# The One-dimensional Polyselenide Compound CsGaSe<sub>3</sub>

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Abstract. A new one-dimensional phase, CsGaSe<sub>3</sub> has been synthesized and characterized by single crystal X-ray diffraction, differential thermal analysis, and single crystal UV/Vis spectroscopy. The structure contains infinite chain anions,  $[GaSe(Se_2)]^-$  separated by Cs cations. The Ga<sup>3+</sup> cation is in a distorted tetrahedral environment coordinated by each two Se<sup>2-</sup> and Se<sub>2</sub><sup>2-</sup> ions. The red crystals of CsGaSe<sub>3</sub> absorb visible light at energies above 2.25 eV. Differential thermal analysis revealed that the compound does not melt below 1000 °C. Crystal data: CsGaSe<sub>3</sub>, monoclinic, space group  $P2_1/c$  (No 14), a=7.727(1), b=13.014(3), c=6.705(1),  $\beta=106.39(3)^\circ$ , Z=4, R1=0.0469.

Keywords: Semiconductors; X-ray diffraction; Crystal structure; Thermal analysis

# Die eindimensionale Polyselenid-Verbindung CsGaSe<sub>3</sub>

**Inhaltsübersicht**. Eine neue eindimensionale Phase, CsGaSe<sub>3</sub>, wurde synthetisiert und durch Einkristall-Röntgenbeugung, Differentialthermoanalyse sowie durch Einkristall-UV/Vis-Spektroskopie charakterisiert. Die Struktur besteht aus unendlichen Anionen-Ketten, [GaSe(Se<sub>2</sub>)]<sup>-</sup>, die durch Cs-Kationen getrennt sind. Das Ga<sup>3+</sup>-Kation ist in verzerrt tetraedrischer Anordnung durch je zwei Se<sup>2-</sup>- und Se<sub>2</sub><sup>2-</sup>-Ionen koordiniert. Die roten Kristalle von CsGaSe<sub>3</sub> absorbieren im sichtbaren Licht bei Energien über 2,225 eV. Die Differentialthermoanalyse zeigte, dass die Verbindung nicht unter 1000 °C schmilzt. Die Kristalldaten von CsGaSe<sub>3</sub> sind: monoklin, Raumgruppe  $P2_1/c$  (No 14), a=7,727(1), b=13,014(3), c=6,705(1) Å,  $\beta=106,39(3)^\circ$ , Z=4, R1=0,0469.

#### 1 Introduction

A large number of ternary group 13 chalcogenide compounds with a variety of metal cations including alkali metals has been reported. Depending on the reaction conditions and the size of cations, structures with discrete molecules [1-6], chains [7-11], layers [12-15], or frameworks [16-19] are formed. In the case of gallium, examples include discrete molecules,  $[Ga_nQ_{2n+2}]^{(n+4)-}$  (Q = S, Se, Te; n = 1, 2, 4, 6) in K<sub>5</sub>GaSe<sub>4</sub>[1], A<sub>6</sub>Ga<sub>2</sub>Q<sub>6</sub> (A = Na, K, Cs; Q = S, Se, Te) [2-5],  $Cs_8Ga_4Se_{10}$  [6] and  $Cs_{10}Ga_6Se_{14}$  [6]. The chain-shaped molecules,  $[Ga_nQ_{2n+2}]^{(n+4)-}$  (Q = S, Se, Te; n = 1, 2, 4, 6 have different lengths depending on the number of n, and are built up of edge-sharing tetrahedral  $GaQ_4$  units. The compounds  $KGaQ_2$  (Q = S, Te) [12-13], CsGaTe<sub>2</sub> [14], and TlGaSe<sub>2</sub> [15] are composed of linked adamantane-like  $Ga_4Q_{10}$  units that form  $[GaQ_2]^-$  layers.  $LiGaS_2$  [16] and  $AGa_3Q_5$  (A = Li, Na; Q = Se, Te) [17–19] have open framework structures which consist of GaS4 tetrahedra sharing corners or edges. Also, two kinds of chain anions are known in  $CsGaS_2$  [7],  $TlGaQ_2$  (Q = Se, Te) [8-10] and  $Na_4Ga_2S_5$  [11]. In CsGaS<sub>2</sub> and TlGaQ<sub>2</sub> (Q = Se, Te), the  $[GaQ_2]^-$  chain is constructed by con-

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necting  $GaQ_4$  tetrahedra sharing their edges, while  $[Ga_2S_5]^{4-}$  chain in  $Na_4Ga_2S_5$  is formed by  $GaS_4$  tetrahedra sharing corners and edges.

In this paper, we report the polychalcogenide flux synthesis and characterization of the new ternary gallium selenide compound, CsGaSe<sub>3</sub>. To the best of our knowledge this rather simple compound has not been reported. It possesses a novel chain structure with tetrahedral  $[GaSe_2(Se_2)_2]^-$  anions linked to each other by sharing corners as well as linking corners (via Se-Se bonds) to form infinite  $[GaSe(Se_2)]^-$  chains.

# 2 Experimental

#### 2.1 Reagents

The following reagents in this work were used as obtained: Ga (shots, 99.999 %; Cerac, Milwaukee, WI), As<sub>2</sub>Se<sub>3</sub> (99.9 %; Strem Chemicals, Newburyport, MA), Se (99.999 %; Noranda Advanced Materials, Quebec, Canada). N,N-dimethylformamide (Spectrum Chemicals, ACS reagent grade); diethyl ether. The Cs<sub>2</sub>Se starting material was prepared by a stoichiometric reaction of cesium metal and selenium in liquid NH<sub>3</sub>. Ga<sub>2</sub>Se<sub>3</sub> was prepared by heating a stoichiometric ratio of the elements in an evacuated silica ampule. The mixture was heated to 800 °C in 10 h and kept for 24 h. It was cooled to 50 °C in 10 h. The Ga<sub>2</sub>Se<sub>3</sub> was ground and stored in a nitrogen filled glovebox.

#### 2.2 Synthesis of CsGaSe<sub>3</sub>

Compound  $CsGaSe_3$  was initially synthesized from a mixture of 0.344g (1.0 mmol)  $Cs_2Se$ , 0.094g (0.25 mmol)  $Ga_2Se_3$ , 0.193g

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(0.5 mmol) As<sub>2</sub>Se<sub>3</sub>, and 0.317g (4.0 mmol) Se. The reagents were mixed, sealed in an evacuated silica tube, and heated at 550 °C for 4 days. The tube was cooled at a rate of 5 °C/h to 250 °C followed by rapid cooling to room temperature. The solid products were washed with N,N-dimethylformamide (DMF) and diethyl ether. Product isolation afforded red rod-shaped single crystals of CsGaSe<sub>3</sub> as a single phase. Electron microprobe analysis of the crystals gave an average composition of Cs<sub>0.90</sub>Ga<sub>0.97</sub>Se<sub>3.00</sub>. The structural details of the compound were determined by a singlecrystal X-ray diffraction study. The product slowly decayed in air but is stable in water and common polar solvents, such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). A reaction without  $As_2Se_3$  ( $Cs_2Se:Ga_2Se_3:Se = 4:1:16$ ) also gave a single phase of CsGaSe<sub>3</sub>. In addition a quantitative synthesis of pure CsGaSe<sub>3</sub> was achieved by a reaction of the stoichiometric amounts of Cs<sub>2</sub>Se/ Ga<sub>2</sub>Se<sub>3</sub>/Se at 550 °C for 4 days.

### 2.3 Characterization

Elemental analysis on the products was performed with a JEOL JSM-35C scanning electron microscope (SEM) equipped with a Tracor Northern energy dispersive spectroscopy (EDS) detector. The sample was carbon coated and analyzed using a 20kV accelerating voltage and an accumulation time of 30s.

UV/Vis optical transmission measurements were performed at room temperature on single crystals using a Hitachi U-6000 microscopic FT spectrophotometer with an Olympus BH-2 metallurgical microscope over a range of 400-800 nm.

Differential thermal analysis (DTA) was performed on Shimadzu DTA-50 thermal analyzer. Samples (~30 mg) of ground crystalline material was sealed in a carbon coated silica ampoule under vacuum. A similar ampoule of equal mass filled with Al<sub>2</sub>O<sub>3</sub> was sealed and placed on the reference side of the detector. Sample was heated to 1000 °C at 10 °C/min, isothermed for 3 min followed by cooling at -10 °C/min to 50 °C. Residues of the DTA experiments were examined by X-ray powder diffraction. The reproducibility of the sample was checked by running multiple heating and cooling cycles.

Raman spectra were recorded on a Holoprobe Raman spectrograph equipped with a CCD camera detector using 633 nm radiation from a HeNe laser for excitation. Laser power at the sample was estimated to be about 5 mW and the focused laser beam diameter was ca. 10  $\mu$ m. The resolution of the spectra was 4 cm<sup>-1</sup>. Sixty four scans were allowed to obtain good quality spectra.

## 2.4 X-ray Diffraction

The crystal structure of CsGaSe<sub>3</sub> was determined by single-crystal X-ray diffraction methods. Preliminary examination and data collection were performed on a SMART platform diffractometer equipped with a 1K CCD area detector using graphite monochromatized Mo K<sub>a</sub> radiation at room temperature. A hemisphere of data was collected with narrow scan widths of  $0.30^\circ$  in  $\omega$  and an exposure time of 30 s/frame. The data were integrated using the SAINT program [20]. The program SADABS was used for the absorption correction [20]. The initial positions for all atoms were obtained using direct methods and the structures were refined by full-matrix least-squares techniques with the use of the SHELXTL crystallographic software package [20]. The final R values are R1 =0.0469 [I >  $2\sigma(I)$ ] and wR2 = 0.1361 [all data]. Crystallographic details are given in Table 1. The fractional atomic coordinates, equivalent isotropic and anisotropic displacement parameters are given in Table 2 and 3.

Table 1	Crystallographic de	etails for CsGaSe
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formula weight	439.51
space group	$P2_1/c$ (No. 14)
a, Å	7.727(1)
b, Å	13.014(3)
c, Å	6.705(1)
$\beta$ , deg	106.39(3)
$V, Å^3$	646.8(2)
Z	4
<i>T</i> , K	293(2) K
λ, Å	0.71073
$\rho_{\text{calcd}}, \text{g/cm}^3$	4.513
$\mu$ , cm <sup>-1</sup>	265.35
F(000)	752
Measured reflections	9184
Independent reflections	1496
crystal size, mm <sup>3</sup>	0.30 x 0.12 x 0.10
$\theta$ range, deg	2.75-27.91
GOF on $F_0^2$	1.058
R1 $[I > 2\sigma(I)]$	0.0469
wR2 <sup>a)</sup> (all data)	0.1361

<sup>a)</sup> wR2 =  $[\Sigma w (|F_0| - |F_0|)^2 / \Sigma w |F_0|^2]^{1/2}; w = 1/[\sigma^2 (F_0^2) + (0.084P)^2 + 3.04P];$  $P = [Max(F_o^2, 0) + 2F_c^2]/3$ 

Table 2 Atomic coordinates  $(x \ 10^4)$  and equivalent isotropic displacement parameters ( $Å^2 \times 10^3$ ) for CsGaSe<sub>3</sub>

	X	у	Z	$U_{eq}^{\ \ a)}$
Cs	7458(1)	4187(1)	2120(1)	43(1)
Ga	1821(1)	2720(1)	1420(1)	22(1)
Se(1)	2930(1)	762(1)	-1543(1)	29(1)
Se(2)	9973(1)	6714(1)	1901(1)	28(1)
Se(3)	4491(1)	1752(1)	1380(1)	30(1)

<sup>a)</sup>  $U_{ea}$  is defined as one third of the trace of the orthogonalized  $U_{ii}$  tensor.

**Table 3** Anisotropic displacement parameters ( $Å^2 \times 10^3$ ) for CsGaSe<sub>3</sub>

	$U_{II}$	$U_{22}$	U33	U <sub>23</sub>	$U_{I3}$	$U_{12}$
Cs	35(1)	34(1)	61(1)	-9(1)	17(1)	1(1)
Ga	22(1)	21(1)	24(1)	-1(1)	6(1)	0(1)
Se(1)	36(1)	19(1)	32(1)	1(1)	9(1)	5(1)
Se(2)	27(1)	28(1)	27(1)	3(1)	6(1)	10(1)
Se(3)	21(1)	26(1)	39(1)	0(1)	1(1)	3(1)

The anisotropic displacement factor exponent takes the form:  $-2\pi^2 \left[h^2 a^{*2} U_{11} + k^2 b^{*2} U_{22} + l^2 c^{*2} U_{33} + 2kl b^*c^* U_{23} + 2hl a^*b^* U_{13} + 2hk a^*b^* \right]$  $b^* U_{12}$ ]

Powder X-ray diffraction analyses were performed using a calibrated CPS 120 INEL X-ray powder diffractometer (Cu K<sub>a</sub> radiation) equipped with a position-sensitive detector, operating at 40kV/20mA with a flat sample arrangement.

### **3** Results and Discussion

### 3.1 Structure of CsGaSe<sub>3</sub>

The structure of CsGaSe<sub>3</sub> is CsAlTe<sub>3</sub>-type [21] and is built up of infinite  $\frac{1}{\infty}[GaSe_3]^-$  chains separated by Cs<sup>+</sup> cations, Figure 1. There is one crystallographically independent gallium atom in a slightly distorted tetrahedral coordination surrounded by each two  $\text{Se}^{2-}$  and  $\text{Se}_2^{2-}$  ions. The GaSe<sub>4</sub> tetrahedra are connected to each other by sharing corners and also by forming Se-Se bonds involving Se atoms of an-



Fig. 1 View of the unit cell along the c axis, 30% thermal ellipsoids. Cesium and gallium atoms are shown as black circles. Selenium atoms are shown as empty circles.



Fig. 2 View of a [GaSe(Se<sub>2</sub>)]<sup>-</sup> chain, 30 % thermal ellipsoids.

other corner. Therefore, each gallium atom is linked by each two Se<sup>2–</sup> and Se<sub>2</sub><sup>2–</sup> ion to form  $\frac{1}{\infty}$ [GaSe(Se<sub>2</sub>)]<sup>–</sup> chains along the *c*-axis, Figure 2. The Ga-Se bond lengths range from 2.383(1) to 2.424(1) Å and the interchain distances are above 3.816(2) Å (Se3-Se1). The crystallographically unique Cs<sup>+</sup> cation is eleven-coordinate by Se atoms in the range of 3.686(1)-4.200(1) Å, Figure 3.Other compounds that have the same structure include TIBS<sub>3</sub> [22].

Many known A/Ga/Q (A = alkali metals, Q = chalcogen) structures are based on GaQ<sub>4</sub> tetrahedra, which are connected to each other sharing their corners and edges. Unlike other known compounds the unique feature of CsGaSe<sub>3</sub> is the presence of diselenide groups in the structure. This is a rare example of a compound containing polychalcogenide bonds in the A/Group13/Q system (A = alkali metals, Q = chalcogen). Compound (Ph<sub>4</sub>P)[Ga(Se<sub>6</sub>)<sub>2</sub>] is another example that contains polychalcogenide Se<sub>6</sub><sup>2-</sup> ligands and adopts a very open framework [22]. The structure of CsGaSe<sub>3</sub> is closely related to CsGaS<sub>2</sub> [7], TlGaQ<sub>2</sub> (Q = Se, Te) [8–10] and Na<sub>4</sub>Ga<sub>2</sub>S<sub>5</sub> [11] containing [GaQ<sub>2</sub>]<sup>-</sup> chains, which are constructed by connecting tetrahedral GaQ<sub>4</sub> sharing their edges. Substitution of one Se<sup>2-</sup> ion in the [GaSe<sub>2</sub>]<sup>-</sup> chains for Se<sub>2</sub><sup>2-</sup> ion results in the [GaSe(Se<sub>2</sub>)]<sup>-</sup>



Fig. 3 Local environments of the Cs atom, 30 % thermal ellipsoids.

Table 4 Selected bond lengths/Å and angles/° for CsGaSe<sub>3</sub>

Cs-Se(1)#1	3.6858(12)	Cs-Se(2)#2	3.7408(12)		
Cs-Se(2)	3.8436(12)	Cs-Se(1)#3	3.8497(13)		
Cs-Se(3)	3.8602(12)	Cs-Se(3)#1	3.9090(12)		
Cs-Se(2)#4	3.9500(14)	Cs-Ga	4.0157(12)		
Cs-Se(1)#5	4.0676(14)	Cs-Se(3)#6	4.0725(16)		
Cs-Se(2)#7	4.1104(16)	Cs-Se(1)#8	4.2001(13)		
Ga-Se(2)#4	2.3834(13)	Ga-Se(2)#2	2.4051(12)		
Ga-Se(1)#5	2.4179(12)	Ga-Se(3)#9	2.4238(12)		
Se(1)-Se(3)	2.3712(13)				
Se(2)#4-Ga-Se(2)#2	110.21(5)	Se(2)#4-Ga-Se(1)#5	107.15(4)		
Se(2)#2-Ga-Se(1)#5	109.85(4)	Se(2)#4-Ga-Se(3)#9	115.02(5)		
Se(2)#2-Ga-Se(3)#9	109.11(5)	Se(1)#5-Ga-Se(3)#9	105.31(5)		
Symmetry transformations used to generate equivalent atoms:					

chain. Recently and during the revision of this paper the isostructural  $CsGaS_3$  was also reported. [24]

#### 3.2 Characterization of CsGaSe<sub>3</sub>

 $CsGaSe_3$  does not dissolve in polar solvents such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).  $CsGaSe_3$  exhibits an optical absorption edge at 2.25 eV determined by single-crystal optical transmission measurements, and this energy is consistent with the red color of the compound, Figure 4.

Preliminary differential thermal analysis showed that the compound CsGaSe<sub>3</sub> attacks the silica tube above  $\sim$ 700 °C. Thus, carbon-coated silica tube was used and the experiment indicated no melting below 1000 °C. Visual inspection



**Fig. 4** Optical absorption spectrum showing absorption edges at 2.25 eV. The sharp noises at high absorbance are due to the very low transmission of light at those energies.



Fig. 5 Raman spectrum of CsGaSe<sub>3</sub>. The peak at 238 cm<sup>-1</sup> is due to Se-Se stretching.

of the sample after the DTA experiment confirmed the lack of melting of the sample.

The Raman spectrum of CsGaSe<sub>3</sub> shows shifts at ~187, ~226, ~238, ~259, ~272 cm<sup>-1</sup>, Figure 5. Most probably the absorptions at 187 and 238 cm<sup>-1</sup> can be assigned to the Cs-Se and Se-Se stretching vibrations, respectively. The shifts at 226, 259 and 272 cm<sup>-1</sup> can be assigned to the Ga-Se vibrations because the Ga-Se vibrations of  $\beta$ -Ga<sub>2</sub>Se<sub>3</sub> containing GaSe<sub>4</sub> tetrahedra occur in the region at 220, 240, 250, 280, and 300 cm<sup>-1</sup> [25].

We made efforts to prepare ion-exchanged compounds such as LiGaSe<sub>3</sub> using a method described earlier [26]. CsGaSe<sub>3</sub> was mixed with LiI at a ratio of 1:30 (CsGaSe<sub>3</sub>: LiI) in a nitrogen-filled glovebox. The mixture was ground into a fine powder and pressed into a pellet to allow better interphase contact. The resulting pellet was sealed in an evacuated pyrex tube, and heated at various temperature for 2 days. The X-ray powder diffraction pattern of resulting product was identical to CsGaSe<sub>3</sub> indicating no lithium exchange.

In conclusion, a rather simple one-dimensional compound  $CsGaSe_3$  containing diselenide ions in A/Group13/ Q (A = alkali metals; Q = chalcogen) system has been synthesized and fully characterized. The presence of diselenide anions in the compound obtained from a polychalcogenide flux suggest possible new phases formed by combinations of various polychalcogenide anions and tetrahedral building units of gallium cations.

*Note added in proof:* While this manuscript was in review the related isostructural sulfur analog CsGaS<sub>3</sub> was reported: M. S. Devi, K. Vidyasagar, J. Chem. Soc., Dalton Trans. **2002**, 4751.

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