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

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Introduction

Figure: Solar cell panel.

In recent years there has been a growing interest in alternative energies and the research to improve efficiency and reduce costs in the manufacture of photovoltaic solar cells 1 is one of the most important ways to go.
The combination of wide Gap semiconductors and organic dyes are the main candidates in the construction of cheap hybrid 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, but the mechanical milling is a useful and effective way of doing it [2].
Like the ZnO, ZnSe and ZnTe have good opto-electrical properties, so this two semiconductors of type II-VI, are potentially the main components for future solar cells. In this work we present preliminary studies of these two pure systems to establish the basis, before further doping.

Experimental procedure

Sample preparation

- Starting materials:
  - *ZnSe* (99.99%) and *ZnTe* (99.99%) powders from Aldrich Chemistry (Sigma-Aldrich Co.).
- The mechanical milling was performed in a Retsch MM2 horizontal vibratory mill (with a frequency of 30 Hz) during 10 h. As milling proceeds, a clearly reduction of grain size was observed..
- The mixtures were milled, in air atmosphere, in a steel cylinder (8 cm^3) with one steel ball (diameter 12mm) being the ball mass to powder mass ratio of 10/1.

Applied Techniques

- *X-Ray Diffraction (XRD)* was carried out using a Philips PW 1710 with Cu K_α radiation in the National Diffraction Laboratory (LANADI-UNLP).
- *X-ray Absorption Full Spectrocopy (XAFS)* measurements were taken at room temperature in transmission mode at the Zn K-edge, using a Si(111) monochromator at the XAFS1 beamline of LNLS (Campinas, Brazil).
- *Positron Annihilation Lifetime* was measured in a conventional fast-fast coincidence system with two scintillator detectors (one BaF2 and one plastic BURLE). A time resolution (FWHM) of 260ps and a time calibration of 24.4 ps/channel was used. Positron lifetime spectra of 3x106 counts each were recorded at room temperature and analysed with the POSITRONFIT program [3].

Previous work

In previous works we have analyzed the effects of mechanical milling on pure and doped ZnO powders.
XRD Measurements: for both kind of powders, as milling time increase, the peaks became broader, obtaining ZnO nanoparticles (20nm). In addition, for the pure system, no changes in the crystalline structure were observed. It was found, for doped powders, a progressive diminution of the diffraction peaks corresponding to the minority phase in the powder mixture. Which is an indication of cation substitution at the final state of milling.
PALS: For pure powders, positron lifetimes increase due to induced mechanical defects. For doped powders, at short milling times, a similar beheavior is observed due to different inittial crystalline structures and induced mechanical defects. For larger milling times, the average lifetime diminishes sice the ZnO wurtzite structure is achieved.

Results and Discussion

XRD Measurements

The ZnSe and ZnTe among others, have typically a cubic crystal structure or zinc blende (see Figure 2). The XRD patterns for the ZnSe and ZnTe powders, as received and after 10 hours of mechanical milling, are shown in Figure 3. The diffractograms display the reflection lines of cubic ZnSe and ZnTe.
In Figure 3 we can appriciate the broadening of the peaks (consequence of the grain size reduction).

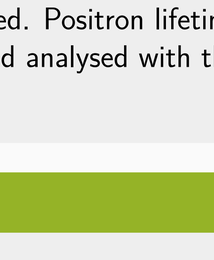

Figure: Zinc-blende structure.

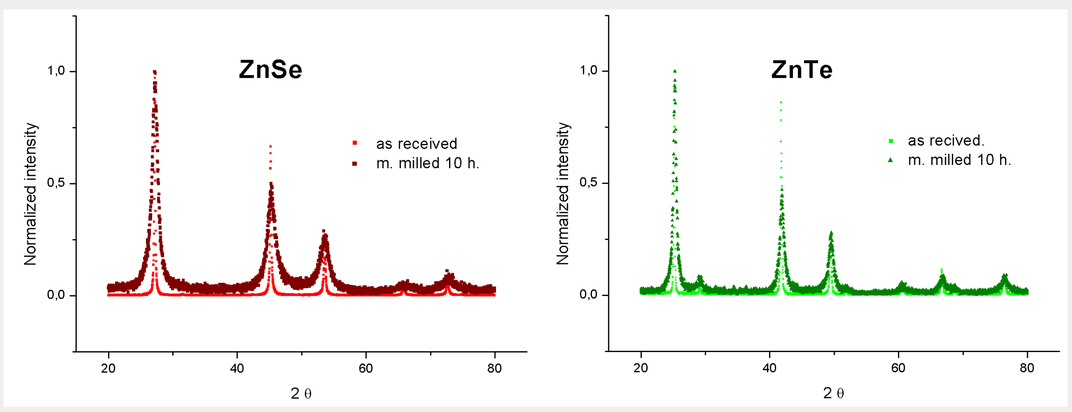

Figure: XRD patterns for *ZnSe* and *ZnTe* powders as received and after 10 hours of mechanical milling.

XAFS

The results were analyzed using the IFFEFIT software, with the Athena and Artemis implementation. This analysis shows, in a very preliminary way, that the distance of the first Zn neighbours do not change with milling time (see Figure 4).

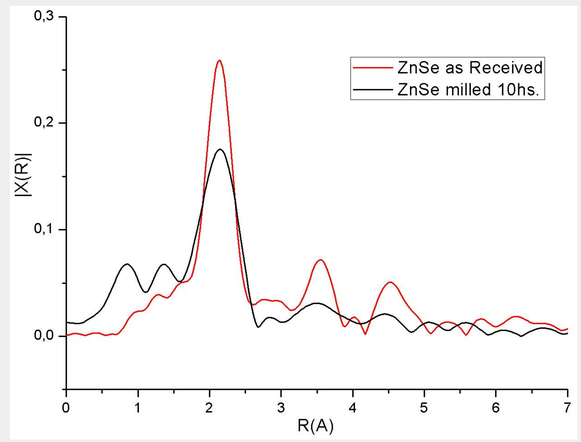

Figure: The effect of mechanical milling in the *ZnSe* sample.

Positron annihilation lifetime spectroscopy (PALS)

The lifetime spectra for this samples consist in various exponential decays:

$$n(t) = \sum_i I_i exp(-t \ / \ \tau_i)$$

being the relative intensities I_i , normalized. Obtained parameters from fitting procedure are shown in Table 1 together with calculations results, and are largely consistent with previous results.

Ab-initio calculations

It was used the implementation MIKA wich works within the framework of the two-component density functional theory (TCDFT) [4]. The positron annihilation rate is proportional to the electronic density at the positron and can be calculated from the overlap integral as

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

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.
To solve the electron and positron densities, a two-component generalization of the density functional theory (TCDFT) can be used. For the exchange-correlation energy, in this work we uses the approximations LDA (local density approximation) and GGA (generalised gradient approximation).

System	Milling Time (hs)	Lifetime PALS (ps)	Intensity (%)	Lifetime MIKA GGA (ps)	Lifetime MIKA LDA (ps)
ZnSe	0	229(7)	69,2(4)	250,25	233,42
	10	239(2)	72,6(4)	-	-
ZnTe	0	241(3)	65,9(2)	274,89	254,11
	10	257(3)	69,2(5)	-	-

Table 1: Experimental and calculated positron lifetime.

In summary

- From XRD measurements grain size reduction due to milling process was verified. The cubic structure is not modified with milling times.
- XAFS analysis confirm, in a preliminary way, that milling has no effects on *Zn* first neighbours distances.
- The trend of positron lifetime and intensity is to increase commensurate the milling time increases.
- Ab-initio calculations indicate that the LDA approximation matches better with PALS results, non the less, the GGA approximation shows the desired trend for both systems.

Future Work

- Complete the XAFS studies on ZnTe with Athena Implementation. Perform the fits with Artemis in all compounds.
- Increase the simulated cell size and incorporate dislocations and defects to represent the effects of milling.
- Incorporate dopants: ZnTe and ZnSe + In and Al, initially.
- Perform bandwidth measurements (GAP) and carrier density.

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