



# Al-doped ZnO mechanical milled powders for dye sensitized cells

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## ABSTRACT

Mixtures of  $\text{Al}_2\text{O}_3$  and ZnO powders were prepared by mechanical milling. The resulting samples were analyzed and characterized by X-ray diffraction (XRD), positron annihilation lifetime spectroscopy (PALS), scanning electron microscopy (SEM) and optical reflection spectroscopy (OPS). XRD and PALS measurements confirm Al incorporation into ZnO wurtzite structure. Powders obtained from  $\text{Al}_2\text{O}_3$  precursors display better reflectivity than those prepared from Al metal so they might be better materials for implementation in photovoltaic solar devices.

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## 1. Introduction

In the last years, a growing interest in the development of cheap hybrid organic/inorganic photovoltaic cells consisting of a wide band gap semiconductor and conjugated polymer as sensitizer has been arisen [1–4]. It is proven that ZnO is an excellent material because of its good optical and electronic properties for the development of solar cells [5]; which can be improved by n-type doping with aluminium and indium [6,7]. Since semiconductor doping is not an easy task, a variety of methods have been tested such as electrodeposition, pulsed laser deposition, radio frequency magnetron sputtering, etc., for obtaining ZnO films and powders with different dopants [8–16]. In this study we present zinc oxide nanoparticles which optical and electrical properties have been modified by the  $\text{Al}_2\text{O}_3$  presence acting as small quantities of dopant using mechanical milling. Milling has been proved to be an effective and simple technique to produce nanocrystalline powders with the possibility of obtain large quantities of materials [17,18] and also as a method of doping [19]. The aim of this study is to improve the compatibility of both compounds present in the bulk heterojunction in blend films based photovoltaic solar cells. The phases formation depends on the initial conditions and enthalpy of phase's formation [17–20]. Fe-doped semiconductors were recently prepared by

mechanical milling starting from oxides and pure metal powders. These preliminary results [21] showed that ternary oxides of the form  $\text{Zn}_{1-x}\text{Fe}_x\text{O}$  can be obtained by this method. Also in a previous work [22], we have successfully obtained the ternary  $\text{Zn}_{1-x}\text{Al}_x\text{O}$  oxide using Al metal and ZnO as starting materials. Al is a trivalent dopant so it will be interesting to use its oxide as precursor and compare the obtained final product for both cases. Parameters such as initial concentrations, atmosphere and milling times were varied. Structural and optical characterization of ZnO-doped powders by X-ray diffraction (XRD), positron annihilation spectroscopy, scanning electron microscopy and optical reflection spectroscopy were done. Undoped ZnO nanocrystalline powders prepared in similar way were analyzed for comparison.

## 2. Experimental procedure

Stoichiometry quantities of commercially obtained ZnO powder (purity 99.99%) and  $\text{Al}_2\text{O}_3$  (purity 99.9%) powders from Alfa Aesar, Johnson Matthey Co; were used as starting materials to obtain samples with 5 at%  $\text{Al}_2\text{O}_3$ . The samples were milled in air atmosphere in a Retsch MM2 horizontal vibratory mill inside a steel cylinder ( $8\text{ cm}^3$ ) with one steel ball (diameter 10 mm). The milling frequency was maintained at 30 Hz while the milling time was varied from 1 to 32 h.

The resulting samples were characterized by X-ray diffraction carried out using a Philips PW 1710 with  $\text{Cu K}_\alpha$  radiation. Scanning electron microscopy (SEM) on a JSM-6300 (JEOL scanning microscopy) operating at 10 kV was used to characterize the morphology and composition of samples. The optical properties were analyzed using a Newport UV–vis spectrophotometer in the 300–850 nm wavelength range at room temperature. The milled powders were compacted under uniaxial pressure of 1.7 GPa into disk-shaped pellets (diameter 8 mm) in order to carry out positron annihilation lifetime (PALS) measurements. The PALS spectra were recorded using a conventional fast-fast coincidence system at room temperature with two scintilla-

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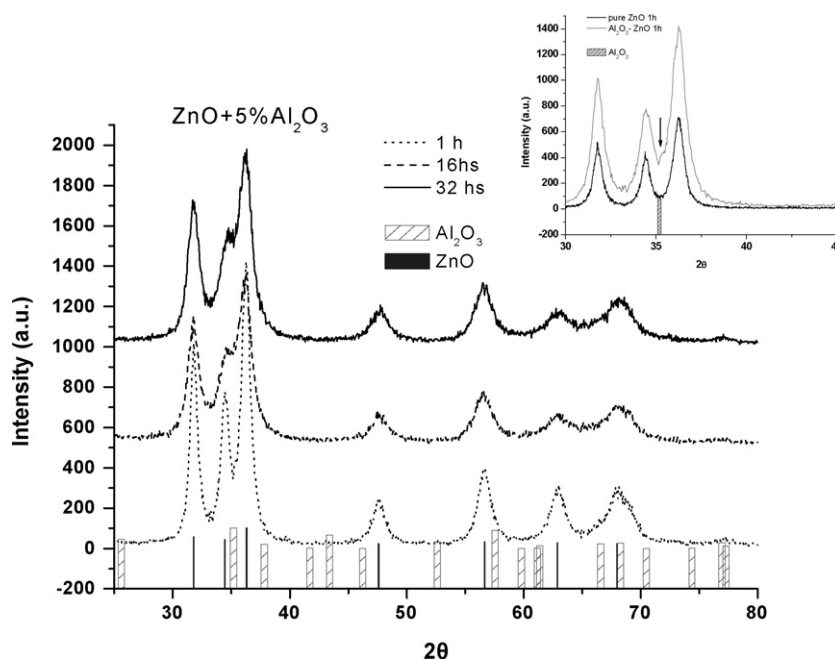


Fig. 1. XRD spectra for  $\text{Al}_2\text{O}_3$ -doped ZnO powders at various milling times. The inset shows the corresponding pattern for 1 h milled pure ZnO for comparison.

tors detectors (FWHM, 260 ps), acquiring  $3 \times 10^6$  counts at RT using the radioactive source of  $^{22}\text{NaCl}$  ( $10 \mu\text{Ci}$ ), onto a kapton foil ( $1.42 \text{ g/cm}^3$ ).

### 3. Results and discussions

#### 3.1. XRD and SEM

The incorporation of Al into the ZnO crystal network with increasing milling times was followed by X-ray diffraction. Fig. 1 displays the XRD reflections lines of the different samples after 1, 16 and 32 h of milling, showing mainly the hexagonal structure of ZnO (*P63mc*) and also the broadening of the peaks with increasing milling time due to grain size reduction. The inset in that figure shows the pattern for 1 h milled pure ZnO together with the 1 h  $\text{Al}_2\text{O}_3$ -doped ZnO in a different scale in order to appreciate the main alumina diffraction peak. For this sample the aluminum oxide diffraction peaks are slight seen, while for the other two samples no signal of this oxide is observed. Moreover, Rietveld refinements are in agreement with this assumption since when alumina oxide

phase is proposed for the two latest milling step, its percentage drop down. This fact can be considered as evidence of Al incorporation in the host material.

Scanning electron microscopy (SEM) was also performed. From the obtained images, shown in Fig. 2, as milling proceeds, grain size diminution and agglomeration are observed.

#### 3.2. Positron annihilation lifetime spectroscopy

The positron lifetime spectrum obtained is a multiexponential decay of the form:

$$f(t) = \sum_{i=1}^N \frac{I_i}{\tau_i \cdot \exp(-t/\tau_i)}$$

where  $N$  is the number of traps where the positron annihilates,  $\tau_i$  is the  $i$ th value of the positron lifetime and  $I_i$  is its corresponding intensity. Source contribution (20% of 386 ps) corresponding to positron annihilation onto the kapton foil and the response func-

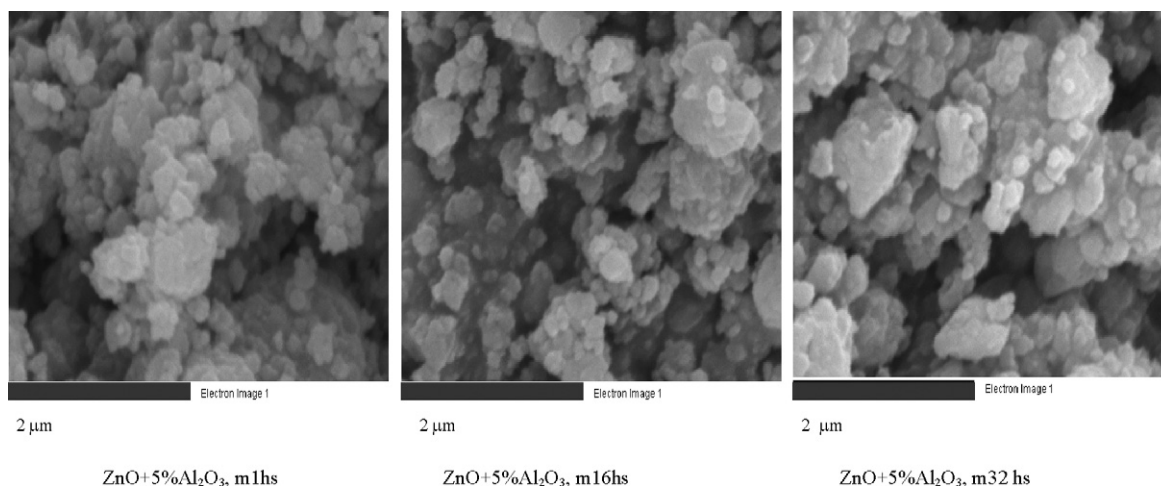


Fig. 2. SEM micrographs for Al-doped ZnO at increasing milling times: (a) 1 h, (b) 4 h and (c) 16 h.

**Table 1**

Positron annihilation parameters obtained after fitting procedure. Also included results from Refs. [18] and [22] for pure milled ZnO and mixtures of Al and ZnO, respectively.

| Sample                                    | $\tau_1$ (ps)    | $I_1$ (%)       | $\tau_2$ (ps)     | $I_2$ (%)       | $\tau_3$ (ns)    | $I_3$ (%)        |
|-------------------------------------------|------------------|-----------------|-------------------|-----------------|------------------|------------------|
| ZnO, as received                          | 158 <sub>7</sub> | 38 <sub>3</sub> | 343 <sub>6</sub>  | 61 <sub>3</sub> | 2.2 <sub>1</sub> | 1.4 <sub>1</sub> |
| ZnO, m.m.1 h                              | 193 <sub>9</sub> | 37 <sub>4</sub> | 357 <sub>8</sub>  | 61 <sub>4</sub> | 2.2 <sub>1</sub> | 1.4 <sub>1</sub> |
| ZnO+5%Al <sub>2</sub> O <sub>3</sub> 1 h  | 188 <sub>6</sub> | 55 <sub>5</sub> | 311 <sub>9</sub>  | 44 <sub>5</sub> | 1.5 <sub>2</sub> | 0.5 <sub>1</sub> |
| ZnO+5%Al <sub>2</sub> O <sub>3</sub> 16 h | 197 <sub>8</sub> | 58 <sub>8</sub> | 322 <sub>16</sub> | 40 <sub>8</sub> | 1.3 <sub>4</sub> | 0.4 <sub>1</sub> |
| ZnO+5%Al <sub>2</sub> O <sub>3</sub> 32 h | 199 <sub>6</sub> | 39 <sub>3</sub> | 362 <sub>6</sub>  | 60 <sub>3</sub> | 1.7 <sub>1</sub> | 0.5 <sub>1</sub> |
| ZnO+10%Al 1 h                             | 137 <sub>7</sub> | 20 <sub>2</sub> | 297 <sub>5</sub>  | 61 <sub>2</sub> | 1.1 <sub>1</sub> | 4 <sub>1</sub>   |
| ZnO+10%Al 4 h                             | 193 <sub>4</sub> | 45 <sub>2</sub> | 357 <sub>7</sub>  | 38 <sub>2</sub> | 1.7 <sub>1</sub> | 2 <sub>1</sub>   |
| ZnO+10%Al 16 h                            | 178 <sub>7</sub> | 37 <sub>3</sub> | 330 <sub>8</sub>  | 45 <sub>4</sub> | 1.6 <sub>1</sub> | 2 <sub>1</sub>   |

tion were evaluated from a Hf pure metal reference sample using the RESOLUTION code [6,7]. Fitting procedure with three different lifetime components yield good results. The obtained positron annihilation lifetime parameters are shown in Table 1, together with the corresponding ones for undoped ZnO milled powders [18] and Al-doped ones [22]. The longlive lifetime (around 1 ns with less than 1% of intensity) corresponds to positron annihilation in the surroundings of the source. The other two can be associated with positron annihilation in the sample itself. Semiconductor materials were characterized by the presence of two lifetime components usually assigned to bulk and vacancy-like defects even in pure single-crystals, due to the presence of certain native defects.

In the presence case, for short times of milling two positron annihilation lifetimes with different values and intensities than the corresponding ones to pure ZnO were observed. Since, from X-ray diffraction patterns, at this milling step both starting oxides are present, the annihilation lifetime  $\tau_1$ , in consequence, may take into account bulk annihilation in both starting oxides, ZnO and Al<sub>2</sub>O<sub>3</sub>, while the second observed lifetime, the presence of different point defects as interstitial atoms, vacancies, etc. in both crystalline structures. After 16 h of milling annihilation lifetime parameters for Al<sub>2</sub>O<sub>3</sub>-doped ZnO sample reach almost those parameters yielded for milled pure ZnO powder. Similar trends and in consequence similar statements were previously arises for other dopants as Mg, Cd and Al [19,22].

Since no monotonically evolution with milling time was observed for each lifetime component, the average lifetime defined by:

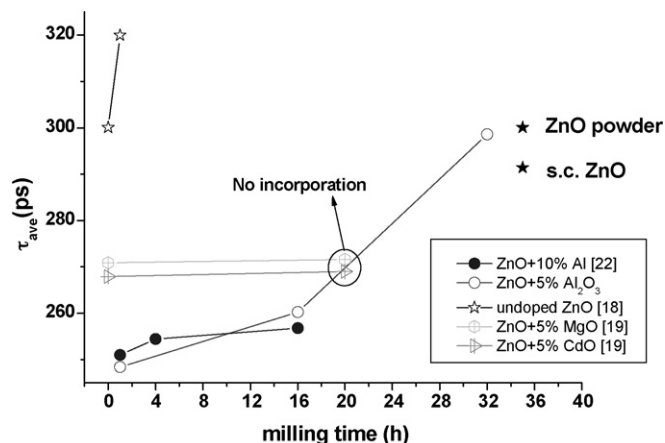
$$\tau_{ave} = \sum_{i=1}^N I_i \tau_i,$$

was evaluated in order to analyze the positron traps behaviour with milling time.

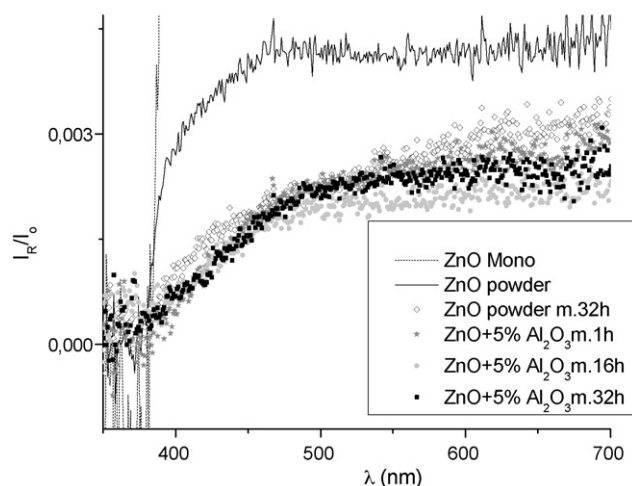
This evolution can be seen in Fig. 3 together with resulting values for pure ZnO powder. Previous results [22] on mixture of metallic Al powder with ZnO and other dopants [19] are also included for comparison. For the present case, it can be seen that  $\tau_{ave}$  has a similar value to the one corresponding to other oxides mixtures already reported. This means that when two oxides are present positrons sense almost similar electronic densities. After prolonged milling times, the value for  $\tau_{ave}$  increases up to reach a similar value to milled pure ZnO powder. This fact can be assumed as an evidence of dopant incorporation into the ZnO lattice.

### 3.3. Optical spectroscopy

The optical reflection spectra for the doped ZnO samples after different milling times are displayed in Fig. 4. The results for pure powder ZnO, ZnO powder milled 32 h and single crystal powders of ZnO are also included for comparison. The ZnO single crystal



**Fig. 3.** Average positron lifetime for different doped ZnO powders versus milling time.



**Fig. 4.** Optical reflectance for Al-doped ZnO and pure ZnO powders and single crystal.

sample shows the sharp absorption onset around 390 nm that is expected for intrinsic zinc oxide with good structural quality, but this shape and value changes for the milled powders samples. For undoped ZnO powder there still a sharp transition that diminishes its slope after 32 h of milling. As dopants are included the sample properties are modified since the absorption onset is no longer sharp. The doped powders are light yellow coloured, the intensity of their reflectivity is poor due to its milled powder character. No major difference is observed for doped powders with milling time, although a slight decrease in slope with respect milled pure ZnO can be appreciated. This means that light absorbed transitions increase as milling time decreases. Similar results with dopants incorporation were observed in a previous work for Al-doped ZnO powders, and also for films prepared by electrodeposition [22–24]. Comparing Al<sub>2</sub>O<sub>3</sub>-doped ZnO powders with Al-doped ZnO powders, those Al<sub>2</sub>O<sub>3</sub>-doped ZnO powders seems to have better reflectivity being, in principle, proper basic elements for the development of solar cells.

### 4. Conclusions

Ternary nanocrystalline oxides Zn<sub>1-x</sub>Al<sub>x</sub>O powders were efficiently obtained by mechanical milling from Al<sub>2</sub>O<sub>3</sub> and ZnO. As milling proceeds a clear reduction of grain size and homogenization is observed. X-ray diffraction reports the Al incorporation in

the wurtzite ZnO structure for either Al or Al<sub>2</sub>O<sub>3</sub> as starting materials. PALS measurements can also be an additional technique to probe dopant incorporation through the evaluation of the average lifetime parameter. The optical properties seem to be different; in the case of the aluminum oxide the powders have a better reflectivity. As a general conclusion, the powders obtained from mixture of ZnO and Al<sub>2</sub>O<sub>3</sub> may be the useful ones for photovoltaic solar devices.

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