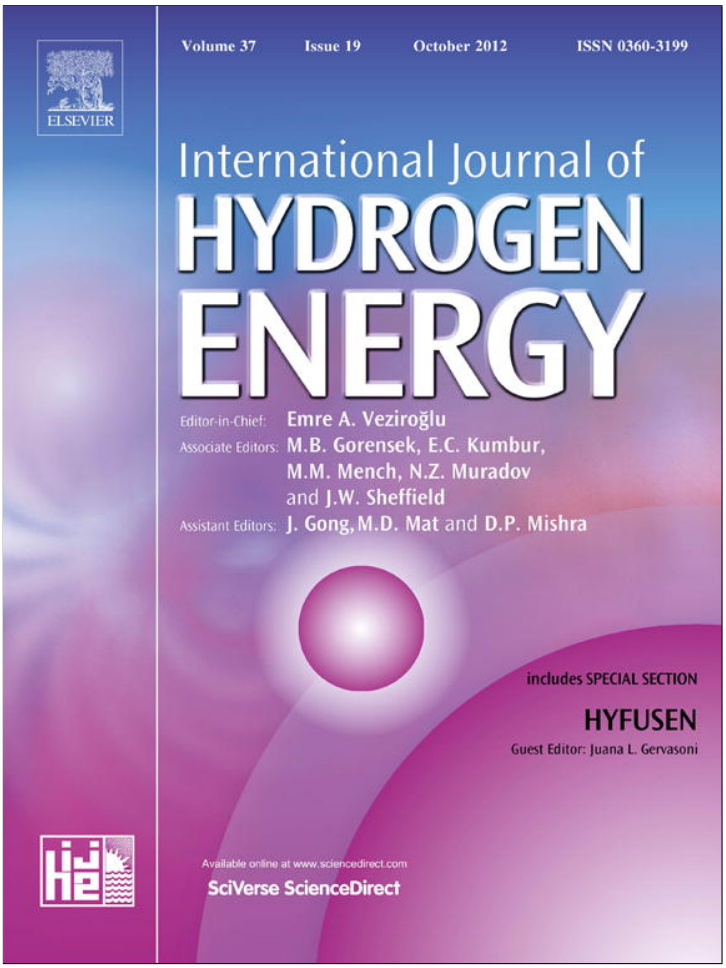

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# Structural characterization of mechanical milled ZnSe and ZnTe powders for photovoltaic devices

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ABSTRACT

II–VI semiconductors are of interest due to their potential application as photovoltaic devices like hybrid solar cells. The efficiency of these devices may be improved mainly increasing charge carriers densities and interfacial processes. In order to reach this last purpose nanocrystalline materials are the best option as solar cells constituents. In this work we present a structural characterization of nanocrystalline ZnSe and ZnTe semiconductors obtained by mechanical milling. The samples were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and positron annihilation lifetime (PALS) measurements. PALS results were compared with ab-initio simulations using the MIKA program. The two-component density functional theory framework (TC-DFT) with the generalized gradient approximation (GGA) and the local density approximation (LDA) was applied.



## 1. Introduction

In recent years there has been a growing interest in alternative energies, in particular solar energy, being the research to improve efficiency and reduce costs in the manufacture of photovoltaic solar cells one of the most important ways to go. The combination of wide bandgap semiconductors and organic dyes are the main candidates in the construction of cheap hybrid solar cells. A lot of work has been done with ZnO for its opto-electrical properties, and it were found improvements in electron transport after doping it with elements of group III (Aluminum or Indium) [1]. There are a variety of doping techniques, such as implantation, but the mechanical milling has proved to be a very useful and effective one [2]. In this sense, we have previous analyzed the effects of mechanical milling on pure [3] and doped ZnO powders with a variety of doping elements [4,5]. From X-ray measurements the general observed behavior in the zincite structure was diminution of grain size as milling time increases. While for doped powders, a progressive diffraction peaks intensity diminution corresponding to the minority phase was found, indicating cation substitution at the final state of milling. This conclusion was also arrived from positron annihilation lifetime experiments [6]. Among others II–VI semiconductors, ZnSe and ZnTe have also good opto-electrical properties and may be potentially the main components for new categories of solar cells. It is important for future technological application the knowledge of defect structure of each material constituent a solar cell device. In this work we present preliminary studies of these two pure systems to establish the basis, before further

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doping. The structural properties on these mechanical milled powders were investigated by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and positron lifetime annihilation spectroscopy (PALS). The PALS technique has advantages respect other experimental procedures, is non-destructive and the radiation of annihilation is appropriate to investigate atomic size defects. In addition, both in metals and semiconductors, positron annihilation parameters can give useful information about density, type, size of positron capture sites.

## 2. Experimental procedure

Commercially powders of ZnSe (99.99%) and ZnTe (99.99%) from Aldrich Chemistry, Sigma–Aldrich Co, were milled in a steel cylinder (8 $cm^3$) with one steel ball (diameter 12 mm). The mechanical milling was performed in a Retsch MM2 horizontal vibratory mill during 10 h. Milled powders were compacted under uniaxial pressure of 150 MPa into disk-shaped pellets (diameter 8 mm). Starting and milled powders were characterized by X-Ray diffraction (XRD) performed with a Philips PW1710 Diffractometer with CuK$\alpha$ radiation in the National Diffraction Laboratory (LANADI-UNLP). Powder microstructure was also investigated by scanning electron microscopy (SEM) with a JSM6300 (JEOL Scanning Microscopy) operating at 10 kV. Positron Annihilation Lifetime measurements (PALS) were done in a conventional fast–fast coincidence system with two scintillator detectors (one $BaF_2$ and one plastic BURLE) provided a time resolution (FWHM) of 260 ps. A $^{22}$NaCl (10 μCi) radioactive source deposited onto a kapton foil (1.42 g/$cm^3$) and sandwiched between two identical samples was used. The source contribution and the response function were evaluated from a Hf metal reference sample using the RESOLUTION code [7,8]. Positron lifetime spectra of $3 \times 10^6$ counts each were recorded at room temperature and analyzed with the POSITRONFIT program [7,8].

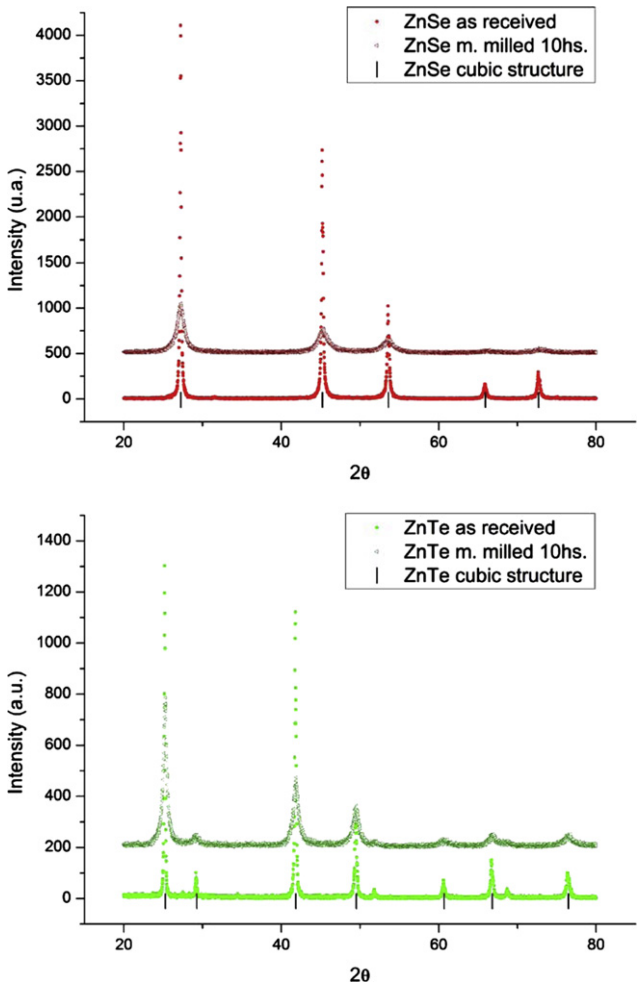


**Fig. 1 – XRD patterns for ZnSe and ZnTe powders as received and after 10 h of mechanical milling. (top) ZnSe as received and after 10 h of milling; (bottom) ZnTe as received and after 10 h of milling.**

## 3. Results and discussion

### 3.1. Sample characterization

X-ray diffraction patterns for ZnSe and ZnTe powders, as received and after 10 h of mechanical milling, are shown in Fig. 1. They display the characteristic reflection lines of cubic ($F\bar{4}3m$) ZnSe and ZnTe. After 10 h of milling, a broadening of the peaks is observed as consequence of grain size reduction and internal strain induced by severe mechanical work [3].

SEM resulting images for all powder samples are shown in Fig. 2. For both semiconductors the results are quite similar. For the starting materials large and wide distribution of sizes are observed. The mechanical work process clearly changes this heterogeneity, reducing the grain size and yielding a more homogeneous powder with a certain degree of agglomeration.

Pressed unmilled and milled powders were analyzed by positron annihilation lifetime spectroscopy in order to identify the mechanically induced defects. After background and source contribution correction, the lifetime spectra for all samples

$$n(t) = \sum_i I_i e^{-t\tau_i},$$

were decomposed into two exponential decays, being each positron state characterized by a positron lifetime, $\tau_i$, with certain intensity, $I_i$ (normalized). The first lifetime component, associated to positron annihilation in the bulk of the material, is in agreement with reported values [9]. The second one, around 550 ps with intensities lower than 10%, take into account positron trapping at different intrinsic defect as is usually observed in semiconductor materials. During mechanical milling, the powders suffer severe plastic deformation giving rise to particle and grain refinement. Different kinds of defects, such as vacancies, vacancy clusters, dislocations, etc., are simultaneously created. This process gives place to an increase in both lifetime contributions modifying also their relative intensities. In Table 1 the resulting fitted positron parameters are shown.

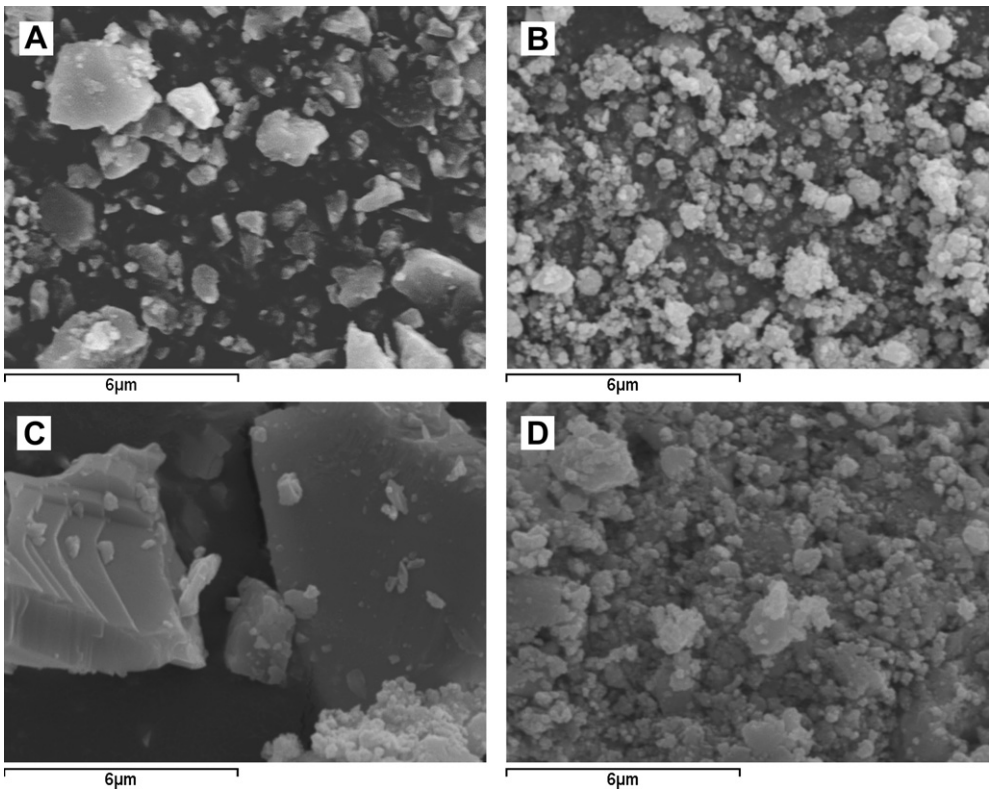


**Fig. 2 – SEM micrographs of ZnSe and ZnTe powders as received and after 10 h of mechanical milling. (A) ZnSe as received; (B) ZnSe after 10 h; (C) ZnTe as received; (D) ZnTe after 10 h.**

### 3.2. *Ab-initio calculations*

In order to obtain a better knowledge of the intrinsic and mechanical induced defects ab-initio calculation of bulk lifetime positron annihilation using the MIKA implementation were performed. This program allows to obtain the positron and electron densities working within the framework of the two-component density functional theory (TCD-FT) [10]. As it is known, the positron annihilation rate is proportional to the electronic density at the positron annihilation region and can be calculated from the overlap integral as

$$\lambda = \frac{1}{\tau} = \pi r_0^2 c \int n_+(r) n_-(r) g(0; n_+; n_-) \mathrm{d}r,$$

where $r_0$ is the classical electron radius, $c$ is the speed of light, $n_+$ and $n_-$ are the positron and electron densities and $g(0; n_+; n_-)$ the electron-positron pair correlation functional evaluated at the positron annihilation region. Basically, this calculation requires solving one-particle Schrödinger equations for electron and positron wavefunctions. For the positron

$$-\frac{1}{2}\nabla^2 \psi_i^+(r) + V_{eff}(r)\psi_i^+ = \varepsilon_i \psi_i^+(r),$$

where $V_{eff}$ is the effective potential which includes three terms, a repulsive Coulomb, an exchange-correlation and a positron–electron correlation potentials. For the last two terms, being unknown, different approaches can be used. In this work, the Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA) were applied for this purpose.

The final calculated lifetimes are shown in Table 1. Comparing these values with the measured lifetime $\tau_1$ a better agreement for the LDA approximation is observed. Similar values were reported by Plazaola et al. [11] under the LDA approximation with Linear Muffin-Tin Orbital Method (LMTO-ASA) calculations for the electron and positron densities. It is known from literature that GGA approximation well described positron properties for metals materials and results less accurate for semiconductors.

**Table 1 – Experimental and calculated positron annihilation lifetime parameters. $\tau_1$ [ps], $I_1$ [%] are the measured lifetimes and intensities. $\tau_{GGA}$ [ps] and $\tau_{LDA}$ [ps] are the calculated lifetime with MIKA implementation using the approximations GGA and LDA, respectively.**

| Sample | M. Time [h] | $\tau_1$ [ps] | $I_1$ [%] | $\tau_2$ [ps] | $I_2$ [%] | $\tau_{GGA}$ [ps] | $\tau_{LDA}$ [ps] |
|---|---|---|---|---|---|---|---|
| ZnSe | 0 | $221_2$ | $67_1$ | $530_{10}$ | $8_1$ | 250 | 233 |
| | 10 | $241_1$ | $74_1$ | $940_{50}$ | $1_1$ | | |
| ZnTe | 0 | $235_3$ | $66_1$ | $560_{20}$ | $9_1$ | 274 | 254 |
| | 10 | $254_3$ | $70_1$ | $582_{30}$ | $4_1$ | | |

## 4. Conclusions

Nanocrystalline ZnTe and ZnSe powders were obtained by mechanical milling. XRD and SEM measurements confirmed grain size reduction as milling proceeds. The observed trend of

positron lifetimes and intensities is to increase commensurate the milling time rises, points out the formation of different kind of defects. Ab-initio calculations indicate that the LDA approximation matches better with PALS results, nonetheless, the GGA approximation shows the desired trend for both systems.

These results constitute a first step of a systematic study on these semiconductors in order to characterize their defect structure for their potential application as solar cells components.

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