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Characterization of geometrically frustrated $Zn_{1-x}Mn_xAl_2O_4$ thin films prepared by Metalorganic Aerosol Deposition

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Abstract. We present the results on the structure and magnetoelectric properties of $Zn_{1-x}Mn_xAl_2O_4$ thin films ($0 \leq x \leq 1$), prepared by metalorganic aerosol deposition (MAD) technique. The films have been grown epitaxially on MgO(100) substrates and characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis (EDX), magnetization, electron paramagnetic resonance (EPR) and capacitance as a function of temperature and magnetic field. For large x values ($x = 0.75$ and 1), we observed a deviation of the magnetization from a Curie-Weiss law below 40K, indicating the expected magnetic ordering of the spinel. In the proximity of this magnetic characteristic temperature the capacitance as a function of temperature shows a peak, which infers a multiferroic character of these spinels.

1. Introduction

In the geometrically frustrated magnets the spins are located in a well defined lattice, but the geometric constraints make an antiferromagnetic arrangement of spins impossible. Recently, these materials have been proposed to show a multiferroic behavior[1,2] with the coexistence and coupling between ferroelectric and magnetic order parameters. This is manifested, on one hand, by an anomaly in the static dielectric constant at magnetic phase transition. On the other hand, a magnetization in an insulating oxide can be induced by long-range ferroelectric ordering. The spontaneous electric polarization frequently appears when inversion symmetry is broken by magnetic order. This often takes place in so-called frustrated magnets, where competing interactions between spins favor unconventional magnetic orders. Microscopic mechanisms of magnetically induced ferroelectricity due to: 1) polarization of electronic orbitals and 2) relative displacement of ions in response to magnetic ordering is a subject of actual debate.

In the cubic spinel oxides with AB_2O_4 stoichiometry, the transition metal ions (A and B) occupy tetrahedrally and octahedrally coordinated sites, respectively. While the $ZnAl_2O_4$ is a non magnetic insulator, the $MnAl_2O_4$ is a geometrically frustrated ferrimagnet with Mn ions forming a geometrically frustrated corner-sharing tetrahedral network (3D). The dominating

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interaction between the Mn^{2+} (S=5/2) ions is antiferromagnetic, resulting a phase transition with a Neel temperature of T_N=40K[3].

2. Experimental, structural and morphological characterization

Thin films were prepared by means of MAD technique[4]. The aerosol of the precursor solution is generated by a pneumatic nozzle, which produces the drops with a mean diameter of approximately 20 μm at characteristic gas flows of about 10-15 l/min. By means of a carrier gas (dry air) aerosol flux is transferred into the reaction zone where a substrate is placed on a resistive polycrystalline SiC heater. The deposition temperature is controlled by a double-wavelength pyrometer. To grow the films we used a 0.02 M solution of metal organic precursors: acetylacetonates (AA) of Mn^{2+}, Zn^{2+} and Al^{3+} with a desired stoichiometric ratio in dymetylformamide. The substrates were freshly cleaved single-crystalline plates of MgO (100). The films were deposited at ambient atmosphere conditions, substrate temperature of T_s=1050 °C, and deposition rate of 60 nm/min. After deposition, films were cooled down to room temperature in 40 min. They looked smooth and shiny and do not contain any defects, as observed by optic microscopy.

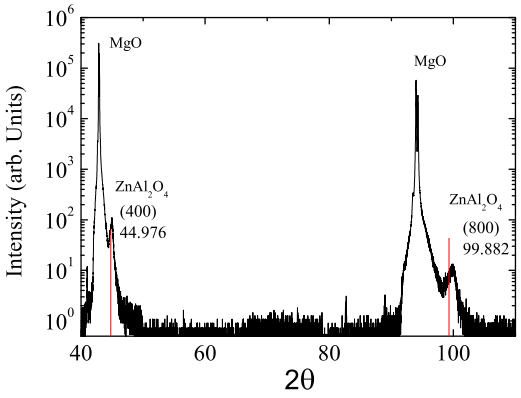


Figure 1. X-ray diffraction pattern of the x =0 thin film. The principal contributions are the MgO reflections and the secondary broad peaks correspond to the spinel.

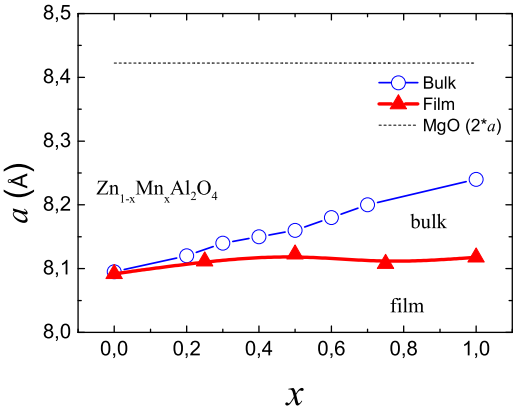


Figure 2. Lattice parameters of the synthesized films comparing with bulk results of Ref.[5]. The (- - - -) indicates the double of the MgO lattice parameter ($2{\cdot}a$)

The structure of the films was characterized by XRD analysis, (θ-2θ patterns and rocking curves), performed by means of Siemens D-5000 diffractometer with Cu K_α radiation and graphite monochromator. The XRD 2θ scans, between 40° to 110°, show two principal peaks that correspond to the (200) and (400) reflections of the MgO, both with the $K_{\alpha 1}$ and $K_{\alpha 2}$ structure. Two weak extra peaks (see Fig. 1), are assigned to the (400) and (800) reflections of the $Fd\bar{3}m$ cubic $ZnAl_2O_4$ phase. In Fig. 2 we show the obtained lattice parameter for all the $Zn_{1-x}Mn_xAl_2O_4$ series as a function of x and compared them whith those reported for the bulk[5] and the doubled lattice parameter of the MgO($2a_{MgO}$). The lattice parameter of the films differ from the bulk values and it is expected to be due to the substrate-film mismatch stress, which can be estimated as: $\varepsilon = (2a_{MgO} - a_{ZnAlO_4})/2a_{MgO}$=3.8 - 2 %. No extra diffraction peaks from impurity phases or randomly oriented grains were detected in the diffractograms, indicating that the films are single phased and out-of-plane oriented. The electron paramagnetic resonance (EPR) spectra of the Mn for the film with x =0.75 show three extra lines in addition

to those observed for a Mn^{2+} impurities in the MgO substrate. We associate the extra EPR lines in the films with Mn^{2+} in the spinel structure. The angular dependence of these extra lines confirms that the films grow epitaxially.

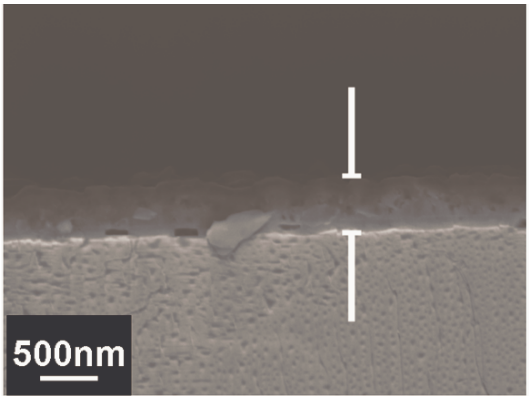


Figure 3. SEM image of the cross-section in the x=1 sample. The marks show the film thickness (≈ 450 nm).

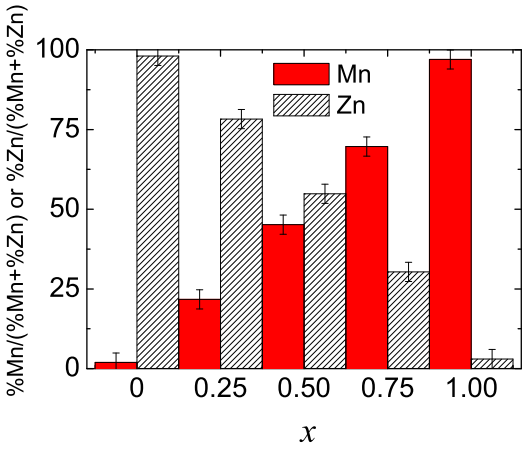


Figure 4. EDX analysis showing the expected composition for each x.

The cross-section of the samples were observed by SEM (i.e. see Fig. 3) and we obtained the films have a thickness between 300 and 450 nm. The EDX spectra, taken at different surface positions show the homogeneous metal composition. In Fig. 4 the relative composition ratio Mn/Zn is shown, which follows the nominal composition for each sample.

3. Magnetic and electrical capacity characterization

The dc magnetization was measured with a commercial superconducting quantum interference device magnetometer in the temperature range 5- 300 K and H up to 50 kOe. The temperature variation of the magnetization (M) was taken at a magnetic field of H = 10 kOe. The data show a significant temperature independent diamagnetic contribution due to MgO substrate. To determine these constant contribution we plot M·T vs T (see inset Fig. 5) and took the negative slope value -4.83 10^{-4} (emu) at high temperature and subtract it from the experimental magnetization data. As a result we calculate the magnetic susceptibility as the ratio χ= M/H (normalized by magnetic field and film area) as it is shown in Fig. 5. The χ(T) looks like a Curie-Weiss curve with some deviations at low temperature. The remaining curve reflects only the behavior below 40K. At this temperature a magnetic order in the sample sets in in agreement with the reported Neel temperature for the bulk spinels of the same composition.

For the electrical capacity experiments we deposit the spinel films onto a high conductivity manganite films, which were grown previously with the same MAD technique. On the spinel surface we deposited two gold electrodes separated by 10 μm. Between these contacts we measured. The electrical capacity was measured between these Au electrodes at f =1 kHz with an Andeen-Hagerling 2500A ultra high precision capacitance bridge, using a commercial He cryostat in a temperature range, T=5-400 K and applied magnetic fields (H) up to 50 kOe. In Fig. 6 we present a C(T) dependence at H=10 kOe, measured by warming up the sample. A peak at about 40 K is clearly seen; it corresponds to the magnetic ordering temperature.

4. Conclusions

We prepared epitaxial thin films of the geometrically frustrated $Zn_{1-x}Mn_xAl_2O_4$ with the thickness between 300 and 450 nm and Mn content in the range $0 \leq x \leq 1$. For samples with high

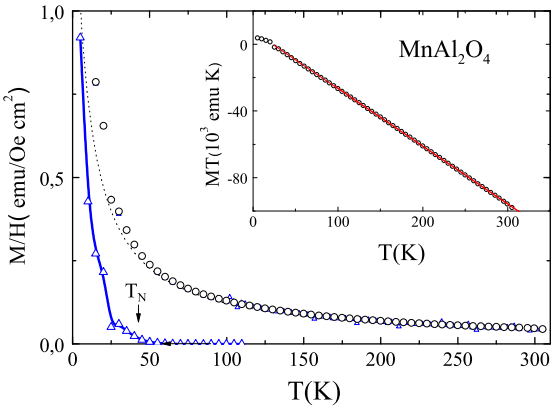


Figure 5. Magnetic properties of x=1 sample at H = 10 kOe. Inset: The negative slope of the M·T vs T plot is the diamagnetic contribution. (○): M/H vs T data after the diamagnetism subtraction. (△): deviation of the Curie-Weiss law below T_N.

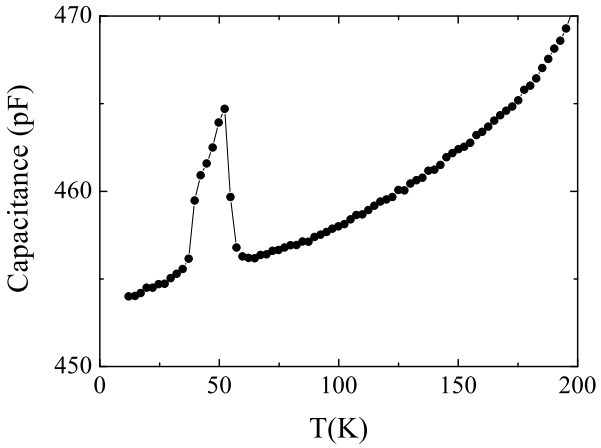


Figure 6. Electrical capacity as a function of temperature of x=0.75 sample at H = 0 kOe. The base of the peak is between 38K and 58K with a maximum at 52K.

Mn content, i.e. x= 0.75 and x =1, we observed an anomalous behavior in electrical capacity with a peak at 52K and a width about 20K. As magnetic ordering was also observed in the same temperature region, we interpret these capacity and magnetization features within a multiferroic behavior, which seems to be relevant for these geometrically frustrated and Mn-reach spinel.

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