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Summary

of the

Contributions to the investigation of photostructural phenomena in chalcogenide materials

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Introduction

In the last decades, the non-crystalline solid state has received more and more attention in the literature. The reasons are the fundamental scientific interest, as well as the potential applications. Already since the early 19th there were glasses looked for, showing transparency in the infrared (IR) spectral region. The oxide glasses were found to be IR-transparent till 3-5 μ m, while the heavy-metal oxides showed values up to 7-8 μ m [1, 2]. Systematic research has been performed including combinations of elements from the VIth main group of the Periodic Table, especially those containing sulfur (S), selenium (Se) and tellurium (Te). They have as generic name the term *chalcogenides* [3].

The field of physics of the chalcogenides grew with the support of the large variaty of caracteristic properties of the non-crystalline chalcogenides [3, 8]. The photo-induced modifications are the most remarkable among them. Great interest present the reversible photoinduced phenomena. Such examples are: the reversible change of the absorption coefficient, or of the refractive index in the amorphous arsenic chalcogenides.

This thesis discusses the problem of the structure of non-crystalline chalcogenides, emphasizing the structural changes induced by light in some amorphous compositions. For this purpose the X-ray diffraction (XRD) experimental method is used, along with the computer assisted hand-made modelling and structural simulations, with the Monte-Carlo-Metropolis method.

Chapter 1 presents the non-crystalline solid state. Starting from the definition of the ideal crystal, we discuss the posibility to define the ideal non-crystalline structure. The experimental and the conceptual limitations are remarked, and the non-unicity of the non-crystalline structure is underlined.

Chapter 2 discusses the XRD method for solid state structure study, according to the literature. Here there is presented also the contribution of the author to improve the measurement procedure in the case of the amorphous chalcogenide films.

Chapter 3 presents the photoinduced modifications which may occur in the non-crystalline chalcogenide materials. These changes practically do not appear in the correspondent crystalline phase. The influence of the ultra-violet (UV) light on some amorphous films is presented, showing also the contribution of the author.

Chapter 4 gives the energetically relaxed nano-phase-type structural model of As_2S_3 . Also here we present a model for the photo-induced structural changes.

Chapter 5 presents the conclutions and summarizes the contributions of the author to a better understanding of the non-crystalline state.

Chapter 1

The non-crystalline solid state

1.1. Ideal crystal and ideal non-crystal

As concerning the sterical relative displacement of the atoms to each other, the solid may take two fundamentally different structural states: ordered (crystalline) or disordered (non-crystalline, amorphous or vitreous).

In the crystalline state the constituents (atoms, molecules) are disposed in a net-like structure having translational symmetry. It is possible to define a structural building unit in this case, the so-called elementary cell, which can reproduce the whole net through the translational symmetry. The elementary cell will have just a limited number of constituents, with well-known positions inside the cell [3, 14]. The real crystall will differ from the ideal crystalline structure, presenting imperfections and defects.

In the non-crystalline state the constituent atoms or molecules are no longer disposed in a periodic structure. There will be a lack of translational symmetry. In time, attempts have been made to define an

ideal non-crystalline state [15, 16]. We have to notice, that it is not easy to find a scalar parameter to characterize the degree of crystallinity or non-crystallinity (order-disorder) of a structure. A reason for this is, that at one end of the scale there are all the possible ideally ordered crystalline structures, while at the other end of the scale one have the practically unlimited number of disordered structural configurations. Therefore, the possible order-disorder transitions are not unique. Exactly this feature of existence of multiple metastable states of the non-crystalline structure allow the interesting photo-induced phenomena, which have not correspondent in the crystalline state.

1.2. Short range order (SRO), medium range order (MRO) and long range order (LRO)

If the translational symmetry of a structure is lost, than what remains is not a total disorder, a chaos, but a special type of order which has been called short-range order (SRO). It describes and characterizes the structure on a distance of one bond length. Here the first coordination sphere, the number and relative sterical positions of the first neighbours will be preserved, because of the same kind and type of chemical bond, like in the crystalline state. This is why the SRO describes a nearly perfect crystalline local structure corresponding to the first coordination shell, which is slowly "fergot" at lareger distances from the origin.

In some chalcogenide compositions there was observed a special type of order (MRO), which expresses the extension of the short-order to longer distances, through the next 2-3 structural neighbours [17, 18].

Elliott proposed a classification for the different type of orders:

- Short-range order (SRO, 0.3-0.5 nm),
- Medium-range order (MRO, 0.5-0.8 nm), and
- Long-range order (LRO, 0.8-1 nm).

Chapter 2

The study of the non-crystalline structures by the X-ray diffraction method

In the following three subsections the classical treatment for the calculation of the diffracted beam intensity is given [14, 20].

2.1. Scattering of X-rays by the electrons of an atom. The atomic form factor

The atomic form factor characterizes the electron density and the shape of the electron distribution around an atom. It also gives the ratio of the scattered intensities by the electrons of the whole atom, and one single isolated electron: $f=I_{at} / I_e$. Because the size of the atoms are in the same range with the scattered wavelength, a phase difference will be inroduced along the different scattering directions from an atom. The atomic form factor decreases non-linearly with the scattering anle 20.

2.2. Scattering intensity by a group of atoms. The structure factor

The scattered intensity by a group of atoms is

 $I \sim |F|^2 = F F^*$,

where F is called the structure factor of the scattering center distribution:

$$\mathbf{F} = \sum_{i=1}^{N} \mathbf{f}_i \ \mathbf{e}^{-i\vec{k}\cdot\vec{r}_i} \ .$$

Here, f_i are the atomic form factors of the scattering atoms.

2.3. The radial distribution function

The radial distribution function (RDF) gives the mean number of scattering centers in a spherical shell of dr thickness at an r distance from any given origin:

$$RDF = 4\pi r^{2} \rho(r) = 4\pi r^{2} \rho_{0} + \frac{2r}{\pi} \int_{0}^{\infty} ki(k) \sin kr \, dk \, \cdot$$

It also describes the density fluctuation characteristic to the amorphous state.

2.4. Contributions to the measuring method of the structure factor for non-crystalline films

The substrate contribution to the X-ray diffraction diagram has been many times observed, especially in the case of films consisting of light or medium weighted elements, which have a lower scattering power. We present in the following a study performed by us and already published [21].

2.4.1. The substrate problem in the case of the thin films

The substrate plays an important role in the thin film deposition process. It may strongly influence the properties and structure of the film deposited onto it (crystallization, oxidation, vitrification, etc.) [22].

For structures with low texture Zevin suggested already a method to avoid the parazit effect of the silicon (Si) substarte [23], introducing a slight assymetry in the scattering geometry. This will "throw" the huge and sharp undesired crystalline peaks outside the counter.

A substrate contribution has been observed also by Collard and Hoyer on carbon nitride hard coatings [24]. They proposed the rotation of the sample to reduce this substarte contribution.

In the case of our amorphous thin films, the strange peak given by the Si substrate was identified to be the so-called escape peak [25]. In this work, a sistematic investigation has been done using the substrate rotation method. Two suggestions are given for minimizing or for avoiding the appearance of the escape peak (EP).

2.4.2. Experimental details

Two series of chalcogenide thin film samples have been investigated: AsSe:Sn (3 samples) and GeSbSe (4 samples). The film thickness were around 5 μ m and 3 μ m respectively. The X-ray diffraction measurement have been performed on a *Seiffert XRD* 7 diffractometer, with Cu target tube, operated at a high voltage of U=40 kV. It is important to remark, that the goniometer of this diffractometer allowed the sample rotation in its own plane.

2.4.3. Results and interpretation

In the frame of the disordered layer model of the amorphous structure, the first sharp diffraction peak (FSDP) reagion in the diffraction diagram characterizes the medium range order (MRO) of the investigated structure.

The XRD diagrams presented in our case large differences in shape and intensity, exactly for the FSDP. The specific angular region was from 13 to 16 degrees in 2 θ , corresponding to a cvasi periodicity of 5,5-6,8 Å. In order to set a reference relative to each sample, the counter has been positioned to $2\theta=15^{\circ}$, where the fluctuations have been found to be the largest. Figure 1 and 2 show the results of the Φ -scans for the two saple series.



Fig. 1. The substrate influence. ϕ -scans for the AsSe:Sn at 2θ =15 deg.

Fig. 2. The substrate influence. ϕ -scans for GeSbSe samples at 2θ =15 deg.

It can be observed, that in the case of no substrate contribution, the diagrams in Figs. 1 and 2 given by the amorphous structure, might consist only in horizontal line shapes, slightly oscillating around a mean scattering intensity. Also, one can see angular regions with minimum and maximum substrate contributions, along with many transient situation between them.

The next step in the systematic study was to make θ -2 θ XRD scans, with the substrates beeing Φ -rotated so, to be in the two extreme situations: an optimal one (the flat region), and the undesired case (the region of the maxima). Figures 3 and 4 show the results:



It is important to stress, that the asymmetric maxima appear always at the same angular position, while the FSDP can "migrate" according to the actual MRO caracteristics of the measured amorphous sample. In some unfavourable situation it amight happen the FSDP to be eclipsed completely by the large EP. In such cases, the FSDP cannot be identified, without filtering the substrate given EP.

In the following Table 1 and 2 we summarize the angular positions and the corresponding quasiperiod for the two sample series, given by the substrate:

Table 1. EP parameters of the AsSe:Sn samples			
Probele	Pozitie maxim	Oasi-perioada	
AsSe:Sn	2θ (deg)	d (Å)	
A 0	15.05	5.88	
A 1 N	14.99	5.90	
A 4 T	15.06	5.07	

Table 2. EP parameters of the $Ge_{27}Sb_{13}Se_{60}$ samples

Probele Ge ₂₇ Sb ₁₃ Se ₆₀	Poziție maxim, 2θ (deg)	Qasi-perioada, d (Å)
F N	14.96	5.92
ΓL	15.06	5.88
AN	14.90	5.94
A L	15.00	5.90

A tight statistics is observed for the angular position distribution of the escape peaks. Taking into account an observation error of $\pm 0,02$ (°2 θ) for the peak position, one can consider that in all cases the EP is given by the same (common) structure, in our case the substrate.

The EP is produced inside the counter by the secondary fluorescence, triggered by the incoming scattered quanta, which have enough energy after the fluorescence to fit the energy threshold and window value conditions set in the electronic measuring chain. Such quanta are commonly present in the white spectrum of the X-rays generated at the high voltage of 40 kV.

Observing, that the appearance of the EP is a threshold phenomena, one can suggest to use high voltages of lower values than 40 kV, to avoid completely the EP.

The possibility to minimize the EP if it appears, may also be very effective through rotating the sample in its own plane to an optimal angular Φ position.

2.4.4. Conclusions

For the investigation of the MRO features of amorphous films by XRD measurements, the diffraction conditions have to be carefully choosed. This is especially important in the case of the non-crystalline compositions for which the FSDP region is situated in the same angular range where the escape peak appears. Two methods have been proposed to minimize or to avoid the escape peak.

Chapter 3

Photoinduced modifications in non-crystalline chalcogenides

3.1. Description of the photoinduced modifications

A classification of the photostructural modifications may be made from different points of view. One of them is related to the reversibility of the changes. An other criteria can be the isotropic or the anisotropic caracter of the change induced by light.

For possible applications the most interesting phenomena are the reversible photoinduced modifications. The most important among them is the photo-darkening (PD). It usually appears along with other reversible modifications, like those of the hardness, density, glassy temperature, elastic constants and dissolution rate [27]. Reversibility has been observed also in the photo-induced anizotropy [28, 29].

As irreversible changes we can note the following: photoevaporation [30], photocrystallization [32], photoamorfization [33], the photocontraction and photoexpantion [34], photo-decomposition [36] or photopolimerisation [40, 41].

3.1.1. Scalar (isotropic) photoinduced modifications

Scalar modifications are those which does not involve a reorganisation of the structure along some preferential directions after the illumination.

The most representative scalar transformation is the photo-darkening (PD).

3.1.2. Vectorial (anisotropic) photoinduced modifications

The most representative vectorial transformation is the photoinduced anizotropy. Vectorial effects are generated mostly by polarized light [28]

3.2. Atomic scale interpretation of the photoinduced modifications

3.2.1. Mechanism of the scalar photoinduced changes

Band-gap light irradiations were found to produce the most important photoinduced effects, through chemical bond breaking [42-44]. Many investigations have been performed to reveal the mechanism of these photoinduced structural changes. Though, the exact mechanism is still not completely clear. It shows certain common features [45] but it is also composition dependent. The non-bonding p-electrons have a key role in the photoinduced phenomena [46].

Based on the data from the literature we suppose that photo-darkening and photo-bleaching can be explained as follows: at the irradiation process the lone-pair (LP) electrons of the chalcogen atoms are excited and they determine a slight repositioning of the atom. Two competitive processes can occur simultaneously. One of them is the bond breaking, while the other one is the bond reconstruction in the immediate vecinity. This mechanism can explain the wide variety of evolution possibilities, where some regions may extend on the expense of the other structural formations of the neighbours.

We assume, that these structural changes modify the energy band structure near the limits of the gap, and so can determine the shift of the absoption edge, i.e. the PD or PB.

3.2.2. Mechanism of the photoinduced vectorial changes

One of the first observations of the photoinduced vectorial changes has been done by Zhdanov and coworkers [70, 71]. They are induced by polarized light. Lyubin and Tikhomirov have found that photodarkening and photo-induced anizotropy are independent processes [76].

We consider, that the mechanism of the photo-induced anizotropy is possibly related to the chirality of the chalcogenide material.

3.3. The effect of the UV radiation on the Ge-As-S thin films

Chalcogenide thin films present a great interest, because of their ability to modify the structure upon the irradiation with appropriate wavelength. We have performed a study about the modifications which can happen in Ge-As-S thin film samples. The results have been published in *Journal of Non-Crystalline Solids* [35]. We summarize below the results.

3.3.1. Introduction. Experimental data.

Arsenic based chalcogenide glasses are an important class of IR tranparent materials. Their structure can be changed by irradiation with appropriate radiation. This is why they are good candidates for photolitografic or phase-change recording materials [85, 86].

The thin films of $Ge_xAs_{40-x}S_{60}$ (0<x<40) of a thickness of ~ 4 µm have been deposited on silicon wafers by thermal evaporation. They have been irradiated by UV light of wavelenght between 300-400 nm. The power density at the film surface was 0.05 W/cm². The temperature did not exceed 40 °C.

XRD, microhardness and IR reflexion spectra measurements have been carried out.

3.3.2. Results and discussion.

The figures below show the behaviour of the measured parameters.



Fig. 7. a. Microhardness; b. Distances corresponding to FSDPs; c. Contraction caused by UV radiation.

Figure 7c shows the contraction of the supposed layer-like units for each composition. This behaviour can be explained if we admit S-bond breaking induced by the UV light. As a consequance, sulfur will be released from the sample, which is to be smelled as well. The idea of the sulfur release is supported also by the microhardness measurement results plotted on Fig. 7a.

Rajagopalan has also mentioned photo-contraction in thin films [90].

Chapter 4

Modelling structure and photostructural changes in non-crystalline chalcogenides

4.1. General considerations

Atomic-scale structure of the non-crystalline chalcogenide (Ch) materials is still not completely understood. Sustained efforts have- and are being made to elucidate it [3, 6, 26, 91]. The most investigated representatives of the Ch materials family are As₂S₃ and As₂Se₃.

There are many models, proposed for the structure of the chalcogenide materials, and all of them try to reveal the relative position of the constituent atoms of a given structure.

Here a model is proposed for the $a-As_2S_3$ composition. This composition has a correspondent one in crystalline form, $c-As_2S_3$, with a well known structure and properties [94]. The $a-As_2S_3$ composition presents a sharp FSDP, which characterizes its medium range order (MRO).

Finding the atomic scale structure of an amorphous composition is not an easy task. XRD measurements can indicate only averaged structures. Because of the large number of particles and related data, the use of the computer is necessary, taking as start data those well known from the literature, and making a set of assumptions regarding the relative disposal of the constituent units. A valid model has to keep the right number of valencies, bond length distribution, as well as bond angle distribution. What remains unclear is the interlink system between the atoms. This must be also included in the model, and it will caracterize the MRO of the amorphous material.

A Monte-Carlo-Metropolis procedure has been adopted in the model construction and refinement through energetical relaxation. The procedure begins with the geometrical construction of the model from plastic units. Then, the cartesian coordinates of each simbolic atom is determined and introduced as data columns in the PC. Dedicated programs are used to do the energetical relaxation, which leeds to a different, but more realistic set of coordinates of the atoms.

To estimate the free energy of the disordered structure the interaction potential has been supposed to have two terms:

 $U = U_{streeh} + U_{bend},$ with $U_{streeh} = (1/2)\alpha (L-L_0)^2$ and $U_{bend} = (1/2) \beta (\theta - \theta_0)^2 L_0^2$, where L stays for the current bond length, L_0 is the experimental bond length, θ is the current angle between the bonds of an atom, θ_0 is its experimental value, while α and β are the intensities of the given potentials and have different values for different pairs of atoms.

4.2. Nano-phase structural model of As₂S₃

The basic idea of the model proposed here is the coexistence of various structural units, with closed ends, i.e. with no unsatisfied bonds. In the case of the As_2S_3 it is supposed, that these units may be: smaller or bigger cage-like molecules (As₄S₆; As₈S₁₂ with its two models: As atoms "looking" toward the cluster center, or outside; As₂₀S₃₀), disordered planar fragments of As₂S₃, nanotube-like segment of As₂S₃ with closed ends or with open ends connected to other kind of building units, single- or twin lens-like clusters of As₂S₃.



Reduced intensity, RDF and bond angle distribution has been computed for each configuration, and they show the possibility of the physical existence of these building units.

An open question remains the weight of each kind of these building units in a practical case.

4.3. Modelling of the photoinduced processes in As₂S₃

The illumination of the amorphous chalcogenides with band-gap or sub-band-gap light induces important modifications in the structure. Experimentally, these changes, mainly in the MRO, are visible in the shape and position modifications of the FSDP [3, 6, 8].

4.3.1. Modelling of the scalar photoinduced processes

The main idea of possible photostructural scalar processes consists of transformation of cage-like clusters into planar-like ones, connecting themselves to other, already existing planar configurations. An article has been published of our group about this possibility [95].



Fig. 8. Photoinduced connection of an As₄S₄ cluster with a-As₂S₃ layers

4.3.2. Modelling of the vectorial photoinduced processes

In this case we suppose the formation of very small crystalline-like units, wich are stressed at the interface were they are embedded in the major amorphous phase. These tiny units are supposed to "germinate" in the whole mass of the chalcogenide glass, but in a very small qantity (experimentally hard to be observed), and they may be randomly oriented. This idea might be acceptable, if we admit, that in these random positions the optimal stoichiometry is locally fulfilled. Then, it might be the result of a natural crystallization tendency the appearance of these stressed crystalline-like units, which can not develop further, because of the quick finish of the cooling process. The polarised light may than interact selectively with these units.



Fig. 9. Photoinduced structural anizotropy.

Chapter 5

Conclusions

The experimental XRD research and the PC-assisted structural modelling of the chalcogenide materials show, that this combination of the two methods gives a useful tool to find out more about their possible intimate structural and photo-structural features [97].

These results are important for a better understanding of the non-crystalline state of solids, and for optimizing the material properties for applications.

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