

# COORDINATION DEFECTS IN VITREOUS $As_2S_3$ INDUCED BY $\gamma$ -IRRADIATION

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*(Received January 24, 1997; revised version May 29, 1997)*

Destruction-polymerization transformations in vitreous  $As_2S_3$ , associated with coordination defects formation processes induced by  $\gamma$ -irradiation, were studied by the IR Fourier spectroscopy method in the region of  $400\text{--}100\text{ cm}^{-1}$ . All topological variants of these processes, statistically possible in the investigated samples, were taken into account for physical consideration of the real structural changes.

PACS numbers: 71.55.Jv

## 1. Introduction

Amorphous chalcogenide semiconductors (AChS), studied by Kolomiets and Goryunova more than forty years ago, are unique solid state materials showing changes of physical properties stimulated by external factors as absorbed light (photoinduced effects [1, 2]),  $\gamma$ -quanta of  $^{60}Co$  radioisotope or accelerated electrons with average energy  $E > 1\text{ MeV}$  (radiation-induced effects [3–8]). Reversible changes in optical properties of AChS are observed in multiple cycles of irradiation and thermal annealing at temperatures near the glass transition.

The reason of this similarity between photo- and radiation-induced effects in AChS is their structural character connected with the so-called coordination defects (CD) [9, 10]. These defects are created in the form of diamagnetic pairs of over- and undercoordinated atoms in the structural matrix with positive and negative electrical charge, respectively. The process of CD formations is due to covalent bond switching or destruction-polymerization transformations without changing average covalent linking.

In spite of a large number of scientific publications on photo- and radiation-induced processes in AChS [1–8], the detailed analysis of bond switching leading to the CD formation, supported by direct experimental data, have not been carried

out yet. This situation is caused by the difficulties in local atomic structure investigation in disordered solids (AChS, in particular) using "traditional" amorphographical techniques. The structural changes related to radiation-induced effects in AChS, called radiation-structural transformations (RST), are very weak. They comprise no more than 10% of the atomic sites [1, 2, 11]. Optical spectroscopy methods providing useful information at the background of the integral signal are less informative for such investigations.

The necessary information on the RST may be accurately obtained using the so-called "differential" Fourier spectroscopy technique in the long-wavelength region of  $400\text{--}100\text{ cm}^{-1}$ . This technique was applied previously to amorphous  $\text{As}_2\text{S}_3$  films in order to study the mechanism of the reversible photoinduced transformations [12]. Unfortunately, this technique is not applied for structural investigation of vitreous samples, which reveal the maximum amplitude of the reversible RST [5–8], because of very high optical absorption. The method of IR Fourier spectroscopy of induced reflectivity modified to reflection measurements is expected to be quite suitable for such investigations in vitreous samples.

## 2. Experimental

Vitreous  $\text{As}_2\text{S}_3$  (v- $\text{As}_2\text{S}_3$ ) is considered as a model object for investigation of the induced destruction-polymerization transformations in AChS. It is chosen because of good distinction of vibrational bands for structural complexes with chemical bonds of different types, in particular the pyramidal  $\text{AsS}_3$  units with heteropolar As–S bonds ( $335$  to  $285\text{ cm}^{-1}$ ) and molecular units containing "wrong" homopolar As–As ( $379$ ,  $340$ ,  $231$ ,  $210$ ,  $168$  and  $140\text{ cm}^{-1}$ ) or S–S bonds ( $243$  and  $188\text{ cm}^{-1}$ ) [13–15].

The investigated v- $\text{As}_2\text{S}_3$  samples were synthesized from 99.999% purity constituents in evacuated quartz ampoules. All ingots were air-quenched at  $420$  to  $430\text{ K}$  during  $3$  to  $5\text{ h}$ . The sample surfaces were polished with  $1\text{ }\mu\text{m}$  alumina.

The  $\gamma$ -irradiation of the v- $\text{As}_2\text{S}_3$  samples was carried out using  $^{60}\text{Co}$  isotope ( $1.25\text{ MeV}$ ) at the dose rate of  $25\text{ Gy/s}$  and the absorbed dose of  $10^7\text{ Gy}$ . As it was established earlier these radiation treatment conditions cause maximum changes in physical properties in AChS [5–8].

The mechanism of the reversible RST was studied in v- $\text{As}_2\text{S}_3$  after two cycles of  $\gamma$ -irradiation with the dose of  $10^7\text{ Gy}$  and thermal annealing at the temperature above thermal bleaching threshold ( $423\text{ K}$ ) [16]. Thus, the own irreversible component of the RST was excluded due to the described initial treatment of the investigated samples (however, the impurity irreversible component [17] was present in our experiment).

The IR Fourier spectroscopy measurements were carried out using v- $\text{As}_2\text{S}_3$  in the form of  $1$  to  $2\text{ mm}$  thick plates with polished surfaces. The IFS-113V "Bruker" instrument was used for recording of reflectivity spectra in the region of the vibrational bands of the v- $\text{As}_2\text{S}_3$  main structural fragments ( $400$  to  $100\text{ cm}^{-1}$ ). The previously intensified reflection spectra of v- $\text{As}_2\text{S}_3$  before and after  $\gamma$ -irradiation were subtracted. Positive values of  $\Delta R > 0$  (additional reflectivity) correspond to complexes appearing under irradiation and negative ones of  $\Delta R < 0$ , on the contrary, correspond to complexes disappearing under irradiation. The advantage

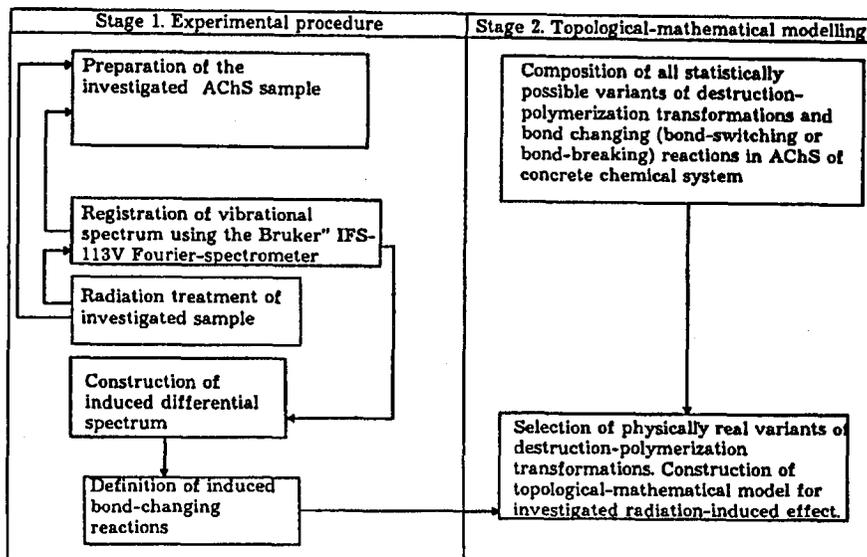


Fig. 1. Scheme illustrates the experimental conditions of determination of the RST in AChS.

of the differential IR Fourier spectroscopy method consists in that the part of the vibrational spectrum induced by external influence is investigated, but not the whole spectrum. Multiple accumulation of the differential signal, when fast Fourier transformation is used, allows to reach a sensitivity of this technique at the breaking bonds level of  $\approx 1\%$ .

The whole scheme of the experimental procedure used for the RST study in the AChS (not only in  $v\text{-As}_2\text{S}_3$ ) is presented in Fig. 1.

### 3. Results and discussion

First we shall analyse all topological variants of the CD statistically possible in  $v\text{-As}_2\text{S}_3$  taking into account the main types of its initial structural units: heteropolar As-S bonds in the framework of pyramidal  $AsS_3$  or bridge As-S-As complexes, homopolar As-As or S-S bonds in different, fully or partially polymerized, molecular fragments (see Fig. 2) [10].

Since the final AChS state depends not only on the destroyed bond, but also on its nearest neighbours (it means that 2 initial units take place in the CD formation), there are 16 topological schemes of the CD for 4 various initial units mentioned above. In other words, the whole number of the statistically possible CD variants is equal to the permutations of 4 taken 2 at a time (from 4 initial structural units of  $v\text{-As}_2\text{S}_3$ ).

These schemes show homopolar and heteropolar bond breaking and are presented in Fig. 3. It is suggested that absence of such statistical consideration for AChS of concrete chemical composition leads to the incorrect conclusions on the mechanism of the structural transformations, especially in the cases of multiple influences such as photoexposure and thermal annealing of the AChS

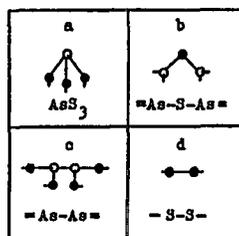


Fig. 2. Main initial structural units in  $v\text{-As}_2\text{S}_3$  based on heteropolar As-S bonds: pyramidal  $\text{AsS}_3$  complex (a), bridge As-S-As complex (b), as well as homopolar As-As (c) and S-S (d) ones (the covalent chemical bond is denoted by hyphen).

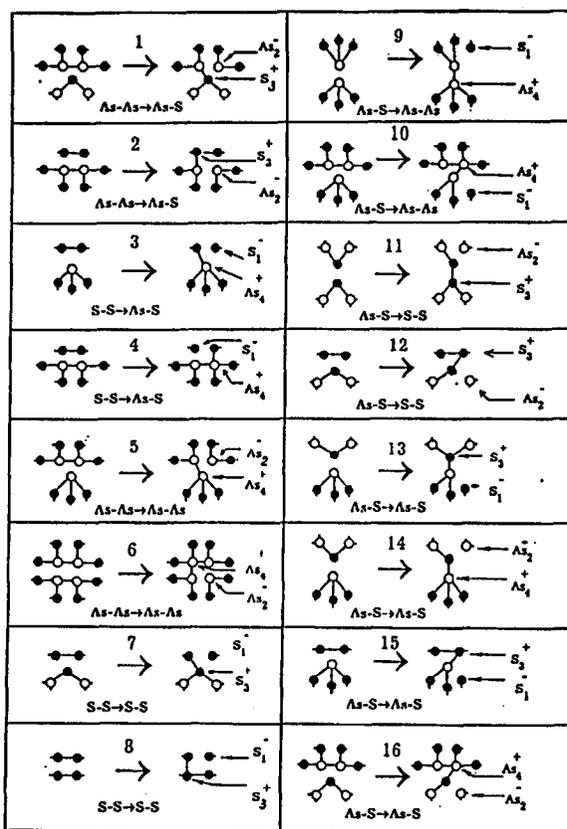


Fig. 3. Statistically possible topological schemes of the CD formation in  $v\text{-As}_2\text{S}_3$  connected with homopolar (1)–(8) and heteropolar (9)–(16) chemical bond breaking.

films at the reversible changes stage [1, 2, 18–20]. Some possible topological variants of the CD remain out of our physical consideration and we cannot explain the whole scheme of studied structural transformations [19, 20].

Each scheme in Fig. 3 corresponds to one CD pair. The upper index in the defect signature (superscript) means the charge state of the atom, and the lower one (subscript) – the coordination number. The CD appear in AChS matrix in pairs (negative and positive) providing conservation of the sample electroneutrality. The whole variety of these defects in  $v\text{-}As_2S_3$  are denoted by  $S_1^-$ ,  $S_3^+$ ,  $As_2^-$  and  $As_4^+$ .

Schemes 1–4 in Fig. 3 are connected with transformations (switchings) of homopolar covalent bonds into heteropolar ones and schemes 9–12, at the contrary, are connected with switchings of heteropolar bonds into homopolar ones. Schemes 5–8 and 13–16 do not change the chemical bond type (one bond is destroyed, but the same bond forms again). The latter situation is the most difficult for experimental observation as only intermediate-range ordering transformations may be associated with it. However, in previous case (schemes 1–4 and 9–12) we have the RST at the level of short-range ordering and the essential changes of vibrational bands intensities in the  $400\text{--}100\text{ cm}^{-1}$  Fourier spectrum are expected.

By the way, each CD pair can be characterized by not only the electrical charge and the coordination number, but also “wrong” homopolar bonds near anomalously coordinated atoms. The number of such “wrong” bonds determines the so-called ordering of the defects pair. Thus, for example  $(As_2^-, S_3^+)$  CD pair, presented by first topological scheme in Fig. 3, is 0-ordering pair as there are no homopolar chemical bonds in its nearest vicinity. At the same time  $(As_2^-, S_3^+)$  CD pair presented by second topological scheme in Fig. 3 is 1-ordering pair as  $S_3^+$  defect has one S–S “wrong” homopolar bond in its vicinity. Taking into consideration all topological variants of the CD in  $v\text{-}As_3S_3$ , shown in Fig. 3 with the corresponding bonds switching reactions and defect characteristics, the following conclusions can be drawn:

1) If the type of the covalent chemical bonds is not changed (topological schemes 5–8 and 13–16 in Fig. 3), the appeared CD pair is homoatomic, i.e. both defects have the same nature —  $(S_1^-, S_3^+)$  or  $(As_2^-, As_4^+)$ . If the bond type changes during the RST (schemes 1–4 and 9–12 in Fig. 3), the appeared CD pair is heteroatomic, i.e. both defects have different chemical nature —  $(S_1^-, As_4^+)$  or  $(As_2^-, S_3^+)$ .

2) There are 4 CD pairs of 0-ordering, 8 pairs of 1-ordering and 4 pairs of 2-ordering among 16 reactions shown in Fig. 3.

The obtained signal of the additional reflectivity  $\Delta R$  of  $v\text{-}As_2S_3$  induced by third cycle  $\gamma$ -irradiation with the dose of  $10^7$  Gy is shown in Fig. 4. Irradiation leads to the increase in the vibrational bands at 379, 231, 168 and  $140\text{ cm}^{-1}$  corresponding to structural fragments with homopolar As–As bonds, while intensities of another bands corresponding to structural fragments with homopolar S–S and heteropolar As–S bonds decrease. In other words,  $\gamma$ -irradiation are really accompanied by structural transformations connected with destruction and forming of chemical bonds or CD formation. In the case under consideration our experimental results can be explained by two processes of chemical bond switching



and homopolar S–S bond into heteropolar As–S one



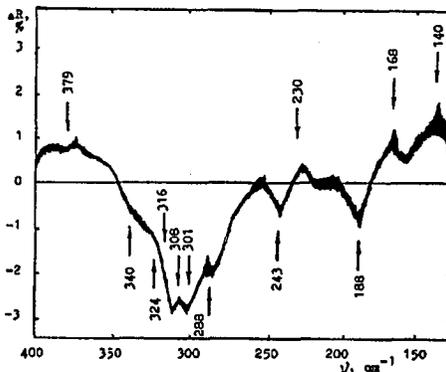


Fig. 4. Spectral reflectivity of  $\nu$ -As<sub>2</sub>S<sub>3</sub> induced by third cycle  $\gamma$ -irradiation with  $10^7$  Gy dose.

It is clear from inspection of the obtained spectrum that statistical weight of switching reaction (1) is greater than that of reaction (2).

Four various types of the CD formation correspond to these data: the topological schemes 9 and 10 are described by the switching reaction (1), whereas schemes 3 and 4 are described by the switching reaction (2). However, the concentration of "wrong" homopolar bonds in  $\nu$ -As<sub>2</sub>S<sub>3</sub> is so small [21] that the CD schemes 4 and 10 may be excluded from the further consideration. Thus only the topological schemes 9 and 3 correspond to physically possible RST in  $\nu$ -As<sub>2</sub>S<sub>3</sub>. In both cases (As<sub>4</sub><sup>+</sup>, S<sub>1</sub><sup>-</sup>) CD are formed. The energy activation barrier of the switching reaction (1) and (2) for the topological schemes 9 and 3, estimated as difference of bond energies after and before irradiation, is negative because the bond energies in the binary As-S system are:  $E_{As-As} = 2.07$  eV,  $E_{As-S} = 2.48$  eV and  $E_{S-S} = 2.69$  eV [22]. The essential difference between the CD formation schemes 9 and 3 in Fig. 3 is that the (As<sub>4</sub><sup>+</sup>, S<sub>1</sub><sup>-</sup>) pair is 1-ordering in the first case and 0-ordering in the second one.

The following thermal annealing of this sample causes the completely opposite changes in the chemical bonds distribution. It means that the thermoinduced IR Fourier spectrum has the same form as shown in Fig. 4, but positive components transform into negative ones and the other way round without any sufficient differences in the vibrational bands intensities. Hence, the observed RST in  $\nu$ -As<sub>2</sub>S<sub>3</sub> are really reversible.

#### 4. Conclusion

This paper presents the experimental data on the RST in  $\nu$ -As<sub>2</sub>S<sub>3</sub> observed at the reversible stage of  $\gamma$ -irradiation and thermal annealing. It was shown, using the IR Fourier spectroscopy method, that these transformations were connected with the (As<sub>4</sub><sup>+</sup>, S<sub>1</sub><sup>-</sup>) CD formation in the structural matrix.

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