

MÖSSBAUER SPECTROSCOPY AS A POWERFUL TOOL TO STUDY LOCAL ELECTRONIC STRUCTURE

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Mössbauer Spectroscopy, the recoil-free resonant absorption of γ -rays, is really suitable for the study of local electronic structure. Its hyperfine parameters, the isomer shift δ and quadrupole splitting Δ , respectively proportional to the *s electronic density* at the nucleus and to the *electric field gradient*, allow one to characterize the oxidation state and coordination of the probed element. Several examples illustrate the capabilities of this powerful technique for different elements (Sn, Fe, Sb) in tin oxide glasses as electrode materials for Li-ion batteries, iron phosphate glasses used for the treatment of inorganic waste and antimony chalcogenide glasses for optoelectronic applications.

(Received December 9, 2004; accepted January 26, 2005)

Keywords: Mössbauer spectroscopy, Amorphous tin composite oxide, Phosphate coacervates, Amorphous Ge-Sb-S, Thin films

1. Introduction

In the field of materials, most of the synthesis processes and properties are governed by electronic transfers between elements. In this case, the local electronic structure is modified and the study of such mechanisms requires the use of local characterisation techniques such as X-ray absorption spectroscopy, X-ray photoemission spectroscopy or Mössbauer spectroscopy.

In particular Mössbauer spectroscopy, the recoil-free resonant absorption of γ -rays [1], is optimally suited to this application. The interactions between the nuclear charge and magnetic moment on one side and the electronic charges and moments of the absorber atom itself and on surrounding atoms on the other side are known as hyperfine interactions. These interactions influence the nuclear levels (and thus also the transition energies) in a characteristic way, and allow one to obtain valuable information about the absorber atom and its surroundings. Three main hyperfine interactions can be distinguished: *i*) the electric monopole interaction, detectable as a line shift (isomer shift, δ); *ii*) the electric quadrupole interaction, detectable as a line splitting (quadrupole splitting, Δ) and *iii*) the magnetic dipole interaction, detectable as a line splitting (nuclear Zeeman effect). The hyperfine parameters, δ and Δ , respectively proportional to the *s electronic density* at the nucleus and the *electric field gradient*, allow one to characterize the oxidation state and coordination of the probed element. The *f* recoil-free fraction, which governs the intensity of the Mössbauer absorption, gives information about the network rigidity and bonding.

Here, we give three examples selected in the field of glasses or amorphous materials, to illustrate the capabilities of this powerful technique for different elements (^{119}Sn , ^{57}Fe and ^{121}Sb).

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2. Amorphous tin oxide composites as electrode materials for Li-ion batteries

The increasing demand for electric energy for many applications motivates intensive research on batteries [2, 3]. The graphitic carbon anodes used in lithium cells appeared the most relevant, but they have a relatively low storage capacity for new applications (372 mAh/g). Among them, tin based anode materials [4] seem very promising, because of the expected large specific capacity and low potential (<0.8 V/Li). These materials have significantly higher reversible specific (> 600 mAh/g) and volumetric (>2200 mAh/cm³) capacities, as compared to carbon-based ones. The main problem is the large irreversible loss of storage capacity for the first discharge.

2.1. Experimental details

The amorphous tin oxide composite glass $\text{SnB}_{0.6}\text{P}_{0.4}\text{O}_{2.9}$ was prepared by solid state reaction. Stoichiometric amounts of SnO, $\text{H}_2\text{PO}_4\text{NH}_4$ and B_2O_3 were dry-blended and heated in a vitreous carbon boat inside a horizontal tube furnace. The sample was first heated at 800°C for 15h in a constant flow of argon, and then quenched at room temperature by removing the heating boat from the furnace. The glass formed was almost clear and gave a white powder after grinding.

Electrochemical lithium tests were performed in SwagelokTM-type cells assembled in an argon-filled dry box. Such cells consisted of a composite electrode containing the active material mixed with 10% acetylene black, a Li metal disk as a negative electrode and a Whatman borosilicate glass microfiber separator with LiPF_6 (1M) in PC/EC/DMC as the electrolyte.

^{119}Sn Mössbauer spectra were recorded by transmission in the constant acceleration mode. The absorbers, containing 1-2 mg of ^{119}Sn per cm², were prepared by mixing powder samples and apiezon grease inside a glove box, and sealed with parafilm to avoid contact with air. The source was $^{119\text{m}}\text{Sn}$ in a BaSnO_3 matrix. Isomer shift values are given relative to BaSnO_3 .

2.2. Results and discussion

Fig. 1 shows the discharge/charge curve obtained by using glass $\text{SnB}_{0.6}\text{P}_{0.4}\text{O}_{2.9}$ as the active electrode material. We can see that the material presents a broad capacity and a good cyclability, but shows an irreversible loss in the 1st cycle.

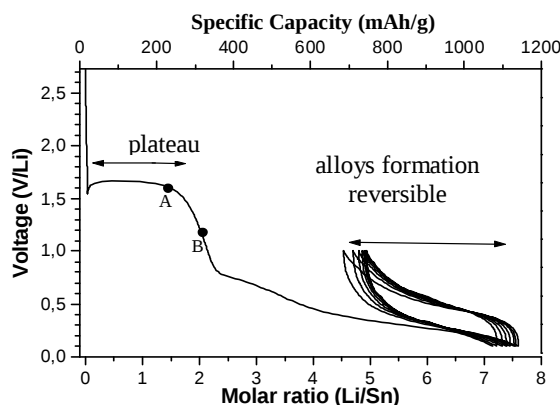


Fig. 1. First charge curve obtained with $\text{SnB}_{0.6}\text{P}_{0.4}\text{O}_{2.9}$ glass as the active electrode material.

Fig. 2 shows the Mössbauer spectra for $\text{SnB}_{0.6}\text{P}_{0.4}\text{O}_{2.9}$ and $\text{Li}_{2.06}\text{SnB}_{0.6}\text{P}_{0.4}\text{O}_{2.9}$ at room and liquid nitrogen temperatures. The hyperfine parameters for Figs. 2a and 2b are in agreement with the known literature values for tin atoms in non-crystalline solids ($\delta_1=3.12$ mm/s, $\Delta_1= 2.01$ mm/s; $\delta_2= 3.33$ mm/s, $\Delta_2=1.66$ mm/s). The values obtained from spectra a) and b) are very similar, because the f Lamb Mössbauer factors [5] for the Sn^{II} species hardly vary. Figs. 2a or 2b can be described by two different environments of two types of atoms. Tin atoms 1, Sn_1 , with a large quadrupole

splitting ($\delta_1 = 2.01$ mm/s), are expected to be bonded to bridging oxygen atoms (Sn-O-M with M= Sn, B, P), and can be considered as network formers. Tin atoms 2, Sn_2 , with lower quadrupole splitting ($\delta_2 = 1.66$ mm/s), are expected to be bonded to non-bridging oxygen and can be considered as network modifiers. The spectra in Figs. 2c and 2d can be regarded as containing three components: Sn_1^{II} , Sn_2^{II} and Sn^0 . The values for the Sn^{II} species are very similar. On the other hand, a strong difference between spectra 2c and 2d can be observed. This is mainly due to the differences in the f factors for Sn^0 . The contribution of Sn^0 to the Mössbauer spectrum at 300 K is very small ($< 7\%$) compared to the lithiated compound (44%) resulting from the reduction of the Sn^{II} atoms.

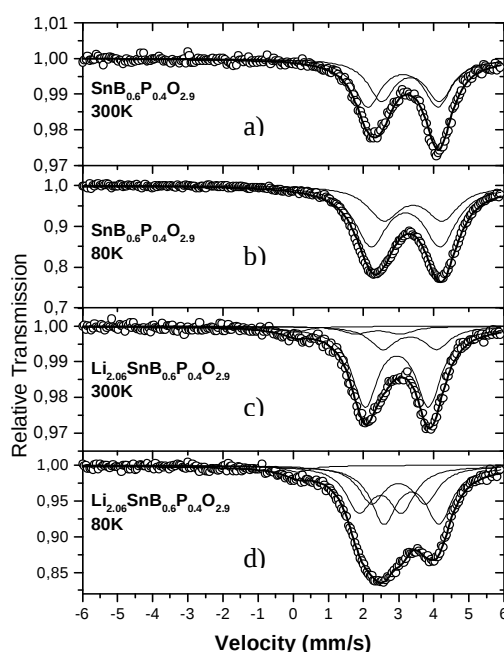


Fig. 2. ^{119}Sn Mössbauer spectra for a) $\text{SnB}_{0.6}\text{P}_{0.4}\text{O}_{2.9}$ at 300 K; b) $\text{SnB}_{0.6}\text{P}_{0.4}\text{O}_{2.9}$ at 80 K; c) $\text{Li}_{2.06}\text{SnB}_{0.6}\text{P}_{0.4}\text{O}_{2.9}$ at 300 K and d) $\text{Li}_{2.06}\text{SnB}_{0.6}\text{P}_{0.4}\text{O}_{2.9}$ at 80 K.

The mechanism takes place in two stages: for $x < 2.06$, lithium atoms act as network modifiers; for $x > 2.06$, the insertion of lithium leads to a total reduction $\text{Sn}^{\text{II}} \rightarrow \text{Sn}^0$ and induces the formation of composite alloys of Li-Sn [6] in interaction with the glass matrix. The Sn^0 species are expected to be nearly β -Sn nanoparticles. The rather high value of $\Delta > 2$ mm/s suggests interaction between the active species and oxygen of the glass matrix, by an increase in the number of non bridging oxygen atoms due to the breaking of M-O-M bonds (M= Sn, B, P).

3. Iron as a probe of phosphate glasses in inorganic waste

Polyphosphate glasses may be used for the immobilization of inorganic wastes, e.g. nuclear waste or fibrous ceramics like asbestos [7]. In this kind of application, the system $\text{P}_2\text{O}_5\text{-Na}_2\text{O-FeO}$ may present interesting advantages [8]. Among the hazardous inorganic wastes, asbestos presents an important problem for health. Sodium polyphosphate glasses, which are soluble in water, present three properties for asbestos treatment: *i*) an important wet ability towards asbestos fibers, *ii*) the feasibility to give coacervates with bivalent ions which act as a glue for fiber immobilization and *iii*) an important reactivity towards the Si-O-Si bridge present in the asbestos at a temperature around 600 °C, allowing destruction of the asbestos fiber structure.

Generally, polyphosphate glasses are obtained by melting, at a temperature higher than 800-1000°C, of metallic oxides with dihydrogen orthophosphates, ammonium orthophosphate, or

phosphoric acid. An alternative must be found by using a colloidal route. Considering the interest in polyphosphate glasses based on the system $\text{FeO}-\text{Na}_2\text{O}-\text{P}_2\text{O}_5$, we have developed a new technique similar to the sol gel process: the coacervation of polyphosphates. Starting from a polyelectrolyte solution such as sodium polyphosphate in water, the modification of the solvent properties by the evolution of the dielectric constant or by addition of an electrolyte, gives a flocculation phenomenon. The denser phase containing most of the polymeric chains is the coacervate. This method permits us to keep and to isolate the long chains in polyphosphate coacervates. They have a behavior like glue, and may be use for sealing purposes [9]. Another interest in the use of a coacervate for the immobilization of inorganic waste lies in the fact that it has a very good wetting ability relative to the inorganic oxide [10]. Thus, it is possible to obtain polyphosphate coacervate formation in a waste bulk with the coating of each particle [11]. After curing, we obtain a glass which contains the wastes. In accordance with the ratio between the inorganic wastes and the polyphosphate quantity, and the temperature treatment, it is possible to digest the waste [12].

3.1. Experimental details

A coacervate based on iron II is easily obtained from the mix of sodium polyphosphate and ferrous chloride in water [10]. ^{57}Fe Mössbauer spectroscopy was carried out in order to get information on the species obtained at the various stages of the treatment. Measurements were performed using a ^{57}Co in Rh matrix source, on an EG>M constant acceleration spectrometer in transmission mode. The zero isomer shift was defined from the spectrum of a reference $\alpha\text{-Fe}$ foil.

3.2. Results and discussion

By ^{57}Fe Mössbauer spectroscopy, we show the stability of Fe^{II} during the coacervate's formation and its drying. Fig. 3 shows two doublets with the following hyperfine parameters: $\delta_1 = 1.29(1)$ mm/s, $\Delta_1 = 1.59(1)$ mm/s and $A_1 = 40\%$, $\delta_2 = 1.29(1)$ mm/s, $\Delta_2 = 2.39(1)$ mm/s and $A_2 = 60\%$. Both sites correspond to Fe^{II} species. Differences in the quadrupole splitting values suggest the presence of Cl^- and/or OH^- in the coordination sphere of low spin Fe^{II} . The lower value of QS may be attributed to octahedral iron sites surrounded by 4 oxygen and 2 chlorine atoms in a *trans* configuration, while the greater value of QS may be attributed to the *cis* configuration. The relative amount of the two Fe^{II} sites indicates that there is no preference for the *cis* or the *trans* configuration. The high value of the full width at half maximum (0.38 mm/s) of the lines is due to the amorphous state of the coacervate.

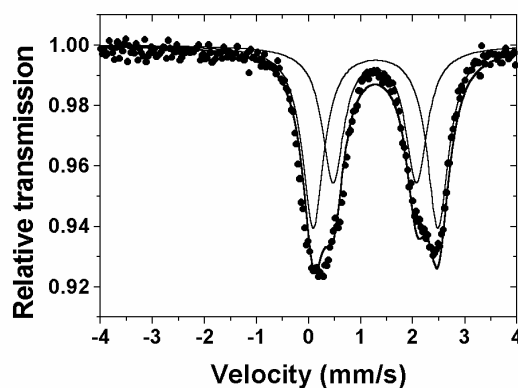


Fig. 3. ^{57}Fe Mössbauer spectrum of a coacervate dried for two months, with initial formulation 33.13 moles H_2O , 3.17 moles NaPO_3 , 0.8 moles FeCl_2 .

The treatment at 900 °C for various times of curing induces the oxidation of Fe^{II} to Fe^{III} . The amount of Fe^{III} increases from 29% ($\delta=0.35$ mm/s, $\Delta=0.69$ mm/s) to 46% ($\delta=0.36$ mm/s, $\Delta=0.63$ mm/s) with the curing time. Changes in the nature of the atmosphere do not modify the

relative amounts of $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$. In the case of an argon atmosphere, about 24% of the iron species are oxidized, but if the curing is performed in air the amount increases to 28% for a short curing time.

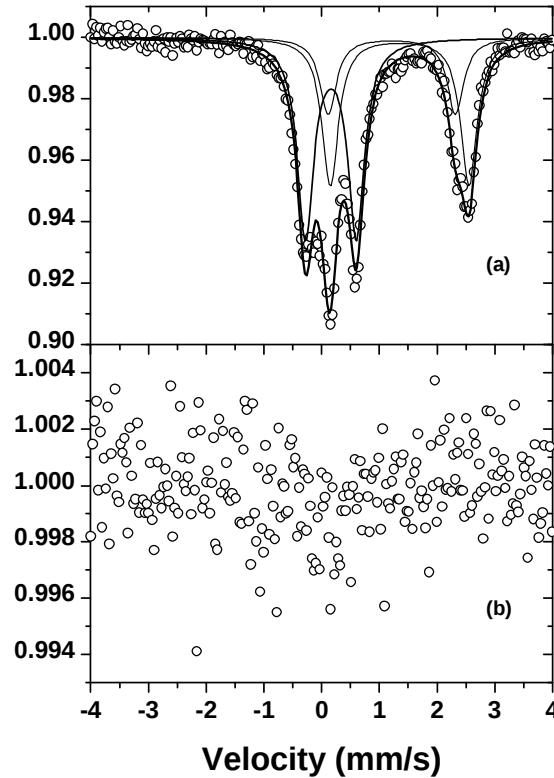


Fig. 4. ^{57}Fe Mössbauer spectra recorded at room temperature for untreated crocidolite fibers (a) and at liquid nitrogen temperature for the corresponding wet coacervate (b).

Our process may be used for crocidolite. In this case, the asbestos fibers contain iron in both the Fe^{III} and the Fe^{II} oxidation state. By Mössbauer spectroscopy, we can observe a reaction between crocidolite and coacervate based on calcium instead of iron. In Fig. 5b, the ^{57}Fe Mössbauer spectrum of the coacervate clearly shows differences from that of the pristine crocidolite sample (Fig. 4a). The spectrum in Fig. 4b indicates that chemical impregnation of the fibers with phosphate extracts iron cations from the structure. The results suggest that iron atoms are located near the surface of the fibers in the crocidolite, and/or that the diffusion of iron is increased in the presence of phosphate. Similar observations are obtained for the fired coacervate.

4. Antimony chalcogenide glasses for optoelectronics

Many applications of chalcogenide glasses are related to photoinduced changes (PIC). PIC in Ge-M-S (M= As, Sb) glasses have also been studied [11-14]. As can be expected, they are compositional dependent. In the present investigation, Ge-Sb-S glasses and films were studied. The local electronic structure of amorphous $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ films was characterized by means of ^{121}Sb Mössbauer spectroscopy.

4.1. Experimental details

The compositions studied are situated on the $\text{Sb}_2\text{S}_3\text{-Ge}_2\text{S}_3$ pseudo-binary line. The appropriate quantities of the constituent 5N elements were sealed in quartz ampoules after

evacuating to 10^{-3} Pa. The ampoules were heated to 950 °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 (~ 80 -100 Å/s) was previously chosen to ensure the nearest composition of the films to that of the parent glass.

The ^{121}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 absorber were simultaneously cooled to liquid helium temperature, to increase the fraction of recoil-free absorption and emission processes. The small amount of Sb in the total mass of the sample caused additional difficulties. For this reason, many slices of the film were arranged one onto another in the sample holder, thus increasing the mass of the absorber.

4.2. Results and discussion

The ^{121}Sb Mössbauer spectra of the amorphous $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ films are shown in Fig. 5, and the parameters obtained from the experimental data are reported in Table 1.

Table 1. ^{121}Sb Mössbauer parameters of amorphous $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ films. The isomer shift δ is given with respect to InSb Γ is absorber linewidth.

Composition	δ (mm/s)	Δ (mm/s)	Γ (mm/s)
$\text{Ge}_{35}\text{Sb}_5\text{S}_{60}$	- 4.20 (15)	+ 9.3 (5)	2.3 (3)
$\text{Ge}_{27}\text{Sb}_{13}\text{S}_{60}$	- 4.45 (10)	+ 14.0 (2)	1.4 (3)
$\text{Ge}_{20}\text{Sb}_{20}\text{S}_{60}$	- 4.30 (10)	+ 10.0 (5)	1.9 (3)
$\text{Ge}_5\text{Sb}_{35}\text{S}_{60}$	- 4.41 (10)	+ 11.8 (7)	1.8 (1)

Broad asymmetric lines, indicating unresolved quadrupole split spectra, were observed for all compositions of the amorphous $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ films. All spectra were fitted supposing only one antimony site, although in almost all crystalline and vitreous compounds several different environments are present. Thus, all values of δ and Δ (Table 1) should be regarded as averaged. The values of δ are characteristic of the Sb^{III} species [15]. Both the large values of Δ , denoting a strong asymmetry of the electron density around the Sb, and the range of values of δ are typical of SbS_3 local environments which are expected to be predominant in the glasses [16]. The broadening of the absorption reflects the distribution of bond lengths and angles involving the Sb atoms. The other local environments are also pyramidal, but can include both Sb–S bands and Sb–Sb or Sb–Ge bonds.

The observed decrease of δ from - 4.2 to - 4.5 mm/s is related to the increase in the number of Sb 5s electrons and/or to the decrease of the number of Sb 5p electrons [17]. This could be due to changes in the local geometry of the SbS_3 units, or to a decrease in the number of Sb–Sb or Sb–Ge bonds. The variations of the different Mössbauer parameters vs. composition of the amorphous $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ thin films (Fig. 6) characterize a special behaviour for the $\text{Ge}_{27}\text{Sb}_{13}\text{S}_{60}$ thin film. This is the composition for which PIC are maximum in the films from the isomorphous $\text{Ge}_x\text{As}_{40-x}\text{S}_{60}$ system.

Thus, the isomer shift and quadrupole splitting provide reliable information on the local structure in this Ge–Sb–S amorphous system, which could be useful in gaining a better understanding of the photoinduced properties.

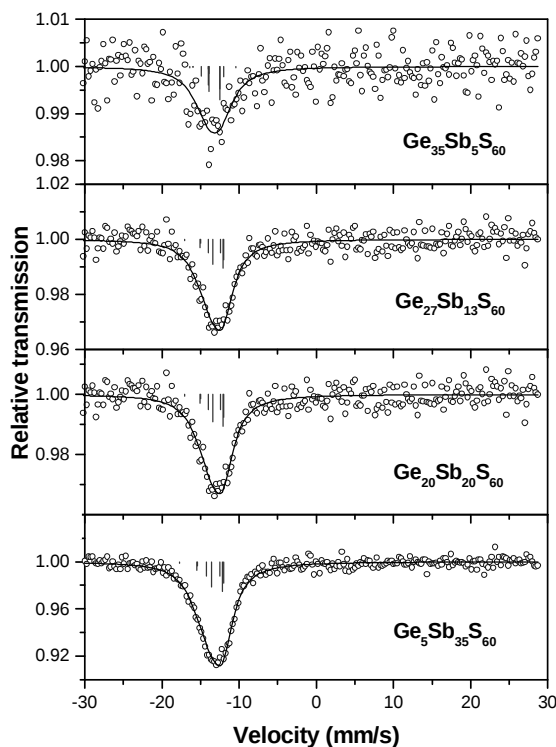


Fig. 5. ^{121}Sb Mössbauer spectra of the amorphous $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ thin films.

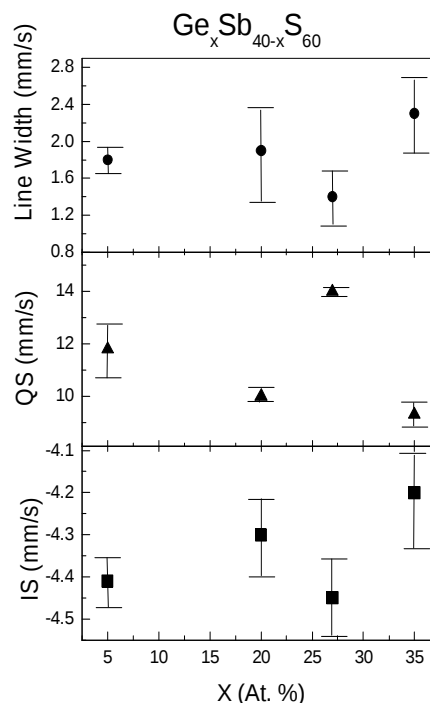


Fig. 6. Variation of the ^{121}Sb hyperfine Mössbauer parameters of the $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ thin films, vs x .

5. Conclusions

Mössbauer spectroscopy is a powerful tool for characterizing the local electronic structure around the probed element in crystalline, glassy or amorphous materials, by the determination of the oxidation state, the local coordination and bonding. It allows the identification of intermediate phases to study reaction mechanisms with experimental facilities (in situ measurements, variable temperatures).

^{119}Sn Mössbauer spectroscopy allows the identification of various reaction mechanisms during the first electrochemical discharge of the new tin amorphous composite oxide $\text{SnB}_{0.6}\text{P}_{0.4}\text{O}_{2.9}$.

The use of solutions of sodium polyphosphate or polyphosphate coacervates permits us to propose a new method for asbestos treatment. A two step process has been proposed: immobilisation of the fibers in the glue-like coacervate followed by the curing at 900 °C to destroy the fiber structure. The resulting glasses contain the waste, and ^{57}Fe Mössbauer spectroscopy provides valuable information on the oxidation state ($\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$) and environment of the probed atoms.

The ^{121}Sb Mössbauer study of amorphous $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ thin films has shown changes in the local electronic structure of the Sb atoms versus composition. The differences in the electronic structure could be related to the different rates of the photoinduced structural changes in the Ge–Sb–S glass compositions.

This spectroscopy is really well suited for the study of complex materials such as glasses or amorphous composites, to characterize the local electronic surrounding of the probed element. However, like all other types of spectroscopy, Mössbauer spectroscopy has to be used complementarily with other experimental techniques.

Acknowledgments

The authors would like to thank “CNRS and Ministère délégué à la Recherche (France)” for funding. Part of this work was performed in the frames of a NATO CLG 980343. It was also partially supported by Grant F-1309 of the Bulgarian Ministry of Education and Science.

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