

## MÖSSBAUER STUDY OF THE DEGREE OF DISORDER IN AMORPHOUS Ge-Sb- S

E. Skordeva<sup>\*</sup>, P. E. Lippens<sup>a</sup>, J. C. Jumas<sup>a</sup>, J. Olivier-Fourcade<sup>a</sup>, V. Pamukchieva

Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria

<sup>a</sup>LAMMI CNRS UMR5072, Université Montpellier II, Place E. Bataillon, CC015, F-34095 Montpellier Cedex 5, France

The local electronic structure of Ge-Sb-S glasses and films has been studied by means of <sup>121</sup>Sb Mössbauer spectroscopy. The films were treated by bandgap illumination and/or annealing. Differences between the Mössbauer parameters in states with different degree of disorder were checked and are discussed.

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### 1. Introduction

The renewed interest in the investigation of amorphous chalcogenide materials is related to the arising variety of possible applications. A considerable number of these applications are based on the photoinduced transformations, i.e. on changes of their structure and related properties under irradiation and/or thermal treatment. During these processes, a relative improvement in or decrease of the amount of the regular bonds in the disordered matrix can be achieved.

Chalcogenide non-crystalline materials exist in several structural forms that differ by their relative degrees of disorder. As a rule, the “most ordered” amorphous materials are the bulk glasses while the fresh (as-evaporated) thin films are considered as the most disordered ones. Annealing at temperatures near to the glass transition temperature,  $T_g$ , induces changes in the film matrix. The structure of the film becomes nearer to that of the parent glass. Bandgap illumination can also alter the film structure, inducing both ordering and disordering effects with respect to its technological prehistory (irreversible or reversible photoinduced changes, PIC).

PIC in the short and medium range order of Ge-Sb-S glasses have been studied by many investigators [1-4]. Related changes in the optical transmission, far IR, Raman and x-ray diffraction spectra have been found. When PIC occur, the local environment of the constituent atoms, as well as their electronic structure, is also supposed to change. The local electronic structure of solid state materials can be successfully studied by various methods, Mössbauer spectroscopy being one of them. Its hyperfine parameters allow one to characterize the oxidation state and coordination of the probed element.

We have made use of <sup>121</sup>Sb Mössbauer spectroscopy to study the Sb electronic population in Ge-Sb-S glasses and thin films. The differences between the Mössbauer parameters in states with different degrees of disorder, including photoinduced structural changes, have been checked and are discussed.

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\* Corresponding author: skordeva@issp.bas.bg

## 2. Experimental details

The compositions studied belong to the glass-forming Ge-Sb-S region, and are situated on the  $\text{Sb}_2\text{S}_3\text{-GeS}_2$  and the  $\text{Sb}_2\text{S}_3\text{-Ge}_2\text{S}_3$  pseudo-binary lines. The appropriate quantities of the constituent 5N elements were sealed in evacuated quartz ampoules. The ampoules were heated to  $950^\circ\text{C}$  in a rotary furnace, and were quenched in air after 24 hours. Thin films were obtained by thermal evaporation at  $10^{-3}$  Pa onto very thin mica substrates. The rate of evaporation ( $\sim 80\text{-}100$  Å/s) was chosen to ensure compositions of the films nearest to those of the parent glass.

The choice of the irradiation source (HBO 500 Mercury lamp or Xenophot HLX 64640) was made in accordance with the differences in the optical transmittances of the samples: bandgap illumination was used for all compositions. The time of illumination was chosen to be 45 min., in order to achieve saturation of the PIC. The samples were annealed at temperatures  $\sim (T_g - 20^\circ\text{C})$  for 45 min., in ampoules filled with  $\text{N}_2$ . After annealing, the ampoules were cooled in air.

The  $^{121}\text{Sb}$  Mössbauer measurements were carried out in a standard transmission geometry, using a  $\text{Ba}^{121\text{m}}\text{SnO}_3$  source. During the measurements, both the source and the absorber were simultaneously cooled to liquid helium temperatures to increase the fraction of recoil-free absorption and emission processes. The calibration and the zero isomer shift were checked carefully, since the changes of the Mössbauer parameters were relatively small. Since the source and the absorber were in a “separated” configuration, the small film thickness ( $\sim 2$  μm), i.e. the small amount of Sb in the total mass of the sample, caused additional difficulties. For this reason, many slices of the film were ranged one onto another in the sample holder, thus increasing the mass of the absorber. Even using this configuration, a long period of time (5-10 days) was necessary in order to obtain reliable spectra for the films. The Mössbauer parameters: isomer shift  $\delta$  quadrupole coupling  $\Delta = eqV_{zz}$  ( $q$  and  $V_{zz}$  are the nuclear quadrupole moment and the electric field at the nucleus, respectively) and absorber linewidth (WHFM)  $\Gamma$  were obtained from the experimental data by using the fitting program of Rubenbauer and Birchall [5]. For simplicity, the asymmetry parameter  $\eta$  was fixed to 0.

## 3. Results

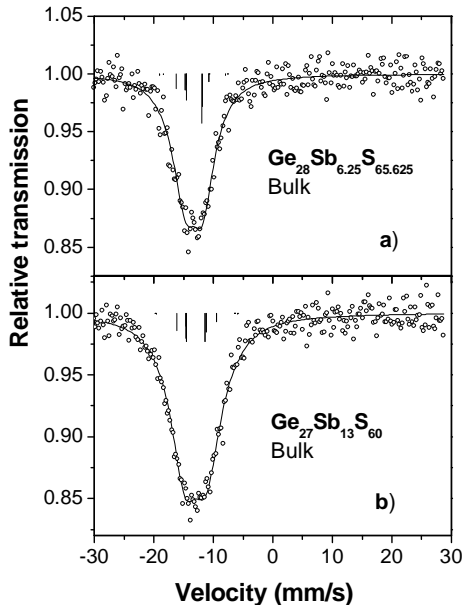


Fig. 1.  $^{121}\text{Sb}$  Mössbauer spectra of bulk glasses with compositions  $\text{Ge}_{28}\text{Sb}_{6.25}\text{S}_{65.625}$  (a), and  $\text{Ge}_{27}\text{Sb}_{13}\text{S}_{60}$  (b).

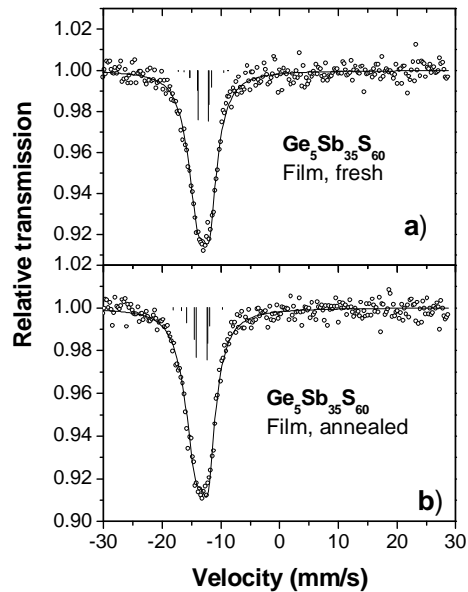


Fig. 2.  $^{121}\text{Sb}$  Mössbauer spectra of  $\text{Ge}_5\text{Sb}_{35}\text{S}_{60}$  thin films before illumination (a), and after illumination and annealing (b).

In order to compare the degrees of disorder due to deviations from stoichiometry, two bulk glasses,  $\text{Ge}_{28}\text{Sb}_{6.25}\text{S}_{65.625}$  and  $\text{Ge}_{27}\text{Sb}_{13}\text{S}_{60}$ , were considered. The samples were found to be

amorphous by x-ray diffraction. The former belongs to the  $\text{GeS}_2\text{-Sb}_2\text{S}_3$  family, and the latter to the  $\text{Ge}_2\text{S}_3\text{-Sb}_2\text{S}_3$  one (to the  $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$  family). Thus, the first composition contains more heteropolar bonds than the second one, and comparison allows one to check the influence of chemical disorder on the Mössbauer parameters. The  $^{121}\text{Sb}$  Mössbauer spectra are shown in Fig. 1 and the parameters obtained from the experimental data are reported in Table 1.

Table 1.  $^{121}\text{Sb}$  Mössbauer parameters of amorphous Ge-Sb-S [f=film; ill.= illuminated; ann.=annealed]. The isomer shift  $\delta$  is given with respect to InSb (-8.70mm/s relative to  $\text{Ba}^{121\text{m}}\text{SnO}_3$  source).

Composition	$\delta$ (mm/s)	$\Delta$ (mm/s)	$\Gamma$ (mm/s)
$\text{Ge}_{27}\text{Sb}_{13}\text{S}_{60}$ bulk	- 4.36(7)	+ 17.0(2)	4.8(3)
$\text{Ge}_{28}\text{Sb}_{6.25}\text{S}_{65.625}$ bulk	- 4.58(4)	+ 18.4(9)	3.2(2)
$\text{Ge}_5\text{Sb}_{35}\text{S}_{60}$ f, untreated (a)	- 4.41(3)	+ 11.8(3)	1.8(1)
$\text{Ge}_5\text{Sb}_{35}\text{S}_{60}$ f, ill. (b)	- 4.50(4)	+ 12.2(4)	1.6(1)
$\text{Ge}_5\text{Sb}_{35}\text{S}_{60}$ f, ill. +ann. (c)	- 4.76(4)	+ 13.0(5)	1.8(1)
$\text{Ge}_5\text{Sb}_{35}\text{S}_{60}$ f, ill. +ann. +ill. (d)	- 4.67(3)	+ 11.5(3)	1.7(1)

An example of the effect of illumination/annealing on the degree of disorder in Ge-Sb-S thin films is given for the composition  $\text{Ge}_5\text{Sb}_{35}\text{S}_{60}$ . The  $^{121}\text{Sb}$  Mössbauer spectra were recorded for fresh, (a), illuminated, (b), illuminated and annealed, (c), illuminated, annealed and re-illuminated, (d), samples. Two spectra are shown in Fig.2 and the parameters are reported in Table 1. The values of the absorber linewidths  $\Gamma$  can be considered as identical within the experimental errors in the four cases. The quadrupole coupling constant  $\Delta$  increased from the sample (a) to (c) and decreased from (c) to (d). The isomer shift  $\delta$  decreased from (a) to (c) and increased slightly from (c) to (d).

#### 4. Discussion

The values of the Mössbauer absorber linewidth obtained for the two bulk glasses (Table 1, rows 1-2) are typical for Sb based glasses [6, 7]. The broadening reflects the distribution of the bond lengths and angles involving the Sb atoms.  $\Gamma$  is greater in the  $\text{Ge}_{27}\text{Sb}_{13}\text{S}_{60}$  glass that is supposed to have a greater degree of disorder. For both compositions, the values of  $\Delta$  are rather large and denote a strong asymmetry of the electron density around the Sb nucleus, as expected with 3-fold coordination. This result is in agreement with the common opinion, based on various experimental studies, that in the amorphous Sb-chalcogenides the Sb is predominantly 3-fold coordinated [7-9]. Both the large values of  $\Delta$  and the range of values of  $\delta$  are typical of  $\text{SbS}_3$  local environments in the Sb-containing glasses. The observed decrease of  $\delta$  from  $\sim -4.4$  to  $\sim -4.6$  mm/s is related to the increase in the number of Sb 5s electrons, and/or to the decrease in the number of Sb 5p electrons [10]. Differences in the local geometry of the  $\text{SbS}_{3/2}$  units, or a decrease in the number of Sb-Sb bonds, could be the reason for this result. The later interpretation is consistent with the expected decrease in the relative number of regular  $\text{SbS}_{3/2}$  units in the respective glass matrix (from  $\text{Ge}_{28}\text{Sb}_{6.25}\text{S}_{65.625}$  to  $\text{Ge}_{27}\text{Sb}_{13}\text{S}_{60}$ ). This shows the high sensitivity of the  $^{121}\text{Sb}$  Mössbauer spectroscopy to changes in the types of bonds involving the Sb atoms when  $\delta$  is considered.

The high sensitivity of the  $^{121}\text{Sb}$  Mossbauer experiment allows us to interpret the results obtained for the thin films (Table 1, rows 3-6). Our interpretation is based on a correlation between the  $^{121}\text{Sb}$  Mössbauer experimental values of  $\delta$  and the calculated values of the electronic density at the nucleus [10]. The observed decrease of  $\delta$  from sample (a) to sample (b) can be explained by the

increase in the number of Sb-S bonds compared to those of Sb-Sb and/or Sb-Ge bonds. The  $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$  films in the as-evaporated state contain a large density of homopolar bonds, due to dissociation of the glass in the course of evaporation and quenching of the vapor on the substrate. As stated in [11], the atoms can be partly statistically distributed and the densities of individual chemical bonds can be described by a random covalent network model. Thus the light exposure could result in homo-to-heteropolar as well in hetero-to-homopolar bond switching depending on the conditions of the film preparation and/or the conditions of light exposure. Our results clearly show that illumination tends to increase the chemical ordering in the present non-illuminated film. The decrease of  $\delta$  from sample (b) to (c) can also be interpreted by the formation of Sb-S bonds improving the ordering. This is in accordance with our IR spectra as well as with other Raman and IR scattering investigations of  $\text{Ge}_{30}\text{Sb}_{10}\text{S}_{60}$  films [11, 12]. Finally, the increase of  $\delta$  from sample (c) to sample (d) reflects the decrease in the number of the Sb-S bonds. This decrease is related once more to changes towards the structural disorder in the film matrix. The  $\delta$  value is smaller than that after the first film illumination. This indicates that the first annealing has led to structural changes that are partially irreversible. In contrast, the post-annealing illumination creates new homopolar bonds, destroying the achieved ordering. The photostructural changes induced by this illumination are smaller, and can be recovered by substantial annealing (reversible photostructural changes).

## 5. Conclusions

The Mössbauer study of Ge-Sb-S glasses and films has shown changes in the local electronic structure of the Sb atoms, depending on the degree of disorder of the amorphous matrix. These changes are induced by appropriate illumination and heating. They are the reason for PIC in various physical and physicochemical properties of the films and glasses. The highest degree of ordering is observed in glasses belonging to the pseudo-binary  $\text{GeS}_2\text{-Sb}_2\text{S}_3$  line. The degree of disorder of the films is very sensitive to the technology, the composition and the prehistory treatment. However, in all of the compositions studied the Sb is predominantly 3-fold coordinated. The isomer shift has turned out to be the main Mössbauer parameter that provides reliable information on the electronic structure and its photoinduced changes in Ge-Sb-S glasses and films.

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