

# **Evolution of the structural properties of sol-gel synthesized ZnO with solid phase and solution-based aluminum doping at different annealing temperatures.**

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## **Abstract**

We report here on the effect of aluminum doping and annealing temperature on the structural properties of ZnO, synthesized using the Sol Gel method. Aluminum doping was performed in two ways, either by adding AlCl<sub>3</sub> to the Zn solution or by mixing the obtained gel with Alumina prior to the annealing step. It was found that both methods of doping yield very similar results. Aluminum doping does not affect ZnO crystals dimensions for an annealing temperature of 500°C, while it induces a significant reduction in grain size, as well as the appearance of the ZnAl<sub>2</sub>O<sub>4</sub> spinel phase for annealing at 700°C and above. These results suggest that no ZnAl bonds are formed in the solution, when doping with AlCl<sub>3</sub>. Aluminum doping of ZnO yields a heterogeneous material if annealed at 500°C, while diffusion and subsequent alloy formation occur only at higher temperatures.

## **I. Introduction**

Zinc oxide is a II-VI semiconductor with very attractive mechanical, chemical, optical and electronic properties allowing it to be used in a wide range of technological applications. In particular, ZnO has a large band gap and hence a low absorption in the visible range. Increase in its electrical conductivity by doping allows it to be used as a window layer in solar cells and an active layer in thin film transistors [1]

Aluminum is the most extensively used n type dopant in ZnO. It allows to achieve high electrons concentration but also induces a reduction of crystals size and hence degrades carriers mobility. Despite the extensive research devoted to the subject, the exact mechanism of aluminum incorporation and its atomic environment in the ZnO matrix is still not fully understood.

In order to further understand Aluminum doping mechanism, we studied here the effect of Aluminum introduction on the grain size of SolGel synthesized ZnO nanocrystals. Both the Aluminum source and the

annealing temperature were varied in order to shed light onto its microscopic incorporation mechanism.

## **II. Experiment**

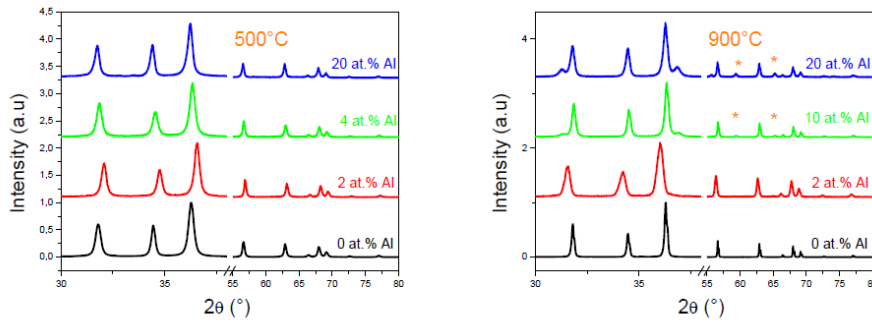
Nanocrystalline ZnO powder was prepared using the SolGel route. A first mix containing 0.5g of glacial acetic acid dissolved in 120ml of pure ethanol was added to a second solution of 25.05g of zinc acetate dihydrate dispersed in 120ml of distilled water. The two solutions were made to react for 5 hours at 50°C under continuous magnetic stirring. The gel was then heated at 80°C for a sufficient duration until it dried completely. Aluminum doping in the range of 0.5 at.% to 20 at.% was achieved either by adding AlCl<sub>3</sub> during magnetic stirring or by mixing the dried gel with nanometric Al<sub>2</sub>O<sub>3</sub> powder. Samples were then annealed at temperatures of ranging between 500°C and 900°C for 1 hour. It has been verified that organic phase was completely eliminated at 450°C and that the material reaches steady state in less than one hour.

The samples were characterized using X-ray diffraction in the q-2q configuration. Results were also confirmed using SEM, FTIR and Raman measurements (not shown here for the lack of space, will be presented in the final conference paper).

## **III. Results and discussion**

Figure 1 shows XRD patterns for pure ZnO as well as for samples doped using AlCl<sub>3</sub>, and annealed at 500°C and 900°C. Spectra from samples with Al<sub>2</sub>O<sub>3</sub> doping are very similar.

It could be seen that diffraction peaks are consistent with the wurtzite structure of ZnO. No amorphous ZnO peaks were observed, neither do we observe the characteristic peaks of carbonated impurities in our samples, indicating that our samples are fully crystallized and calcinated at these temperatures. For the samples annealed at 700°C (not shown here) and 900°C, and containing at least 10 at.%, of aluminum, additional XRD peaks are observed, which are ascribed to the ZnAl<sub>2</sub>O<sub>4</sub> spinel phase. No such peaks are observed for the samples annealed at 500°C.



**Figure 2 :** XRD patterns for ZnO samples doped with AlCl<sub>3</sub> and calcinated at 500°C and 900°C. ZnAl<sub>2</sub>O<sub>4</sub> peaks are highlighted with asterisks.

The grain size of undoped ZnO particles inferred from XRD data (not shown here) is found to increase monotonically with the annealing temperature, from about 30 nm at 500°C to 50 nm at a temperature of 900°C. SEM images of the samples also confirm that undoped ZnO is constituted of nanometric spherical particles, whose size increases monotonically with temperature. This behavior is expected from basic thermodynamic considerations, through defects curing and enhanced mobility at higher temperature. Grain size is also expected to increase above the densification threshold of 600° [2].

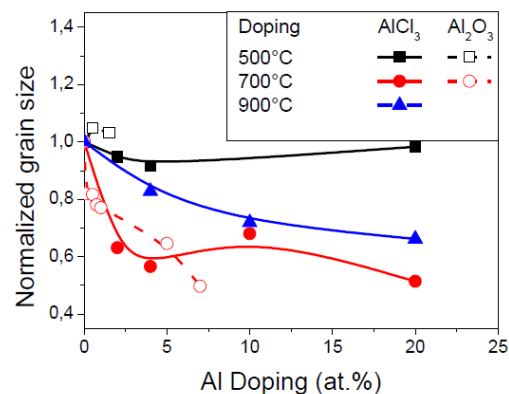
Figure 2 shows the evolution of nanoparticles size, normalized to the value of pure ZnO, as a function of doping for various annealing temperatures. One could observe that the two methods of doping, namely solution and solid phase doping, yield strikingly similar trends. No evolution of particles size with doping is observed when annealing at 500°C. On the other hand, particles size decreases sharply at 700°C and 900°C.

The similarity between the trends for the two doping methods suggests that no Zn Al bonds are directly formed in the solution when adding AlCl<sub>3</sub>. Calcination at 500°C induces the formation of a ZnO/AlO<sub>x</sub> biphasic material. Diffusion of metals seems to happen only at 700°C or above.

Aluminum solubility in ZnO is about 3 at.%. Beyond that doping concentration the ZnAl<sub>2</sub>O<sub>4</sub> spinel phase is commonly observed. The exact atomic environment of atomic Al incorporated in ZnO crystals is still

not fully understood, and a homogeneous (ZnO)<sub>3</sub>Al<sub>2</sub>O<sub>3</sub> phase has been proposed for the composite structure [3]. Aluminum doping is however known to reduce crystals size through the increase in defects

concentration and the reduction in precursor surface mobility [4]. This mechanism is clearly at play for the samples calcinated at 700°C and 900°C. ZnO crystals are on the other hand aluminum-free at 500°C and hence its size does not depend on the doping level.



**Figure 3** : Normalized grain size of ZnO crystals, for solid phase and solution doping, as a function of dopant concentration and annealing temperature.

#### IV. Conclusions

We have studied the effect of Aluminum doping using Al<sub>2</sub>O<sub>3</sub> incorporation both into the gel and AlCl<sub>3</sub>- based solution doping. It has been observed that Al doping does not affect ZnO grain size for a calcination temperature of 500°C, while a sharp decrease is seen when annealing at 700°C and 900°C, together with the apparition of the ZnAl<sub>2</sub>O<sub>4</sub> spinel phase. These results suggest that AlCl<sub>3</sub> doping occurs through the oxidation of Aluminum without the formation of ZnAl bonds. No diffusion is induced by annealing at 500°C and a heteroneous material constituted from pure ZnO crystals and Alumina is obtained. On the other hand, exposure to temperatures of 700°C or higher leads to the formation of doped ZnO nanocrystals, whose structural properties are extremely sensitive to the level of doping.

#### V. Références

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