Mechanical milled doped Zn-based semiconductors powders for photovoltaic devices

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Introduction

It is known that solar cells efficiency may be improved by increasing charge carriers densities and interfacial processes. We are interested in nanomaterials, nanopowders and nanocolumns, prepared by low cost methods [1, 2] and its doping with donor elements.
Nanosized doped semiconductors were obtained by mechanical milling from metal oxides (In_2O_3) or the pure metal (In) [3] together with ZnO or $ZnTe$ as starting materials in adequate proportion to obtain the desired concentration.
Structural and optical characterization of doped powders by X-ray diffraction, X-ray Absorption Full Spectroscopy (XAFS), Scanning Electron Microscopy (SEM) and optical reflection spectroscopy were done. Undoped ZnO and ZnTe nanocrystalline powders prepared in a similar way were analyzed for comparison.

Experimental procedure

Sample preparation

- Starting materials:
  - ZnO (99.99%), In_2O_3 (99.9%) and In powders from Alfa Aesar (Johnson Matthey Co.)
  - $ZnTe$ (99.99%) from Aldrich Chemistry (Sigma-Aldrich Co.).
- Stoichiometric quantities were weighed to obtain mixtures of ZnO and $ZnTe$ with 5 at%, In_2O_3 and In.
- The mechanical milling was performed in a Retsch MM2 horizontal vibratory mill (with a frequency of 30 Hz) at different milling times.
- 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).
- *Scanning Electron Microscopy (SEM)* was done on a JSM-6300 (JEOL Scanning Microscopy) operating at 10kV, in the UPV (Valencia - Spain).
- *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).
- *Optical Reflection Spectroscopy* was measured with a Newport UV-VIS spectrophotometer in the 300-850 nm wavelength range at room temperature, in the UPV (Valencia - Spain).

Results and Discussion

XRD Measurements

The XRD patterns for the ZnTe powders, as received and milled 1h and 10h with In_2O_3 or In, are shown in Fig. 1 and 2. The diffractograms display the reflection lines of cubic $ZnTe$, in the samples of $ZnTe$ as received and after 10h of milling. Also show the broadening of the peaks (consequence of the grain size reduction). In the samples doped with In_2O_3, we can associate the new peaks with the reflection lines of cubic In_2O_3. There were no new peaks in the samples doped with In.

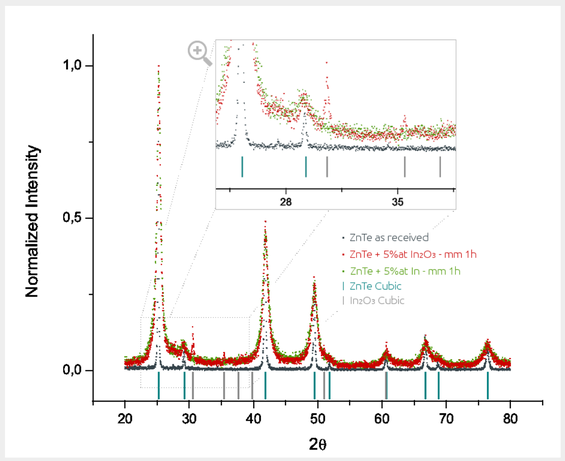

Figure: XRD for $ZnTe$ as received and after 1h of mechanical milling with In_2O_3 and In.

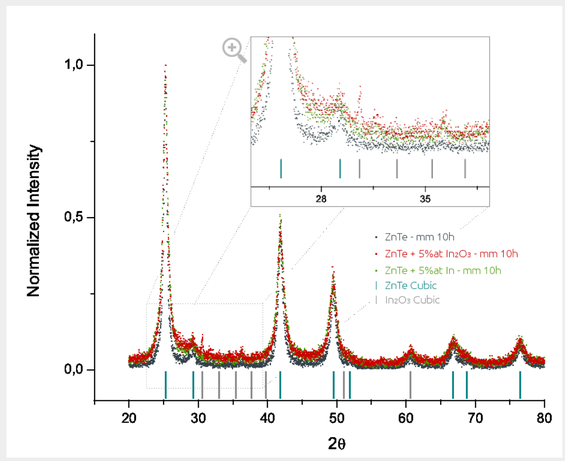

Figure: XRD for $ZnTe$ after 10h of mechanical milling alone and with In_2O_3 and In.

Scanning Electron Microscopy - SEM

The figures 3 and 4 shows the SEM micrograph for $ZnO + In_2O_3$ after 1h and 32h of milling.
As milling proceeds, grain size diminution and agglomeration are observed.
The presence of Fe atoms is evidenced from EDS analysis in those samples doped with In_2O_3.

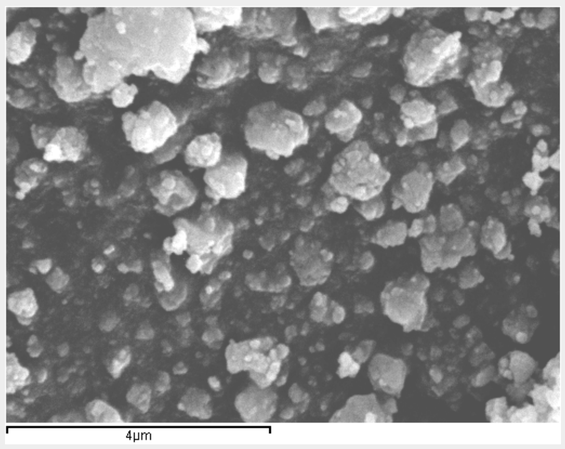

Figure: SEM micrograph of $ZnO + In_2O_3$ particles formed after **1h** of milling.

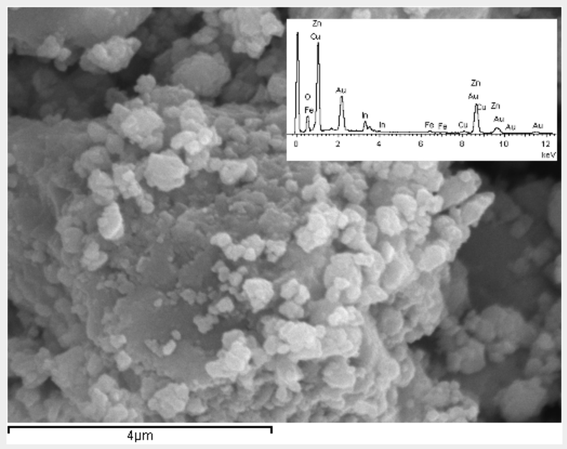

Figure: SEM micrograph of $ZnO + In_2O_3$ particles formed after **32h** of milling. Inset show EDS analysis.

XAFS

The results were analyzed using the IFFEFIT software, with the Athena implementation.
Figures 5 and 6 shows the effect of the dopants after 1h and 10h of mechanical milling.
Figures 7 and 8 shows the effect of the milling in the doped samples.
In a very preliminary way, we conclude that the distance from Zn to first neighbours do not change, neither with milling time nor with the addition of dopants.

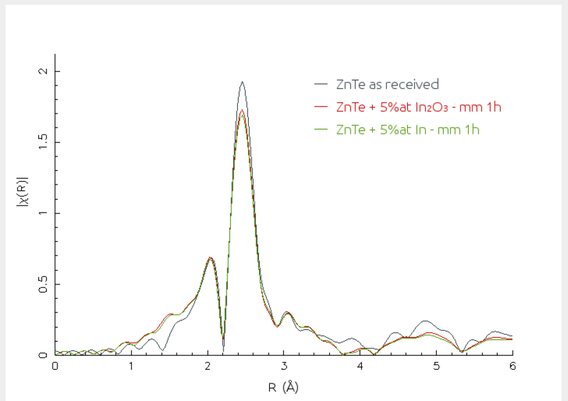

Figure: After 1h of mechanical milling, there is no difference in the effect of doping with In or In_2O_3.

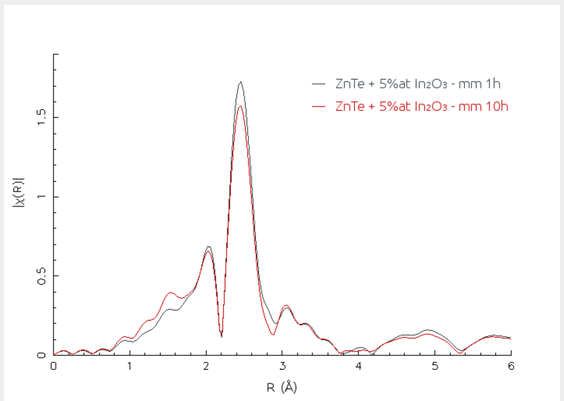

Figure: The effect of mechanical milling in the doped (In_2O_3) sample. Distances to first neighbours remains the same.

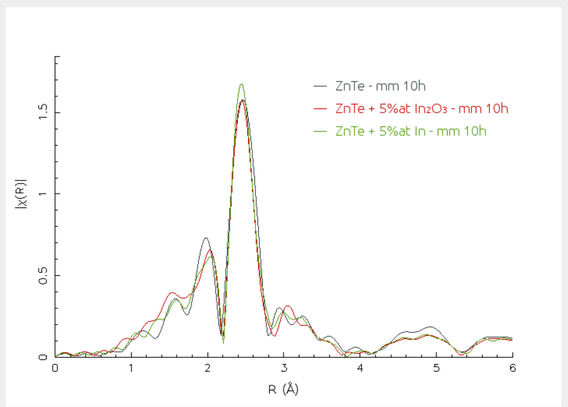

Figure: After 10h of m.m., we see a difference doping with In or In_2O_3, but distances to first neighbours remains the same.

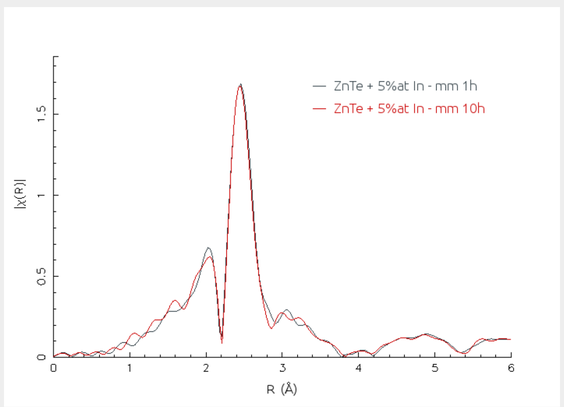

Figure: The effect of mechanical milling in the doped (In) sample. Distances to first neighbours remains the same.

Optical Reflection Spectroscopy

In figure 9 we present the results for severals samples of ZnO, doped and undoped.

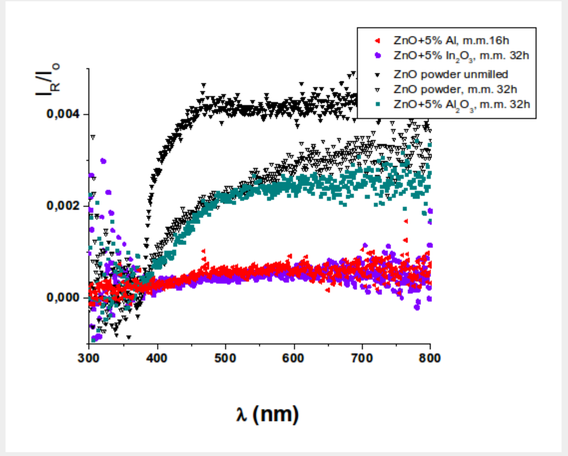

Figure: Reflection patterns for ZnO-doped samples.

- Reflection intensity is poor due to its powder character.
- Results obtained for pure ZnO, ZnO powder milled 32 hours and single crystal ZnO samples are included for comparison.
- The $In_2O_3 - ZnO$ samples after a prolonged milling time show a reduced reflectivity intensity and a change in its slope. A possible reason for this behaivour is, as it can be seen in the EDS analysis, that the $In_2O_3 - ZnO$ samples were contaminated with Fe from the milling tools.

In summary

- From XRD measurements grain size reduction due to milling process was verified. The cubic structure of $ZnTe$ is not modified with milling times. The reflection lines of cubic In_2O_3 appears in the $In_2O_3 - ZnTe$ diffractograms.
- SEM micrographs shows grain size reduction and agglomeration after 32h of milling. Fe contamination from milling tools in $In_2O_3 - ZnO$ samples is observed from EDS analysis.
- XAFS analysis confirm, in a preliminary way, that milling and doping has no effects on Zn first neighbours distances. Nonetheless, some differences can be appreciated at other distances.
- Optical reflectivity is a sensible technique to dopant incorporation and contamination.

Future Work

- Continue with the analysis of $ZnSe + In$.
- Incorporate Al as a dopant.
- Continue with the comparison between pure and doped ZnO.
- Perform MIKA's Supercell simulations.
- Determine the source of the contamination with Fe.
- Study the meaning of the In_2O_3 lines in the XRD spectrum.

References

[1] M. D. Reyes Tolosa, J. Orozco-Messana, L. C. Damonte, and M. A. Hernandez-Fenollosa.
Zno nanoestructured layers processing with morphology control by pulsed electrodeposition.
J. Electrochem. Soc., 158:D452–D455, 2011.

[2] J.Hoya, J.I.Laborde, and L.C. Damonte.
Structural characterization of mechanical milled znse and znte powders for photovoltaic devices.
International Journal of Hydrogen Energy, 37:14769–14772, 2012.

[3] L.C. Damonte, V. Donderis, S. Ferrari, M. Meyer, J. Orozco, and M.A. Hernández Fenollosa.
Zno-based nanocrystalline powders with applications in hybrid photovoltaic cells.
International Journal of Hydrogen Energy, 35:5834–5837, 2010.