (100% reflectance). Absorption data were calculated from the reflectance data using the Kubelka–Munk function:[6]

$$\alpha/S = (1 - R)^2/2R$$

where R is the reflectance at a given wavelength, α is the absorption coefficient and S is the scattering coefficient which 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.

Single crystal X-ray diffraction analysis

X-Ray diffraction data collection was performed at 293 ± 2 K on an Enraf Nonius CAD4 X-ray diffractometer by standard procedures for a needle shaped single crystal of $CsGaS_3$ of dimensions 0.1 × 0.075 × 0.05 mm. Crystal data: $M = 298.831$, monoclinic, space group $P2_1/c$, $a = 7.558(3)$, $b = 12.502(7)$, $c = 6.411(5)$ Å, $\beta = 107.75(4)°$, $U = 576.9(6)$ Å^3, $Z = 4$, $\mu = 11.445$ mm^{-1}, total reflections 1168, independent reflections 1014 ($R_{int} = 0.0442$), $R_1 = 0.0433$ and $wR_2 = 0.1174$. The structure solution and refinement were performed by the programs SHELXS 86[15] and SHELXL 93,[16] respectively. All the five atoms of the asymmetric unit were located by direct methods and refined anisotropically. The only four peaks, found to have electron density of >1 e Å^{-3} in the final difference Fourier map, were the ghosts of caesium. The bond lengths and selected bond angles are given in Table 1. The graphic programs ORTEP[17] and ATOMS[18] were used to draw the structures.

CCDC reference number 191450.

See http://www.rsc.org/suppdata/dt/b2/b207741h/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis

Synthesis of $CsGaS_3$, as pure single crystals, from a reactant mixture of Cs_2CO_3, Ga_2S_3 and S, involves the use of molten flux of caesium polysulfide, generated *in situ*[2,19] from Cs_2CO_3 and S. This compound could also be prepared, but in poor yield, at lower temperatures such as 400 °C or even from a mixture of Cs_2CO_3, Ga and S. It is to be noted that the synthetic procedures for similar caesium polysulfide compounds of other ternary and quaternary systems have been reported[4,6–8,20] to employ Cs_2S_3 or a mixture of Cs_2S and S for the molten Cs_2S_x flux.

X-Ray diffraction and crystal structure

The monophasic nature of the compound $CsGaS_3$ was established by comparing its powder XRD pattern with that simulated, by the program LAZY PULVERIX,[21] from the single crystal X-ray structure. However, the observed and simulated values of relative intensities for some of the reflections are different, indicating the preferred morphological orientations of the crystallites, which is not uncommon for compounds with such low-dimensional structures. $CsGaS_3$ is a new one-dimensional polysulfide containing linear GaS_3^- anionic chains and Cs^+ cations (Fig. 1). The anionic chains are parallel to the c-axis and contain trivalent gallium ions, each tetrahedrally coordinated to two sulfide and two disulfide ions. Each of these sulfide and disulfide ions is bonded to two gallium ions and thus spirocyclic, non-planar five-membered Ga_2S_3 rings are fused at gallium centers to form the linear GaS_3^- anionic chains. This compound is isostructural with the known[22,23] boron polychalcogenides, ABS_3 (A = Cs, Rb, Tl) and $ABSe_3$ (A = Cs, Rb).

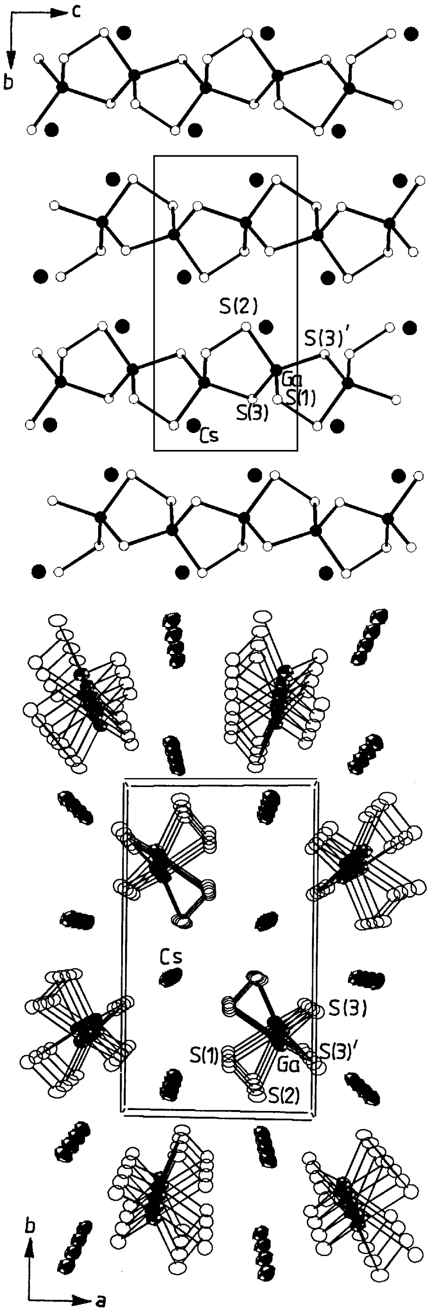

Fig. 1 Unit cell diagram of $CsGaS_3$ viewed along the a-axis (top) and along the c-axis (bottom), showing the atom labeling.

Gallium forms shorter bonds with sulfide ions than with disulfide ions and the values of the S–Ga–S bond angles indicate that GaS_4 tetrahedron is largely undistorted (Table 1). The S–S bond length of 2.099(3) Å for the disulfide ion compares well with those reported in the literature.[1,4,6–8] Caesium ions are six coordinated with the values of Cs–S bond lengths ranging from 3.584(3) to as high as 3.764(3) Å. These structural features of $CsGaS_3$ are similar to those of the known[11] one-dimensional sulfide, $CsGaS_2$. Only half of the sulfide ions of $CsGaS_2$ are replaced by disulfide ions in $CsGaS_3$ and, therefore, edge-sharing of GaS_4 tetrahedra, present in the GaS_2^- chain, is not possible in the GaS_3^- chain. The average volume of an atom, in both the compounds, is as large as 29–31 Å^3 and seems to indicate that the linear anionic chains are loosely held.

Table 1 Bond distances (Å) and selected bond angles (°) in $CsGaS_3$

Ga–S(1)	2.296(2)	Cs–S(2)	3.706(3)
Ga–S(2)	2.282(2)	Cs–S(3)	3.707(3)
Ga–S(3)	2.254(3)	Cs–S(1)	3.764(3)
Ga–S(3)′	2.265(2)	Cs–S(2)	3.584(3)
S(1)–S(2)	2.099(3)	Cs–S(3)′	3.603(3)
Cs–S(1)	3.746(3)		
S(1)–Ga–S(2)	105.80(9)	S(3)′–Ga–S(3)	111.19(10)
S(1)–Ga–S(3)	112.64(8)	S(2)–S(1)–Ga	95.80(11)
S(1)–Ga–S(3)′	109.27(9)	S(1)–S(2)–Ga	94.75(11)
S(2)–Ga–S(3)	109.11(8)	Ga–S(3)–Ga	91.90(8)
S(2)–Ga–S(3)′	108.62(8)		

Symmetry operation for S(3)′: $-x + 2, y - 1/2, -z + 1/2$.

Ion exchange reactions

The one-dimensional structure and the relatively large average atomic volume of $CsGaS_3$ are the two features that prompted us to investigate its ion-exchange properties. Furthermore, it is known that $KFeS_2$,[24] isostructural with $CsGaS_2$, undergoes ion-exchange reactions. $CsGaS_3$ is found to undergo, at room temperature, quantitative ion-exchange reactions with aqueous solutions of NH_4Cl and RbCl to yield NH_4GaS_3 and $RbGaS_3$ phases, respectively. The powder XRD patterns of these three $AGaS_3$ (A = Cs, Rb and NH_4) compounds are similar with small, but significant, changes in the relative intensities and the values of 2θ of the reflections. This is indicative of the retention of the parent one-dimensional structure and the topotactic nature of these ion-exchange reactions. Ion-exchange reactions with divalent ions (A = Ca, Sr, Ba, Mn, Fe, Co, Ni and Cu) are also successful and, as inferred from the similarity of powder XRD patterns of $CsGaS_3$ and AGa_2S_6 compounds, topotactic. Furthermore, Cs^+ ions in $CsGaS_3$ undergo ion-exchange with Me_4N^+ ions also, to yield Me_4NGaS_3. Its powder XRD pattern, as expected for replacement of monoatomic ion by spherically symmetric polyatomic ion, is more significantly different from, but still similar to, that of $CsGaS_3$. It is noteworthy that all of these ion-exchanged products could not be synthesized by any other method and thus $CsGaS_3$ could be regarded as a precursor for the synthesis of various, metastable, one-dimensional compounds. Our unsuccessful attempts at ion-exchange reactions with aqueous solutions of NaCl and KCl seem to indicate that ion-exchange is possible only when the A^+ ion is as big as Rb^+.

Thermogravimetry

The thermogravimetric results of the four $AGaS_3$ (A = Cs, Rb, NH_4 and Me_4N) compounds studied are, as expected, different from one another and only some of the initial stages of decomposition could be reasonably accounted for. $CsGaS_3$, for example, undergoes an incongruent weight loss of about 10%, in two stages, around 166 and 410 °C and this decrease in weight is probably due to the loss of one sulfur and the formation of $CsGaS_2$. The thermogravimetric curve of $RbGaS_3$ shows the completion of the first weight loss of 22.5% around 270 °C and is thus distinctly different. On the other hand, a major weight loss of approximately 36%, starting from 150 to 300 °C, has been observed in the case of NH_4GaS_3 and, as deduced from the powder XRD pattern of a sample heated at 200 °C for 24 hours in a flowing nitrogen atmosphere, corresponds to the formation of essentially Ga_2S_3 from NH_4GaS_3. Further weight loss observed at temperatures beyond 300 °C could probably be due to decomposition of Ga_2S_3. The weight loss at 320 °C, in the case of Me_4NGaS_3, is as high as 80%. The vastly different thermal behavior of these four compounds is supportive of the quantitative exchange of caesium ions in $CsGaS_3$.

Infrared spectroscopy

The infrared spectra of the parent $CsGaS_3$ and all the ion-exchanged solid products could be only partially assigned.[6,25] The common features observed in the spectra of all these compounds are a peak around 460 cm^{-1}, due to the stretching vibrations of the S–S bond, and a broad band at 3400 cm^{-1} and a peak at 1620 cm^{-1}, due to stretching and bending modes of water, presumably adsorbed on the surface. The infrared spectrum of the ammonium ion-exchanged solid product shows peaks at 3163 and 1400 cm^{-1}, which can be assigned to the symmetric γ_1 and asymmetric γ_4 stretches of the tetrahedral ammonium ion. The peak at 3000 cm^{-1}, in the tetramethylammonium ion-exchanged product, is due to $N–CH_3$ vibration and peaks at 1399 and 1428 cm^{-1} can be ascribed to symmetric γ_1 and asymmetric γ_2 C–H vibrations of the tetramethylammonium ion.

UV-Vis-Near IR spectroscopy

The energy band gap of the four $AGaS_3$ (A = Cs, Rb, NH_4, Me_4N) compounds were examined by analyzing their diffuse reflectance data. The values of absorption function α, converted from the diffuse reflectance data, were plotted *versus* the energy and band gap values, estimated from the sharp absorption edges, for all four compounds they are in the range of 2.8 to 3.0 eV, revealing their insulating nature.

Concluding remarks

A new one-dimensional compound, $CsGaS_3$, has been synthesized using a molten flux of caesium polysulfide and characterized by single crystal X-ray diffraction. It represents the first example of a polysufide of an alkali metal/Ga/S system and undergoes facile ion-exchange, in aqueous solution, with various mono- and di-valent cations. Our synthetic efforts for other alkali metal analogues led to the isolation of twinned crystals of approximate composition $AGaS_{2.25}$ and their structural characterization by single crystal X-ray diffraction is underway.

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