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Raman spectroscopy of chalcogenide thin films prepared by PLD

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ABSTRACT

Chalcogenide glasses have many technological applications as a result of their particular optical and electrical properties. Ge–Se and Ag–Ge–Se systems were recently studied and tested as new materials for building non-volatile memories. Following these ideas, thin films of Ge–Se and Ag–Ge–Se were deposited using pulsed laser deposition (PLD). Ag was sputtered over binary films (for a composition between 0.05 and 0.25 Ag atomic fraction) and photo-diffused afterwards. Thus, three kinds of samples were analyzed by means of Raman spectroscopy, in order to provide information on the short- and medium-range order: PLD binary films before Ag doping, after Ag doping and PLD ternary films.

Before Ag doping, binary films exhibited Ge–Se corner-sharing tetrahedra modes at 190 cm^{-1}, low scattering from edge-sharing tetrahedra at 210 cm^{-1}, and Se chains at 260 cm^{-1} (stretching mode). However, after the diffusion process was complete, we observed an intensity reduction of bands centered at 210 cm^{-1} and 260 cm^{-1}. The spectra of the photo-diffused films were similar to those of films deposited using a ternary target. Relaxation effects in binary glasses were also analyzed. Results were compared with those of other authors.

1. Introduction

Se-rich Ag–Ge–Se films have been recently studied because of their application in programmable metallization cell devices [1,2]. These devices are made using Ge–Se thin films with the addition of photo-diffused Ag. Mitkova et al. reported some structural data about these Ag-diffused Ge–Se thin films deposited using the sputtering technique. However, their glass structure and how it is modified with Ag incorporation have not been completely analyzed yet.

The structure of Ge_xSe_{1-x} bulk glasses and films has been investigated by means of Raman scattering [1–6]. Bulk glasses scattering over a wide composition range ($x < 0.40$) were investigated by different authors [3–5]. Three main bands were reported in these spectra and were associated to the stretching mode of $GeSe_{4/2}$ corner-sharing tetrahedra (CS mode), the vibrations of Se atoms that form the edge-sharing Ge–Se tetrahedra (ES mode) and Se–Se bonds in Se chains (Chain mode). These three modes also appeared in Raman results for Se-rich Ag–Ge–Se glasses in bulk and film form. A reduction of intensity is reported for ES and CM with the addition of Ag [7]. These authors observed that Ag–Ge–Se bulk glasses are intrinsically phase separated into a Ag_2Se-rich glass and a residual Ge_tSe_{1-t} with Ag as a network modifier. Although this idea was recently ratified using scanning electron microscopy, resistivity measurements and Mössbauer spectroscopy [8,9], these heterogeneities in bulk glasses are associated to liquid immiscibility and consist of zones with different compositions, basically due to Ag concentration: Ag-rich zone and Ag-poor zone.

In this work, Raman spectroscopy results are analyzed and compared on three kinds of thin films: PLD Ge–Se films before Ag doping, PLD Ge–Se films after Ag photo-diffusion and PLD films obtained using ternary targets.

2. Experimental

2.1. Sample preparation

Amorphous Ge_xSe_{1-x} (named Ge*u* with $u = 100x$) and $Ag_{0.25}(Ge_{0.25}Se_{0.75})_{0.75}$ (named Ag25-T) thin films (90–288 nm thick) were prepared by pulsed laser deposition (PLD) using bulk chalcogenide glasses with a composition of Ge_xSe_{1-x} ($x = 0.15$, 0.20 and 0.25) and $Ag_{0.25}(Ge_{0.25}Se_{0.75})_{0.75}$ as targets. Target glasses were prepared by direct synthesis from pure elements (4N) in evacuated silica ampoules, followed by melt quenching. 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 surfaces, inside a vacuum chamber (about 6×10^{-8} Pa). PLD was performed using a pulsed Nd:YAG laser (quanta-ray spectra-physics), operating at a 266 nm wavelength, with a 5 ns pulse duration and a 10 Hz repetition rate. The laser beam had an angle of incidence of about 45° with the static target surface and its energy density varied from 1.56 to 2.77 J cm^{-2} on the target.

In order to dope binary films with 0.05 and 0.25 Ag atomic fraction a Ag film (2–80 nm thick) was deposited on top, using RF or DC sputtering techniques. This sandwich structure was illuminated with two types of radiations: monochromatic

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Table 1
$Ag_y(Ge_xSe_{1-x})_{1-y}$ samples identification (ID) and film preparation, x was determined using electron disperse X-ray and wavelength dispersive spectrometer, y is nominal. The films were prepared by PLD technique using binary or ternary targets. A silver film was deposited using RF or DC sputtering technique on top of some binary films. Then, these sandwich structures were illuminated using monochromatic light (M) or Mercury lamp (Hg).

ID	Composition (at.%)		PLD targets	Thickness (nm)	Sputtering technique	Illumination source	Exposure time (min)
	x	y					
Ge12	0.12	0	Binary	207	–	–	–
Ge22	0.22	0	Binary	150	–	–	–
Ge27	0.27	0	Binary	150	–	–	–
Ag25-T	0.25	0.25	Ternary	50	–	–	–
Ag25-Hg	0.27	0.25	Binary	150	DC	Hg	40
Ag5-M	0.30	0.05	Binary	90	RF	M	10
Ag25-M	0.27	0.25	Binary	288	DC	M	30

light (365 nm wavelength) and UV light (Hg-lamp with wavelength between 200 and 350 nm). Typical illumination time was between 10 and 40 min. Ag remaining on the surface of the sandwich structure was removed employing a $Fe(NO_3)_3$ (0.16 g/ml) solution (dipping time about 120 s). Films irradiated with monochromatic light are named Agν-M (with $\nu = 100y$) whereas films irradiated with a mercury lamp are named Agν-Hg (with $\nu = 100y$). Table 1 summarizes sample preparation.

2.2. Samples characterization techniques

Film composition was analyzed using electron disperse X-ray (EDX) JEOL JSM-6300F microscope and Cameca 100SX wavelength dispersive spectrometer. Film thickness was measured using a Dektak 3 Veeco profilometer.

The amorphous nature of thin films was confirmed by X-ray diffraction (XRD) using a Rigaku diffraction system in grazing incidence (incidence angle = 2°) with monochromatized Cu Kα radiation.

Raman spectra were recorded, at room temperature, with a LABRAM 1B from Horiba (Jobin–Yvon–Dilor–Spex) using a He–Ne laser (632.818 nm).

3. Results

Table 1 shows the characteristics of the films: composition and thickness. The relative composition between Ge and Se (x), obtained by the above mentioned techniques is reported. Compositions of binary films differ from their target compositions in about ±3 at.%. In the case of ternary films, composition measurement does not remain constant and Ag content rises during the experiment. This is due to the high mobility of the Ag ion as was previously reported in [8,9]. So, the composition of Ag (y), reported in Table 1, is nominal for these films.

Typical X-ray patterns of thin films are shown in Fig. 1. XRD patterns of both targets and films present a notable pre-peak at the diffraction angle $2\Theta \approx 14°$ ($q = (4\pi/\lambda)\sin\Theta \approx 1\,\text{A}^{-1}$). This pre-peak is a characteristic of amorphous chalcogenide glasses and is associated with medium-range order. Pre-peak intensity decreases with Ag content, as it is shown in Fig. 1 and previous works [10,11]. This behavior is also observed in Ag–Ge–Se bulk glasses. This fact points out that silver addition to the binary glass breaks down the medium-range order.

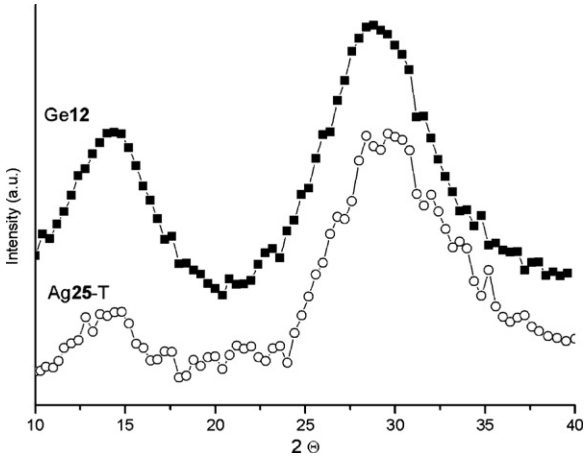

Fig. 1. X-ray diffraction of the $Ge_{0.12}Se_{0.88}$ film (sample Ge12) and $Ag_{0.25}(Ge_{0.25}Se_{0.75})_{0.75}$ film (sample Ag25-T).

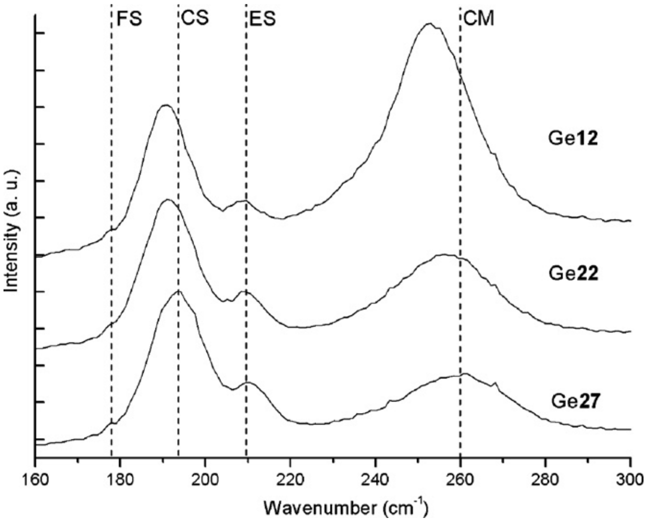

Fig. 2. Raman spectra of PLD Ge_xSe_{1-x} films with $x = 0.12$ (sample Ge12), 0.22 (sample Ge22) and 0.27 (sample Ge27) atomic fraction.

Raman spectra of the films are shown in Figs. 2–4. All Raman spectra exhibit similar behavior. The dominant features are a band

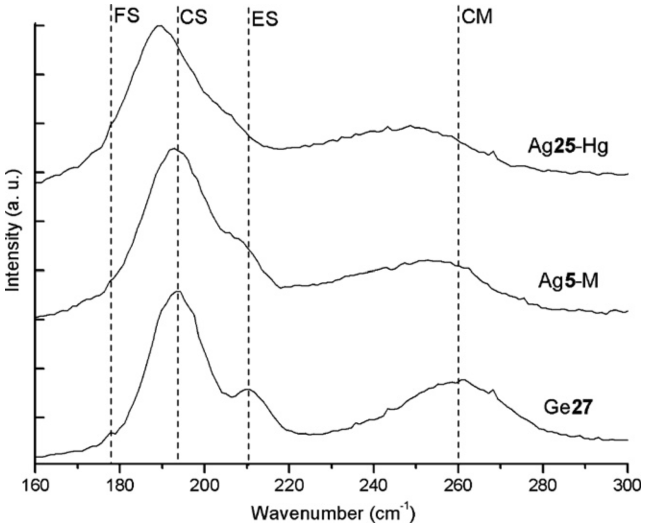

Fig. 3. Raman spectra of Ag photo-diffused thin films $Ag_{0.25}(Ge_{0.27}Se_{0.73})_{0.75}$ (sample Ag25-Hg) and $Ag_{0.05}(Ge_{0.30}Se_{0.70})_{0.95}$ (sample Ag5-M). This figure shows the influence of adding photo-diffused Ag ($y = 0.05$ and 0.25 Ag atomic fraction) to binary film $Ge_{0.27}Se_{0.73}$ (sample Ge27).

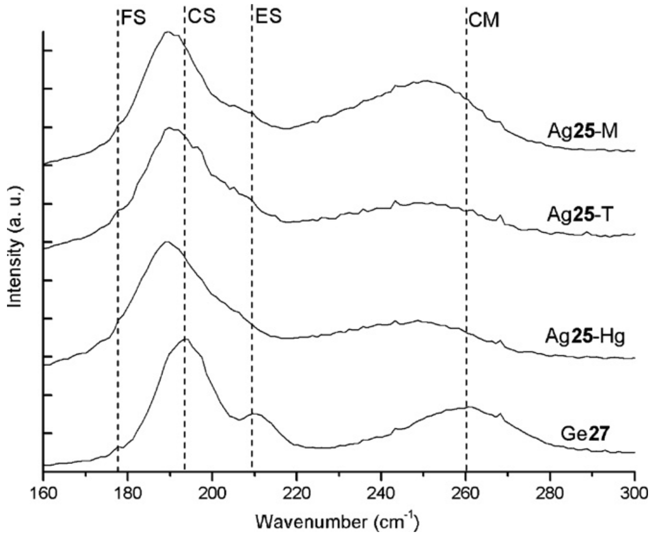

Fig. 4. Raman spectra of $Ge_{0.27}Se_{0.73}$ film (sample Ge27) and $Ag_{0.25}(Ge_xSe_{1-x})_{0.75}$ film ($x = 0.25$ and 0.27) prepared using different procedures: (a) using mercury lamp to illuminate a Ag film deposited on binary Ge–Se film (sample Ag25-Hg), (b) using ternary target: $Ag_{0.25}(Ge_{0.25}Se_{0.75})_{0.75}$ (sample Ag25-T) and (c) using monochromatic light for to illuminate a silver film deposited on binary Ge–Se film (sample Ag25-M).

I at 189–194 cm^{-1}, with a shoulder at about 178–180 cm^{-1}, a band II at 205–210 cm^{-1} and a broad band III at about 248–260 cm^{-1}. Our Raman results of both binary and ternary thin films are similar to those of Ge–Se and Ag–Ge–Se bulk glasses obtained in previous works [3–5,7,12]. Four main modes are observed in Ge_xSe_{1-x} bulk glasses (depending on Ge content x). Firstly, a broad band at 192–201 cm^{-1} that is assigned to the stretching mode of $GeSe_{4/2}$ corner-sharing tetrahedra (CS mode). It is accompanied by a side band near 210–218 cm^{-1} that arises from the vibrations of Se atoms that form the edge-sharing tetrahedra (ES mode). Also, a broad band is observed near 255–270 cm^{-1} and is associated with Se–Se bonds in Se chains (CM). An additional band with low intensity is observed at 178 cm^{-1}. This peak is associated to Ge–Ge mode in $Ge_2(Se_{1/2})_6$ ethane-like units (face sharing, FS) [5,12].

Raman spectra of binary films are shown in Fig. 2. If x decreases, we can observe: (1) a red shift (lower wave numbers) of CS mode, (2) intensity of ES mode decreases slightly, (3) an important red shift (lower wave numbers) and intensity increase of CM mode.

Fig. 3 shows the influence of adding photo-diffused Ag (0.05 and 0.25 at. fraction) to $Ge_{0.27}Se_{0.73}$ films. When Ag is added to these films, we observe two effects: firstly, intensity decrease of ES and CM modes. Second, red shifts (lower wave numbers) are observed in CS and CM modes.

The influence of film preparation procedures for $Ag_{0.25}(Ge_xSe_{1-x})_{0.75}$ films (with $x = 0.25$ and 0.27) is shown in Fig. 4. Raman spectra of ternary films are similar. In particular, Ag25-T film Raman spectrum shows the same features to those of Ag25-Hg. However, one can observe a difference in the Ag25-M film spectrum: the peak associated with CM mode shows larger intensity than in both Ag25-T and Ag25-Hg samples.

4. Discussion

4.1. Binary thin films

The spectra of binary thin films (Fig. 2) show the specific Raman features closely matching those reported by other authors in binary bulk glasses [3,4,12,13]: FS, CS, ES and CM modes.

Boolchand et al. [12] observed in Ge_xSe_{1-x} bulk glasses that CS and ES modes shift to lower wave numbers (red shift) with decreasing Ge concentration. They found three different Ge content dependence of these modes wave number: (a) floppy regime for $0.08 < x < 0.20$ (lineal dependence), (b) a transition region for $0.21 < x < 0.25$, and (c) rigid regime for $0.26 < x < 0.33$ (power-law dependence). For the binary films, we observed a CS mode shifts to lower wave numbers with decreasing Ge concentration as it was previously observed in bulk glasses [12]. Following previous arguments [12], CS mode red shift with decreasing Ge concentration (shown in Fig. 2) leads to a more floppy glass structure in the binary films. On the other hand, we found that CS mode wave numbers of the films are lower than bulk glasses having equal Ge content (see Table 2), indicating that film structures are more floppy than bulk ones. Besides these similarities, a red shift of ES mode in the binary films could not be confirmed.

Table 2
CS Mode wave numbers (cm^{-1}) of Ge_xSe_{100-x} binary samples.

x	Thin film	Bulk glasses [12]
12	190.6	192.8
22	191.4	194.4
27	193.4	195.2

The FS mode peak is present in all the binary films (see Fig. 2), it comes up at lower Ge content than the results reported for bulk ones ($x > 0.30$) [12,13]. FS mode was also reported for PLD films for $x = 28$ [15]. An exhaustive study shows a slightly intensity increase of this mode with x. It is related to the increase of Ge–Ge bonds.

The CM mode intensity of binary thin films increases with Se concentration. This fact is due to higher Se content increases homopolar Se–Se chains. This line is asymmetric due to contribution of almost two single lines as was observed in bulk glasses [3,12]. Also, a red shift (higher wave numbers) of CM mode is observed, with increasing Se concentration. It could be explained in terms of different contributions of single lines with x.

4.2. Ternary thin films

The Raman spectra of ternary thin films (PLD Ge–Se binary films after Ag photo-diffusion and PLD films obtained using ternary targets) show similar Raman features to those reported by other authors in $Ag_y(Ge_{0.25}Se_{0.75})_{1-y}$ bulk ternary glasses [7]. We observe (Figs. 3 and 4): FS mode at 178 cm^{-1}, CS mode at 189–192 cm^{-1}, ES mode at 205–206 cm^{-1} and CM mode at 248–258 cm^{-1}.

After Ag photo-diffusion in Ge–Se binary films, spectra (Fig. 3) of thin films show the following features: (a) CS mode presents a shift toward lower wave numbers (red shift) with the silver content. It is centered at 190 cm^{-1} in films with $y = 0.25$ (Ag atomic fraction), (b) the intensity of ES mode, centered at 205–206 cm^{-1}, decreases when Ag is added and diffused in the binary films, (c) the peak corresponding to CM mode presents a red shift and a intensity decrease with y (silver content). Similar features are also observed in ternary films made with ternary targets (Ag25-T sample).

Besides the similarity, there are discrepancies between the Raman spectra of $Ag_{0.25}(Ge_{0.25}Se_{0.75})_{0.75}$ thin films (for both PLD Ge–Se films after Ag photo-diffusion and PLD films obtained using ternary targets) and those of the bulk. First, the position of the CS mode in our $Ag_{0.25}(Ge_{0.25}Se_{0.75})_{0.75}$ thin films (at 189–190 cm^{-1}) is red shifted with respect to those of the $Ag_{0.25}(Ge_{0.25}Se_{0.75})_{0.75}$ bulk glass (at 195 cm^{-1}). Second, we observe a red shift of the CS mode in ternary thin films when Ag is added, but it is not reported in ternary bulk glasses. Third, Mitkova et al. [7] reported little or no scattering from CM mode in $Ag_{0.25}(Ge_{0.25}Se_{0.75})_{0.75}$ bulk glasses. However, CM mode is clearly observed for $Ag_{0.25}(Ge_xSe_{1-x})_{0.75}$ (with $x = 0.25$ and 0.27) thin films. These discrepancies indicate that amorphous structure in ternary thin film is lightly different to those of bulk samples.

Summarizing, the main differences between ternary and binary films are:

- CS mode: We observed a red shift when Ag is added to binary thin film. Following mentioned ideas for binary samples, the CS mode red shift indicates that glass structure is more floppy in case of a silver addition to binary films. This consequence is in agreement with previous Mössbauer results [8,9]. Lower Debye temperatures (more floppy glass structures) were observed for glass phases rich in silver.
- ES mode: Red shift and intensity decrease when Ag is added to binary thin films. ES mode disappears practically for $y = 0.25$.
- CM mode: In ternary films, the intensity is lower than in binary films and is shifted toward lower wave numbers (red shift). The position of CM band in ternary samples is at about 248–256 $\mathrm{cm^{-1}}$ while in $Ge_{0.27}Se_{0.73}$ binary films the peak position is at about 260–261 $\mathrm{cm^{-1}}$. The CM mode red shift suggests that Ag atoms interact with Se atoms and change the vibration state modifying the peak position of CM mode. As the amount of Ag is raised, Ag atoms interact with dangling bonds of Se chains at first, and then break Se–Se bonds, shortening Se chains.
- The analysis of the influence of film preparation procedures on the Raman spectra of $Ag_{0.25}(Ge_{0.25}Se_{0.75})_{0.75}$ films show an increase in CM band intensity for Ag25-M sample, as compared to Ag25-Hg and Ag25-T (see Fig. 4). This fact could be related to the use of a Hg-lamp, in the photo-diffusion process, which produces an additional heating of the thin film. Thermally and photo-induced irreversible changes were observed in Ge–Se thin films [6], a decrease of CM intensity is observed in heated films and is associated to relaxation effects in these glasses. We suppose that Ag25-Hg and Ag25-T samples have more stable glass structure than Ag25-M sample. In the case of Ag25-T, it is more stable because it was obtained using a ternary target. In the cases of Ag25-M and Ag25-Hg films (obtained with Ag photo-diffusion in binary films) binary glass structure is modified (silver diffusion changes it) and therefore a less stable ternary glass structure is obtained. The additional heating of Hg-lamp stabilizes the structure of Ag25-Hg thin film.

The main result of our work is that main features of 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 [3,4,7,12,15]. However, our results are not in agreement with those previously reported in Ag photo-diffused $Ge_{30}Se_{70}$ and $Ge_{20}Se_{80}$ thin films [1,2]. These authors showed that Ag photo-diffusion causes a significant reorganization on the structure of the initial binary films evidenced by important changes in Raman spectra. They reported a FS Mode in Ag doped films related with the formation of Ag_2Se. In our results, Raman spectra of ternary thin films are similar between them and with those reported by other authors in bulk ternary glasses. It indicates that production procedure of our ternary films using two different methods is suitable and does not modify perceptibly the glass structure. Moreover, in our case, FS mode is hardly observed in binary films, as was reported by [13–15], and its intensity does not present significant variation with Ag doping.

Our Raman results can be also compared with Raman studies [16] in $Ag_y(Ge_{0.25}S_{0.75})_{1-y}$ thin film. GeS_4 corner-sharing (CS) and edge-sharing (ES) modes and thio-germanate units Q_1, Q_2 and Q_3 are reported. Authors observe also the presence of sulfur-ring (S_8) mode in Ag–Ge–Se thin films (but not in bulk glasses). This is attributed to the low vaporization temperature of sulfur. S_8 mode disappears in a thermal annealing. We do not observe either Se_8 mode or thio-germanate units in Raman result of AgGeSe thin films.

5. Conclusions

Compositions of Se-rich Ge–Se films prepared by PLD differ from their target compositions in about ±3 at.%.

Raman results of both binary and ternary thin films are similar to those reported for Ge–Se and Ag–Ge–Se bulk glasses in previous works. $GeSe_{4/2}$ tetrahedra remains the basic structural element in the heavily Ag doped Ge–Se amorphous films.

The main differences between ternary and binary films are the change of homopolar Se–Se chain mode intensity and the disappearance practically of ES mode in the Raman spectrum. A red shift of the different excited modes is observed for ternary films spectra when compared to the spectra of binary films. Ternary films have a more floppy glass structure than binary films. FS mode is hardly observed in the binary films analyzed in this work. Ag doping does not modify FS mode. Two types of Ag photodoped were compared. The Raman spectra were similar but a difference were found in CM band, and it is attributed to relaxation effects.

References

[1] M. Mitkova, M.N. Kozicki, J. Non-Cryst. Solids 299–302 (2002) 1023–1027.
[2] M Mitkova, M.N. Kozicki, H.C. Kim, T.L. Alford, J. Non-Cryst. Solids 338–340 (2004) 552–556.
[3] S. Sugai, Phys. Rev. B 35 (3) (1987) 1345–1361.
[4] Y. Wang, K. Tanaka, T. Nakaoka, K. Murase, Physica B 316–317 (2002) 568–571.
[5] X. Feng, W.J. Bresser, P. Boolchand, Phys. Rev. Lett. 78 (23) (1997) 4422–4425.
[6] E. Sleeckx, L. Tichy, P. Nagels, R. Callaerts, J. Non-Cryst. Solids 198–200 (1996) 723–727.
[7] M Mitkova, Y. Wang, P. Boolchand, Phys. Rev. Lett. 83 (19) (1999) 3848–3851.
[8] B. Arcondo, M.A. Ureña, A. Piarristeguy, A. Pradel, M. Fontana, Appl. Surf. Sci. 254 (1) (2007) 321–324.
[9] B. Arcondo, M.A. Ureña, A. Piarristeguy, A. Pradel, M. Fontana, Physica B 389 (1) (2007) 77–82.
[10] A. Piarristeguy, M. Mirandou, M. Fontana, B. Arcondo, J. Non-Cryst. Solids 273 (2000) 30.
[11] A Piarristeguy, M. Fontana, B. Arcondo, J. Non-Cryst. Solids 332 (2003) 1–10.
[12] P. Boolchand, X. Feng, W.J. Bresser, J. Non-Cryst. Solids 293–295 (2001) 348–356.
[13] P Boolchand, W.J. Bresser, Philos. Mag. B 80 (10) (2000) 1757–1772.
[14] P. Boolchand, W.J. Bresser, Philos. Mag. B 84 (9) (2004) 877–885.
[15] P. Nemec, J. Jedelsky, M. Frumar, M. Stabl, Z. Cernosek, M. Vlcek, Philos. Mag. 84 (9) (2004) 877–885.
[16] F. Wang, W.P. Dunn, M. Jain, C. De Leo, N. Vicker, R. Svage, X. Jim, S. Mamedov, P. Boolchand, J. Phys. Chem. Solid 70 (2009) 978–981.