

EARLY STAGES IN SOLID STATE REACTIONS: A STUDY

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ABSTRACT

Aim of the work is to show that fluorescence XAFS can be used as a tool for investigating the *initial* stages of solid state reactions, when local chemical equilibrium is not yet attained at the interfaces. A very classical solid state reaction, *i.e.* the formation of Zn-Al spinel starting from the parent oxides ($\text{ZnO} + \text{Al}_2\text{O}_3 \rightarrow \text{ZnAl}_2\text{O}_4$) has been investigated by monitoring the time evolution of the local chemical environment of Zn in a reacting ZnO thin layer, by means of Zn-K edge fluo-EXAFS. At 800 °C, a progressive evolution from a ZnO environment to a spinel environment has been obtained with increasing firing times. It can be shown that differently oriented Al_2O_3 single crystals show impressive different reactivity towards ZnO.

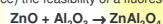
INTRODUCTION

Solid-state reactions are of extreme interest both for technological applications and from the point of view of basic science. For instance, almost all ceramic materials are obtained by this way, while reactions in the solid state occur in many geological processes. The kinetics and mechanisms of these reactions are typically studied with mono-dimensional chemical diffusion experiments on macroscopically thick layers. The theory underlying such experiments [1] assumes that in this regime local chemical equilibrium is attained at both interfaces (*i.e.* between each reagent phase and the product phase) as well as inside the product layer. In this approach, the agreement between the rate constant measured in this way and (independently measured) diffusion coefficients gives a reliable assessment of the reaction mechanism in the long time scale regime.

On the other hand, little is known about the very early stages, *i.e.* when the local chemical equilibrium is not yet attained at the interfaces and the chemical kinetics is not driven by long range diffusion.

To obtain some insights into these important aspects of solid state reactions, a local probe is needed. Here "local" should be intended as 1) capable of monitoring changes in the proximity of the interface between the reacting compounds; 2) sensitive to the local chemical environment, as required by the need of monitoring transient stages, when local chemical equilibrium is not yet attained.

In a recent experiment carried out at GILDA beamline (ESRF – Grenoble, France) the feasibility of a fluorescence Zn-K edge XAFS investigation on the very initial stages of solid state reaction:



of a 150 Å thick film of ZnO deposited onto Al_2O_3 single crystals (with different orientation has been investigated).

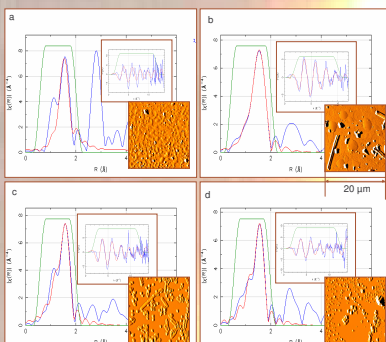
EXPERIMENTAL SECTION

Fluorescence EXAFS data were collected on the dedicated chamber operative at the GILDA beamline (ESRF – Grenoble, France). The monochromator was equipped with a Si(111) crystal pair and was run in dynamically focusing mode. The rejection of higher order harmonics was achieved by using a pair of Pt mirrors with an energy cutoff of 10 keV. X-ray fluorescence of the samples was measured by means of a thirteen elements Ge detector.

The samples were obtained according to the following protocol:

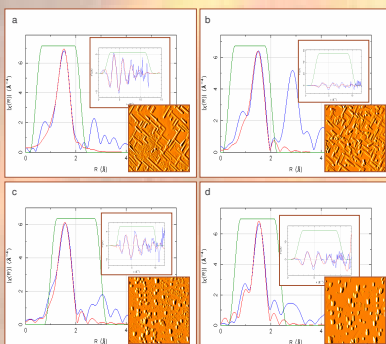
i) Sputtering in vacuum (10^{-4} mbar) and at room temperature of ZnO onto Al_2O_3 single crystals, having the following orientations: (11-20), (0001) and (1-102). The layer thickness was checked by X-ray reflectivity and resulted to be 150 Å. The chemical state of the layer was checked by X-ray diffraction and resulted to be ZnO.

ii) Firing of the ZnO layer with the substrate. The treatments were carried out at 300°C for 20 minutes and 800°C for different amount of time in air. For comparison purposes the EXAFS spectra in conventional transmission mode of ZnO and ZnAl_2O_4 powders were also collected.



Heating time (minutes) at 800 °C	Zn – O distance (Å)	Zn – O distance (Å)
20	1.82	2.01
40	1.80	2.05
60	1.77	2.00
120	1.71	1.99

Fig. 1 : Fourier Transforms of Zn K-edge EXAFS spectra of ZnO onto Al_2O_3 (0001) single crystal after different treatments: a) 800 °C for 20 minutes, b) 800 °C for 40 minutes, c) 800 °C for 60 minutes and d) 800 °C for 120 minutes. The blue lines represent the experimental data while the red lines represent the theoretical data. The insets show the Zn K-edge EXAFS spectra and the AFM images. The table shows the Zn-O distances for the first coordination shell (one short and three long bonds).



Heating time (minutes) at 800 °C	Zn – O distance (Å)	Zn – O distance (Å)
20	1.80	2.04
40	1.79	2.01
60	1.80	2.09
120	1.79	2.05

Fig. 2 : Fourier Transforms of Zn K-edge EXAFS spectra of ZnO onto Al_2O_3 (1-102) single crystal after different treatments: a) 800 °C for 20 minutes, b) 800 °C for 40 minutes, c) 800 °C for 60 minutes and d) 800 °C for 120 minutes. The blue lines represent the experimental data while the red lines represent the theoretical data. The insets show the Zn K-edge EXAFS spectra and the AFM images. The table shows the Zn-O distances for the first coordination shell (one short and three long bonds).

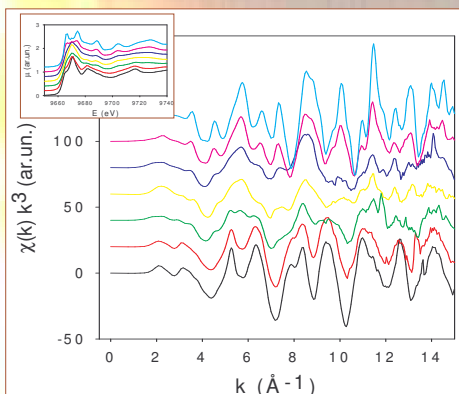


Fig. 3: Zn K-edge EXAFS spectra of ZnO onto Al_2O_3 (11-20) single crystal after different treatments. For comparison purposes the figure also shows the spectra of ZnO and ZnAl_2O_4 powders. The insets shows the Zn K-edge XANES spectra.

CONCLUSIONS

The most striking result that can be easily observed looking at figures 1 – 3 is that differently oriented Al_2O_3 single crystals show impressive different reactivity towards ZnO. In particular:

- (11-20) orientation: at 800 °C the spinel is formed and the amount of spinel increases with time, the sample appearing almost totally reacted after 2 hours at 800 °C.
- (0001) orientation: at 800 °C a chemical reaction takes place, the product of which is different from both the spinel and ZnO. At the moment the chemical nature of this product has been not yet identified but the local coordination of Zn is almost identical to that of the wurtzite phase of ZnO. In addition EDS analyses on the crystals shown in Figures 1 and 2 evidenced the presence of Zn and O only. Therefore we can speculate that in this case a new crystal phase of ZnO is formed.
- (1-102) orientation: the behaviour of this orientation is strongly resembling of that previously described for the (0001) orientation.
- In addition, linear dichroism measurements at the Zn K-edge for the samples treated at 300°C showed that the ZnO thin film is highly oriented when deposited onto Al_2O_3 (11-20) and (0001) surfaces (the orientation of the film is with the c-axis of the wurtzite crystal structure perpendicular to the surface), while onto the Al_2O_3 (1-102) surface a polycrystalline film is formed.

REFERENCES

- 1) H. Schmalzried, *Solid State Reactions* Verlag Chemie ed. 1981.