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Structural study by Raman spectroscopy and ^{77}Se NMR of $GeSe_4$ and $80GeSe_2$–$20Ga_2Se_3$ glasses synthesized by mechanical milling

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ABSTRACT

Amorphous powders of $GeSe_4$ and $80GeSe_2$–$20Ga_2Se_3$ compositions have been prepared by mechanical alloying of raw Germanium, Selenium and Gallium. The amorphization process and structural evolution of the powder during mechanical alloying have been studied by XRD, DSC, Raman spectroscopy and ^{77}Se NMR. The role of Gallium in the amorphization process has been pointed out. Similar structures and thermal properties of amorphous powders and respective glasses synthesized by melt-quenching method have been observed.

1. Introduction

Chalcogenide glasses (ChG) are transparent in near and mid infrared (IR) ranges and have proven their effectiveness in different fields of applications as sensors, laser amplifier and especially as lenses for the night vision devices [1–4]. ChG are usually synthesized under vacuum in order to avoid their contamination by the molecules that vibrate in their range of transparency. Nevertheless, the use of ChG is still restricted by their low mechanical properties and especially their high final price which is due to the use of expensive purified elements and non-reusable silica tubes. We have recently demonstrated the feasibility to obtain bulk ChG by combining mechanical milling and sintering [5,6]. This new technology avoids the use of silica tubes, allows a glass synthesis at room temperature and leads to the production of new compositions and bigger size samples. Moreover, by adjusting sintering parameters, this process also permits the fast and simultaneous synthesis of glass-ceramics having higher mechanical characteristics than glasses. The first step of this process consists in making an amorphous powder by grinding raw metallic elements in a planetary grinder. This work was focused on the understanding of the amorphization process and of the structural evolution along the milling using XRD, DSC, Raman spectroscopy and solid state NMR analyses. Indeed, over the past 10 years, ^{77}Se NMR was found to be a very good technique for probing the structure of ChG [7–11].

2. Experimental procedures

2.1. Glass powder synthesis

Amorphous chalcogenide powder of $GeSe_4$ and $80GeSe_2$–$20Ga_2Se_3$ compositions has been synthesized using the same conditions of mechanical alloying by introducing stoichiometric amounts of pure raw metallic Germanium (5 N, Umicore), Selenium (5 N, Umicore) and Gallium (5 N, Materion) in a tungsten carbide (WC) grinding jar containing 6 WC milling balls, with a ball-to-powder weight ratio 18.75:1. The jar was introduced into a planetary grinder (Retsch PM100, Germany). Rotation cycles of 3 min at 300 rpm were scheduled with direction reversal and a pause of 3 min between each cycle. The milling process has been periodically stopped and a small amount of the powder (~0.1 g) has been taken out for analysis.

2.2. Powder characterizations

X-ray diffraction was carried out on the powder taken out after different milling durations using a Philips PW3710 diffractometer (Cu $K\alpha_{1,2}$ 1.5418 Å) in the range of 10–90° (2θ). Thermal properties of the powders were analyzed by Differential Scanning Calorimetry (DSC) using 10 mg of the sample and a ramp of 10 °C/min (DSC Q20; TA Instruments, New Castle, DE). A HR800 (Horiba/Jobin-Yvon) micro-raman spectrometer was used to collect unpolarized Raman spectra of all $GeSe_4$ and $80GeSe_2$–$20Ga_2Se_3$ glassy powders in backscattering geometry at ambient temperature. These Raman measurements have been performed with a He–Ne laser at 633 nm for $GeSe_4$ samples and with

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a laser diode at 785 nm for $80GeSe_2–20Ga_2Se_3$ powders. Optical density filters were used to decrease the laser power to avoid heating at the focus point of the laser on the sample. The spectral dispersion was less than 1 cm^{-1} per CCD pixel. The ^{77}Se ($S = 1/2$) NMR spectra were recorded at room temperature on an Avance 300 Bruker spectrometer operating at 57.28 MHz with a 4 mm MAS probe spinning at 14 kHz. Full echoes were used to refocus the whole magnetization and avoid base line distortion. The time delay between the both pulses corresponds to one rotor rotation period. The recycle time was 300 s in agreement with recent results showing that long time is essential to get some quantitative spectra [12].

3. Results and discussions

3.1. Coloration of the powder

The evolution of the color of $GeSe_4$ and $80GeSe_2–20Ga_2Se_3$ ($Ge_{23.53}Ga_{11.76}Se_{64.71}$) components is presented in Fig. 1. One can see that in the case of the ternary system the color changes from gray to brick-red after only 30 min of milling (Fig. 1b) which indicates a fast reaction between elements. On the contrary, in the case of the binary system, the change of the color occurs after around 30 or 50 h of milling (Fig. 1a). This latter result underlines that the interaction between Germanium and Selenium is slow during mechanical milling.

Such a behavior of these two compounds observed in the same conditions of milling (ball-to-powder ration, rotation speed) indicates that Gallium plays an accelerator role in the amorphization process. Taken into account the very low melting point of Gallium (29.76 °C) and the transformation of the mechanical energy into a thermal one during milling, the melting of Gallium may be supposed, acting as a liquid medium which facilitates the diffusion of elements. The very fast amorphization of the ternary system could be explained by both a local melt-quenching of elements and their progressive diffusion during impacts.

3.2. X-ray diffraction

XRD analyses have been performed on the powder extracted all along the milling process, as presented in Fig. 2. In both cases, $GeSe_4$ and $80GeSe_2–20Ga_2Se_3$, diffraction pattern corresponding to Germanium has only been observed. Selenium and Gallium react relatively fast forming an amorphous powder. Completely amorphous powders have been obtained after 110 h of milling in the case of $GeSe_4$ composition and after 50 h for $80GeSe_2–20Ga_2Se_3$. This result is in complete agreement with the evolution of the color of the two compounds, which has already pointed out the much faster interaction of Germanium and Selenium in the presence of Gallium.

3.3. Differential scanning calorimetry

The evolution of the transition temperature during the milling has already been discussed in several previous papers [5,6]. In this work the T_g values have been registered on the powder obtained at the end of the milling which have been identified as completely amorphous using XRD analysis. The two T_g are 168 °C for the $GeSe_4$ composition and 370 °C for the $80GeSe_2–20Ga_2Se_3$ one, which are similar to the values registered for these two glasses obtained by the melt-quenching method (165 °C for $GeSe_4$ and 370 °C for $80GeSe_2–20Ga_2Se_3$) [13–15].

3.4. Raman spectroscopy

3.4.1. $GeSe_4$

Raman spectroscopy has been used in order to study the structure of the completely amorphous powder. In Fig. 3, three bands can be identified at 195 cm^{-1}, 215 cm^{-1} and 260 cm^{-1}. The band at 195 cm^{-1} corresponds to the A_1 breathing mode of corner-sharing (CS) $GeSe_{4/2}$ tetrahedral units and the band at 215 cm^{-1} is associated to the A_1^c breathing like motions (companion peak) of edge-sharing (ES) $GeSe_{4/2}$ units [16–18]. The difference in the intensities of these bands indicates that the structure of the amorphous material is mainly based on CS tetrahedral units while ES units are presented in a small quantity. The third band at 260 cm^{-1} corresponds to the A_1 and E_2 modes of Se–Se bonds from chains or cycles constituted of Se atoms [16–19]. This peak indicates the presence of Selenium-rich phases in the final structure of $GeSe_4$ glass.

A comparison between this spectrum and the one corresponding to the same glass made by the melt-quenching method has also been done. The same bonds are observed on both spectra indicating that the same structure is reached in both materials synthesized using the two different methods.

3.4.2. $80GeSe_2–20Ga_2Se_3$

Spectra presented in Fig. 4 have been normalized according to the most intense band (200 cm^{-1}).

One can see that the interaction between the three elements occurs fast. Already after 1 h of milling, bands associated with $GeSe_{4/2}$ units can be distinguished together with Se–Se and metal–metal interactions. With the increase of the milling time, the shape of spectra is not changing, only the intensity of bands is modified.

Three areas can be identified on the Raman spectra: 75–150 cm^{-1}, 150–230 cm^{-1} and 230–350 cm^{-1}. In the first domain several distortional vibrations of Ge–Se or Se–Se bonds give such a broad band as in the case of $GeSe_4$ composition [20,21].

In the second area an intense band centered at 200 cm^{-1} with two shoulders at 178 and 215 cm^{-1} can be distinguished. The peak at 200 cm^{-1} is associated with the A_1 symmetric mode of CS $GeSe_{4/2}$ units [20,21]. Two shoulders correspond respectively to the stretching of Ge–Ge bond in the ethane-like units $(Se_{3/2})Ge–Ge(Se_{3/2})$ (178 cm^{-1}) and

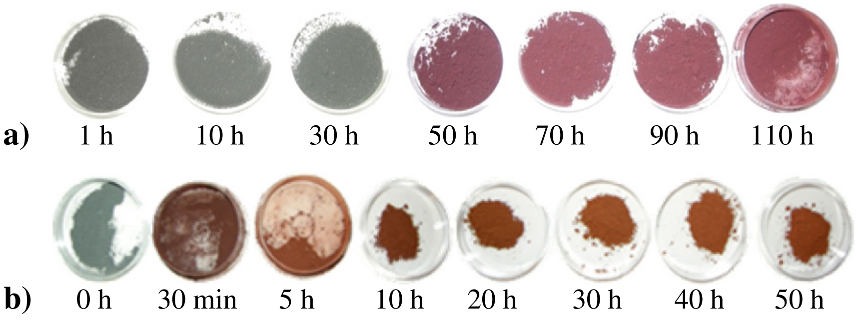

Fig. 1. Evolution of the color of the a) $GeSe_4$ and b) $80GeSe_2–20Ga_2Se_3$ powder with the milling duration.