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DISORDER IN $Ge_xAs_{40-x}S_{60}$ GLASSES AND FILMS: AN EXAFS STUDY

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X-ray absorption spectroscopy has been used to study $Ge_xAs_{40-x}S_{60}$ glasses and films at the K edges of As, Ge and S. The spectra obtained for glasses with different compositions as well as those for glasses and films are compared. The spectra of films before and after illumination or thermal treatments are compared in order to study the effect of annealing and/or illumination upon the disorder. The results are discussed in terms of the degree of chemical and structural disorders of the amorphous matrices.

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1. Introduction

Since the chalcogenide amorphous materials are promising for a wide range of technological applications, a variety of their properties is still intensively studied. A considerable part of the studies is carried on with respect of the possibility to induce changes in their structure and related properties under irradiation and/or thermal treatment. It is well known that the structural ordering in the amorphous materials depend strongly on the technological pre-history. As a rule the term "degree of disorder" is used in a relative sense. Hence, the well-annealed glasses are more ordered than the films evaporated from them. The latter are preferred for investigation of the photoinduced structural changes due to the limited possibility of the light to penetrate into the sample's depth. The photostructural changes, irreversible or reversible, can be obtained by bandgap illumination. The first illumination of the as-prepared (fresh) films, as well as their annealing near the respective glass-transition temperature, T_g, leads to a certain degree of structural ordering. The most ordered state in the film structure can be obtained by an appropriate annealing although the degree of ordering of the parent glass can not be achieved. By the reversible photostructural changes the post-annealing illumination induces new structural disorder in the film matrix that can be subsequently recovered by the next annealing. The mentioned changes of the structural order in the films reflect in changes of various physical and physicochemical properties.

During the process of photostructural changes the local environment of the constituent atoms as well as their electronic structure are also changed. Results from extended X-ray absorption fine structure (EXAFS) studies on the photoinduced changes, mainly in binary chalcogenides, have been already published [1-6]. In [1, 2] the formation of "wrong bonds" during the reversible photostructural changes in As_2S_3 was confirmed. The rearrangement of the bonds induced by thermal treatment and/or illumination is one of the reasons for the photostructural changes. *In situ* EXAFS measurements [5] have shown that the coordination geometry around the chalcogen atoms

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leads to formation of dynamic interchain bonds via interaction of photoexcited electrons from selenium lone-pair orbitals.

EXAFS has been successfully used to define the homopolar bonding, chemical order and topology in Ge-As-S chalcogenide glasses [7, 8]. Photoinduced changes in films from this system have been largely studied by us [9, 10] and are also recently reported in [11, 12].

In the present work we report preliminary results of an EXAFS study on $Ge_xAs_{40-x}S_{60}$ glasses and films at the K edges of the constituent elements. The compositional trends in structural ordering as well as the degree of disorder in technologically different states are analyzed.

2. Experimental

The appropriate quantities of the constituent 5N elements were sealed in quartz ampoules and glasses were prepared by a standard method [see e.g. 9]. The glassy ingots were ground and sieved to 5 μm to obtain a homogeneous granular powder. Thin films were thermally evaporated in a vacuum of 10^{-3} Pa onto Si, kapton and mica substrates. The rate of evaporation (~100 Å/s) was previously chosen to ensure the nearest to the parent glass composition of the films. Bandgap illumination from a HBO 500 Mercury lamp was used. The time of illumination was chosen to be 45 min. These conditions are necessary to achieve saturation of the optical photoinduced changes. The samples were annealed at temperatures ~ (T_g-20°C) for 45 min. in ampoules filled with Ar. After annealing the ampoules were cooled in air.

X-ray absorption spectra at the As and Ge K-edges were recorded using the synchrotron radiation of the D42 beamline of the DCI storage ring at Orsay, France. The beamline was equipped with a channelcut Si(111) monochromator. The spectra were recorded in transmission geometry with an energy step width of 2 eV in the EXAFS region and of 0.5 eV in the XANES region. Absorption spectra at the S K-edge were measured on the SA32 beamline of the SACO ring at the same synchrotron, equipped with a Ge(111) double crystal monochromator. The spectra were recorded with energy step widths of 5 and 0.2 eV in the EXAFS and XANES regions, respectively. All spectra were first corrected for a linear baseline and then for atomic absorption by fitting a polynomial function to the spectral region above the absorption edge. The spectra were normalised with respect to a point far above the absorption edge, where EXAFS oscillations are sufficiently attenuated.

3. Results

Figs. 1-3 show the conduction band states for the glasses studied. The curves are based on the XANES measurements for the K edges of the constituent elements. The absorption curves are shifted one upon another for clarity. As can be seen, almost no differences with the change of the composition are observed in the case of the As K and Ge K edges. However, compositionally dependent changes are present in the curves obtained for the S K edge (Fig. 3). The evolution of the shape of the white band from As_2S_3 to Ge_2S_3 is well expressed, especially in the small peak at 2475 eV. In Fig. 4 the Ge and S K edges are plotted for Ge_2S_3 and GeS_2. The differences in the curves are once more better expressed for the sulphur K edge. Thus, the main differences for all the Ge-As-S curves in Figs. 1-4 are in the shape of the white line while almost no shift in the position of the absorption edge is found.

In Fig. 5 XANES spectra of glasses and films evaporated from them are compared. In the example the compositions $Ge_{20}As_{20}S_{60}$ (at the As K edge) and $Ge_{27}As_{13}S_{60}$ (S K edge) are chosen. The respective normalized spectra of the conduction band states show different structures with varying intensities and slight shifts of the white line maximum. Here, and in the next figures, the letters indicating different states of the films, related to the treatments, are used as follows:

f - untreated (fresh) film ,
fi – first illumination
fa - annealed film
fai - film, illuminated after annealing.

In all the cases the shape of the absorption curves is characteristic for the respective element environment.

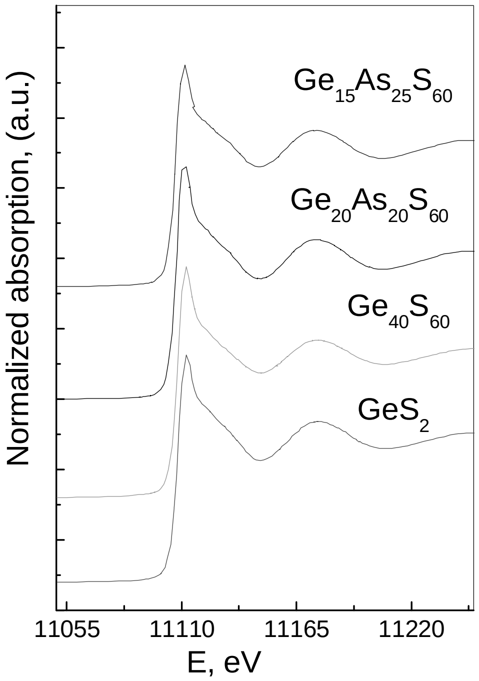

Fig. 1. Comparison between the spectra of the glasses, Ge K edge

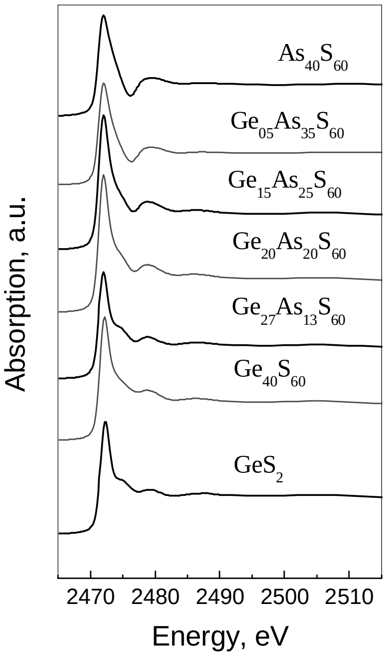

Fig. 3. Comparison between the spectra of the glasses (S K edge)

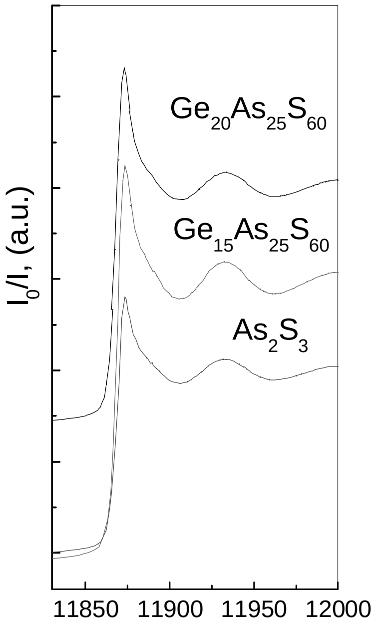

Fig. 2. Comparison between the glass spectra, As K edge

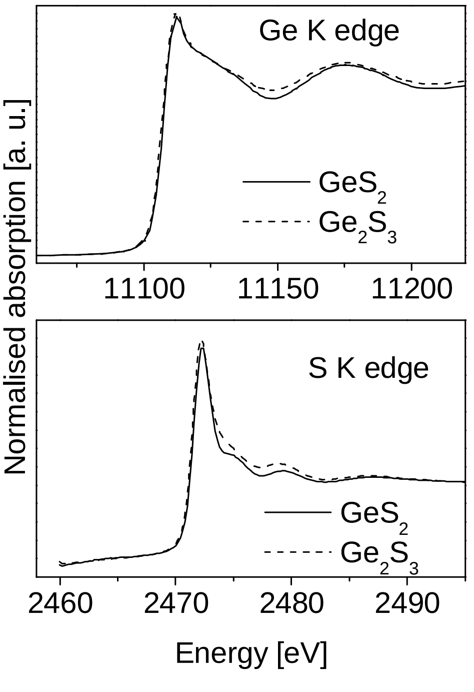

Fig. 4. Ge K and S K edges spectra for Ge_2S_3 and GeS_2

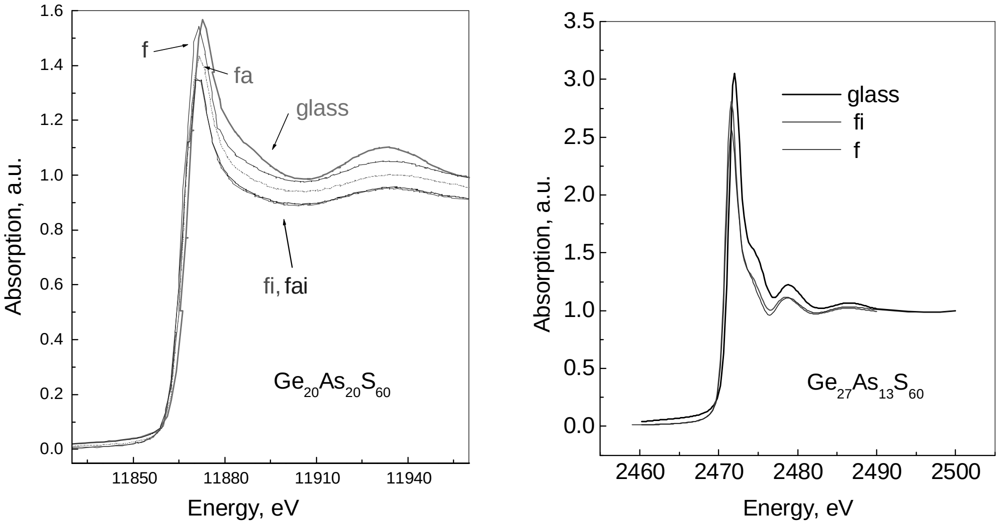

Fig. 5. Conduction band states for the glasses $Ge_{20}As_{20}S_{60}$ (As K edge) and $Ge_{27}As_{13}S_{60}$ (S K edge) and the respective evaporated from them films

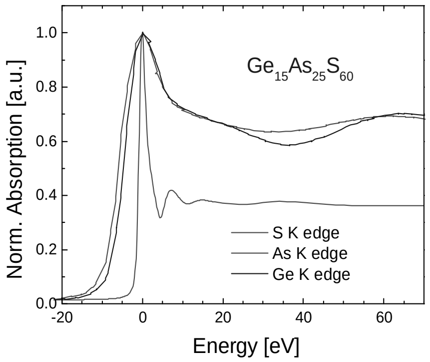

Fig. 6. Differences in the shape of the white line for the K edges of the three constituent elements in $Ge_{15}As_{25}S_{60}$.

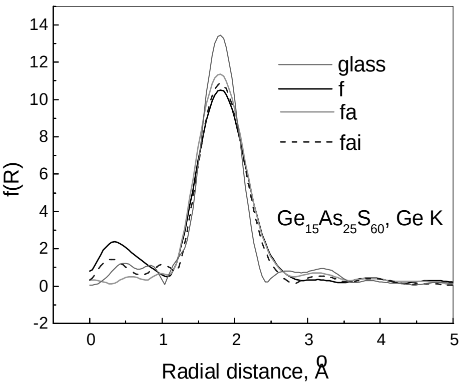

Fig. 7. Fourier transform for the $Ge_{15}As_{25}S_{60}$: glass; evaporated from it film, (f); annealed film, (fa); and film, illuminated after annealing, (fai). The curves are obtained from the Ge K edge.

An example of typical radial distribution functions f(R) for one of the investigated glasses ($Ge_{15}As_{25}S_{60}$) and for the films evaporated from it is presented in Fig. 7. The peak positions are almost identical. The curve related to the glass has a better expressed maximum with a narrower radial distribution than the films. Differences are observed in the intensities of the main peak as well as in the range beyond the main Fourier peak (second co-ordination shell).

Changes have been also observed in the K-edge EXAFS spectra. The amplitudes of the k^3 weighted curves of the glass spectra higher than for the films. In most cases illumination and annealing increased the amplitudes, although differences between the results for different elements have been observed. The detailed study of these changes will be published later.

4. Discussion

The comparison of the Figures 1-3 shows that the main changes in the short range order of the sulphur are due to changes in the composition from x=0 to x=40 at.%. The sulphur in the $Ge_xAs_{40-x}S_{60}$ glasses is connected partially with both the As and Ge atoms, thus it is the most influenced by variations of the composition. The investigated compounds belong to the As_2S_3-Ge_2S_3 line of the Ge-As-S ternary diagram. The main structural units are the pyramidal As_2S_3 and the tetrahedral GeS_2 ones. Our IR and Raman scattering results on the same compositions lead us to the conclusion that a small amount of homopolar wrong bonds is also present in the glass matrix. Some of the obtained bands can be assigned to As-As bonds in As_4S_4 structural units and Ge-Ge bonds in ethane-like $Ge_2(S_{1/2})_6$ structures [9]. With the increase of the Ge-content the sulphur deficit increases. As has been pointed out in [7, 8], the fraction of As-As and Ge-Ge bonds in S-deficient Ge-As-S glasses increases with the sulphur deficit. At the same time neither the Ge-S and Ge-Ge bond lengths, nor the As-S and As-As ones do show any significant compositional variations and are typical of the Ge-sulphide and As-sulphide binary phases. On the other hand, As-As bonds are the first to appear in these conditions and the Ge-Ge bonds begin to form at a much higher S deficiency [7, 13]. Our Raman scattering spectra have shown that in the As_2S_3 glass, prepared by the same technology, exist already at least 2% of wrong (As-As) bonds [14]. With the increase of the Ge-content (and, hence, of the S-deficiency) the appearance of new As-As bonds should not change essentially the shape of the curves. Finally, Ge-Ge bonds are formed in an amount that is sufficient to enlarge the white line of the spectra. In GeS_2 the predominant bonds are the Ge-S ones and only a small percent of Ge-Ge bonds are available. That is the reason for the differences between the curves observed in Fig. 4.

Another reason for the higher sensibility of the S K edge spectra to the compositional change lies in the higher spectral resolution at the S K edge as compared to the As and Ge K edges (Fig.6), due to the lower line broadening by the finite life time of the core hole.

Recent XPS studies on $Ge_xAs_{40-x}S_{60}$ glasses and films have also supported the concept of a structure based on the mentioned above main structural units [15]. Both Raman and XPS results pointed on the structural similarity between the films and their parent glasses. However, the identity is far to be reached: the films are in any state more disordered than their parent glasses.

Fig. 5 illustrates the influence of the degree of disorder on the XANES absorption edge. For both $Ge_{20}As_{20}S_{60}$ (at As K) and $Ge_{27}As_{13}S_{60}$ (S K) compositions the position of the freshly evaporated films is slightly shifted to lower energies, while the illuminated (first illumination, it has an ordering action as well as the annealing) and the annealing do shift the edge position to higher energies (closer to the position of the glass curve). The intensity of the respective peaks increases but does not reach the value of the glass edge. The post-annealing illumination leads to a decrease of the intensity and to a re-shift towards the lower energy position. This picture confirms the concept about the ordering/disordering of the film structure when reversible photoinduced changes occur.

Figs. 7 also confirms this statement. The radial distribution function f(R) for the glass is higher and narrower, illustrating the most ordered among the samples under examination. The films, more disordered than the glass, exhibit larger and lower curves. The annealed sample is more ordered than the fresh and the post-annealing illuminated ones. As concerning the second co-ordination shell, the nearest curve to that of the glass is again that of the annealed film.

The changes of the EXAFS amplitude can derive from changes in the coordination number as well as from modifications in the local order. Should the second reason be the main one, the differences in the respective curves confirm in most of the cases the above listed changes to more or less ordered states in dependence on the thermal treatments: the degree of disorder in the films is directly connected with the photo- and thermoinduced changes.

As has been mentioned above the photo- and thermally induced structural changes result from rearrangements in the bonds between the nearest neighbours. The most ordered state is that one that has a minimal amount of wrong (in our compositions – homopolar) bonds. The glasses are representative for. When the films are well annealed, the amount of the homopolar bonds decreases. A subsequent illumination increases the amount of the wrong bonds, thus leading to a more disordered state. These processes have been supposed and proved for binary compositions by many investigations, in particular in almost all the references quoted in this work. Our EXAFS and XANES results on the ternary $Ge_xAs_{40-x}S_{60}$ compositions give also an experimental support to this statement. A detailed analysis of the local environments of the Ge, As and S atoms will be published soon in another paper.

5. Conclusion

EXAFS and XANES study at the Ge, As and S K edges on $Ge_xAs_{40-x}S_{60}$ glasses and thin films has shown the possibility to use these methods to check the degree of disorder in the amorphous matrix. Differences have been found in the electronic structure of the films and their parent glasses, as well as of the films after various treatments. The changes in the absorption curves for the S K edge are the most pronounced.

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