	Experiment title:	Experiment number:
	Experiment title: Role of texturation and hybridization of the Ce 4f states on the luminescence of ZnAl2O4 undoped and doped with Ce, Nd films on poly and monocrystalline Al2O3	**Experiment number**: 25-02-1012
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Report:

$ZnAl_2O_4$ spinel compound has been extensively studied and used in different applications such as catalytic support or as active material for automobile catalysis, as a transparent conductive oxide, sintering aid and as photo-catalytic material. Among its multiple applications as pure material, the employment of dopants gives a variety of functional properties[1]. Besides, $ZnAl_2O_4$ is an appropriate host for luminescence due to the transparency to wavelengths > 320 nm, that promotes its use in lighting, optoelectronic devices or electroluminescent displays. $ZnAl_2O_4$, also called gahnite, has a spinel structure belonging to Fd3m space group and can have a direct or an inverse structure. Recent investigations showed blue and white luminescence in the pure phase[5–7]. However, there is a lack of evidence of which defect centers are the responsible of the emission of the pure matrix. This reason encourages us to an in-depth correlation between the structural characteristic and the luminescence properties. Here, $ZnAl_2O_4$ undoped in air atmosphere films were obtained by screen printing route over sapphire subtrates with different orientation c and a-plane. The modulation of the luminescence emission on $ZnAl_2O_4$ oriented films is a challenge in the science community. The results obtained by using conventional XRD employing a 1D detector show that the films are preferential oriented. Th XRD analysis and omega and beta scan that shows the preferred orientation of the films. However, the understanding of the azimuthal intensity distributions and Debey –Sherrer rings of 111, 422 plane of the spinel by GI-XRD studies can draw conclusions about preferred orientation as a function of the substrate and synthesis temperature.

Over the past decades, the focus has been on development of epitaxial layers using complex methods. But we wanted to depomnstrate that epitaxial growth is posiible by empoying a cost-efficient route such as screen printing process.

This experiment was performed at the SpLine beamline BM25 at the European Synchrotron Radiation Facility (ESRF) in Grenoble. An incidence angle of the illuminating x-rays of 0.5◦ sufficiently suppresses strong scattering by the substrate, and thus makes this method highly surface sensitive. A primary x-ray photon energy of 25 keV enables the inspection of a comparatively large area in reciprocal space, which is important to probe also multiple reflections of the same lattice plane family. Six samples were measured during the beamtime, five of them were grown in c-cut and one in a- cut sapphire subtrates obtained at 1200 and 1300 ºC and with different thickness.

The main challenge found during the beamtime was to obtain the orientation matrix of the a-cut sapphire. For this reason, it was not posisble to measure all the samples expected. It is essential to study the microstructures of epitaxially grown materials; to characterize the dislocations and defects, which are essential issues for the application of materials in device fabrication.

By modulating the processing parameters, the thickness is adjusted and different growth is obtained. SEM micrographs of the $ZnAl_2O_4$ films deposited on c- plane substrate by modulating the thickness showed that by changing the temperature of the anealing and the thickness of the film it is possible to obtain epitaxial nano structures on the surface and when the thickness is higher these nanostructures are not present. The prominent structures are aligned in three specific in-plane directions with an angle of 120° between.

Figure 1a-d shows SEM micrographs of the $ZnAl_2O_4$ films deposited on c- plane substrate by modulating the thickness. Figure 1a exhibits the cross section and Figure 1b top surface of the films that have nanoblades on the top. We have observed prominent structures with a linear appearance with a high secondary electron contrast, aligned in three specific in-plane directions with an angle of 120° between them, designated as nanoblades. The symmetric distribution of these microstructures with a three-fold symmetry suggests an epitaxial relationship to the hexagonal sapphire c-plane substrate. The microstructure of the deposited layer is strongly affected by the thickness obtained. Figure 1c shows the cross section of the film that has higher thickness, the nanoblades are gone but there is a slightly faceting on the film. Figure 1d shows intial symmetric structures, some of which appear to be in an intermediate stage of transformation support. However further studies are needed to establish the main factor that causes the presence of the three-fold symmetric line structures.

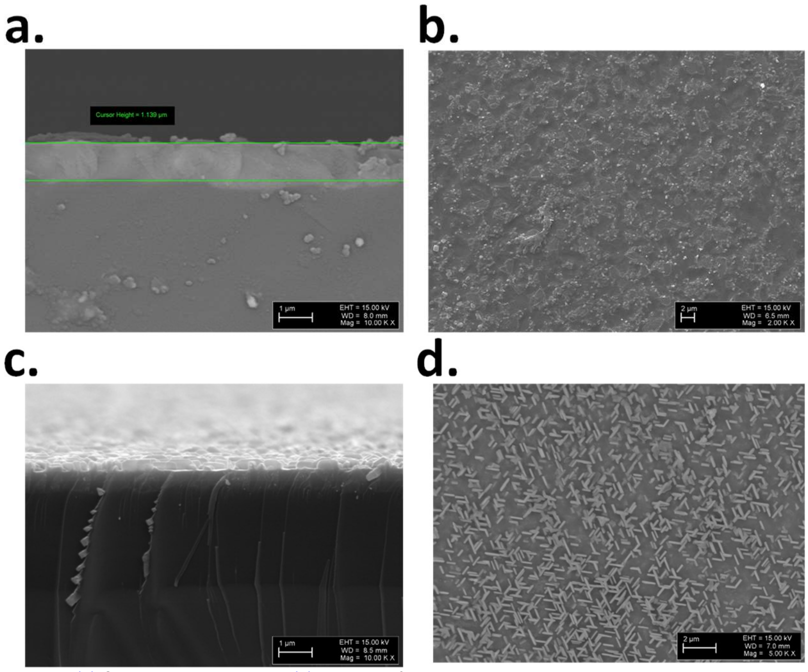

Figure 1. FE-SEM micrographs of the films grown: (a) Cross- section view and (b) top view of the layer grown on c-plane sapphire substrate with nanoblades on the top showing three-fold symmetric microstructures. (c) Cross- section view and and (b) top view $ZnAl_2O_4$ layer grown on c-plane with higher thickness and without nanoblades on the top.

Figure 2 shows the L-H RSMs for $ZnAl_2O_4$ layer grown on c-plane sapphire substrate. (a) RSM maps is related to a film that show nanoblades on the top and the (b) RMS maps belong to a film that has no nanoblades. These preliminary RSM results showed that an incommensurate growth based on the non-coincidence of the spinel layers and the c-cut sapphire.

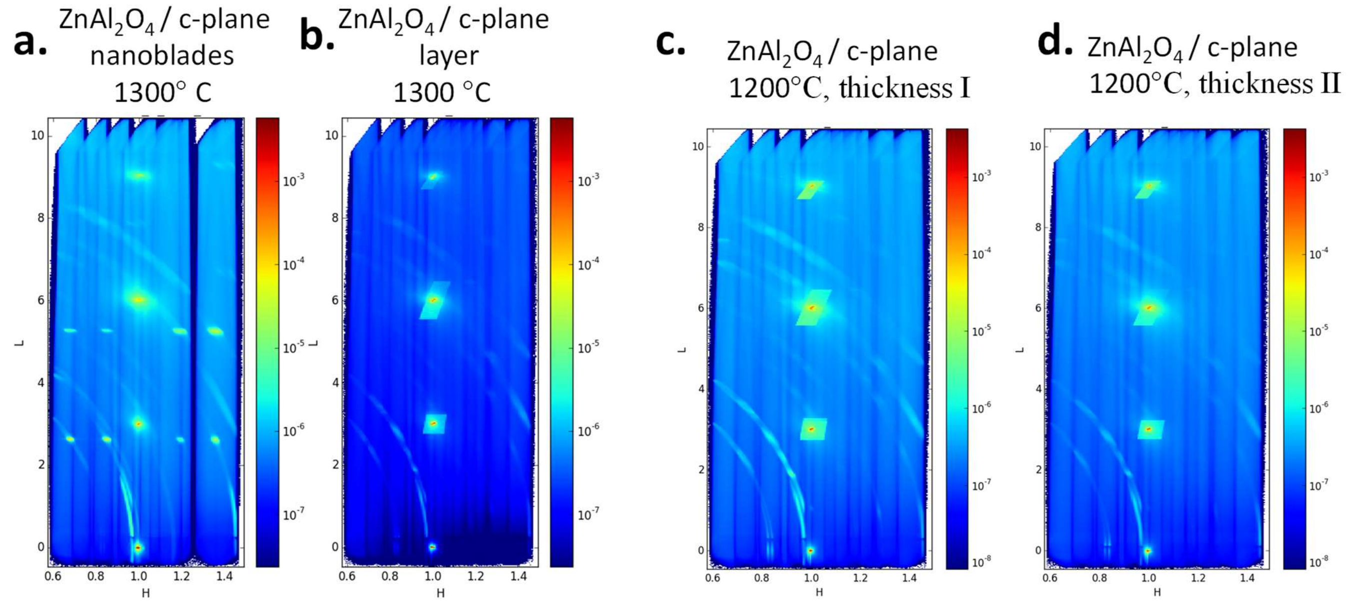

Figure 2. (a) RSMs for a film grown over a c-cut sapphire that has nanoblades on the top and (b) the film that has no nanoblades that have been synthesized at 1300 ºC . (c-d) And the films obtained with two different thickness at 1200 ºC The axes are in reciprocal lattice units of the substrate (1 r.l.u.= 2π/4,758 ˚A).

Regarding the films synthesized at 1200 ºC, the films shows certain degree of mosaicity and the out of planes scan at high angle reflectivity reveals a prefrential orientation of the planes 111 and 422.

HR-TEM studies were done of the Focused Ion Beam (FIB) prepared sample correlate the twinning relationships. We are trying to understand the epitaxial relationships of the twin boundary of the zinc aluminate grain with the surface is a line parallel to the sapphire.

Theoretically, the lattice structures of the spinel layer on the C-plane has a less matching mismatch meanwhile the a-plane has no such similar symmetry relationship. However the RSM of the a-plane shows a coincidence of the in-plane diffraction peak as in show in Figure 3a-b; but further studies are needed to clarify the growth and correlate the luminescence characterization employing the a and r- cut.

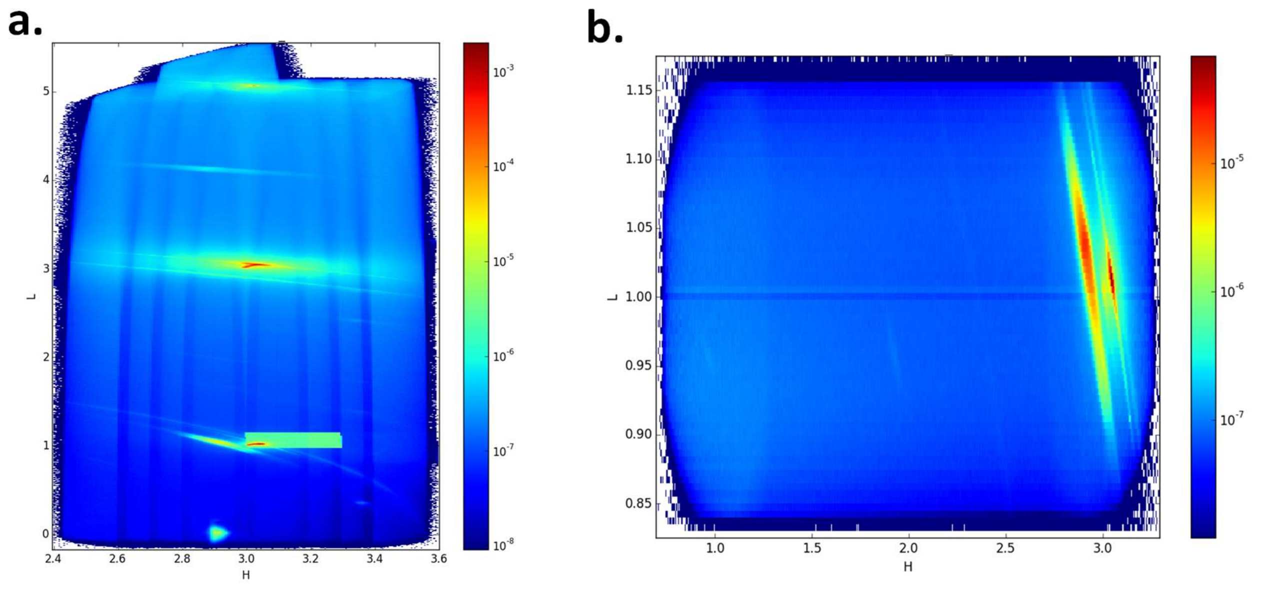

Figure 2. (a) RSMs for a film grown over a a-cut sapphire obtained at 1200 ºC The axes are in reciprocal lattice units of the substrate (1 r.l.u.= 2π/4,758 ˚A)