



Structural studies of technologically modified GeS₂ glasses and film

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Abstract

This paper is aimed at combining quantum-chemical calculations of the frequency spectra of clusters and spectroscopic studies of vibrational spectra of GeS₂ glasses, obtained at different conditions, and films, prepared on their base. The optimized geometries and Raman spectra of edge- and corner-sharing, and ethane-like Ge–S clusters have been obtained from ab initio calculations with RHF/6–31G* basis set. The most intensive bands of calculated Raman spectrum of such clusters are in good agreement with experimental Raman data.

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1. Introduction

Working out and construction of stable optical coatings, holographical elements, high-resolution resists based on chalcogenide glassy semiconductors (ChGS) require information concerning the nearest-order structure of ChGS-based thin films. At vacuum thermal deposition of thin layers based on glasses (g) g-As₂S₃ their structure differs from that of the bulk glasses [1–3]. The vapour phase of ChGS contains ~10% of clusters [2]. Being deposited on the heated substrate, not all of the clusters merge into a continuous matrix which results in the formation of micro-non-uniform

films [2]. When the films are formed from the cluster beams the level of the cluster merging on the surface increases due to their ionization and subsequent considerable increase in kinetic energy by acceleration in electric field [2]. A slight increase in the kinetic energy of the clusters is also achieved at the transition from common to flash thermal deposition of films [4]. For strongly dissociate materials one can manage to reduce the non-uniformity size at the film–substrate boundary [2].

Among the ChGS glassy g-GeS₂ belongs to the glasses composed of the components with drastically different vapour pressure [2]. The specific feature of its structure is the presence of GeS₄ tetrahedra, linked together in the matrix by both an edge and angles [6]. At the deviation of Ge_xS_{1–x} glass composition towards germanium-rich material a new structural unit (s.u.) in the matrix arises,

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the coordination of germanium in it being a subject of a long discussion [2,6–9]. The authors of Refs. [6,7] consider that at the increase of germanium content in $\text{Ge}_x\text{S}_{1-x}$ glasses with respect to stoichiometric $\text{Ge}_{33}\text{S}_{67}$ interpenetration of GeS_4 tetrahedra in the glasses occurs, leading to the formation ethane like clusters with Ge–Ge bonds. In this case the coordination of Ge does not change, remaining four-fold. In Refs. [2,8] it is stated that at the enrichment of $\text{Ge}_x\text{S}_{1-x}$ glasses by germanium, part of Ge atoms changes their coordination with respect to sulphur from four-fold to three-fold, and in the structure matrix $\text{GeS}_{3/3}$ s.u. are formed along with $\text{GeS}_{4/2}$.

In order to increase the degree of reliability of interpretation of vibrational spectra in the recent years quantum-chemical methods are used to calculate the frequency spectra of clusters [9,10].

The aim of this work is comparing quantum-chemical calculations of clusters and vibrational spectra of GeS_2 glasses, obtained at different conditions, and films, prepared on their base. We calculated geometries with energy minimum of tetrahedral GeS_4 clusters connected by an edge, corner and ethane-like Ge–S clusters. Then Raman spectra were calculated with the same basis sets. The most intensive bands of calculated Raman spectrum of such clusters are in good agreement with experimental Raman data.

2. Experimental technique and calculations

The glasses for the investigation were synthesized by melt quenching from $T_1 = 1173$ and $T_2 = 1373$ K with cooling rate $V = 10^2$ K/s. The technique of GeS crystal synthesis is described in Refs. [2,8].

Raman spectra of GeS_2 glasses and crystalline powder GeS were measured by RENISHAW SYSTEM 1000 Raman spectrometer with CCD (Charge Coupling Device) detecting cell. Raman scattering was excited by a diode laser with the wavelength 785 nm and output power 25 mW. The spectra were measured in a 180° geometry. Raman spectra of $\beta\text{-GeS}_2$ were measured using a Spectra Physics Model 168 (Ar) laser with the wavelength 488 nm and output power 1 W.

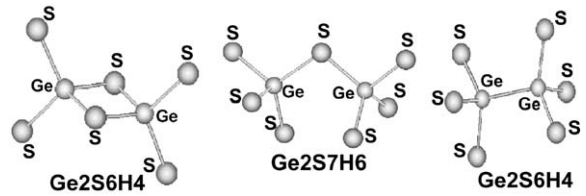


Fig. 1. Structure of germanium sulphide clusters.

The films for the studies were $\sim 1 \mu\text{m}$ thick, obtained by flash evaporation on the substrates of Si and polished quartz. Raman spectra were measured using a RENISHAW SYSTEM 1000 spectrophotometer, wavelength 785 nm, resolution 2 cm^{-1} .

Optimized geometries and vibrational spectra of clusters were calculated by ab initio RHF (restricted Hartree-Fock) method using GAMESS (US) software, the basis set 6–31 G with polarization d-functions for Ge and S atoms. Terminal sulphur atoms were saturated by hydrogen. After Raman calculation the frequencies were recalculated to minimize hydrogen influence. The optimized geometries of the clusters are given in Fig. 1.

3. Results and discussion

Fig. 2 shows the Raman spectrum of a g- GeS_2 (T_1 , V). The bands with the maxima at 430, 368, 340 cm^{-1} are clearly seen in the spectrum. The comparison of the shape and frequency position of the bands from the measured spectra with the data given in Refs. [5,6,9,11] shows a good agreement. The band at 340 cm^{-1} is related to the vibrations of corner-shared tetrahedra, and the bands at 430 and at 368 cm^{-1} —to the vibrations of atoms in the edge-shared tetrahedra. The calculations of the Raman spectrum of a Ge_2S_6 ($\text{Ge}_2\text{S}_6\text{H}_4$) cluster of the tetrahedra with a common edge have shown the most intense band in the frequency spectrum to be localized at 363 cm^{-1} (Fig. 3). In the calculated spectrum a low-frequency shift of the most intense band by 5 cm^{-1} with respect to the experimental spectrum (Fig. 2) is observed.

The calculated frequency spectrum of $\text{Ge}_2\text{S}_7\text{H}_6$, cluster of the corner-sharing tetrahedra (Fig. 3), contains the most intense band of valence

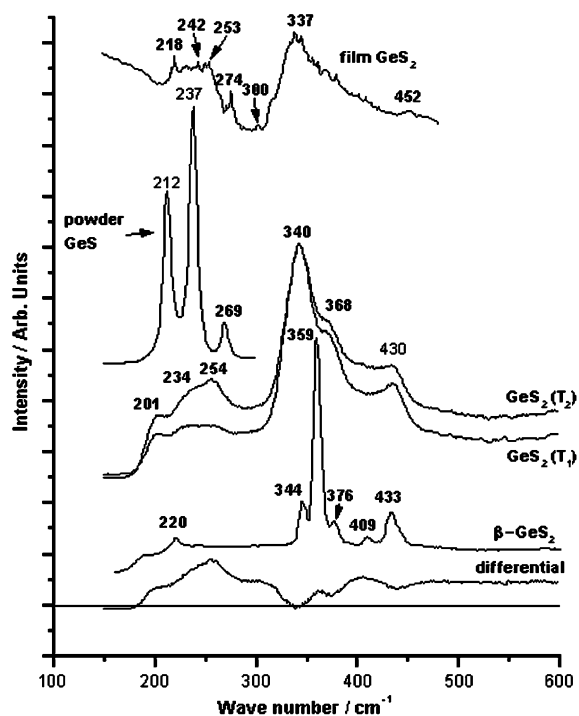


Fig. 2. Raman spectrum of GeS_2 glasses, GeS_2 film, crystalline powder GeS , crystalline powder $\beta\text{-GeS}_2$ and differential $(I(\text{GeS}_2(T_2)) - I(\text{GeS}_2(T_1)))$ spectra.

vibrations at 333 cm^{-1} . This band is also shifted by 7 cm^{-1} to the low-frequency range with respect to the experimental data for the vibrations of clusters of corner-sharing GeS_4 tetrahedra. Such discrepancies are within typical errors of the calculations by this method. However, the shift may also be explained by the interaction of clusters in the matrix of the bulk glass structure. According to the data of Refs. [2,4], the free GeS_4 tetrahedron vibration band in solution is centred at 386 cm^{-1} , and that of an ideal tetrahedral group in Cd_4GeS_6 crystal—at 396 cm^{-1} . When a chain of corner-sharing GeS_4 tetrahedra is formed, the tetrahedra vibration frequency shifts downward and the maximum of the valence vibrations of Ge–S bonds in the chain clusters is observed near 340 cm^{-1} [2]. The role of edge-linked clusters consists in connecting the chain clusters and formation of layer-chain fragments, similar to those in $\beta\text{-GeS}_2$ [2,4]. The above slight deviations of the calculated spectrum from the experimental data can possibly

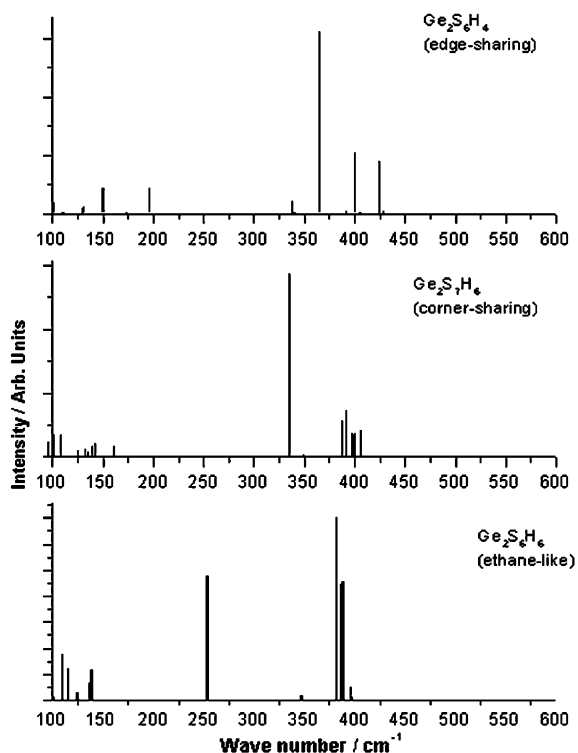


Fig. 3. Calculated Raman spectrum of clusters.

result from the simplified representation of the glass structure, consisting in a separate consideration of clusters in the form of corner-sharing and edge-sharing tetrahedra.

We proceed considering the case of GeS_4 tetrahedra interpenetration (formation of so-called ethane-like s.u.) and formation of Ge–Ge bonds ($\text{Ge}_2\text{S}_6\text{H}_6$ cluster). The frequency spectrum of such cluster is characterized by intense vibrations at 250 and 380 cm^{-1} . The increase of the band intensity at 250 cm^{-1} is observed in the Raman spectrum of $g\text{-GeS}_2$ (T_2V) at the increase of the temperature, from which the melt was quenched. This is specially pronounced at the differential spectrum (the lower curve in Fig. 2). Hence, the calculations of the vibrational spectrum enable the band at 250 cm^{-1} to be assigned to the vibration of atoms in the ethane-like clusters. Though we have not observed a distinct appearance of the band at 380 cm^{-1} in the spectra of such glasses, but, taking into account the calculations error and the broad-

ening of the main band centred at 340 cm^{-1} in the Raman spectrum of g-GeS₂ (T_2V), the contribution of the vibrations of homopolar-bond clusters into the high-frequency wing of the band broadening is quite possible. Thus, the performed calculations of vibrations of the cluster with the interpenetrating tetrahedra confirm the assumption [7] on the formation of s.u. in germanium-rich Ge_xS_{100-x} glasses. In some papers [8] the existence of s.u. SGe_{3/3} with three-fold coordinated Ge in g-GeS₂ was assumed. As follows from the resonant Raman data for As-GeS₂ glasses, an intense band at 290 cm^{-1} corresponds to such s.u. [12]. Our resonant Raman data on g-GeS₂, excited by 488 nm laser [13], registered band at 285 cm^{-1} , but their intensity was very low. Hence, very small quantity of three-fold coordinated germanium s.u. exists in glasses GeS₂.

An interesting feature, clearly seen in the differential spectrum of GeS₂ glasses, is revealed in the presence of very slight bends in the range of 400 and 500 cm^{-1} (Fig. 2). It is in this spectral range, where, according to the data of quantum-chemical calculations, the frequencies of sulphur atoms at the ends of Ge–S and S–S bond frequencies, respectively, are expected (Fig. 3).¹ Hence, the contribution of the terminal sulphur and S–S inclusions in the chains is possible, and the low intensity of the peaks is the evidence for the small number of such bonds in the glass structure matrix. A similar situation was observed in the analysis of arsenic trisulphide films [14].

The temperature $T_2 = 1373\text{ K}$ exceeds the melting point of the components loaded in the quartz ampoule. Hence, the process of obtaining GeS₂ glass from the overheated melt should be similar to the process of obtaining amorphous GeS₂ film by discrete thermal evaporation in vacuum at the evaporator temperature 1373 K. Indeed, the maximum position and shape of a complex band at 337 cm^{-1} in the Raman spectrum of GeS₂ (T_2) film (Fig. 2) does not undergo a considerable transformation compared to the glass spectrum while the band centred at 253 cm^{-1} somewhat broadens and

contains a number of peaks at 218, 242 and 274 cm^{-1} . The frequency positions of these bands are close to the most intense bands in the Raman spectrum of crystalline GeS powder (Fig. 2) where germanium is three-fold coordinated with respect to sulphur [15]. Weaker bands at 300 and 452 cm^{-1} are close to the positions of the bands in Ge [10] and sulphur S_n [2], respectively.

Since the evaporation of g-GeS₂ is of dissociative character [2]



then at the deposition of the film the vapour phase components are partially taken and continuous structure matrix is formed. Hence, according to the above structural interpretation of the Raman spectrum of the a-GeS₂ film, the structure of the film is non-uniform and contains tetrahedral, ethane-like, three-fold coordinated s.u., free germanium and sulphur.

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¹We also calculated geometries and Raman frequencies of some Ge–S clusters with S–S bonds. The frequencies of vibrations of such bonds are at 500 cm^{-1} .

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