

## RAMAN SPECTROSCOPY OF GeSe AND AgGeSe THIN FILMS\*

J.M. CONDE GARRIDO, A. PIARRISTEGUY<sup>a</sup>, R. LE PARC<sup>b</sup>, M.A. UREÑA, M. FONTANA, B.ARCONDO\*, A.PRADEL<sup>a</sup>

*Laboratorio de Sólidos Amorfos, INTECIN, Facultad de Ingeniería, Universidad de Buenos Aires – CONICET. Paseo Colón 850, (1063) Buenos Aires, Argentina.*

<sup>a</sup> *ICG, UMR 5253 CNRS UM 2 ENSCM UMI équipe PMDP CC3, Université Montpellier 2, 34095 Montpellier Cedex 5, France.*

<sup>b</sup> *Laboratoire Charles Coulomb, UMR 5587, Université Montpellier 2, F-34095 Montpellier Cedex 5, France*

The structural properties of  $\text{Ag}_y(\text{Ge}_{0.25}\text{Se}_{0.75})_{1-y}$  thin films ( $y=0, 0.07, 0.10, 0.15, 0.20$  and  $0.25$  at. fraction) were studied. The films were prepared by pulsed laser deposition using bulk glass targets of the studied ternary system and deposited onto microscope slides. Their amorphous structures were confirmed by XRD (X-ray Diffraction). The effect of silver content on films structures was analysed by Raman spectroscopy. Typical Raman vibration modes were observed in the  $\text{Ge}_{0.25}\text{Se}_{0.75}$  binary film: Ge-Se corner-sharing tetrahedra mode (CS) at  $199\text{ cm}^{-1}$ , edge sharing tetrahedra mode (ES) at  $217\text{ cm}^{-1}$ , and Se-Se rings and chains mode at  $255\text{-}265\text{ cm}^{-1}$  (CM). In the  $\text{Ag}_y(\text{Ge}_{0.25}\text{Se}_{0.75})_{1-y}$  ternary thin films, the same modes were observed but with a red shift and an intensity reduction in the ES and CM bands.

(Received October 8, 2013; Accepted November 11, 2013)

### 1. Introduction

Alloys of the AgGeSe system have been extensively studied because of their application in programmable metallization cell devices [1, 2]. These devices comprise a AgGeSe thin film placed between two electrodes: an inert one and an active Ag-rich electrode. Structural studies have shown that a covalent network of  $\text{GeSe}_{4/2}$  tetrahedra, as the elementary structural fundamental unit, constitutes the AgGeSe glass structure [3, 4]. Furthermore, Arcondo et al. [5, 6] reported, using Scanning Electron Microscopy, resistivity measurements and Mössbauer Spectroscopy, that AgGeSe bulk glasses are intrinsically separated into two amorphous phases (an Ag-rich and an Ag-poor phase).

The structure of  $\text{Ge}_x\text{Se}_{1-x}$  bulk glasses and films has been investigated by means of Raman scattering [1-2, 7-11]. Bulk glasses of a wide composition range ( $x < 0.40$ ) were investigated by different authors [7-9]. Three main bands were reported in these spectra and were associated to: the stretching mode of Se in  $\text{GeSe}_{4/2}$  corner-sharing tetrahedra (CS mode), the vibrations of Se atoms that form the edge-sharing Ge-Se tetrahedra (ES mode) and the stretching of the Se-Se bonds in the Se rings and chains (CM mode). These three modes also appear in Raman results for Se-rich AgGeSe glasses. A reduction of intensity is reported for the ES and CM modes with the addition of Ag [12-13].

In a previous work, Raman spectroscopy was performed in three kinds of thin films: Ge-Se films before Ag doping, Ge-Se films after Ag doping and photodiffusion and films obtained using ternary targets [14]. A red shift of the different excited modes was observed for the ternary

---

\*Paper presented at 6<sup>th</sup> International Conference on Amorphous and Nanostructured Chalcogenides, Brasov, Romania, June 24-28, 2013

\* Corresponding author: barcond@fi.uba.ar

films spectra when compared to the spectra of the binary films. Morphology and optical properties of the  $\text{Ag}_y(\text{Ge}_{0.25}\text{Se}_{0.75})_{1-y}$  films has also been studied [15]. It was found that as the silver content in the films increased, the refractive index also increased and the optical band gap energy decreased. In this work,  $\text{Ag}_y(\text{Ge}_{0.25}\text{Se}_{0.75})_{1-y}$  thin films ( $y = 0, 0.07, 0.10, 0.15, 0.20$  and  $0.25$  at. fraction) prepared by PLD (Pulsed Laser Deposition) were studied by Raman spectroscopy and the effect of silver content on the films structures was analysed.

## 2. Experimental

Amorphous  $\text{Ag}_y(\text{Ge}_x\text{Se}_{1-x})_{1-y}$  thin films (500 to 1100 nm thick) were prepared by PLD using targets of bulk chalcogenide glasses with a composition of  $\text{Ag}_y(\text{Ge}_{0.25}\text{Se}_{0.75})_{1-y}$  ( $y = 0, 0.07, 0.10, 0.15, 0.20$  and  $0.25$  at. fraction, named **Ag0**, **Ag7**, **Ag10**, **Ag15**, **Ag20** and **Ag25**, respectively). The glass targets were prepared by direct synthesis from pure elements (4N) in evacuated silica ampoules, followed by melt quenching [16]. After this process, bulk glasses were sliced and polished to obtain targets with parallel faces.

Thin films were deposited on static substrates (chemically cleaned microscope glass slides) held at room temperature, which were positioned parallel to the target surface, inside a vacuum chamber (about  $6 \times 10^{-8}$  Pa). PLD was performed using a pulsed Nd:YAG laser (Quanta-Ray Spectra-Physics), operating at a 355 nm wavelength, with a 5 ns pulse duration and a 10 Hz repetition rate. The laser beam with an angle of incidence of  $45^\circ$  was spanned horizontally by the movement of a mirror in order to get a uniform ablation of the target surface. The energy density of the laser was  $1.4\text{-}1.7 \text{ J/cm}^2$ .

The film composition was analyzed using Energy-dispersive X-ray Spectroscopy (EDS) in a Carl Zeiss AG - SUPRA 40 electron microscope. The film thickness was measured using a Dektak 3 Veeco profilometer.

The amorphous structure of the thin films was confirmed by X-Ray Diffraction (XRD) using a Rigaku diffraction system in grazing incidence (incidence angle =  $2^\circ$ ) with monochromatized  $\text{Cu}(K_\alpha)$  radiation.

Raman spectra were recorded, at room temperature, with a Jobin-Yvon T64000 using a He-Ne laser (647 nm).

An additional Raman spectra of  $\text{Ge}_{0.25}\text{Se}_{0.75}$  bulk glass was also measured.

## 3. Results

The amorphous structure of the thin films was confirmed by X-ray diffraction as shown in Fig1. XRD patterns of the films present a prominent pre-peak at the diffraction angle  $2\Theta \approx 14^\circ$  ( $q = (4\pi/\lambda)\sin\Theta \approx 1 \text{ \AA}^{-1}$ ) as was previously observed in the bulk glasses used as targets [4, 17]. This pre-peak is characteristic of amorphous chalcogenide glasses and is associated with medium-range order. Pre-peak intensity decreases with increasing Ag content, as shown in Figure 1. This fact points out that silver addition to the binary glass decreases the medium-range order. This behavior is also observed in AgGeSe bulk glasses [3, 17] and thin films obtained by PLD [14].

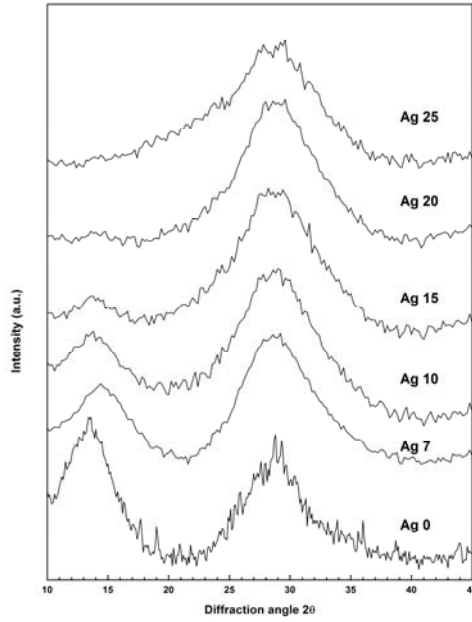


Fig. 1. X-ray diffraction patterns of  $\text{Ag}_y(\text{Ge}_x\text{Se}_{1-x})_{1-y}$  films.

Table 1 shows the composition of the  $\text{Ag}_y(\text{Ge}_x\text{Se}_{1-x})_{1-y}$  thin films. The measured relative composition between Ge and Se ( $x$ ) in the **Ag0** film exhibits an important difference with the nominal composition. Ternary films are mildly selenium-deficient and  $x$  differs from their target compositions in +0.04 atomic fraction. The selenium loss can be explained by the high volatility of selenium. It is worth mentioning that the measured silver composition ( $y$ ) has a higher experimental error due to the high mobility of  $\text{Ag}^+$  ions as was previously reported [5, 6].

Table 1:  $\text{Ag}_y(\text{Ge}_x\text{Se}_{1-x})_{1-y}$  films: identification, films nominal compositions and measured compositions using EDS.

$\text{Ag}_y(\text{Ge}_x\text{Se}_{1-x})_{1-y}$ <b>Identification</b>	Nominal Composition (atomic fraction)		Measured Composition (atomic fraction)	
	<b>x</b> ( $\pm 0.03$ )	<b>y</b> ( $\pm 0.03$ )	<b>x</b> ( $\pm 0.03$ )	<b>y</b> ( $\pm 0.03$ )
Ag0	0.25	0	0.38	0
Ag7	0.25	0.07	0.26	0.08
Ag10	0.25	0.10	0.28	0.16
Ag15	0.25	0.15	0.29	0.24
Ag20	0.25	0.20	0.29	0.25
Ag25	0.25	0.25	0.29	0.31

Fig. 2 shows the Raman spectra of the **Ag0** film and  $\text{Ge}_{0.25}\text{Se}_{0.75}$  bulk glass. Raman spectra of  $\text{Ag}_y(\text{Ge}_x\text{Se}_{1-x})_{1-y}$  films are depicted in Figure 3. All Raman spectra exhibit similar dominant features. A main band at  $194\text{-}200\text{ cm}^{-1}$ , with a shoulder at about  $178\text{-}180\text{ cm}^{-1}$  (very noticeable in the Ag0 film but almost absent in the  $\text{Ge}_{0.25}\text{Se}_{0.75}$  bulk glass and ternary films). A second band at

210-217  $\text{cm}^{-1}$  and a third broad band at 255-265  $\text{cm}^{-1}$ . The Raman results obtained in this work are similar to those of Ge-Se and Ag-Ge-Se bulk glasses obtained in previous works [7-9, 13, 19]. For  $\text{Ge}_x\text{Se}_{1-x}$  bulk glasses, four main modes are observed (depending on the Ge content,  $x$ ): a band at 192-201  $\text{cm}^{-1}$  (CS mode), an accompanying side band near 210-218  $\text{cm}^{-1}$  (ES mode), a broad band near 255-270  $\text{cm}^{-1}$  (CM mode) and a band at 178  $\text{cm}^{-1}$  observed in glasses with high Ge content. This Raman peak is associated to Ge-Ge homopolar bonds mode in  $\text{Ge}_2(\text{Se}_{1/2})_6$  ethane-like units (Ge HB) [9, 19].

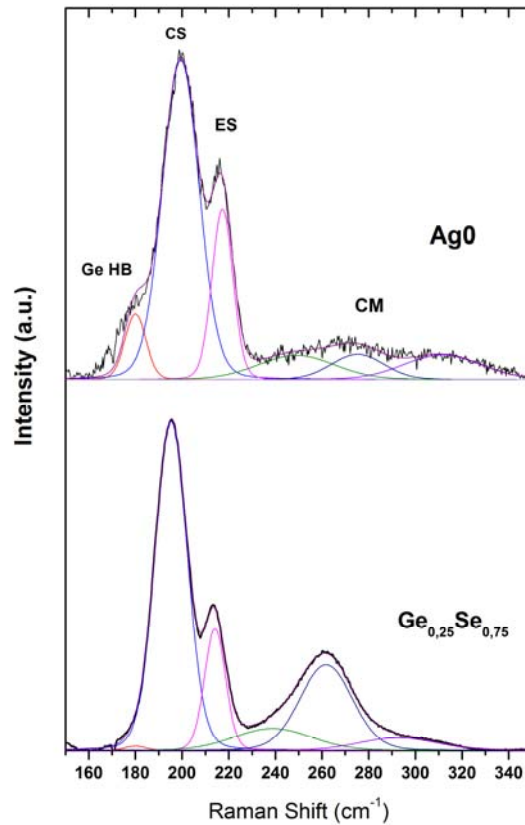


Fig. 2. Raman spectra of Ag<sub>0</sub> film and Ge<sub>0.25</sub>Se<sub>0.75</sub> bulk glass.

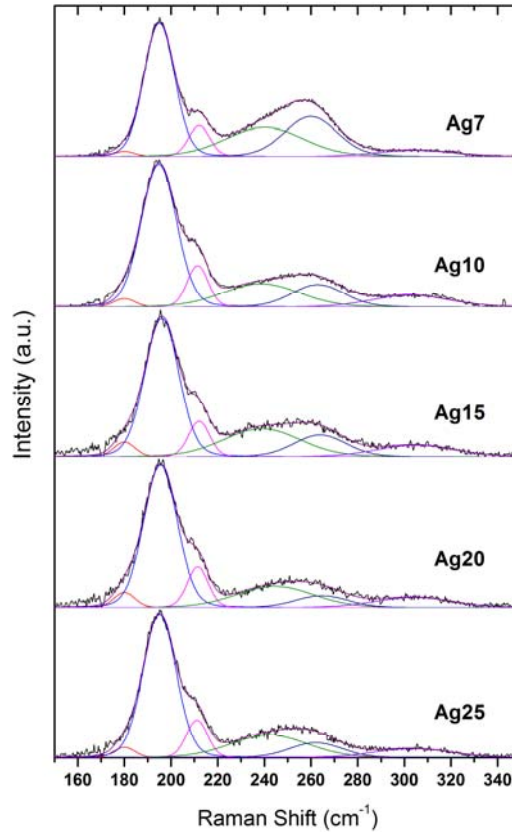


Fig. 3: Raman spectra of  $Ag_y(Ge_xSe_{1-x})_{1-y}$  films (Ag7, Ag10, Ag15, Ag20 and Ag25 films).

#### 4. Discussion

The Raman spectra of the thin films and the  $Ge_{0.25}Se_{0.75}$  bulk glass (Figures 2 and 3) show specific features closely matching those reported by other authors in bulk glasses [7-8, 18-20]: Ge-HB, CS, ES and CM modes.

The Raman spectra of the **Ag0** binary film and the  $Ge_{0.25}Se_{0.75}$  bulk glass (Figure 2) are similar to one another. However, some differences can be observed. The **Ag0** film has: a) a Ge-HB mode with higher intensity, b) a blue shift (towards higher wavenumbers) of the CS and the ES modes, and c) a CM mode with lower intensity. These changes can be explained by a difference in the measured composition of the two (as measured by EDS) (Table 1).

Boolchand et al. [18] observed in  $Ge_xSe_{1-x}$  bulk glasses that CS and ES modes shift to higher wavenumbers (blue shift) with increasing Ge concentration. They found three different Ge content dependences of these modes' wavenumbers: a) a floppy regime for  $0.08 < x < 0.20$  (lineal dependence), b) a transition region for  $0.21 < x < 0.25$ , c) a rigid regime for  $0.26 < x < 0.33$  (power-law dependence). The Ge-HB mode appears at high Ge concentrations ( $x > 0.30$  for bulk glasses [19, 20] and  $x = 0.22-0.28$  for PLD films [11]) and this is related to the increase in the amount of Ge-Ge bonds. As the Se concentration decreases, the amount of homopolar Se-Se bonds decreases and therefore the intensity of the CM mode also decreases. Summarizing for the **Ag0** film, the observed differences (higher intensity of the Ge-HB mode, blue shift of the CS and ES modes and lower intensity of the CM mode) are consistent with the film having a higher Ge concentration than the target. The measured composition of the **Ag0** film (shown in table 1) indicates that the film is selenium deficiency and corroborates the previous idea. This is consistent with the fact that the Raman spectrum of the **Ag0** film is similar to the Raman spectrum of bulk glasses with  $x = 0.33$  reported in the literature [17].

The Raman spectra of the ternary thin films (Figure 3) shows similar Raman features to those reported by other authors in  $\text{Ag}_y(\text{Ge}_{0.25}\text{Se}_{0.75})_{1-y}$  bulk ternary glasses with  $0 \leq y \leq 0.25$  [12, 13] and thin films of compositions  $\text{Ag}_y(\text{Ge}_{0.25}\text{Se}_{0.75})_{1-y}$  with  $y=0.25$  [14] and  $\text{Ag}_y(\text{Ge}_{0.20}\text{Se}_{0.80})_{1-y}$  with  $y=0.06, 0.11, 0.23$  [21]. Comparing with the GeSe binary sample, the  $\text{Ag}_y(\text{Ge}_{0.25}\text{Se}_{0.75})_{1-y}$  ternary thin films show a red shift in CS and ES modes and an intensity reduction of the ES and CM bands. On the other hand, the spectra of **Ag10**, **Ag15**, **Ag 20** and **Ag25** are very similar to one another and there are no clear differences among them (as was observed by Mitkova et al. for bulk glasses with  $y \geq 0.10$  [13]). This fact suggests that the Ge-Se and Se-Se bonds are not significantly influenced by the silver content in the films with  $y \geq 0.10$ . The spectrum of the **Ag7** film is similar to the others but with two differences, i.e., higher intensity of the ES and CM modes (this fact was also observed by Mitkova et al. in bulk glasses [13]).

In a previous work [15], optical properties of AgGeSe thin films in the UV-visible-NIR region were studied. A decrease in the energy of the optical band gap (from 2.03 to 1.45 eV) and an increase in the refractive index (from 2.43 to 2.89) were observed with the increase of silver content. These important changes in the optical properties of  $\text{Ag}_y(\text{Ge}_{0.25}\text{Se}_{0.75})_{1-y}$  thin films do not seem to have any correlation with the Raman spectra, especially in the region of ionic conduction ( $y \geq 0.10$ ) where Raman parameters remain almost unchanged. It was therefore concluded that the observed changes in the optical properties were not caused by a change in the vibration modes of the Ge-Ge, Se-Se or Ge-Se bonds.

## 5. Conclusions

It was found that the main features of the Raman spectra of both binary and ternary thin films are similar to those of Ge-Se and Ag-Ge-Se bulk and film glasses obtained in previous works [7-8, 11, 13-14, 18, 21]. Comparing the  $\text{Ag}_y(\text{Ge}_{0.25}\text{Se}_{0.75})_{1-y}$  ternary thin films with the binary film, the former show a red shift in the CS and ES modes and an intensity reduction in the ES and CM modes. The  $\text{GeSe}_{4/2}$  tetrahedra remains the basic structural element in the heavily Ag doped Ge-Se amorphous films.

Raman results do not seem correlate with the changes of the optical properties measured by UV-visible-NIR, which indicates that the observed optical behavior was not due to a in the studied vibration modes.

## References

- [1] M. Mitkova, M.N. Kozicki, J. of Non-Crystalline Solids **299-302**, 1023 (2002).
- [2] M. Mitkova, M.N. Kozicki, H.C. Kim, T.L. Alford, J. of Non-Crystalline Solids **338-340**, 552 (2004).
- [3] R. Dejus, S.Susman, K. Volin, D.Montague and D.Price, J.Non-Cryst. Solids **143**, 162 (1992).
- [4] A. Piarristeguy, M. Mirandou, M. Fontana, B. Arcondo, J. of Non-Crystalline Solids **273**, 30 (2000).
- [5] B. Arcondo, M.A. Ureña, A. Piarristeguy, A. Pradel, M. Fontana, Applied Surface Science **254(1)** 321 (2007).
- [6] B. Arcondo, M.A. Ureña, A. Piarristeguy, A. Pradel, M. Fontana, Physica B **389(1)** 77 (2007).
- [7] S. Sugai, Phys. Rev. B **35(3)**, 1345 (1987).
- [8] Y.Wang, K.Tanaka, T.Nakaoka, K.Murase, Physica B **316-317**, 568 (2002).
- [9] Xingwei Feng, W. J. Bresser, P. Boolchand, Phys. Rev. Let. **78(23)** 4422 (1997).
- [10] E. Sleetx, L. Tichy, P. Nagels, R. Callaerts, J.of Non-Crystalline Solids **198-200**, 723 (1996).
- [11] P. Nemeč, J. Jedelsky, M. Frumar, M. Stabl, Z Cernosek and M. Vlcek, Philosophical Magazine **84(9)** 877 (2004).
- [12] R. Le Parc, A.Piarristeguy, N.Frolet, M.Ribes and A.Pradel, "Ag-Ge-Se glasses: a vibrational spectroscopy study", J. of Raman Spectroscopy (2013) (in press).
- [13] M. Mitkova, Yu Wang, and P. Boolchand, Phys. Rev. Let. **83(19)**, 3848 (1999).

- [14] M. Erazú, J. Rocca, M. Fontana, A. Ureña, B. Arcondo, A. Pradel, *J. of Alloys and Compounds* **495**, 642 (2010).
- [15] J.M. Conde Garrido, A. Piarristeguy, M.A. Ureña, M. Fontana, B. Arcondo, A. Pradel, "Compositional dependence of the optical properties of chalcogenide glasses thin film of  $\text{Ag}_x(\text{Ge}_{0.25}\text{Se}_{0.75})_{100-x}$  system" *J. of Non-Crystalline Solids* (2013) (in press).
- [16] M.A. Ureña, M. Fontana, B. Arcondo and M.T. Clavaguera-Mora, *J. Non-Cryst. Solids* **320**, 151 (2003).
- [17] A. Piarristeguy, M. Fontana, B. Arcondo, *J. of Non-Crystalline Solids* **332**, 1 (2003).
- [18] P. Boolchand, X. Feng, W.J. Bresser, *J. of Non-Crystalline Solids* **293-295**, 348 (2001).
- [19] T. Edwards, S. Sen and E. Gjersing, *J. of Non-Crystalline Solids* **358**, 609 (2012).
- [20] P. Boolchand, W.J. Bresser, *Phil. Mag. B* **80**(10) 1757 (2000).
- [21] J. Orava, T. Kohoutek, T. Wagner, Z. Cerna, Mil. Vlcek, L. Benes, B. Frumarova, M. Frumar, *Journal of Non-Crystalline Solids* **355**, 1951 (2009).