

# Intrinsic phase separation in low-temperature quenched arsenic trisulfide glass

O. Shpotyuk<sup>1,2\*</sup>, A. Kovalskiy<sup>3</sup>, J. Trimble<sup>3</sup>, M. Vlček<sup>4</sup>, Ya. Shpotyuk<sup>5,6</sup>, S. Kozyukhin<sup>7</sup>

<sup>1</sup> Vlokh Institute of Physical Optics

23, Dragomanov str., Lviv, 79005, UKRAINE

<sup>2</sup>Institute of Physics of Jan Dlugosz University

13/15, al. Armii Krajowej, Czestochowa, PL-42201, POLAND

<sup>3</sup> Department of Physics & Astronomy, Austin Peay State University  
Clarksville, TN 37044, USA

<sup>4</sup> Department of General and Inorganic Chemistry, Faculty of Chemistry  
University of Pardubice, 532 10 Pardubice, CZECH REPUBLIC

<sup>5</sup> Centre for Innovation and Transfer of Natural Sciences and Engineering Knowledge

1, Pigonia str., 35310 Rzeszow, POLAND

<sup>6</sup> Ivan Franko National University of Lviv,  
1, Universytetska str., 79000 Lviv, UKRAINE

<sup>7</sup> N.S. Kurnakov Institute of General and Inorganic Chemistry  
31 Leninsky Pr., Moscow, 199991, RUSSIA

## PACS codes / keywords:

61.43.Fs, 64.70.Pf / chalcogenide glass, Raman scattering, disorder

## Highlights:

Intrinsic phase separation in binary As-S glasses near As<sub>2</sub>S<sub>3</sub> stoichiometry

Chemical disorder in glassy As<sub>2</sub>S<sub>3</sub> under rapid quenching from high temperatures

Phase demixing in As<sub>2</sub>S<sub>3</sub> glass under prolonged low-temperature homogenization

Coordination disordering in As<sub>2</sub>S<sub>3</sub> glass under reduced low-temperature homogenization

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\*Corresponding author. Tel.: +38 032 2638303

E-mail address: [olehshpotyuk@yahoo.com](mailto:olehshpotyuk@yahoo.com)

## Abstract

The nature of intrinsic phase separation initiated under different homogenization routes is studied in arsenic trisulfide As<sub>2</sub>S<sub>3</sub> glass using Raman scattering spectroscopy.

It is shown that As<sub>2</sub>S<sub>3</sub> glass prepared within conventional melt-quenching route is subjected to essential phase separation dependent on the homogenization of elemental constituents sealed in evacuated ampoules. Under condition of low-temperature homogenization at 450-550°C, chemical interaction due to limited solubility of liquid S in solid As results in structurally intrinsic As- and S-rich phases with high content of homoatomic As-As and S-S bonds, respectively, which are “wrong” from the point of As<sub>2</sub>S<sub>3</sub> stoichiometry. This process can be essentially facilitated with more rapid heating and greater amount of initial elemental ingredients taken for synthesis. During prolonged homogenization of this intrinsically-decomposed melt (such as lasting 2 days in a rocking furnace), these products are partially separated giving main glassy phase enriched on As in the form of realgar- and dimorphite-type molecules, isolated As-As bonds in a glassy network and volatilized S-rich phase, which condenses on the walls of ampoules. If such melt is insufficiently homogenized as under 6-hours heating at 500°C with only 2-hours rocking, the coordination disordering is maintained in the ultimate glass. This provides that volatilized S-rich phase does not form, and all decomposition products are stabilized in glassy state as quasi-tetrahedral units and compensating homoatomic As-As bonds.

## Introduction.

Stoichiometric arsenic trisulfide glass g-As<sub>2</sub>S<sub>3</sub> possessing excellent network-forming ability with full saturation of covalent bonding is known to be a model glass former, allowing wide range of related As-S glassy compounds [1,2]. This glass can be prepared by melt quenching or cooling, ensuring some features proper to liquid being frozen in a stabilized solid state [1]. Despite lack of crystalline long-range ordering, the influence of melt-quenching route on properties of g-As<sub>2</sub>S<sub>3</sub> remains still essential in view of some deviations in the distribution of covalent bonds composing glassy network (*chemical disordering*) and interlinking between principal glass-forming structural units (*medium-range disordering*) [3,4]. So changing melt-quenching conditions, it seems possible to synthesize this glass with different content of “wrong” homoatomic As-As and S-S bonds (which appear in addition to regular heteroatomic As-S bonds) and structural-topological perfectness [3-8]. Most frequently, the overall technological process of g-As<sub>2</sub>S<sub>3</sub> preparation is arranged using pure elemental constituents (no worse than three nines) sealed in evacuated ampoules homogenized above 600°C [5-12]. In many cases [5,6,10-12], the melt is kept in rocking furnace for 12-24 hours at the temperatures as high as  $T_q=800\text{-}900^\circ\text{C}$ , which exceed the boiling point of this compound  $T_b=709^\circ\text{C}$  [1,2,13], and further it quenched from this  $T_q$  in a certain temperature-time regime. Under such high-temperature (HT) conditions, the quenching rate attains an essential role to stabilize the finalized glassy state with high (rapidly quenched glass) or low (slowly quenched or cooled glass) level of “wrong” homoatomic bonding. It means, in an alternative formulation, that *structurally-intrinsic phase separation* is frozen in the equilibrium glass as a result of *HT bond dissociation*, this process being temperature dependent provided sharp difference between slowly- and rapidly-quenched glasses with growing homogenization temperature above boiling point [5].

But this technological process can also be performed exploring slow or fast melt-quenching (cooling) technological route from essentially lower  $T_q$  such as 450-550°C [14-19], which are far below boiling point  $T_b=709^\circ\text{C}$ , but above melting temperature  $T_m=310^\circ\text{C}$  of As<sub>2</sub>S<sub>3</sub>. Since elemental sulfur S has  $T_m=113^\circ\text{C}$  and  $T_b=445^\circ\text{C}$  [20], this allows chemical interaction between solid As (with melting point close to  $T_m\approx615^\circ\text{C}$  [21]) and liquid S even at such relatively low temperatures. However, such chemical interaction seems to be highly time-consuming because of limited S solubility in solid As [22]. So it is expected that under reduced melt homogenization at low  $T_q$ , the elemental S is not distributed uniformly in a glassy network composed by three-fold coordinated As-branching sites, producing specific kind of structural imperfections. Thus, as was first shown in [23,24], the g-As<sub>2</sub>S<sub>3</sub> slowly cooled (with a rate of 10°C/h) in low-temperature (LT) regime ( $T_q=450\text{-}525^\circ\text{C}$ ) demonstrated *extended defect structures* filled with inter-coupled “wrong” As-As and S-S chemical bonds, which disrupt a continuity of glassy network like macroscopic internal surfaces or dislocation lines in defective crystals. Recently [25], it was found that insufficiently homogenized g-As<sub>2</sub>S<sub>3</sub> prepared by cooling from  $T_q=500^\circ\text{C}$  possessed *coordination disordering* in the form of quasi-tetrahedral (QT)  $\text{S}_{3/2}\text{As}=\text{S}$  units overcompensated by homoatomic As-As bonding. Possible configurations of such extended defects were examined with *ab-initio* quantum chemical modeling and experimentally verified using micro-Raman spectroscopy and X-ray diffraction patterning in the measuring mode related to the first sharp diffraction peak [25].

In fact, all these cases verify that structural anomalies in the LT-quenched g-As<sub>2</sub>S<sub>3</sub> result from *intrinsic phase separation* due to spatially inhomogeneous distribution of elemental constituents in a bulk glassy matrix. In this work, we continue experimental research on these anomalies in g-As<sub>2</sub>S<sub>3</sub> subjected to different homogenization routes using Raman scattering technique.

## Experimental: sample preparation and measuring procedures.

Samples of g-As<sub>2</sub>S<sub>3</sub> were synthesized in evacuated ( $10^{-5}$  Pa) and sealed fused quartz ampoules by conventional melt-quenching technique in a rocking furnace. Elemental constituents (S and As) additionally purified with distillation (to purity of no worse than three nines) were melted at maximal temperature of 500°C. The synthesis procedure was portioned into few step-wise stages:

- (1) initial heating from room temperature to 250 °C for a few hours,
- (2) heating from 250 to  $T_q=500^\circ\text{C}$  for 6 hours with increment 50°C,

(3) rocking at  $T_q=500^\circ\text{C}$  for 48 hours, and then

(4) cooling from this  $T_q=500^\circ\text{C}$  to room temperature under *rapid quenching* (RQ) by inserting the ampoule in a water bath or *slow cooling* (SC) with a turned-off furnace.

Thus, we prepared two batches of g-As<sub>2</sub>S<sub>3</sub> homogenized in the LT regime at  $T_q=500^\circ\text{C}$  and further stabilized under RQ or SC. Visual inspection testifies that both types of samples have conchoidal fracture characteristic for glasses, but inner walls of ampoules were covered with bright-red layer. So for microstructure study we took large pieces from deeper part of each ingots and remainder of the deposited phase inside the ampoule. The wide-stretched halos on X-ray diffraction patterns registered from these samples provides additional confirmation on their amorphous state.

For a comparison, we also used samples of g-As<sub>2</sub>S<sub>3</sub> prepared in the HT regime, when the ampoules were kept at  $T_q=700^\circ\text{C}$  or  $900^\circ\text{C}$  for 30 hours in a rocking furnace and then subjected to the same RQ stabilization procedure. Other batch of samples was composed by stoichiometric g-As<sub>40</sub>S<sub>60</sub> and near-stoichiometric g-As<sub>42</sub>S<sub>58</sub> and g-As<sub>38</sub>S<sub>62</sub> prepared by cooling from  $T_q=500^\circ\text{C}$ , which were only shortly homogenized at this temperature for 6 hours with 2 hours rocking [25].

The room temperature Raman scattering spectra were measured by using fast Fourier-transform (FFT) spectrometer IFS 55 supplied with FRA 106 accessory (Bruker, Germany). A back-scattering method with Nd:YAG laser line (1064 nm) of 90 mW power was used for the excitation. The resolution of the Raman spectrometer was  $4\text{ cm}^{-1}$  at 300 scans. The raw experimental spectra were processed using the Bruker software, normalized by standard technique of matching the most intensive peaks in the studied spectral region and compared by subtraction method.

## Results and discussion.

The normalized FFT Raman scattering spectra of g-As<sub>2</sub>S<sub>3</sub> synthesized in the LT regime at  $T_q=500^\circ\text{C}$  under RQ and SC are shown in Fig. 1 and 2, respectively. It is obvious these spectra differ essentially for glassy bulk ingots (Fig. 1a and 2a) and remainders of deposited vapour phase taken from the upper part of the ampoules (Fig. 1b and 2b).

In the spectrum of bulk ingots (Fig. 1a, 2a), a group of sharp lines corresponding to Raman-active vibration modes of  $\beta$ -As<sub>4</sub>S<sub>4</sub> molecules can be easily identified due to specific doublet at 345-362  $\text{cm}^{-1}$  completed by relatively slight shoulders near 310 and 380  $\text{cm}^{-1}$  [11,26-33]. The first of these bands (345  $\text{cm}^{-1}$ ) also corresponds to symmetric stretching vibrations of As-S bonds in trigonal AsS<sub>3</sub> pyramids [26], which can be considered as representatives of regular glassy network built of corner-sharing AsS<sub>3/2</sub> pyramids, while the second band (362  $\text{cm}^{-1}$ ) is rather attributed to these vibrations in realgar-type molecules [27-29]. In such configuration, these Raman scattering lines are well pronounced in the As-rich As-S glasses [11,18,25,26,32], as-evaporated (freshly-prepared) thin films of stoichiometric arsenic sulfide As<sub>2</sub>S<sub>3</sub> [30,31], as well as high-temperature  $\beta$ -As<sub>4</sub>S<sub>4</sub> or so-called  $\chi$ -phase, which can be accepted as a precursor of pararealgar appeared in light-induced transformation from realgar [27,28]. So, in fact, the bulk ingot condensed in the LT-regime at  $T_q=500^\circ\text{C}$  is the As-rich glass of As-S system, the As excess being in the form of realgar-type molecules. Presence of homoatomic As-As bonds in these probes follows also from intense scattering bands observed near  $\sim 146$ , 188, 212 and 222  $\text{cm}^{-1}$ , which can be attributed to  $\beta$ -As<sub>4</sub>S<sub>4</sub> [26-30]. The appearance of slight band near 234  $\text{cm}^{-1}$ , which is quite close to one (234  $\text{cm}^{-1}$ ) observed in the Raman spectra of amorphous As [34], can be ascribed in harmony with interpretation [32,35] to isolated As-As bonds within glassy network (network-type As-As bonds). Other band slightly pronounced near 275  $\text{cm}^{-1}$  can be attributed to dimorphite As<sub>4</sub>S<sub>3</sub> molecules, both cage-type crystalline forms of which possess strong mode in this region [36-38]. An alternative interpretation allows ascribing this band to pararealgar As<sub>4</sub>S<sub>4</sub>, but corresponding Raman activity of this mode in this crystalline state is only weak [29].

Thus, at the basis of this analysis, the bulk ingots obtained in the LT regime can be classified as As-rich arsenic sulfide glass, where excess of As is mainly present in the form of  $\beta$ -As<sub>4</sub>S<sub>4</sub> molecules, as well as isolated As-As bonds incorporated in a glassy network and cage-type dimorphite As<sub>4</sub>S<sub>3</sub> molecules. Noteworthy that no any bands proper to S-rich configurations were observed in the spectra of bulk ingots (Fig. 1a, 2a). In contrast, the Raman scattering spectra of

supplemented vapour phases (Fig. 1b and 2b) contain such bands at  $494\text{ cm}^{-1}$  ascribed to S-S chains and  $474\text{ cm}^{-1}$  ascribed to S<sub>n</sub>-like rings [11,26,30,39], which are superimposed on sharp Raman-active vibrations of regular AsS<sub>3/2</sub> pyramids (umbrella mode stretched around  $\sim 160\text{ cm}^{-1}$  and dominant broad band of symmetric-asymmetric modes at  $\sim 340\text{ cm}^{-1}$  modified by the same shoulders at  $\sim 310$  and  $\sim 380\text{ cm}^{-1}$  [28]). Therefore, we can certainly declare the vapour phase deposited on the inner walls of the ampoule consist of S-rich entities from binary As-S system. Surprisingly, but no any differences were observed between Raman spectra of g-As<sub>2</sub>S<sub>3</sub> subjected to RQ (Fig. 1) or SC (Fig. 2) procedures, testifying in a favor of insignificant impact of post-technological conditions on the glass stabilized in the LT-regime.

At the same time, no any phase-separation products (neither As-rich, nor S-rich ones) were found in g-As<sub>2</sub>S<sub>3</sub> synthesized in the HT regime ( $T_q=700$  and  $900^\circ\text{C}$ ) under RQ (see Fig. 3). Raman spectra of these glasses demonstrate only main attributes of corner-shared AsS<sub>3/2</sub> pyramids, e.g. the intense high-frequency peak of As-S stretches with centroid near  $343\text{ cm}^{-1}$  and shoulders at  $312$  and  $380\text{ cm}^{-1}$ , as well as weaker low-frequency modes attributed to As-S-As bond-bending vibrations with only slightly pronounced peaks at  $188$  and  $234\text{ cm}^{-1}$ . Insignificant effect of homoatomic bonding follows also from under-margin band near  $494\text{ cm}^{-1}$  (corresponding to S-S vibrations in ring-like configurations) and practically full absence of characteristic As-As stretches typical for spectra on Fig. 1 and 2. It is worthy to note that main centroid of As-S stretches lies near  $343\text{ cm}^{-1}$ , corresponding thereby to the glassy network of corner-shared AsS<sub>3/2</sub> pyramids, but not shifts towards  $340\text{ cm}^{-1}$ , which is character for S-rich As-S glasses (Fig. 1b and 2b) [11,26,33].

By comparing these results with Raman spectra of As-S glasses synthesized in the LT regime under SC, but at condition of reduced melt homogenization (only 6-hours keeping at  $T_q=500^\circ\text{C}$  and 2-hours rocking), close similarity between As-rich g-As<sub>42</sub>S<sub>58</sub> (Fig. 4) and LT-prepared g-As<sub>2</sub>S<sub>3</sub> (Fig. 1a, 2a) is evidenced testifying in favor of correct Raman modes ascribing. Other important feature is great background fluorescence observed in these under-homogenized glasses at such excitation, which essentially prevent reliable identification of some modes, especially at high frequencies (above  $400\text{ cm}^{-1}$ ). As it was shown in [25], under another excitation ( $785\text{ nm}$  diode laser) with careful filtering used to limit output power to  $80\text{ }\mu\text{W}$ , it was possible to register the Raman-active bands of S-rich products in these glasses at  $474$ ,  $494$  and  $530$ - $540\text{ cm}^{-1}$  (Fig. 5). The latter band was ascribed, at the basis of first-principle cluster-modeling calculations [33], to mode of stretch double-bond As=S vibrations at  $537\text{ cm}^{-1}$  within S<sub>3/2</sub>As=S unit (other modes of this QT unit are expected to contribute mainly to modes of normal trigonal AsS<sub>3/2</sub> pyramids). This finding was also concomitant with earlier *ab-initio* Hartree-Fock method calculations for different structural configurations in g-As<sub>2</sub>S<sub>3</sub>, giving As=S group frequencies in  $525$ - $530\text{ cm}^{-1}$  domain [40]. These S<sub>3/2</sub>As=S units introduce coordination disordering in a glassy network built of three-fold coordinated As-branching sites and two-fold coordinated S atoms along with some portion of chemical disordering owing to compensating input of homoatomic As-As bonding. Possible topological configurations of such structural anomalies were examined with *ab-initio* quantum chemical simulation [25], showing that As-As bonds try to be deeper in a glass structure from S<sub>3/2</sub>As=S units. In other words, the network of g-As<sub>2</sub>S<sub>3</sub> prepared under such technological conditions does not dissociate on well-separated heavy As-rich and light-volatilized S-rich products, giving a possibility to stabilize the energetically unfavorable double covalent bonding (As=S) in a glassy network.

Thus, the above results testify that intrinsic phase separation in g-As<sub>2</sub>S<sub>3</sub> can be activated from HT liquid state of melt (above boiling point) as a consequence of thermally-induced dissociation of main glass-forming structural units, e.g. corner-sharing AsS<sub>3/2</sub> pyramids built of heteroatomic As-S bonds. This result is quite well predicted, as we accept the molar fraction of different chemical species in As<sub>x</sub>S<sub>1-x</sub> liquid identified at the HT conditions such as  $T_q=900^\circ\text{C}$  [41]. At this temperature, this liquid melt around stoichiometric As<sub>2</sub>S<sub>3</sub> composition can be considered as a homogeneous mixture of different chemical species, these being AsS<sub>3/2</sub> chain branching units, As<sub>4</sub>S<sub>4</sub> separate molecules, as well as elemental As and S compounds. Only for high S-enriched compositions ( $x<0.3$ ), the liquid evolves two of these species (AsS<sub>3/2</sub> units and elemental S), while in other

concentration range the liquid is composed, at least, by three of them. Since a final glass is frozen from this state, it preserves, with a necessity, some of these species. In this case, the time-consuming phase demixing is essentially governed by melt quenching rate revealing itself in a temperature-dependent manner (the growing difference between rapidly- and slowly-quenched glasses with increased homogenization temperature).

In conditions of metastable liquid-solid equilibria such as realized under LT synthesis regime ( $T_q=500^\circ\text{C}$ ), only quenching at unreally high rates (typical for vapour quenching of  $\sim 10^7 \text{ K/s}$ ) can prevent the mixture from essential phase separation [42]. The metastable liquid-solid immiscibility cannot result in a homogeneous amorphous solution stable to phase separation at melt-quenching conditions employed in typical glass synthesis routes ( $10^{-2}$ - $10^2 \text{ K/s}$ ). In such cases, the phase demixing is not further dependent on quenching/cooling rate showing similar effects for both RQ and SC samples. The only way to affect this process is to modify time durations of the homogenization stage. If the LT-cooling process is arranged under a prolonged homogenization (48-hours keeping in a rocking furnace), the ultimate products can be well decomposed in two distinguished phases, the As-rich phase in bulk glass ingot and light-vaporized S-rich phase deposited at the ampoule walls. But under insufficient homogenization of liquid-solid mixture (reduced or short-term homogenization in a rocking furnace), these phases cannot be well separated in the evacuated ampoule remaining dissolved in the amorphous phase enriched on coordination disordering due to QT  $\text{S}_{3/2}\text{As}=\text{S}$  units and excess of homoatomic As-As bonds.

Thus, the intrinsic phase separation is permanent feature of glassy As-S system in a wide range of compositions. Nevertheless, the stoichiometric  $\text{g-As}_2\text{S}_3$  demonstrates nearly catastrophic response on HT-LT-deviations in the glass preparation technology because of variety of chemical species characteristic for this glass, when coordination anomalies (double As=S bonding) can be fully compensated by chemical ones ("wrong" As-As bonds). This specificity explains numerical misleading attempts to register experimentally double covalent bonding in different glassy arsenic chalcogenides near average coordination numbers of  $Z=2.286$ , which corresponds to exact chemical composition of  $\text{S}_{3/2}\text{As}=\text{S}$  [14,33,43]. This QT unit can appear as a requisite of S-rich phase near stoichiometric  $\text{As}_2\text{S}_3$ , being balanced by chemical disordering due to excess of homoatomic As-As bonds. Absence of such possibility in the HT-stabilized ( $T_q=900^\circ\text{C}$ ) molten  $\text{As}_x\text{S}_{1-x}$  liquid near  $Z=2.29$  [41] is in a good agreement with this conclusion.

In final, these results explain a lot of controversies observed in physical-chemical properties of glassy arsenic trisulfide  $\text{g-As}_2\text{S}_3$  prepared in various laboratories exploring fine-different specifics in their synthesis. Special attention have to be paid to cases, when glass was stabilized in the LT regime under reduced short-term homogenization, since many of anomalies could result from possible coordination disordering realized under such conditions.

### Conclusions.

Intrinsic phase separation in wide range of As-S glasses is shown to reveal catastrophic feedback near stoichiometric  $\text{As}_2\text{S}_3$  composition due to essential differences in the microstructure of glasses quenched from high ( $800$ - $900^\circ\text{C}$ ) and low ( $450$ - $550^\circ\text{C}$ ) temperatures. In respect to FFT Raman scattering spectra, the former ones demonstrate no essential phase decomposition, some portion of chemical disordering in the form of "wrong" homoatomic As-As and S-S bonding being possible in them in dependence on quenching temperature and rate. In contrast, the glasses prepared from relatively lower temperatures do not form homogeneous amorphous solution because of metastable immiscibility of liquid S and solid As, the phase demixing being not dependent on the melt quenching rate. If the melt cooling is arranged with prolonged homogenization (such as under 48-hours heating in a rocking furnace), the ultimate products of low-temperature synthesis can be well decomposed in two distinguished phases, the As-rich bulk glass and S-rich vaporized compound. The first of them are composed of cage-type  $\beta\text{-As}_4\text{S}_4$  and  $\text{As}_4\text{S}_3$  molecules, as well as isolated As-As bonds incorporated in a glassy network, while the second is S-rich As-S glass. In case of insufficient melt homogenization (such as under 6-hours keeping at  $500^\circ\text{C}$  and 2-hours

rocking), the ultimate product close to As-rich glass, where essential coordination disordering in the form of  $S_{3/2}As=S$  units compensated by excess of As-As bonds are present.

### Acknowledgement

AK, JT and MV thank U.S. National Science Foundation, through International Materials Institute for New Functionality in Glass (Grant No. DMR-0844014), for initiating the international collaboration and providing financial support for this work. AK and JT acknowledge also financial support from NSF Grant DMR-1409160. MV thanks to project CZ.1.05/4.1.00/11.0251 „Center of Materials and Nanotechnologies“, cofinanced by the European Fund of the Regional Development and the state budget of the Czech Republic.

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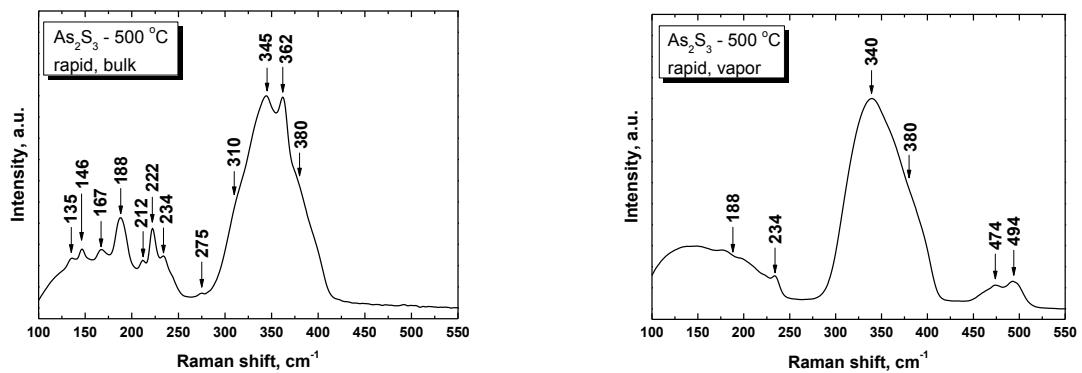
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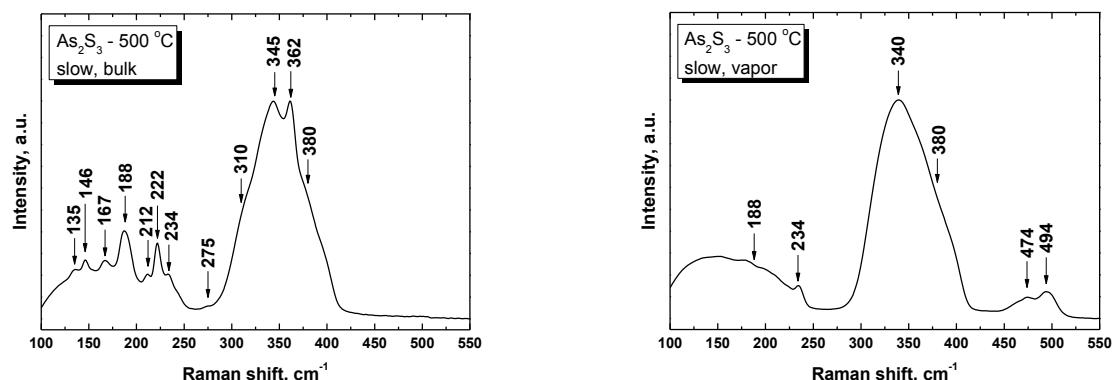
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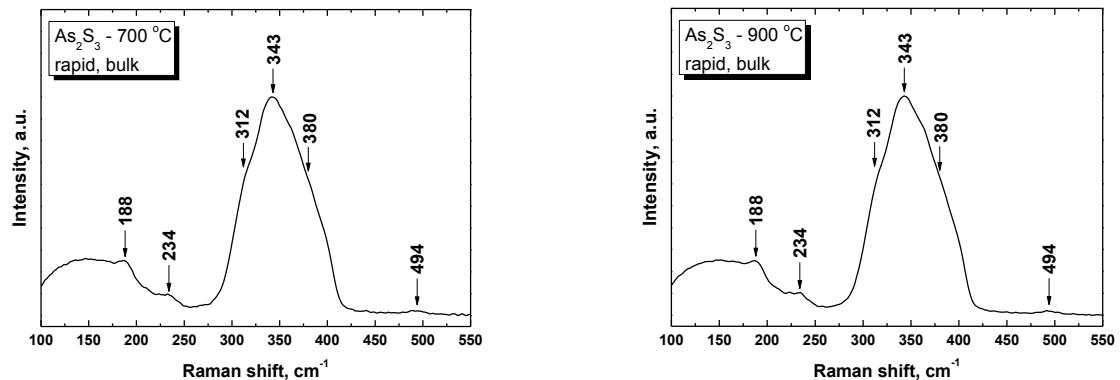
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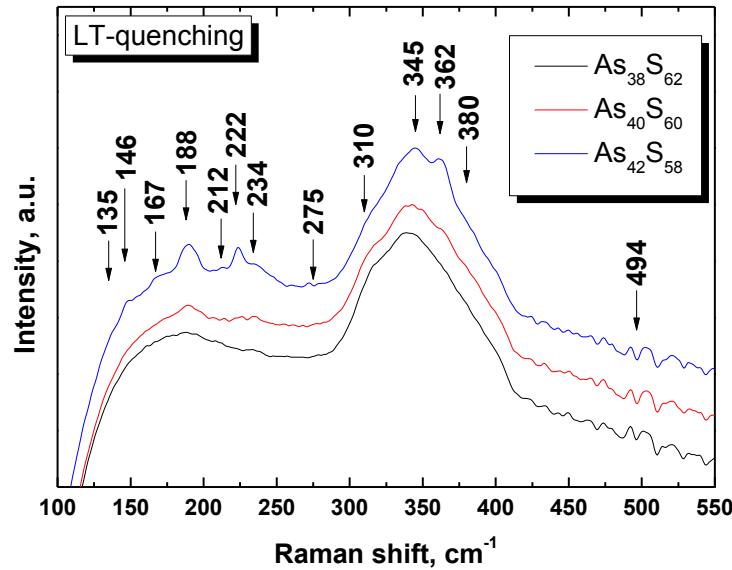
**Fig. 1.** Normalized FFT Raman scattering spectra of g-As<sub>2</sub>S<sub>3</sub> synthesized in the LT regime under RQ: a – bulk glass extracted from ampoule; b – vapor phase condensed on the ampoule walls.



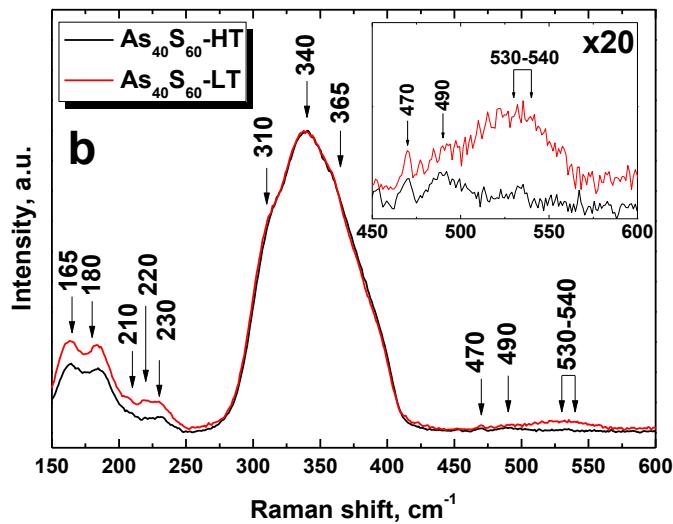
**Fig. 2.** Normalized FFT Raman scattering spectra of g-As<sub>2</sub>S<sub>3</sub> synthesized in the LT regime under SC: a – bulk glass extracted from ampoule; b – vapor phase condensed on the ampoule walls.



**Fig. 3.** Normalized FFT Raman scattering spectra of g-As<sub>2</sub>S<sub>3</sub> synthesized in the HT regime under RQ from 700 °C (a) and 900 °C (b).



**Fig. 4.** Normalized FFT Raman scattering spectra of g- $\text{As}_{38}\text{S}_{62}$ , g- $\text{As}_{40}\text{S}_{60}$  and g- $\text{As}_{42}\text{S}_{58}$  synthesized in the LT regime under SC.



**Fig. 5.** Normalized micro-Raman scattering spectra of g- $\text{As}_{40}\text{S}_{60}$  synthesized in the LT regime under SC (the registration conditions are given in ref. [25]).