



Intrinsic phase separation in low-temperature quenched arsenic trisulfide glass



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ABSTRACT

The nature of intrinsic phase separation initiated under different homogenization routes is studied in arsenic trisulfide As_2S_3 glass using Raman scattering spectroscopy.

It is shown that As_2S_3 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_2S_3 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-h heating at 500 °C with only 2-h 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.

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1. Introduction

Stoichiometric arsenic trisulfide glass $g-As_2S_3$ 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 $g-As_2S_3$ 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 $g-As_2S_3$ 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 h at the temperatures as high as $T_q = 800–900$ °C, which exceed the boiling point of this compound $T_b = 709$ °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

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lower T_q such as 450–550 °C [14–19], which are far below boiling point $T_b = 709$ °C, but above melting temperature $T_m = 310$ °C of As_2S_3 . Since elemental sulfur S has $T_m = 113$ °C and $T_b = 445$ °C [20], this allows chemical interaction between solid As (with melting point close to $T_m \approx 615$ °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 $g\text{-As}_2\text{S}_3$ slowly cooled (with a rate of 10 °C/h) in low-temperature (LT) regime ($T_q = 450\text{--}525$ °C) demonstrated *extended defect structures* filled with intercoupled “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 $g\text{-As}_2\text{S}_3$ prepared by cooling from $T_q = 500$ °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 pattering 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 $g\text{-As}_2\text{S}_3$ 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 $g\text{-As}_2\text{S}_3$ subjected to different homogenization routes using Raman scattering technique.

2. Experimental: sample preparation and measuring procedures

Samples of $g\text{-As}_2\text{S}_3$ 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 $T_q = 500$ °C for 6 h with increment 50 °C,
- (3) rocking at $T_q = 500$ °C for 48 h, and then.
- (4) cooling from this $T_q = 500$ °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 $g\text{-As}_2\text{S}_3$ homogenized in the LT regime at $T_q = 500$ °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 $g\text{-As}_2\text{S}_3$ prepared in the HT regime, when the ampoules were kept at $T_q = 700$ °C or 900 °C for 30 h in a rocking furnace and then subjected to the same RQ stabilization procedure. Other batch of samples was composed by stoichiometric $g\text{-As}_{40}\text{S}_{60}$ and near-stoichiometric $g\text{-As}_{42}\text{S}_{58}$ and $g\text{-As}_{38}\text{S}_{62}$ prepared by cooling from $T_q = 500$ °C, which were only shortly homogenized at this temperature for 6 h with 2 h 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 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.

3. Results and discussion

The normalized FFT Raman scattering spectra of $g\text{-As}_2\text{S}_3$ synthesized in the LT regime at $T_q = 500$ °C under RQ and SC are shown in Figs. 1 and 2, respectively. It is obvious these spectra differ essentially for glassy bulk ingots (Figs. 1a and 2a) and remainders of deposited vapor phase taken from the upper part of the ampoules (Figs. 1b and 2b).

In the spectrum of bulk ingots (Figs. 1a, 2a), a group of sharp lines corresponding to Raman-active vibration modes of $\beta\text{-As}_4\text{S}_4$ molecules can be easily identified due to specific doublet at $345\text{--}362\text{ cm}^{-1}$ completed by relatively slight shoulders near 310 and 380 cm^{-1} [11, 26–33]. The first of these bands (345 cm^{-1}) also corresponds to symmetric stretching vibrations of As–S bonds in trigonal AsS_3 pyramids [26], which can be considered as representatives of regular glassy network built of corner-sharing $\text{AsS}_{3/2}$ pyramids, while the second band (362 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_2S_3 [30,31], as well as high-temperature $\beta\text{-As}_4\text{S}_4$ or so-called χ -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 $T_q = 500$ °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 cm^{-1} ,

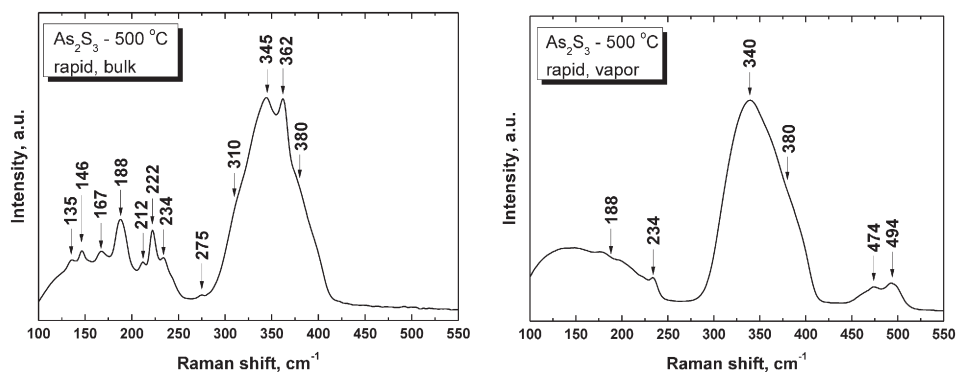


Fig. 1. Normalized FFT Raman scattering spectra of $g\text{-As}_2\text{S}_3$ synthesized in the LT regime under RQ: a – bulk glass extracted from ampoule; b – vapor phase condensed on the ampoule walls.

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