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Structural, optical and thermal characterization of nanostructured CdSe obtained by mechanical alloying

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HIGHLIGHTS

- Mechanical alloying of Cd and Se promoted the nucleation of CdSe with few hours of milling.
- A CdSe polymorphism was quantified by XRD using the Rietveld Method.
- 20 h of milling promoted the nucleation of a metastable Se phase.

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ABSTRACT

A CdSe nanostructured alloy was produced by high energy Mechanical Alloying (MA). The existence of three crystalline phases, two CdSe polymorphs and a small fraction of CdO phase, was revealed through X-ray powder diffraction. With continued MA process, the CdO phase was dispersed between the nanostructures of zinc blende (ZB) and wurtzite (WZ). Differential Scanning Calorimetry (DSC) measurements indicated sublimation at 122 °C confirmed by thermal treatment. Raman spectroscopy revealed that the sublimated material was composed by a trigonal Se. After the thermal treatment, a partial phase transition from ZB to WZ was observed, which is in agreement with that observed by DSC, as well as by nucleation of the $CdSeO_3$.

Introduction

Nanostructured CdSe semiconductors have been extensively studied in both applied and basic researches [1–5]. For applied researches they have been used as opto-electronic devices [6,7], solar cells [1,2,8] and photochemical biosensors [9], whereas the basic researches concentrates mainly on the structural characterization of these materials [4,5,10–12].

CdSe can be synthesized in two different structures, depending on the crystallite size. While in the bulk form exist some preference to form a hexagonal structure, S.G. P63MC (186), better known as wurtzite (WZ), in the nanometer form the trends is to form a face-centered cubic structure, S.G. F4-3 m (216), known as zinc blende (ZB), at any preparation temperature [13,14].

A wide variety of unique CdSe nanostructures have been synthesized using CdSe, such as nanotubes and nanowires [15] nanosheets [16], nanorods and nanofractals [17], nanobelts [18] and quantum dots [19,20], utilizing a variety of techniques such as thermal [21], chemical [22], thermochemical [23,24] and mechanical [25,26]. It is already known that mechanical alloying (MA) can produce simultaneously at least two CdSe structures. A quantitative structural characterization is sometimes difficult due to the structural similarities between WZ and ZB [10] and their stacking faults disorders.

In this work we present a structural study of nanostructured CdSe produced by MA using X-ray Diffraction (XRD), Differential Scanning Calorimetry (DSC) followed by annealing and microRaman spectroscopy.

Experimental methods

CdSe nanostructured semiconductor was produced by MA using a Spex Model 8000 Mixer/Mill (USA). Cd (Alfa Aesar, 99.9%) and Se (Alfa Aesar, 99.9%) were weighed and placed together inside the steel mill. The ratio of the mass of the balls to the powder was

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previously chosen (5:1). The container was sealed under argon atmosphere and the milling was carried out for 2 and 20 h. After each milling time, sample was collected and characterized by X-ray Diffraction (XRD) using a Philips diffractometer, model X'Pert (Netherlands) equipped with Cu radiation (0.154056 nm). Data acquisition of XRD was 1 s per point. Rietveld method [28] was performed using the GSAS [27] package to determine the structural parameters related to the XRD patterns following the recommended IUCr guidelines [29]. Thermal behavior was verified through DSC between 25 and 600 °C with a heating rate of 10 °C/min on a TA equipment, model DSC 2010. Raman spectroscopy was carried out to investigate vibrational behavior of the atoms in crystalline lattice. MicroRaman spectra were obtained with a spectrometer Jobin–Yvon T64000 triple Raman spectrometer equipped with a liquid-nitrogen-cooled charge coupled device multichannel detector. An excitation line of Ar laser (λ = 514.5 nm) was focused down to 5 μm, 100 mW and acquisition time of 5 × 100 s. Spectrometer calibration was performed using a silicon wafer and setting the peak at 521.6 cm^{-1}. Raman frequencies were determined from the peak fit using a Lorentzian profile.

Results and discussion

X-ray diffraction and DSC

Fig. 1 shows the XRD pattern of Cd and Se mixture at the milling times of 2 and 20 h. In the XRD pattern corresponding to 2 h of milling we could verify the nucleation of both structures, WZ and ZB, together with a cadmium oxide of cubic structure, ICSD n°.29290 [30] (indicated by stars in the figure), without any trace of the starting materials, as observed in reference [25]. The filled triangles correspond to the most intense peaks of ZB structure, ICSD n° 41528, while the inverted triangles correspond to WZ structure, ICSD n° 415786. From 2 to 20 h of milling, diffractograms presented only one significant difference related to the disappearance of CdO phase, which can indicate, among many others possibilities, the phase amorphization, dispersion or solubilization on the crystalline matrix [31]. The similarity between both XRD patterns indicates that, if the CdO phase formation is avoided, a milling time of two hours is enough for the process stabilization.

It was noted that from $2\theta \sim 60°$ no peaks of WZ phase the peaks were observed, but only this phase can explain the first peak at $2\theta \sim 24°$ and the shoulder of the most intense peak observed at $2\theta \sim 27°$. The difficulty increases since the major peaks of ZB phase are overlapped with the main peaks of the WZ phase. We also see in Fig. 1 that the WZ structure should have peaks at $2\theta \sim 35°$ and $2\theta \sim 46°$, corresponding to the planes (101) and (103), respectively. The reason why these peaks were not observed can be explained through the structure defects, or stacking faults, which can produce different features in diffraction patterns, such as shift peak, anisotropic enlargement or even their extinction [32,33].

In fact, both structures are based on the stacking faults of two-dimensional planar units, coordinated tetrahedrally with four first neighbors. From this point of view, the main difference is that one is translated relative to each other, generating layers ABABAB along [111] for ZB structure and ABCABC along [001] for WZ structure [10]. Given these characteristics, it was necessary to perform a structural simulation using the Rietveld refinement [28].

Fig. 2 shows the XRD pattern of CdSe milled for 2 h, which was overlapped by their respective Rietveld refinement, together with the deconvolution of its three phases. The refinement results are summarized in Table 1. From this deconvolution it was verified that the relationship between the peaks intensities of the ZB phase does not change significantly from that published in the ICSD and JCPD databases [34]. This indicates that only the WZ phase has stacking faults, highlighted by the difficulty of adjusting the peaks at $2\theta \sim 35°$ and $2\theta \sim 46°$. Crystallite size shown in Table 1 was calculated by Scherrer formula [35] using the more well-defined peaks average for each phase.

Since this stacking fault causes anisotropic features in XRD patterns, it was applied the Stephens anisotropic model [36] to reach the presented refinements. This model proposes to simulate microdeformations dependent on the (hkl) planes. This model is particularly applicable for different enlargements for each family of planes [31]. The variance of the peak widths are modeled by Eq. (1) [36]:

$$[S(hkl)]^2 = \sum_{H,K,L} S_{HKL} h^H k^K l^L \tag{1}$$

where h, k and l are Miller indices and S_{HKL} are coefficients defined by crystal symmetry and can be refined in GSAS program. The function S (hkl) for hexagonal symmetry, which is the case of WZ, is given by the following equation:

$$S(hkl) = \frac{\pi d_{hkl}^2}{18,000}[S_{400}(h^4 + k^4 + 3h^2k^2 + 2h^3k + 2hk^3) + S_{004}l^4 + 3S_{202}(h^2l^2 + k^2l^2 + hkl^2)]^{1/2} \tag{2}$$

where d_{hkl} is the distance between the planes and $H + K + L = 4$ [37]. The three S_{HKL} parameters obtained through Rietveld refinement of the sample milled for 20 h were $S_{400} = 300 \pm 15$, $S_{004} = 0.02 \pm 0.08$

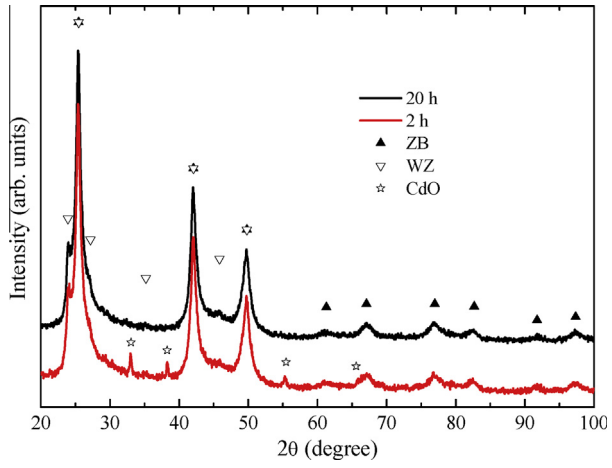

Fig. 1. Structural evolution of the CdSe alloy during the milling process.

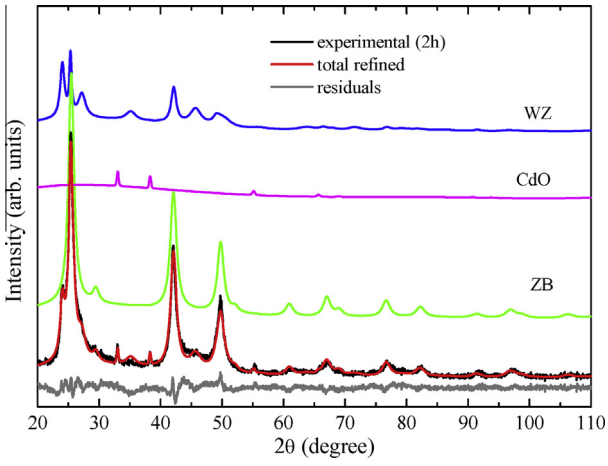

Fig. 2. Experimental XRD pattern of the CdSe sample milled for 2 h overlapped by the best fitting achieved by the Rietveld method using the GSAS package and its discriminated phases.