Pressure-induced effects on the structural properties of iron selenides produced by mechano-synthesis

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Abstract
Extended x-ray absorption fine structure studies were performed to follow the structural behaviour of $FeSe_2$ and $FeSe/Fe_7Se_8$ nanocrystalline phases produced from a mechanically alloyed $Fe_{25}Se_{75}$ mixture when exposed to high pressure. A phase transition from marcasite $FeSe_2$ to NiAs-type $FeSe/Fe_7Se_8$ was previously reported when the milling time was increased from 20 to 62 h; this study proposes to verify the possibility of inducing the same phase transition in high-pressure experiments using a diamond anvil cell.

1. Introduction

As is well known, the mechano-synthesis process, or, as it is better known, mechanical alloying (MA), is based on repeated shocks between hard spheres and powder sample disposed inside a sealed container with a controlled atmosphere [1]. As a result of the ball–powder collisions, basically two effects take place: fracturing and cold welding of the powder particles, which occur mainly due to high pressures (of the order of 6 GPa [1]) applied to the sample particles. After a few hours of milling, the sample presents two distinct regions: one formed from very small crystals (tens of nanometres) and the other highly disordered, with these nanocrystals covered up [2]. The transition metal chalcogenides provide examples of systems that have already been produced by the MA process in the nanocrystalline form [3–5]; they showed interesting structural evolution as a function of milling time. This is a very interesting case because there is a huge difference between the melting points of the components of these systems, which makes it difficult to control the composition of the final product as well as demanding large quantities of energy and long sintering times when the production is by conventional synthesis methods based on fusion [6–10].
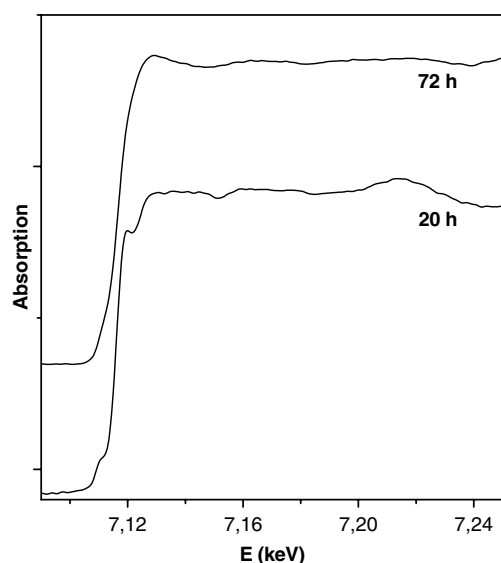
Figure 1. The XANES region of the x-ray absorption spectra of the MA $Fe_{25}Se_{75}$ samples milled for 20 and 72 h.

In the special case of the iron selenides, at least one phase transition (from marcasite $FeSe_2$ to hexagonal NiAs-type $FeSe/Fe_7Se_8$) has been reported in a previous study as the milling time was increased from 20 to 52 h [3]. In a complementary study [11] Mössbauer measurements showed that the amount of iron decreases continuously due to the formation of the paramagnetic marcasite $FeSe_2$ phase, which remains as the only crystalline phase after 20 h of milling. For longer milling time (72 h), the coexistence of two iron selenide phases, FeSe and Fe_7Se_8, both with NiAs-type hexagonal structure, was observed. As the Fe_7Se_8 phase is ferromagnetic and FeSe is paramagnetic [7, 12, 13], the Mössbauer results could be used to determine the relative amounts of each phase, showing that the ferromagnetic phase becomes the majority one after 62 h of milling. The hyperfine parameters determined for the Fe_7Se_8 phase are in good agreement with the literature ones [13], with just a slight distortion in one of the non-magnetically equivalent sites.

The goal of the present study is to verify the stability of the iron selenide phases produced by MA when subjected to high pressure (up to 20 GPa). Since structural evolution of $FeSe_2$ to $FeSe/Fe_7Se_8$ phase had been observed as the milling proceeded, it was expected that the same phase transition could be induced via the action of high-pressure effects produced by a diamond anvil cell (DAC). In order to observe the structural modifications caused by high pressures in the short-range order of the MA samples, extended x-ray absorption fine structure (EXAFS) measurements were performed on the Fe K edge.

2. Experimental details

High pressures on the samples were generated by axial forces acting between two small diamonds of a DAC. The local structure determination for the mechanically alloyed samples as a function of the pressure was performed by x-ray absorption spectroscopy (XAS). Study of phase transformations following the modifications in short-range order, as given in a special region of the XA spectrum—the EXAFS, has several advantages over study of long-range order obtained from diffraction experiments. The main advantage is that it directly provides the coordination numbers around a selected absorbing atom. A visual evaluation of the XA spectra in the XANES region can furnish strong evidence of differences in the electronic character of bonds caused by the absorber atom. The present study provides a good example; figure 1 shows

clearly the different electronic behaviours of the Fe atom when it is in a sample containing $FeSe_2$ (milled for 20 h) and for the $FeSe/Fe_7Se_8$ phase (milled for 72 h). Furthermore, studies following the evolution of the disorder (Debye–Waller) parameter as a function of pressure can probe more accurately for the exact pressure at which a phase transition starts.

XAS experiments were performed at the Fe K edge (7112 eV) at dispersive station D11 of DCI in the Laboratoire pour l'Utilisation du Rayonnement Electomagnétique (LURE), Orsay, France.

The pressure determination during the measurements was performed through the pressure-dependent fluorescence of a ruby chip and a 16:3:1 methanol/ethanol/water mixture was used as the pressure transmitting medium.

The subsequent data treatments were done using the CDXAS-26 [14] and FEFF [15] software packages. The energy calibration in the XAS measurements was done by comparing with the spectra of standard samples, normally metallic foils of pure elements, obtained in dispersive and classical set-ups. Then, the relationship between the pixel position of the detector and the energy of the transmitted photons is determined.

3. Results and discussion

Figure 2 shows x-ray absorption spectra of the $Fe_{25}Se_{75}$ samples milled for 20 h (a) and 72 h (b) as a function of pressure applied during the upstrokes. It can be seen that a good spectral range was obtained in both experiments at about 550 eV beyond the edge. The two series of spectra show important differences between their oscillation patterns, as well as between their behaviours as a function of pressure. The sample milled for 20 h shows a more intense amplitude of oscillations than the sample milled for 72 h; the oscillations become more intense at higher pressures. The spectrum of the sample milled for 20 h at about 19 GPa was compared with that of the sample milled for 72 h in ambient conditions and, in view of several differences observed between them, it can be stated that the phase transition reported with milling time increase was not reproduced.

Figure 3 shows the edge and XANES profiles of the samples milled for 20 h (a) and 72 h (b) as a function of pressure. This region of the x-ray absorption spectra contains information concerning photoelectron multiscattering effects, which gives access to the medium-range order ($\sim$15 Å) of the atomic systems. From this figure one can see huge differences between the signals in the 7.12 and 7.15 keV region: that for the sample milled for 20 h presents several small oscillations and that for the sample milled for 70 h is almost continuous. These effects can be associated with differences in medium-range order of the milled samples. Despite the apparent differences, the XANES patterns of the milled samples presented similar pre-edge effects and the values at the K edge were slightly lower than that for the pure metallic Fe, indicating the existence of electronic features in the MA samples with energy levels smaller than those of metallic form. In general, the XANES patterns of both MA samples suffered just small distortions after the pressure upstroke and no similarities were found between them.

Figure 4 shows the EXAFS profiles $\chi(k)$ of the samples milled for 20 h (a) and 72 h (b) as a function of pressure. Considering the spectra of the samples milled for 72 h and those for the samples milled for 20 h, it can be seen clearly that the oscillations are in contra-phase and that there are substantial differences in the signal amplitudes, even after the upstrokes. For higher pressure values the spectrum of the sample milled for 72 h presented a huge amplification of the EXAFS oscillations, especially after 7.3 keV, and also presented a substantial phase shift typical of a great shortening of the nearest neighbour average distances.

Using the phase and amplitude extracted from the experimental EXAFS signal at ambient conditions and considering the short-range crystallographic information for the $FeSe_2$
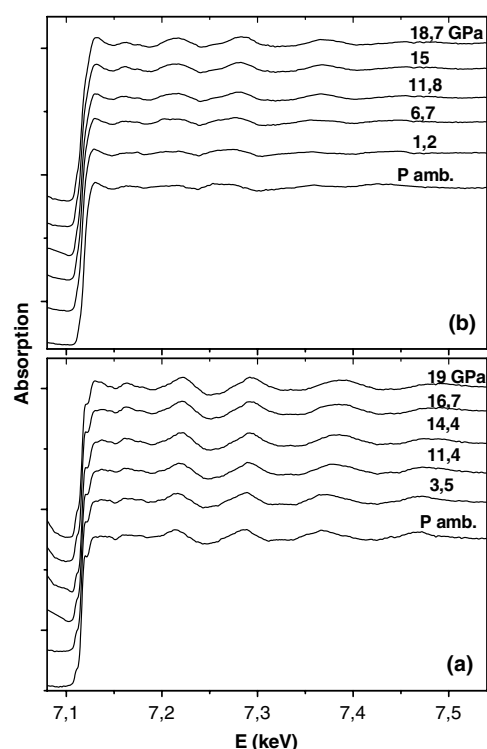
Figure 2. X-ray absorption spectra of the MA $Fe_{25}Se_{75}$ samples milled for 20 h (a) and 72 h (b) as a function of pressure.

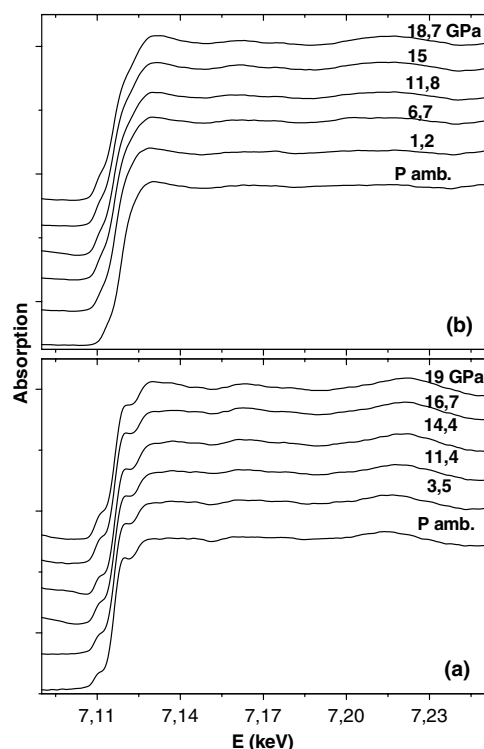**Figure 3.** The XANES region of the x-ray absorption spectra of the MA $Fe_{25}Se_{75}$ samples milled for 20 h (a) and 72 h (b) as a function of pressure.

phase [16][3] (coordination number $N = 6$ and average distance $d = 2.40$ Å), simulated EXAFS signals were proposed for experimental signals collected at higher pressures. The simulations were performed fixing the N and the electronic parameters. From these simulations the variations of d and the pseudo-Debye–Waller ($\Delta\sigma^2$) parameters were determined as a function of the pressure.

The same simulations were performed for the experimental EXAFS signals for the sample milled for 72 h. It is interesting to note that the short-range crystallographic configurations of the FeSe ($N = 6$ and $d = 2.55$ Å) and Fe_7Se_8 phases are practically identical, except for a greater distribution of distances of the Fe_7Se_8 phase ($d = 2.46$–2.75 Å) (see footnote 3) [17]. Since the FEFF [15] simulations, considering only first neighbours of the absorber atom, showed practically identical phase and amplitude patterns for $FeSe_2$ and FeSe/Fe_7Se_8 phases, EXAFS simulations of the sample milled for 72 h were performed using the experimental phase and amplitude files obtained for the sample milled for 20 h under ambient conditions. The fitting quality achieved was satisfactory and the results showed that, even though the simulations were performed using the same phases and amplitudes, the sample milled for 72 h has larger structural distortions and larger neighbour distances than those reported for the sample milled for 20 h. This reinforces the differences between the two samples (crystalline phases) and the absence of pressure-induced phase transitions.

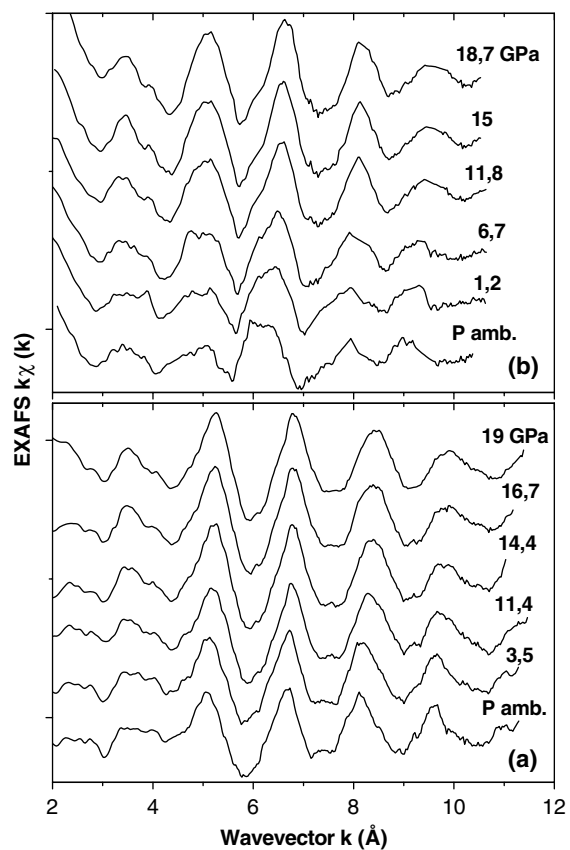[3] Atomic Softek, 70 Longwood Road North, Hamilton, Ontario, Canada L8S 3V4.

Figure 4. The EXAFS region of the x-ray absorption spectra of the MA $Fe_{25}Se_{75}$ samples milled for 20 h (a) and 72 h (b) as a function of pressure.

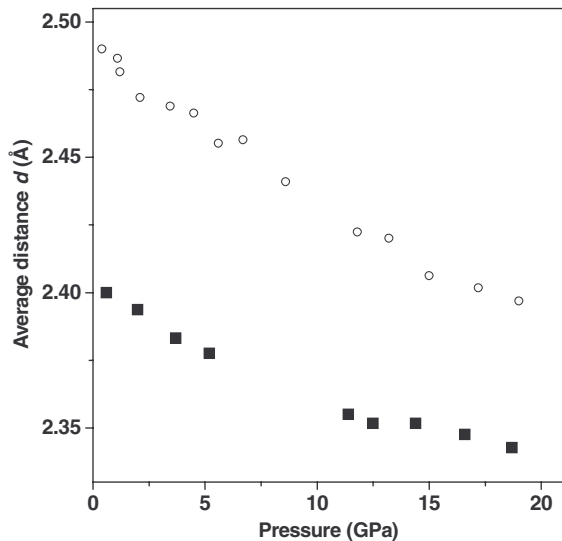**Figure 5.** Fe first-neighbour average distances for the $Fe_{25}Se_{75}$ samples milled for 20 h (squares) and 72 h (open circles) as a function of pressure.

Figure 5 shows the Fe first-neighbour average distances (d) for the sample milled for 20 h—$FeSe_2$ (squares)—and that milled for 72 h—$FeSe/Fe_7Se_8$ (circles)—as a function of pressure. It can be seen that even though the same phase and amplitude patterns were used to

fit the EXAFS spectra of the samples milled for 20 and 72 h, the samples presented different Fe nearest neighbour distances and different structural behaviours with pressure. The volumetric variation is much more important for the sample milled for 72 h for the same pressure range. This shows that the $FeSe_2$ phase is less compressible than the $FeSe/Fe_7Se_8$ one, which is in good agreement with the results for iron sulfides.

4. Conclusions

A local structural determination for $Fe_{25}Se_{75}$ samples milled for 20 and 72 h was carried out, as a function of pressure, and the main conclusions of this study are:

(1) The $FeSe_2$–$FeSe/Fe_7Se_8$ phase transition induced by milling was not reproduced in testing the sample milled for 20 h up to 19 GPa.
(2) The structural disorder (pseudo-Debye–Waller) parameter observed for the sample milled for 72 h is greater than that for the sample milled for 20 h at ambient pressure. It decreases with pressure increase for both samples.
(3) The nanocrystalline $FeSe_2$ phase is less compressible than the $FeSe/Fe_7Se_8$ one.

Acknowledgment

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