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## Raman spectra of gallium sulfide based glasses

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### Abstract

Raman investigation of glasses  $x\text{GeS}_2\text{--Ga}_2\text{S}_3\text{--}y\text{MCl}$ ,  $\text{Ga}_2\text{S}_3\text{--}2\text{MCl}$  (where  $\text{M} = \text{Ag, Tl, Rb, Cs}$ ) and melt  $\text{Ga}_2\text{S}_3\text{--}2\text{CsCl}$  has been carried out for various  $x$  and  $y$ . Raman spectra have been interpreted in the frame of the model that gallium is fourfold coordinated in the chalcogenide/halide glasses and forms complex anions such as  $[\text{GaS}_{3/2}\text{Cl}]^{1-}$ . Stability of these units and type of their interconnection (corner shared or edge shared tetrahedra) depends on cation radius of a metal and correlates with glass-forming ability.

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### 1. Introduction

Germanate and gallate,  $\text{Ga}_2\text{O}_3\text{--M}_x\text{O}$  ( $\text{M}$  – metal), glasses are well known and studied. It was found by nuclear spin resonance (NMR) [1], X-ray absorption [2], infra-red (IR) and Raman spectroscopy [3], that Ge and Ga have tetrahedral environments. The glasses including sulfur instead of oxygen are less studied. The compound  $\text{GeS}_2$  is a network glass former and its IR and Raman spectra can be well interpreted based on the vibrational modes of tetrahedral pseudomolecular subunits  $\text{GeS}_{4/2}$  (breathing mode  $342\text{ cm}^{-1}$ ) [4]. The pure compound  $\text{Ga}_2\text{S}_3$  can be transformed into the glassy state only as film [5]. Recently bulk glasses containing gallium sulfide have been produced [18,9,15]. The structure of these glasses is still a topic of discussion.

The aim of this work is structural investigation of  $\text{Ga}_2\text{S}_3$  based glasses by Raman spectroscopy.

### 2. Experiment

#### 2.1. Sample preparation

The samples were synthesized from metal chloride, gallium and sulfur at a high temperature in a quartz ampoule which had been sealed under vacuum.  $\text{AgCl}$  was produced by dissolving silver in nitric acid and then precipitating it by  $\text{HCl}$ . The other metal chlorides, sulfur and gallium were commercial reagents (Reachem). All the chlorides had been dried thoroughly just before synthesis. The syntheses were carried out at temperatures  $1000\text{--}1150^\circ\text{C}$  for 4–10 h in the rocking furnace. The samples (in an ampoule) were vitrified by quenching in water or air. The choice of cooling rate depended on glass-forming ability.  $\text{TlGaS}_{1.5}\text{Cl}$  melt was quenched by splash

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cooling on a rotating copper wheel (cooling rate  $10^4$ – $10^5$  K/s). The glassy state of all samples was confirmed by X-ray analysis.

## 2.2. Raman spectroscopy

The setup consists of Kr ion laser at 647.1 nm and a 1 m double monochromator (Jobin Yvon U1000, 1800 lines/mm) with photon counting (dark count rate 1/s). Spectra were taken using 512 channels,  $1\text{ cm}^{-1}$  each, at incident beam powers of 100–500 mW, on the Stokes side. Measurements were carried out at  $90^\circ$ , with samples placed into sealed cylindrical quartz ampoules.

## 3. Results

In order to investigate non-crystalline  $\text{Ga}_2\text{S}_3$  structure, we synthesized glass with mixed  $(\text{GeS}_2)_{(0.8)}(\text{Ga}_2\text{S}_3)_{(0.2)}$  composition. In Fig. 1 we present the reduced Raman spectra of  $(\text{GeS}_2)_{(1-x)}(\text{Ga}_2\text{S}_3)_{(x)}$  glasses for  $x = 0$  (pure  $\text{GeS}_2$ ) and  $x = 0.2$  (the procedure of the reduction was proposed by Galeener and Sen [19]). The spectra show that insertion of a relatively small quantity of  $\text{Ga}_2\text{S}_3$  into  $\text{GeS}_2$  glass former leads only to the redistribution of intensity in the  $350$ – $420\text{ cm}^{-1}$  range and to displacement of the lower frequency peak from  $258\text{ cm}^{-1}$  to  $268\text{ cm}^{-1}$ . A similar Raman curve shape was obtained for the samples with  $x \sim 0.18$  and  $x \sim 0.07$  [6]. The glasses which include

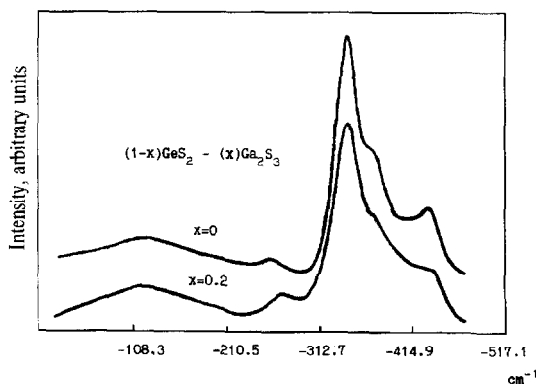


Fig. 1. Reduced Raman spectra of glasses  $(1-x)\text{GeS}_2-(x)\text{Ga}_2\text{S}_3$ , where  $x = 0, 0.2$ .

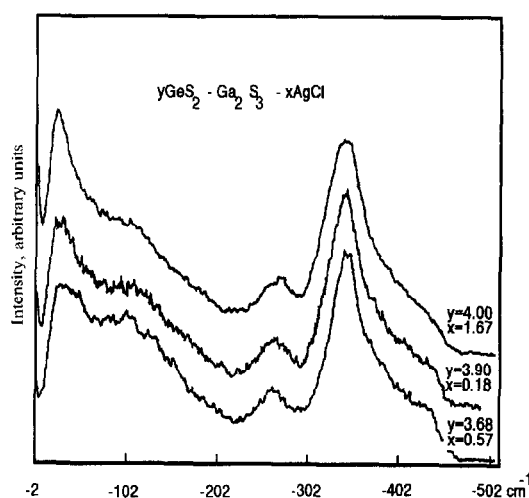


Fig. 2. Raman spectra of  $y\text{GeS}_2-\text{Ga}_2\text{S}_3-x\text{AgCl}$  glasses.

metal ions are of a great significance for applications. However, the glass-forming regions of the mixed systems including metal salts have quite a narrow composition range. Taking into account the tendency of Ga towards fourfold coordination and formation of tetrahedral complexes (e.g.,  $[\text{GaCl}_4]^-$ ), it was of interest for us to add metal halides to glasses containing  $\text{Ga}_2\text{S}_3$ , e.g., to  $\text{GeS}_2-\text{Ga}_2\text{S}_3$ , and also to pure  $\text{Ga}_2\text{S}_3$  in order to bind the metal ions with a fourfold network formed by tetrahedral coordinated Ga. Indeed we have found glass formation in broad composition regions of the gallium sulfide

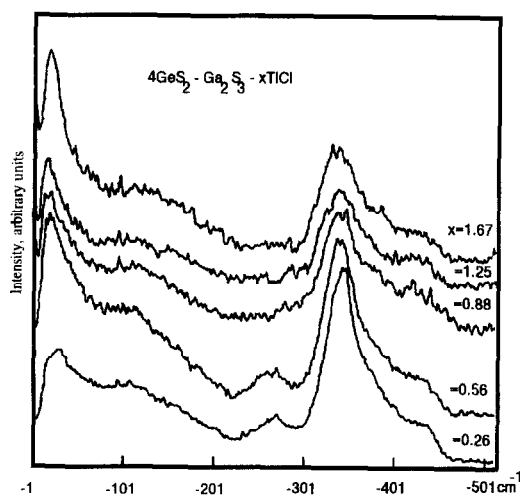
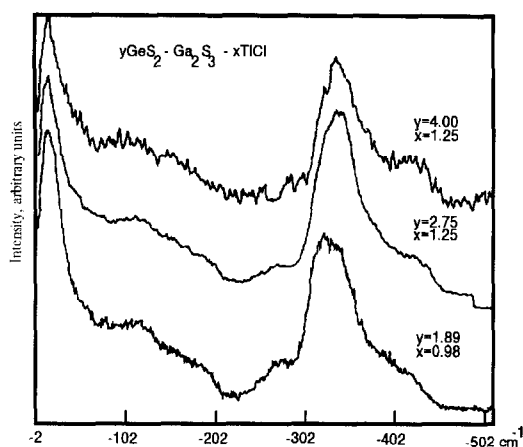


Fig. 3. Raman spectra of  $4\text{GeS}_2-\text{Ga}_2\text{S}_3-x\text{TiCl}$  glasses.

Fig. 4. Raman spectra of  $y\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-}x\text{TlCl}$  glasses.

systems with various metal halides [9]. Here we will discuss AgCl, TlCl, RbCl and CsCl additions.

Phase diagrams show that metal chlorides don't interact with  $\text{GeS}_2$  [10], therefore we assume that metal chloride additions interact with  $\text{Ga}_2\text{S}_3$  only and we can extract the information about the interaction from Raman spectra.

We were able to produce glasses containing up to 39 mol% AgCl in the  $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-AgCl}$  system [9]. Raman spectra are depicted in Fig. 2. If AgCl content is increasing, at an essentially constant ratio of  $\text{GeS}_2$  to  $\text{Ga}_2\text{S}_3$ , the shape of the Raman spectrum shows only negligible changes. This fact seems to

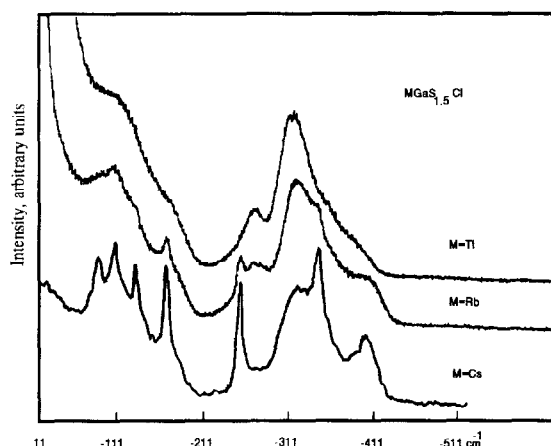
Fig. 5. Raman spectra of glassy  $\text{MGa}_{1.5}\text{Cl}$ , where  $M = \text{Tl}, \text{Rb}$  or  $\text{Cs}$ .

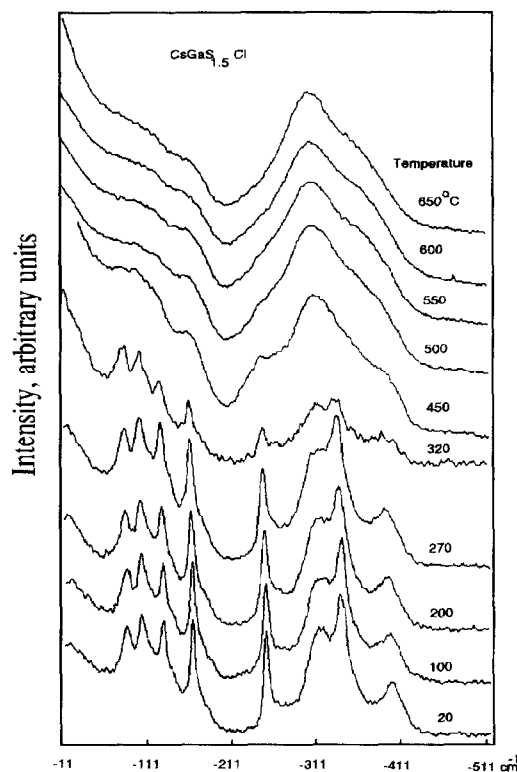
Table 1

Ion radius calculated according to Goldschmidt (\* 1) and Pauling (\* 2)

Metal	Ion radius A	
	* 1	* 2
Ag	1.13	1.26
Tl	1.49	1.44
Rb	1.49	1.48
Cs	1.65	1.69

prove that AgCl does not interact with the  $\text{GeS}_2\text{-Ga}_2\text{S}_3$  glass matrix.

Studying the  $\text{GeS}_2\text{-Ga}_2\text{S}_3\text{-TlCl}$  system, we have found that the glass-forming composition region is broader (viz about a factor of two) than one in the AgCl system [9]. Also, there is some difference from the previous system in the Raman spectra (see Fig. 3). Increasing the TlCl contents at a constant ratio of  $\text{GeS}_2$  to  $\text{Ga}_2\text{S}_3$  (4:1) leads to two major effects. The

Fig. 6. Raman spectra of  $\text{CsGa}_{1.5}\text{Cl}$  in the glassy and melt states at different temperatures (from 20 to 650°C).

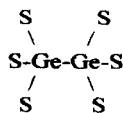
first, the breathing mode line of  $\text{GeS}_2$  glass (structure units  $\text{GeS}_{4/2}$ ,  $342\text{ cm}^{-1}$ ) is broadened to the lower frequency side; later we shall show that this is due to the addition (and/or mixing) of the breathing mode contribution at  $\sim 320\text{ cm}^{-1}$  of  $\text{GaS}_{3/2}\text{Cl}^{-1}$  structure subunits. The second, the peak disappears at  $268\text{ cm}^{-1}$ . Besides, the increase of  $\text{Ga}_2\text{S}_3$  content (at approximately constant  $\text{TlCl}$  content) results in the shift of the band from  $340\text{ cm}^{-1}$  to  $320\text{ cm}^{-1}$  (see Fig. 4).

The glass-forming composition region of systems containing  $\text{Ga}_2\text{S}_3\text{--MCl}$  only ( $\text{M}$  – metal), increases according to increasing of metal ion radius [9]. Raman spectra of glasses  $\text{MGaS}_{1.5}\text{Cl}$ , where  $\text{M} = \text{Tl}$ ,  $\text{Rb}$ ,  $\text{Cs}$ , are represented in Fig. 5. This is a sequence of ions with increasing radius of  $\text{M}^+$  (see Table 1). There is a pronounced difference between the spectra of the glasses containing  $\text{Tl}$  and  $\text{Cs}$  while the spectrum  $\text{Rb}$  including glass is close to a superposition of the two other spectra.

The heating of glassy  $\text{CsGaS}_{1.5}\text{Cl}$  up to melt state results in disappearing of this difference (Raman spectra of both glassy and melt  $\text{CsGaS}_{1.5}\text{Cl}$  are represented in Fig. 6).

#### 4. Discussion

In the Raman spectrum of glassy  $\text{Ge}_x\text{S}_{1-x}$  ( $\text{GeS}_2$  glass for example, see Fig. 1), the peak at  $258\text{ cm}^{-1}$  has been ascribed to the stretching of the direct  $\text{Ge--Ge}$  bond in the subunits of the



type (e.g.,  $\text{Ge}_2\text{S}_{6/2}$ ) [7]. In glassy stoichiometric composition these homobonds exist due to concentration fluctuations. Their content is relatively low and depends on glass preparing regime. Certainly this peak is pronounced in glassy  $\text{Ge}_x\text{S}_{1-x}$  at  $x > 0.33$  (i.e., where there is a chalcogen deficit relative to stoichiometric  $\text{GeS}_2$ ), at  $x = 0.37$  for example [4]. The existence of  $\text{Ge--Ge}$  homobonds in  $\text{Ge--S}$  glasses was also confirmed by Feltz et al. with ESCA [8].

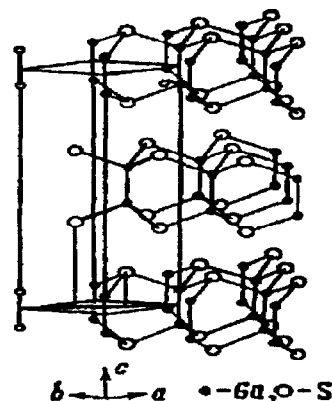
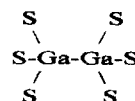
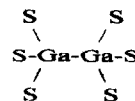


Fig. 7. GaS crystal structure.

We propose to assign the  $268\text{ cm}^{-1}$  line in Raman spectra of gallium sulfide containing glasses (see Fig. 1,  $x = 0.2$ ) to a stretching of the  $\text{Ga--Ga}$  bond in a complex subunit



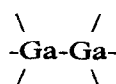
in an analogous way<sup>1</sup>. A slightly higher frequency (by 3.8%) would be in accordance with the somewhat smaller mass of  $\text{Ga}$  compared to  $\text{Ge}$  (by 4.2%), so that 2.1% frequency shift is expected (to  $263\text{ cm}^{-1}$ ). A small discrepancy may be due to the difference between the force constants. We have some additional reasons for such assumption. This complex unit



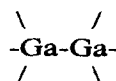
does not contradict  $\text{GaS}$  crystal structure (see Fig. 7). Besides, the peak intensity depends on the ratio of  $\text{Ga}$  and  $\text{S}$  components as in the  $\text{Ge--S}$  system. The increase of  $\text{Ga}$  contents relative to  $\text{S}$  results in the increase of the band intensity [6,15].

<sup>1</sup> At any rate, two sulfur atoms of this structure unit are threefold coordinated ( $\text{Ga}_2\text{S}_{4/2}\text{S}_{2/3}$ ).

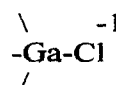
In the gallium sesquisulfide–germanium disulfide–metal chloride glass systems, when the ratio of Ga–X (X – chalcogen or galogen) components amounts to 1:4, i.e., the possibility of fourfold coordination of gallium by chalcogen/halogen takes place ( $\text{GaX}_4$ ), the peak disappears at  $268\text{ cm}^{-1}$  (with the exception of the system with  $\text{AgCl}$ , Fig. 2). The disappearance of the above mentioned mode of the



bond with the increasing  $\text{TlCl}$  content (see in Fig. 3) can probably be explained by the formation of a complex anion: instead of



homobonds,

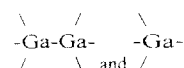


heterobonds appear. This statement is in agreement with the set of spectra shown in Fig. 4, where the ratio of  $\text{GeS}_2$  to  $\text{Ga}_2\text{S}_3$  is changed at approximately constant  $\text{TlCl}$  content. Here one can see an intensity shift from the band at  $340\text{ cm}^{-1}$  (ratio 4:1) to a position around  $320\text{ cm}^{-1}$  (ratio 1.88:1). Summarizing both observations we conclude that, when Cl–Ga bonds become possible due to addition of metal chloride to a  $\text{Ga}_2\text{S}_3$  containing glass, fourfold coordination of Ga by sulfur and chlorine develops, and that the breathing mode of such tetrahedra is about  $320\text{ cm}^{-1}$ . The idea of mixed halogen–chalcogen environment of Ga in the glassy state was also considered [11,17].

Formation of such tetrahedra assists glass formation, therefore there is a possibility of glass formation even without a  $\text{GeS}_2$  glass-forming matrix. In-

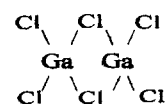
deed we have found wide glass-forming regions in the  $\text{Ga}_2\text{S}_3$ – $\text{MCl}$  systems [9].

According to the previously mentioned facts, we argue that the effects of the interaction of  $\text{Ga}_2\text{S}_3$  with  $\text{TlCl}$  are similar both with and without the  $\text{GeS}_2$  component. It is obvious, for example, of  $\text{TlGaS}_{1.5}\text{Cl}$  glass. The Raman spectrum shown in Fig. 5(a) can be explained satisfactorily within the framework of the above described model as a superposition of the contributions from pseudomolecular subunits



Both our Raman data of glassy  $\text{TlGaS}_{1.5}\text{Cl}$  and the data for  $\text{GaCl}_4^{1-}$  [16,17] are represented in Table 2. The exact agreement is obtained for both sets except for the discussed peak at  $268\text{ cm}^{-1}$ . The formation of tetrahedral complex anion  $\text{GaS}_{1.5}\text{Cl}^{1-}$  seems to be easier with tetrahedral glassy matrix  $\text{GeS}_2$ , so that at a ratio of  $\text{Ga}_2\text{S}_3$  to  $\text{TlCl}$  equal to 1:2, the peak at  $268\text{ cm}^{-1}$  is invisible (Fig. 3), without  $\text{GeS}_2$  one is distinguished yet (Fig. 5(a)) (maybe it is just a result of different resolution and content).

As said before, the increase of the metal ion radius at substitution of Tl by Cs in the glassy  $\text{MGaS}_{1.5}\text{Cl}$  results in radical changes of Raman spectra. Table 3 presents the experimental Raman frequencies of  $\text{CsGaS}_{1.5}\text{Cl}$  glass together with known data and the assignments for  $\text{GaCl}_3$  melt [12,13] (these assignments are based on normal vibrations analysis of bridged  $\text{X}_2\text{Y}_6$  molecules [14]; the observed bands are mostly assigned to the modes of the  $\text{Ga}_2\text{Cl}_6$  dimer



It is really striking that all Raman bands of  $\text{CsGaS}_{1.5}\text{Cl}$  glass except the  $215\text{--}230\text{ cm}^{-1}$  region, correspond precisely to the band of  $\text{GaCl}_3$  melt, i.e., to the vibration frequencies of dimer  $\text{Ga}_2\text{Cl}_6$ . Most dimer modes are assigned to the

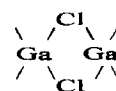


Table 2  
Raman frequencies ( $\text{cm}^{-1}$ )

$\text{GaCl}_4^-$ melt [16]	$\text{CsGaCl}_4$ melt [17]	$\text{TlGaS}_{1.5}\text{Cl}$ glass (this work)	$\text{CsGaS}_{1.5}\text{Cl}$ melt, $T = 650^\circ\text{C}$ (this work)
115	120	$\sim 107$	122
153	153	$\sim 174$ $\sim 271$	172
346	343	$\sim 316$	315
380	370	$\sim 384$	381

ring, that is, to the edge sharing tetrahedra. Hence we assume (taking into account similarity of S and Cl atoms weights) that in the  $\text{Ga}_2\text{S}_3$ –CsCl glass tetrahedral  $\text{GaS}_{3/2}\text{Cl}$  subunits are linked into chains by sharing common edges (Fig. 8(c)). Assumption about chain like structure in the system  $\text{Ga}_2\text{S}_3$ – $\text{Na}_2\text{S}$  was proposed [15]. As the temperature is increased to  $650^\circ\text{C}$  ( $T_L = 550^\circ\text{C}$ ), the Raman spectrum of  $\text{CsGaS}_{1.5}\text{Cl}$  changes, especially between  $270^\circ\text{C}$  and  $400^\circ\text{C}$  (see Fig. 6). We propose that in accordance with the proposed chain model the chains are destroyed and at about  $500^\circ\text{C}$  the spectrum is similar to the case of Tl-containing glass for which we propose the structure formed by the corner connected tetrahedra. However, in contrast to the glasses containing  $\text{TlCl}$ , the band at  $268\text{ cm}^{-1}$  appears to be absent (unless it is drowned by very broad main peak at  $\sim 320\text{ cm}^{-1}$ ). This absence points to the possibility that each Ga atom is saturated by fourfold coordina-

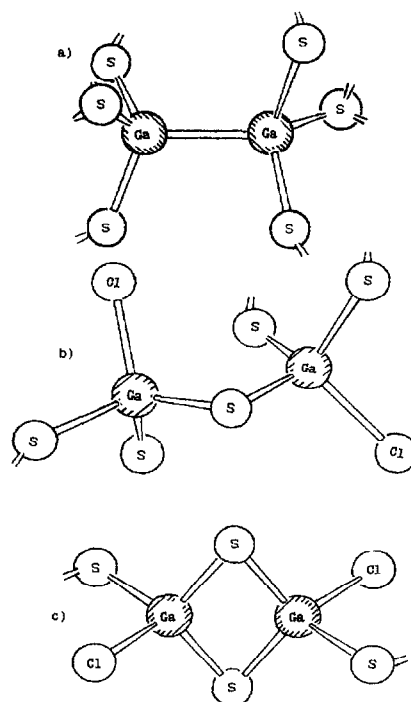


Fig. 8. Models of structure units proposed for  $\text{Ga}_2\text{S}_3$ – $\text{MCl}$  (M – metal) glasses.

tion of S plus Cl. As can be seen from the Raman data for  $\text{GaCl}_4^-$  [16,17] in Table 2, there appear the same vibration energies as in the high temperature spectrum of  $\text{CsGaS}_{1.5}\text{Cl}$ .

Table 3  
Raman frequencies ( $\text{cm}^{-1}$ )

$\text{CsGaS}_{1.5}\text{Cl}$ (glass), this work	$\text{Ga}_2\text{Cl}_6$ (melt), data and assignment [12]		$\text{Ga}_2\text{Cl}_6$ (melt), data and assignment [13]	
86	96 vs	$\nu_{12}$ rocking	100 s	$\nu_4$ deformation
106	107 sh	$\nu_7$ wagging	113sh	$\nu_{12}$ rocking
131			128 sh	$\nu_7$ wagging
165	167 s	$\nu_4$ deformation	167 m	$\nu_3$ ring in-plane bend
	228 w	$\nu_{15}$ symmetric twisting	215 sh	$\nu_{15}$ symmetric twisting
			231 w	$\nu_6$ ring in-plane stretching
253	268 w	$\nu_9 * 2 = 246$ rocking	268 w	$\nu_3 + \nu_4$
317	321 m	$\nu_3$ ring in-plane bend	318 mw	$\nu_2$ ring breathing
343	342 ms	$\nu_2$ ring breathing	344 m	$(\nu_3 + \nu_4) * 2$
400	412 vs	$\nu_1$ symmetric stretching	413 s	$\nu_1$ symmetric stretching
	464 m	$\nu_{11}$ antisymmetric stretching	462 m	$\nu_{11}$ antisymmetric stretching

## 5. Conclusion

Gallium in the chalcogenide/halogenide glasses is fourfold coordinated as in oxide glasses. At insufficient chalcogen/halogen content for tetrahedral environment of Ga, the fourth neighbour of gallium is gallium too (structure unit is shown in Fig. 8(a)). The addition of metal chloride to gallium sesquisulfide results in the formation of complex anion  $\text{GaS}_{3/2}\text{Cl}^{1-}$ . Stability of this complex depends on the cation size and increases along with increasing of the cation radius. The  $\text{Ag}^+$  cation has the smallest radius of the above mentioned cations — such a complex is not typical for Ag as for an outside cation. One is stable for Tl, but gallium–gallium coordination exists; for Cs with the largest radius among the discussed cations, the complex is stable up to 650°C and Ga is fully tetrahedral coordinated by chalcogen/halogen. The structure of  $\text{TlGaS}_{1.5}\text{Cl}$  glass and  $\text{CsGaS}_{1.5}\text{Cl}$  high temperature liquid is determined by corner connected tetrahedra (Fig. 8(b)), but the structure of  $\text{CsGaS}_{1.5}\text{Cl}$  glass is defined by tetrahedra connected by common edges into chains (Fig. 8(c)). The structure of Rb-containing glasses is determined by corner connected tetrahedra as well as by edge connected. Glass-forming ability follows the same sequence as complex stability.

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