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Mössbauer and XPS structural study of (Ge, Sn)-As-S glasses

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The local structure and the electronic properties of three Ge-As-S glasses are studied by ^{119}Sn Mössbauer and X-ray photoelectron spectroscopies. For the former method, a small fraction of the Ge atoms are substituted by Sn atoms. Mössbauer spectroscopy shows that the glasses contain Sn(IV) and Sn(II) ions with isomer shifts in the range of those found for tin sulphides. The quadrupole splittings found for Sn(IV) and Sn(II) are very different and indicate that Sn(IV) is symmetrically surrounded by S atoms, whereas the local environment of Sn(II) is strongly distorted. Based on these results, and on XPS results obtained for As, Ge and S atoms in the glasses, a simple model describing the local environment of the Sn atoms, and, respectively, of the Ge ones is discussed

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1. Introduction

Ge-As-S amorphous materials are extensively studied, due to their high sensitivity to photoinduced structural changes (PIC) and prospective applications. In order to find the compositions showing the highest sensitivity to PIC, we studied many different glasses and thin films from this ternary system. The greatest changes were obtained in stress-rigid compositions with an average coordination number Z ($2.6 < Z < 2.8$), nearly independent of to which line in the glass-forming region they belong [1]. Among the compositions studied, those from the As_2S_3-Ge_2S_3 line exhibited giant photoinduced structural changes.

In this work, we present the results obtained in a Mössbauer study of three Ge-As-S glasses with Z in the above-mentioned region. A small fraction of the Ge atoms are substituted by ^{119}Sn atoms. The aim of the study was to check what kind of structural units the Sn (Ge) atoms form, in order to clarify the structure of the films evaporated from these glasses and used in PIC experiments. Some XPS studies were also performed to enlarge the knowledge of the electronic structure of the constituent elements.

2. Experimental settings

$Ge_{19.8}Sn_{0.2}As_{20}S_{60}$, $Ge_{30.72}Sn_{1.28}As_5S_{63}$ and $Ge_{31.68}Sn_{0.32}As_5S_{63}$ glasses were prepared by a standard procedure. The constituent elements with 5*N* purity were heated to 950^0C in a rotary furnace for 24 hours and quenched in air [2].

In the XPS study, the glassy samples were analysed just after being fractured. A SSI 301 spectrophotometer and focused Al K_α radiation (1486.6 eV) were used. More details can be found in Ref. [2].

For the ^{119}Sn Mössbauer measurements, the glass slices were ground into powder. The ^{119}Sn Mössbauer spectra were recorded in transmission mode in the constant acceleration mode at room temperature. The source used for this experiment was ^{119m}Sn embedded in a $CaSnO_3$ matrix. The velocity scale was calibrated with the magnetic sextet of a high purity iron foil as a reference absorber, and ^{57}Co (Rh) was used as source. The spectra were fitted to Lorentzian profiles by a least-squares method. The isomer shift values δ are given relative to the δ value of the $BaSnO_3$ spectrum recorded at room temperature.

3. Results

The ^{119}Sn Mössbauer spectra of the glasses studied are shown in Fig. 1. The respective hyperfine parameters are reported in Table 1.

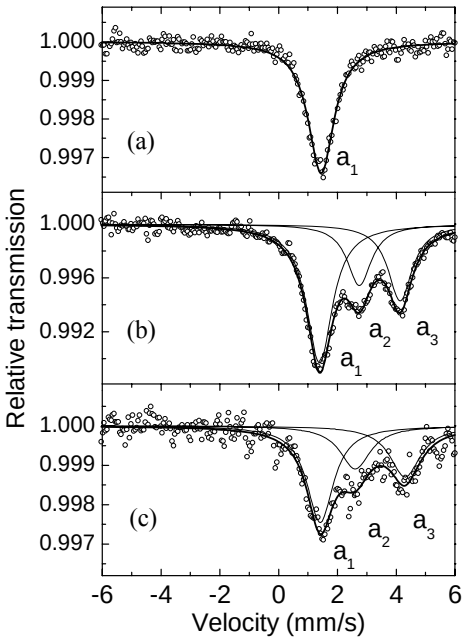

Fig.1. The ^{119}Sn Mössbauer spectra of: (a) $Ge_{19.8}Sn_{0.2}As_{20}S_{60}$; (b) $Ge_{30.72}Sn_{1.28}As_5S_{63}$; (c) $Ge_{31.68}Sn_{0.32}As_5S_{63}$.glasses

The Mössbauer spectrum of $Ge_{19.8}Sn_{0.2}As_{20}S_{60}$ glass, Fig.1 (*a*), shows only one peak (a_1) at 1.45 mm/s that can be attributed to Sn(IV) sites with a symmetrical environment. The spectrum obtained after two weeks of measurements for $Ge_{31.68}Sn_{0.32}As_5S_{63}$ glass, Fig.1 (*c*), is rather noisy, but clearly shows two peaks at about 1.4 (a_1) and 4.3 mm/s (a_3) and a shoulder at about 2.6 mm/s (a_2). Since 4.3 mm/s lies beyond the usual values of isomer shifts observed for tin sulphides, we must consider a_3 as one peak of a doublet, split by electric field gradients due to the asymmetrical environment of tin sites. Taking a_2 as the second peak of this doublet, we obtain for (a_2+a_3) a set of hyperfine parameters which is typical of Sn(II) while the peak a_1 can be attributed to Sn(IV), both present in the glass [5]. The spectra (*b*) and (*c*) of Fig.1 show the doublet (a_2+a_3) to be asymmetric, with a_3 being more intense than a_2 but with equal line widths for both peaks. We shall return to this point in the discussion. Since the poor signal-to-noise ratio of the spectrum reduces the accuracy of the values of the hyperfine parameters, a Sn-richer glass $Ge_{30.72}Sn_{1.28}As_5S_{63}$, Fig.1 (*b*), was also considered. As shown in Table 1, the isomer shifts are similar to those of the Sn-poor sample but the quadrupole splittings of Sn(II) differ by about 0.3 mm/s. There are also differences between the linewidths of the Sn(II) component which confirm the improvement in the evaluation of the hyperfine parameters caused by the increase in the concentration of Sn. The $Ge_{30.72}Sn_{1.28}As_5S_{63}$ glass, and, consequently, the $Ge_{31.68}Sn_{0.32}As_5S_{63}$, contain at least two types of Sn sites: Sn(IV) sites with symmetrical environments and Sn(II) sites with asymmetrical environments.

Table 1. Mössbauer parameters of the glasses with indicated compositions: isomer shift relative to $BaSnO_3$: δ; quadrupole splitting: Δ; linewidth: Γ and relative areas of the different components: A. All units are in mm/s except for A. The experimental errors are of about 0.03mm/s.

Composition	Peaks	δ	Δ	Γ	A(%)
$Ge_{30.72}Sn_{1.28}As_5S_{63}$	a_1	1.39	0	1.06	52
	a_2+a_3	3.44	1.39	1.00	48
$Ge_{31.68}Sn_{0.32}As_5S_{63}$	a_1	1.42	0	1.09	47
	a_2+a_3	3.45	1.70	1.26	53
$Ge_{19.8}Sn_{0.2}As_{20}S_{60}$	a_1	1.45	0	1.07	100

The XPS Sn 3d core level spectrum for the $Ge_{30.72}Sn_{1.28}As_5S_{63}$ glass is shown in Fig. 2. Some values of core level shifts, both for studied and reference glasses, are reported in Table 2. The XPS results for the $Ge_{32}As_5S_{63}$ glass (not given in the Table) are very close to those of the respective glass, where a small amount of Ge was substituted by ^{119}Sn. The Sn $3d_{5/2}$ core level spectrum was fitted with two components due to its asymmetric shape. These two components can be attributed to Sn(IV) and Sn(II), by comparison with the reference materials. There is a good agreement with the results obtained from Mössbauer experiments, except for the relative contributions of the two types of Sn to the spectrum. The contributions of Sn(IV) to the Mössbauer and XPS spectra are 47% and 68%, respectively, whereas the contributions of Sn(II) to the Mössbauer and XPS spectra are 53% and 32%, respectively.

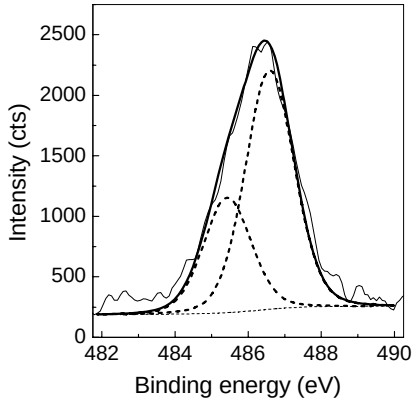

Fig. 2. XPS spectrum of Sn $3d_{5/2}$ for the $Ge_{30.72}Sn_{1.28}As_5S_{63}$ glass.

This could be due to differences between the Lamb-Mössbauer factors of Sn(IV) and Sn(II) which modify the relative areas of the sub-spectra compared to the relative amounts of these two species. This could also be related to the presence of SnO and/or SnO_2 at the surface of the sample (in fact, XPS showed the presence of a small amount of oxygen on the glass surface). Such oxidation is expected to mainly contribute to the XPS Sn(IV) peak, since this technique is surface sensitive but has no

significant influence on the Mössbauer spectra which are obtained in the transmission mode. The absence of a Mössbauer component at $\delta = 0$ mm/s indicates that the amount of Sn atoms in the oxidized layer should be lower than 1-2% of the total amount of Sn atoms in the glasses which are localized in the bulk. The obtained values of the Ge $3p_{3/2}$ and As $3d_{5/2}$ core-level shifts are close to those observed for GeS_2 and As_2S_3 crystalline materials, respectively. These values are also similar to those obtained previously by us [2]. They confirm that most of the Ge and As atoms mainly form $GeS_{4/2}$ tetrahedral and $AsS_{3/2}$ pyramidal units.

Table 2. Core level shifts (in eV) of $Ge_{30.72}Sn_{1.28}As_5S_{63}$, $Ge_{20}As_{20}S_{60}$ glasses and of some reference compounds

Composition	Ge $3p_{3/2}$	As $3d_{5/2}$	Sn(II) $3d_{5/2}$	Sn(IV) $3d_{5/2}$	S $2p_{3/2}$
$Ge_{30.72}Sn_{1.28}As_5S_{63}$	124.1	43.25	485.5 (32%)	486.6 (68%)	162.2
$Ge_{20}As_{20}S_{60}$	124.2	43.6			162.7
GeS_2	124.0[3], 124.2[2]				162.8[2]
GeS	123.3[3]				
As_2S_3		43.4[3], 43.6[2]			162.5[2]
SnS_2				486.5[3, 4]	
SnO_2				486.5[4]	
SnS			485.6[3]		
SnO			486.4		

4. Discussion

The Mössbauer spectra of both $Ge_{30.72}Sn_{1.28}As_5S_{63}$ and $Ge_{31.68}Sn_{0.32}As_5S_{63}$ glasses show the existence of Sn(II) with a strongly distorted environment and of Sn(IV) with isomer shifts in the range 1.4 - 1.45 mm/s. As shown previously, this range of isomer shifts corresponds to $SnS_{4/2}$ tetrahedral units [5]. The absence of quadrupole splitting confirms the symmetrical environments of the Sn(IV) tetrahedral sites and clearly indicates that Sn(IV) atoms are only bonded to S atoms. At first sight it seems rather surprising that the Mössbauer spectrum of $Ge_{19.8}Sn_{0.2}As_{20}S_{60}$ only contains the second contribution (Sn(IV)), since the "undoped" glass belongs to the $Ge_xAs_xS_{100-2x}$ line and according to Ref. [6] homopolar bonds are expected to exist for x>18. Furthermore, As_4S_4 units are formed in the glass matrix [6].Our result suggests that Sn substitutes for Ge preferably in tetrahedral $GeS_{4/2}$ units.

We assign the observed difference between curves (*a*) and (*b*, *c*) in the Mössbauer spectra, Fig.1, to the different As-concentrations in the compositions studied and, mainly, to the differences in the As/Ge ratio. This

supposition can be supported by a simple calculation (involving 100 atoms per composition) based on a model given in Ref. [7]. In this model S atoms are bonded with Ge and As atoms proportionally to the magnitude of the binding energies, coordinations and concentrations of the elements. The Ge, As and S atoms have been supposed to be 4-, 3-, and 2-fold coordinated, respectively.

Using the most probable and energetically advantageous structural units (SU) it can be obtained that

(a) $Ge_{32}As_5S_{63}$ can be presented as

$Ge_{32}As_5S_{63} \rightarrow As_5S_6 + Ge_{32}S_{57} \rightarrow As_2S_3 + 3/4\ As_4S_4 + Ge_{32}S_{57}$

or

$Ge_{32}As_5S_{63} \rightarrow 5/4\ As_4S_4 + Ge_{32}S_{58}$

In both cases the Ge-S compounds ($Ge_{32}S_{57}$ and $Ge_{32}S_{58}$) are enriched with Ge. Thus, except for the tetrahedral SU $GeS_{4/2}$, the amount of the formed GeS (and, respectively, SnS) and/or other non-tetrahedral SU is relatively large. Meanwhile, the As- containing units are in a small amount.

(b) In the case of $Ge_{20}As_{20}S_{60}$:

$Ge_{20}As_{20}S_{60} \rightarrow As_{20}S_{24.4} + Ge_{20}S_{35.6} \rightarrow As_{20}S_{20} + Ge_{20}S_{40} \rightarrow 5As_4S_4 + 20GeS_2$

or

$Ge_{20}As_{20}S_{60} \rightarrow As_{16}S_{16} + As_4S_6 + Ge_{20}S_{38} \rightarrow 4As_4S_4 + 2As_2S_3 + Ge_{20}S_{38}$

Here, the S-atoms are sufficient to form mainly $GeS_{4/2}$ tetrahedral SU, since the homopolar Ge-Ge (or Sn-Sn) bonds are in a small amount (about 1%). SU of both As_4S_4 and As_2S_3 are present.

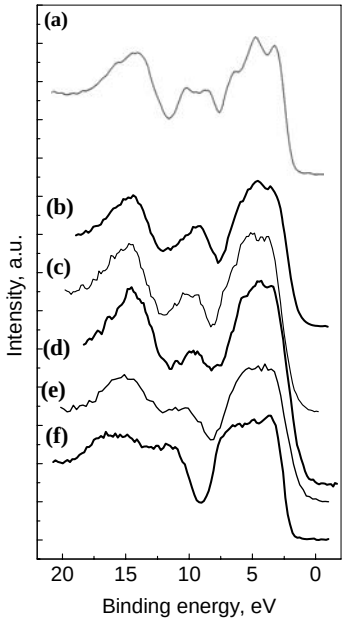

Fig. 3. Valence band spectra of the glasses: (a) GeS_2 , (b) Ge_2S_3 , (c) $Ge_{32}As_5S_{63}$, (d) $Ge_{30.72}Sn_{1.28}As_5S_{63}$, (e) $Ge_{20}As_{20}S_{60}$ and (f) As_2S_3.

XPS results confirm our assumption about the correlation between the main structural units in the matrices of the glasses with different As/Ge concentrations (Fig.3, *c*, *d* and *e*). For comparison three complementary spectra are given in the Figure: the VB spectra of glassy GeS_2, *a*; Ge_2S_3, *b*, and of As_2S_3, *f*. The VB spectra of both glasses with small As-concentration (Fig.3 *c, d*) are very similar. This is an indication that their structural units are of one and the same type, independently of that either Sn or Ge is included in the respective glass matrix. For this reason the conclusions we have draw about the Sn structural units (SnS and SnS_2) are also valid for the Ge structural units.

Similarly to the results reported in Ref. [2], the VB spectra exhibit three broad bands in the range of 0-20 eV:

- The first broad band (1 - 8 eV) can be associated with ionizations involving sulfur lone pairs (at about 3.5 eV) and both (Ge-S and As-S) bonds (at E ≥ 6 eV). The energy associated with the Ge-S bonds is lower than that, related to the As-S one's and a higher value characterizes the photoionization cross section of As 4p orbitals compared to Ge 4p orbitals (0.121 and 0.058 respectively [3]). A certain enlargement on the left site of this band for the $Ge_{20}As_{20}S_{60}$ curve (Fig.3, *e*) towards those for $Ge_{32}As_5S_{63}$ (Fig.3, *c*) and $Ge_{30.72}Sn_{1.28}As_5S_{63}$ (Fig.3, *d*) arises from the augmentation of the amount of As-S bonds in the former composition. This enlargement is well seen in the VB spectrum of As_2S_3, curve *f*.
- The intermediate energy band (9 - 11 eV) corresponds to ionization's characteristics of 3s, 3p orbitals of S, and 4s orbitals of Ge and/or As atoms (with a lower binding energy for 4s orbitals of Ge atoms than of the As atoms). Homopolar Ge-Ge and As-As bonds can be associated with this feature of the VB spectra of the glasses [2]. These bonds arise from structural units like As_4S_4 for As and $Ge_2S_{6/2}$ and/or GeS, as well as $GeS_{6/6}$ distorted cubic units, for Ge [8,10]. In the glasses with small As concentration the most probable structural units are GeS. That is why in the curves *a* – *d* in Fig.3 the intermediate energy band is more pronounced than in the curves *e, f*.
- The third band, at about 14 - 17 eV, is mainly due to ionizations of the 3s orbitals of S atoms. This spectral region is preferentially characterized by the S-S interactions (distances). There is a noticeable difference between the curves *b* - *d* from one side and *e, f* by the other side (Fig.3) in this energy region. This difference is due to the different S-S interactions between the main structural units in the glasses studied. The relative quantity of the structural Ge-S units prevails in the compositions whose VB spectra are presented by the curves in Fig.3 *a* - *d*. The similarity between the curves *c, d* and curve *b* (for Ge_2S_3) is great whereas some differences are seen when the spectra *c, d* are compared with that from curve *a* (GeS_2). This is an indication that S is included in different types of structural units. According to [6, 10] in Ge-S system in the range of 57 - 62 at.% S two types of structural units exist: $GeS_{4/2}$ thetrahedra and GeS-like SU with two valences of Ge^{4+} and Ge^{2+}, respectively. Taking in mind our experimental results we accept this model for the S-environment of our Ge-rich glasses. Meanwhile, it can be seen that with the increase of the relative concentration of As the shape of the curves from (*c*) to (*e*) changes and becomes similar to that of the As_2S_3 glass. This is an indication for the increase of the concentration of structural units that form the glass matrix of the latter, namely, $AsS_{3/2}$ pyramids and As_4S_4 SU. Thus, the amount of the S-atoms that are "free" to connect with the Ge ones decreases and only the energetically more probable GeS_2 tetrahedra are formed.

On the base of the above presented discussion on the obtained experimental results it can be explain why in the $Ge_{32}As_5S_{63}$ and $Ge_{30.72}Sn_{1.28}As_5S_{63}$ glasses Sn and, consequently Ge, are bonded with S as Ge(IV) and Ge(II) while in $Ge_{20}As_{20}S_{60}$ glass Ge atoms are bonded only as Ge(IV).

As has been already mentioned, the Sn(II) sites observed from both studies are supposed to be due to substitution of Sn for Ge in $Ge_2S_{6/2}$ ethane-like units and/or in $GeS_{6/6}$ distorted cubic units as observed in Ge_xS_{100-x} [6] and suggested in Ref. [8, 10]. In the light of the discussion on the obtained XPS spectra it is more probable that the $Ge_2S_{6/2}$ ethane-like prevail in the structure of the $Ge_{20}As_{20}S_{60}$ glass while in the $Ge_{32}As_5S_{63}$ without and with ^{119}Sn glasses the $GeS_{6/6}$ distorted cubic units should prevail. The latter units are also found in crystalline SnS, where distorted SnS_6 octahedra are characterised by a strong vibrational anharmonicity which results in an asymmetric Mössbauer doublet (Goldanskii-Karyagin effect) with a similar isomer shift (δ = 3.4 mm/s) but a lower quadrupole splitting (Δ = 0.9 mm/s) as in the present case. This suggests the existence of SnS-like nanophases in the glass, with a more distorted structure than in the SnS crystalline compound but characterised by a similar vibrational anharmonicity. Such an interpretation could be consistent with the nanoscale phase separation previously proposed for the GeS_2 glass [9].

The presence of two submaxima in the XPS core level peak of Sn 3d can also be explained in this light. The position of the main peak at 486.6 eV is close to the positions of SnS_2 (486.5 eV), SnO_2 (486.5 eV) and SnO (486.4 eV), while the position of the smaller peak at 485.5 eV – to the position of SnS (485.6 eV), see Table 2. However, taking into account that the amount of oxygen in the glasses studied was negligible (a just-formed fracture site of the glass was examined in a high vacuum) we accept that the obtained binding energies represents structures like both SnS_2 (486.6 eV) and SnS (485.5 eV) with a very small influence of SnO_2. Accordingly, the Ge and S atoms are connected in the respective GeS_2 and/or GeS structural units.

It should be pointed out that in both studies we have obtained average results. Moreover, as a rule, the spectra of the glasses due to structural and chemical disorder are somewhat smeared. Nevertheless, the experimental results clearly proved the prevalence of the main structural units characterizing the stoichiometric Ge-S and As-S compositions ($AsS_{3/2}$, $GeS_{4/2}$, As_4S_4) and, also, some structural units enriched in Ge.

5. Conclusions

A substitution of the Ge atoms by ^{119}Sn was used to identify the Ge-environment in (Ge, Sn)-As-S glasses. The combined Mössbauer and XPS study showed differences in the type of the structural units forming the glass matrices in relation to the As/Ge ratio. In $Ge_{20}As_{20}S_{60}$, the Ge atoms are situated preferably in tetrahedral $GeS_{4/2}$. In $Ge_{32}As_5S_{63}$, besides the main $GeS_{4/2}$ tetrahedral structural units, $Ge_2S_{6/2}$ ethane-like and/or $GeS_{6/6}$ distorted cubic units, as well as GeS units (with smaller probability) are present. Nanoscale phase separation is possible in the glasses with low As concentration.

Acknowledgements

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