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# Age-induced phase transitions on mechanically alloyed amorphous GaSe

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#### Abstract

After aging it for four years at room temperature, a mechanically alloyed amorphous GaSe powder was transformed to a multi-phase crystalline alloy, where major phase is the trigonal Se one. The structural, thermal and optical properties of this aged amorphous GaSe were investigated through systematic X-ray diffraction, differential scanning calorimetry and Raman scattering measurements. The X-ray diffraction results on the aged GaSe powder suggest the presence of oxides, and X-ray absorption spectroscopy was employed to further investigate it. © 2007 Elsevier Ltd. All rights reserved.

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#### 1. Introduction

Gallium–selenium (Ga–Se) alloys have a number of interesting optical and electronic properties. When produced in the crystalline form, they have been employed to design several devices with direct technological applications, such as MOSFET type transistors, photodiodes, phototransistors, IR detectors, solar cells, X-ray detectors, photoelectric analyzers of polarized light, high-energy muon detectors, etc. [1,2]. When produced in amorphous form, it is a potential candidate for optical memory type applications, large area flexible solar cells, etc. [1,2]. Faced with a huge interesting technological applications for such Ga–Se alloys, it is very important to find alternative ways to produce them and to study their stability with respect to temperature, pressure, radiation, aging and so on.

GaSe is a layered semiconductor of the III–VI family like GaS and InSe, and its basic units, two dimensional layers, are formed by two hexagonal sheets with gallium and selenium atoms at alternate corners of the hexagons; the hexagonal layers undergo "chairlike" deformations through the bonding of the gallium atoms by strong ionicovalent bonds. At ambient temperature, the layers are bound by weak van der Waalstype interactions. The weakness of this interaction explains the existence of a number of polytypes [3]. According to the phase diagram [4] of the Ga–Se system, there are two congruent compounds Ga<sub>2</sub>Se<sub>3</sub> and GaSe, which melt at 1005 °C and 938 °C, respectively. A monotectic transition occurs at 915 °C in the lower composition region of Se. There is a eutectic between GaSe and Ga<sub>2</sub>Se<sub>3</sub>. There are some controversial reports [4] on the existence of peritectics.

GaSe and Ga<sub>2</sub>Se<sub>3</sub> samples can be prepared by fusion, vapor deposition and molecular beam epitaxy techniques [5–8]. In the case of Ga<sub>2</sub>Se<sub>3</sub>, there is another difficulty: its native surface oxidizes and is thus not stable in air [9]. Recently, our group has successfully used mechanical alloying (MA) [10] to produce amorphous GaSe [11] and nanocrystalline Ga<sub>2</sub>Se<sub>3</sub> alloys [12], starting from their elemental powder mixtures with nominal compositions Ga<sub>50</sub>Se<sub>50</sub> and Ga<sub>40</sub>Se<sub>60</sub>, respectively. More detailed studies on the local atomic structure of the amorphous phases were performed by using techniques related to synchrotron radiation sources (EXAFS, XRD and RMCA modeling) [13].

In 2001, de Lima et al. [14] reported for the first time results on the influence of aging in the structural properties of an amorphous selenium sample (a-Se) produced by MA. They have observed that after some years of aging, the

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atomic structure of a-Se produced by MA partially transforms from the ordinary  $Se_n$  chain-like form to the  $Se_8$  ringlike one, which is commonly found in a-Se produced by the rapid quenching or vapor deposition methods. Based on this interesting observation, more recently, an aged ZnSe sample, also produced by MA, was re-examined [15]. Our main observations in that paper pointed out that the presence of a small quantity of c-Se seeds in the as-milled ZnSe sample, probably in the interfacial region, were responsible for promoting the growth of c-Se clusters/agglomerates, due to migration of Se atoms located on this component with just room temperature energy (< 0.025 eV). The Se diffusion and c-Se re-crystallization due to aging in ambient conditions was not observed even in a pure mechanically alloyed *a*-Se sample [14]. Very recent investigation of the degradation in chalcogenide II-VI semiconductors grown by the high-pressure Bridgman method [16] showed that in order to improve the degradation and short lifetimes of II-VI based devices, the incorporation of beryllium content in II-VI compounds should be ensured (less than 10%), since it is believed that the degradation can be attributed to the recombination-enhanced defect motion, and the beryllium-based bonding can be used to enhance the crystal elastic rigidity in II-VI alloys.

In the present paper, we followed our preliminary studies reporting results on the aging effects of the amorphous GaSe alloy produced by MA in 2002 (named as *aged*-GaSe). X-ray diffraction (XRD) results show a spontaneous amorphous–crystalline transformation four years after mechanical amorphous alloy production. Extended X-ray absorption spectroscopy (EXAFS) was carried out to study the local atomic disorder due to aging and oxidation processes. Differential scanning calorimetry (DSC) and Raman scattering (RS) were employed to verify the amorphous GaSe phase deterioration and to track changes in the vibrational spectra due to aging.

## 2. Experimental procedure

Sample preparation details can be found elsewhere [11]. The aged-GaSe sample was stored in a sub-micrometer powder form and as small pellets for Raman measurements. The powder was analyzed by energy dispersive X-ray (EDX) measurements in a scanning electron microscope, and the mean values obtained were: 41.0 at.% Se, 31.0 at.% Ga and 28.0 at.% O, while in 2002 the results were 48.9 at.% Se and 51.1 at.% Ga. The absence of bulk-Fe or Fe compounds, already reported in 2002, was confirmed in the Mössbauer spectrum of the aged sample. XRD patterns were recorded using a Rigaku powder diffractometer, Miniflex model, with Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å), in an air atmosphere. The EXAFS measurements were performed at room temperature in transmission mode on the D04B-XAFS beamline of an LNLS (Campinas, Brazil), using a channel cut monochromator (Si 111) and two ionization chambers filled with air as detectors, working at 10% and 70% efficiency, respectively, and the beam size at the sample was about  $1 \times 3 \text{ mm}^2$ . This yielded a resolution of about 3 eV on the Ga and Se K edges. At these energies, harmonic Fig. 1. XRD patterns of the *c*-Se, *as-milled*-GaSe (with different periods of time) and *aged*-GaSe (named 15<sup>\*</sup>). The circles represent the  $2\theta$  positions of the most intense peaks of the hexagonal GaSe phase.

rejections are irrelevant for the D04B beamline. The energy and average current of the storage ring were 4.4 GeV and 110 mA. All DSC measurements were carried out from 25 °C up to 600 °C, at a heating rate of 10 °C min<sup>-1</sup>, in a 2010 DSC cell manufactured by TA Instruments, with flowing nitrogen gas. The temperature of the cell was calibrated with an In standard sample with a temperature accuracy better than  $\pm 0.2$  °C. Micro-Raman measurements were performed with a T64000 Jobin-Yvon triple monochromator coupled to an optical microscope and a cooled CCD detector. The 5145 Å and 6470 Å lines of an Ar-Kr laser were used as exciting light, always in backscattering geometry. The output power of the laser was selected at about 3 mW and 0.3 mW for 5145 Å and 6470 Å lines, respectively, in order to avoid overheating samples, and consequently avoiding photo-induced structural modifications. All Raman measurements were performed at room temperature.

## 3. Results and discussion

#### 3.1. XRD measurements

As it is reported in Ref. [11], the hexagonal GaSe phase was formed for a short milling time (3 h), and when increasing the milling time to greater than 10 h its amorphization occurred. Hereafter, the as-milled amorphous sample will be called the *as-milled*-GaSe, and the same sample aged for four years will be called the *aged*-GaSe.

Fig. 1 shows the XRD patterns for the *as-milled*-GaSe measured in 2002 (patterns named as 1/2 h, 3 h and 15 h), and for the *aged*-GaSe measured in 2006 (pattern named 15 h\*). In order to clarify the comparison and discussions that will





Fig. 2. Experimental XRD pattern of the *aged*-GaSe sample (noisy curve) overlapped by the best fitting achieved by the Rietveld method using the GSAS package. The symbols represent the  $2\theta$  positions of the most intense peaks of possible minority phases: ( $\Box$ ) Ga<sub>2</sub>O<sub>3</sub>, ( $\bigcirc$ ) SeO<sub>2</sub>, ( $\diamond e \lor$ ) high-pressure Se phases.

be made, the XRD pattern of trigonal selenium (c-Se) is also shown in this figure. A comparison between the XRD patterns for the as-milled-GaSe and aged-GaSe samples reveals a huge structural evolution from the amorphous pattern to a multicrystalline-phase pattern, where the main phase corresponds to the trigonal Se (c-Se). In addition, several other diffraction lines arise, and they remain unexplained. An exhaustive comparison of these diffraction lines with the many XRD patterns given in the crystallographic databases [17] and [18] (including all compounds of the Ga-Se, Ga-O, Se-O and Ga-Se-O systems) suggests that these new other phases can be the trigonal Ga<sub>2</sub>O<sub>3</sub> (ICSD [17] card no 27431), tetragonal SeO<sub>2</sub> (ICSD card no 24022) and some high-pressure Se phases (JCPDS [18] cards no 471516 and 471515). The XRD patterns for some Ga–Se phases, such as GaSe polytypes or Ga<sub>2</sub>Se<sub>3</sub>, were also compared, and they were discarded.

The attempted identification these new phases in Fig. 2 is shown the *aged*-GaSe pattern together with the main diffraction lines of the possible candidate phases (see symbols). The Rietveld method [19] was applied using the GSAS package [20], and with exception of the *c*-Se phase, no conclusive identification was reached for the *aged*-GaSe pattern. The structural refinement for the *c*-Se was reached for a lattice parameter of a = 4.372 Å and c = 4.955 Å, which is 0.1% greater than that given in ICSD Database, card 22251 (a = 4.366 Å and c = 4.954 Å). The best-fitted pattern obtained is shown in Fig. 2.

# 3.2. EXAFS measurements

Fig. 3(a) shows EXAFS spectra of the *aged*-GaSe (solid lines) and *as-milled* GaSe samples (dashed line) at both Ga and Se K-edges obtained using the iFeffFit package [21]. A comparison of these EXAFS signals reveals important changes with aging; for example, the EXAFS oscillations measured at the Ga K-edge for the *aged*-GaSe shows a huge attenuation for  $k > 7.5 \text{ Å}^{-1}$ , which indicates destructive interferences due to phase coexistence. At the Se K edge, the EXAFS signal for this sample shows only a shift to smaller k values, and practically no attenuation with aging.

Fig. 3(b) shows the Fourier Transformed functions of the *aged*-GaSe (solid lines) and *as-milled*-GaSe samples (dashed line) at both Ga and Se K-edges. For Fourier transformations, the EXAFS oscillations were performed over *k* ranges delimited by Kaiser–Bessel windows from 2 to 16 Å<sup>-1</sup> and from 5 to 17 Å<sup>-1</sup> for Se and Ga K-edges, respectively.

Based on these XRD results, several theoretical models were proposed to fit the EXAFS signals of *aged*-GaSe in direct *d*-space. At the Se K-edge, the best fit was reached by considering the contributions from the an amorphous GaSe phase (fixing their values as those obtained in 2004 [13]) and



Fig. 3. (a) EXAFS spectra of the *aged*-GaSe (solid lines) and as-milled samples (dashed line) at both Ga and Se K-edges. (b) Fourier Transformed functions of the *aged*-GaSe (solid lines) and as-milled samples (dashed line) at both Ga and Se K-edge. The symbols represent the best fits achieved by EXAFS fittings obtained using iFeffFit package (see numerical results in Table 1). The dotted lines indicate Kaiser–Bessel windows used in the fitting processes.

Table 1
Numerical results from EXAFS best fits of as-milled and <i>aged</i> -GaSe samples

Model	Bond type	Ga K edge		Model	Se K edge	
		Ga–Ga	Ga–Se		Se–Ga	Se–Se
	Ν	1.6	2.4		2.4	1.5
a-GaSe	d	2.39	2.46	a-GaSe	2.46	2.40
	$\sigma^2(10^{-2})$	1.26	0.62		0.62	1.78
+		Ga–Ga	Ga–O	+		Se–Se
	Ν	3	3/3/1		-	2
Ga <sub>2</sub> O <sub>3</sub>	d	2.98	1.91/2.17/2.82	Se	-	2.36
	$\sigma^2(10^{-2})$	1.11	1.52/0.57/0.92		-	0.37

N is the coordination number, d is the interatomic distances in Å and  $\sigma^2$  is the Debye–Waller parameter in Å<sup>2</sup>. Sequences of three numbers on the Ga–O column represent the values obtained for the nearest O shells.

*c*-Se, while at the Ga K-edge, the best fit was reached by considering the contributions from the amorphous GaSe and trigonal  $Ga_2O_3$  phases. We tried to consider a contribution from the SeO<sub>2</sub> phase for the EXAFS signal at the Se K-edge, but the fitting shows no realistic numerical results. The symbols in Fig. 3(b) represent the best fits achieved, whose numerical results are listed in Table 1.

## 3.3. DSC measurements

Fig. 4 shows the measured DSC curves for the *as-milled*-GaSe and *aged*-GaSe (1st run and 2nd run — dashed line) samples. The first DSC run on the *aged*-GaSe sample shows several endothermic peaks between 50 and 230 °C, and an exothermic broad band between 300 and 600 °C, which can be decomposed into, at least, three sub-peaks centered at 390, 455 and 520 °C. The endothermic peak located at about 215 °C is attributed to the *c*-Se melting, whose calculated enthalpy change values are 3.4 J g<sup>-1</sup> and 0.6 J g<sup>-1</sup> (g of the sample) in the first and second runs, respectively.

The second DSC run, besides confirming the *c*-Se melting, allowed the association of the endothermic peak with the elimination of intra-molecular water molecules. However, a comparison between the measured DSC curves during the first and second runs reveals the arising of a small endothermic peak at 209 °C, which does not fit precisely the melting points of any selenium oxides in bulk form. The melting point of some selenium oxides are: Se<sub>2</sub>O<sub>5</sub> ( $T_m = 224$  °C), SeO<sub>2</sub> ( $T_m = 316$  °C) and SeO<sub>3</sub> ( $T_m = 394$  °C) [22]. Based on these melting point values, one could attribute the endothermic peak at 209 °C to a probable presence of Se<sub>2</sub>O<sub>5</sub>, but XRD measurements disagree and suggest the SeO<sub>2</sub> as the main Se oxide candidate.

The absence of most of those exothermic features (observed in the first run) in the second run corroborates the structural relaxation and amorphous-crystalline transformation already suggested for the *as-milled* GaSe sample in the DSC results obtained in 2002.

# 3.4. RS measurements

Fig. 5 shows the micro-Raman spectra of the *as-milled* GaSe (named 3 h and 15 h), *aged*-GaSe (named 15 h<sup>\*</sup>), as well as the spectra of polycrystalline trigonal selenium (*c*-Se) and gallium (*c*-Ga). The results show that after aging, just one intense



Fig. 4. DSC curves of *as-milled* GaSe sample (3 h and 15 h) and DSC curves of *aged*-GaSe sample (1st and 2nd runs, solid and dashed lines, respectively). All DSC measurements were carried out with a heating rate of  $10 \,^{\circ}$ C min<sup>-1</sup>.

Raman line remains easily visible in the spectrum, which is located at the same spectral range of *c*-Se features (at about 237 cm<sup>-1</sup>); however, a very weak line at about 140 cm<sup>-1</sup> can be seen in the magnified region of the spectrum shown in the inset of Fig. 5. As well as shown by XRD, no features from the Ga–Se phases are observed in the Raman spectrum for the *aged*-GaSe sample.

The Raman spectrum of the *c*-Se displays two lines located at about 140 cm<sup>-1</sup> and 235 cm<sup>-1</sup>, which can be identified as the E' and  $A_1$  optical modes of the [Se]<sub>n</sub> chains, respectively [23– 27]. There is also some contribution from the E'' mode to the 235 cm<sup>-1</sup> Raman line, as its frequency has been reported to be 231 cm<sup>-1</sup> [24].

The Raman spectrum of the *as-milled*-GaSe 3 h shows at least four broad lines located at 130, 155, 235 and 280 cm<sup>-1</sup>, and several other lines at the lower frequency range ( $<100 \text{ cm}^{-1}$ ). For longer milling times, between 10 and 15 h, the Raman spectra obtained in 2002 were very



Fig. 5. Micro-Raman spectra of *c*-Se, *c*-Ga, as-milled GaSe (3 h and 15 h) and *aged*-GaSe (15 h<sup>\*</sup>) samples.

Table 2 Raman lines observed and their suggested assignments according to GaSe and Ge<sub>2</sub>Se<sub>3</sub> modes

Frequency (cm <sup>-1</sup> )	Mode symmetry assignment			
	GaSe [3]	Ga <sub>2</sub> Se <sub>3</sub> [30]		
~60	E''			
105		TA		
130	$A'_1$			
155	ZB: $A_2''$ and/or $E'$	LA		
235	$E^{\prime\prime}$			
280	$A'_1$			

similar in shape and quite different to those for 3 h of milling, which was explained based on the crystalline–amorphous phase transition detected by the XRD and DSC measurements. As a consequence of the breakdown of the selection rules caused by disorder, Raman scattering can access phonons out of the Brillouin zone center.

The Raman active modes observed in the spectra of the *as-milled*-GaSe were compared to those given in the literature for both crystalline GaSe and Ga<sub>2</sub>Se<sub>3</sub> [9,28], and also with the Phonon Frequency Distribution Function (PFDF) for the GaSe phase [3] (see Table 2).

Two interpretations for the 155 cm<sup>-1</sup> line were pointed out: (i) zone-boundary (ZB)  $A_2''$  and/or E' modes activated by selection rule relaxation due to defects and/or vacancies in the crystalline structures [28–31], and (ii) LA (155 cm<sup>-1</sup>) and TA (105 cm<sup>-1</sup>) modes of the X point of the large Brillouin zone of the Ga<sub>2</sub>Se<sub>3</sub> zinc-blend structure [28]. Moreover, both 155 and 105 cm<sup>-1</sup> lines have been attributed to phonons from the epitaxial Ga<sub>2</sub>Se<sub>3</sub> layers in Ref. [9], where two other lines (at 250 and 290 cm<sup>-1</sup>) are also reported as Raman active modes.

Thus, as already mentioned, only Raman lines at about 140 and 237 cm<sup>-1</sup> were observed for the *aged*-GaSe sample, and this corroborates all attributions done for this sample using the XRD and DSC results, which suggests the *c*-Se as the major crystalline phase. This is a very interesting result that shows the enormous atomic mobility of the Se atoms in the *as-milled*-GaSe, even after it forms amorphous alloys. In some way, this result alerts us to the metastable character of the amorphous GaSe phase produced by MA. Further investigations are underway to discover from where the Se atoms come, and how they get the energy to recuperate their trigonal structure. Our first suggestion is that they are in the interfacial component, where there is sufficient free-energy stored in the defects to promote that structural regeneration.

## 4. Conclusions

The structural evolution of an amorphous GaSe alloy produced by MA in 2002 was investigated in order to detect aging effects in ambient conditions. The main conclusions of this study are the following:

- (i) The XRD measurements of the *aged*-GaSe alloy showed that the major crystalline phase is now the trigonal-Se one. Several indications of oxides (Ga<sub>2</sub>O<sub>3</sub>) and high-pressure Se phases can be also pointed out based on its pattern. An amorphous halo can also be seen, and suggests an amorphous phase coexistence.
- (ii) The EXAFS results supported almost all the XRD results, except those about the selenium dioxide (SeO<sub>2</sub>).
- (iii) The DSC measurements for the *aged*-GaSe are not conclusive, but corroborate a residual amorphous phase coexistence as well as several structural relaxation features. Moreover, a second-run measurement revealed evidence of a hydrophilic character for the *aged*-GaSe sample, and confirmed one of the endothermic features as been from *c*-Se melting.
- (iv) The RS measurements corroborated an age-induced amorphous-polycrystalline phase transition in the *as-milled*-GaSe, also discarding any possibility of the nucleation of Ga–Se crystalline polytypes.

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