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Room temperature charge-ordered phase in $Gd_{0.6}Ca_{0.4}MnO_3$ and $Sm_{0.6}Ca_{0.4}MnO_3$ thin films

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ABSTRACT

We have grown rarely studied Gd_{1-x} Ca_xMnO_3 (GCMO) and $Sm_{1-x}Ca_xMnO_3$ (SCMO) thin films on $SrTiO_3$ (100) single crystal substrates with pulsed laser deposition in order to optimize the magnetic and structural properties for e.g. memristor-like applications. To enable the Mott insulator to metal transition with practicable external stimulus, the previously unstudied $x = 0.4$ doping was chosen. The deposition temperature was 500 °C or 700 °C and the oxygen post-annealing was done *in situ* at 500 °C or 700 °C. All the films were fully textured and (0*b*0) oriented, but the ones made at 700 °C had better crystalline quality. For the same pulse amounts, GCMO films were clearly thinner than the SCMO films. Magnetically, all the films showed a charge/orbital order phase transition around 360 K and a ferrimagnetic transition around 70 K. The saturation magnetization at 10 K was highest in the films deposited and oxygen annealed at 700 °C. The samples deposited and annealed at 500 °C contained an unknown ferromagnetic impurity, which was invisible in structural characterization and not observed in the other samples. The samples made at 700 °C had a hysteretic $I(V)$-curves typical for materials used in memristors.

1. Introduction

All the doped manganites have phase diagrams with several different phases ranging from canted antiferromagnets ($Pr_{1-x}Ca_xMnO_3$, PCMO, with $x = 0.1$) to ferromagnetic metallic phases ($La_{1-x}Ca_xMnO_3$, LCMO, with $x = 0.3$) [1]. The properties depend greatly on the ionic sizes of the rare-earth metals and the dopant. The distortion is quantified with the Goldschmidt tolerance factor [2]. The more the lattice distorts from the cubic perovskite structure, the lower is the one electron bandwidth and with decreasing bandwidth the manganites turn from metals to insulators. For $Gd_{1-x}Ca_xMnO_3$ (GCMO) and $Sm_{1-x}Ca_xMnO_3$ (SCMO) the tolerance factors vary between 0.904–0.977 and 0.912–0.977, depending on the calsium doping, respectively. These tolerance factors are clearly smaller than for example in LCMO. In bulk, both GCMO and SCMO have orthorhombic crystal structures at room temperature.

Even though low bandwidth manganites are insulators in the ground state, a transition to a metallic phase (MIT) can be induced with external stimuli such as magnetic or electric field, light, pressure etc [3–5]. In the MIT, the resistivity can decrease by several orders of magnitude [3]. Low bandwidth manganites also possess an insulating charge- and orbital ordered state (CO/OO-state) at high temperature, where the current carriers are localized in a chequerboard like order [1]. This ordered state can also be destroyed by external stimuli. The upper transition temperature of the CO/OO-state, T_{co}, increases with decreasing bandwidth, which means that in GCMO and SCMO T_{co} is above room temperature enabling potential applications at room temperature.

The low bandwidth manganites have possible applications in e.g. resistive switching (memristors). So far mostly PCMO with $x = 0.3$ has been used [6]. Although most memristors work with filament like conducting paths [7], the PCMO memristors work by oxidating the metal contact interface [8]. Since both mechanisms work by physical movement of ions, there has been some doubt in the endurance of the devices [9]. It would be more beneficial to use real Mott MIT transition, where the electrons are released into the conduction band. To have a room temperature device, the material needs to have an electron correlated state at room temperature. This could be the CO/OO-state of GCMO or SCMO.

The growth of manganite thin films is commonly done with pulsed laser deposition, which allows easy control of the deposition parameters, such as substrate temperature, deposition atmosphere and laser energy. For most materials the parameters have to be optimized on a case-by-case basis, specially the substrate temperature and possible post-annealing treatments. We have pre-

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viously optimized the deposition of $Pr_{1-x}Ca_xMnO_3$ (PCMO) thin films [10], which have a very similar structure to GCMO and SCMO films. PCMO films can be deposited at the quite low temperature of 500 °C, which is advantageous considering potential applications. So far the reports on either SCMO or GCMO films have been scarce. Some reports on SCMO with $x = 0.3$ or $x = 0.5$ have been published [11–14] where the interesting properties of low bandwidth manganites have mostly been observed. On the other hand, the deposition process has not been varied, but the parameters optimized for other manganites have been used. We have found only one report on GCMO ($x = 0.5$) film [15], where the structural properties were not studied. Therefore, a systematic study of deposition parameters and their effect on film properties is called for.

In $Pr_{1-x}Ca_xMnO_3$ (PCMO) thin films the most interesting properties have been observed with $x = 0.4$. These include e.g. a metamagnetic transition at a clearly lower magnetic field than in bulk [16] and photoinduced change in the MIT field [3]. The doping $x = 0.4$ is slightly off the strongest CO/OO-state, thus enabling MIT at magnetic fields reachable in the laboratory [3]. Therefore, we chose the $x = 0.4$ doping for our GCMO and SCMO films. In addition to the doping, also oxygen content has a non-neglible effect on the properties of the thin films.

In this work, we have deposited GCMO and SCMO ($x = 0.4$) thin films on $SrTiO_3$ (100) single crystal substrates with pulsed laser ablation in order to optimize the magnetic and structural properties for e.g. memristor-like applications. We carefully study the structural and magnetic properties with X-ray diffraction (XRD), X-ray reflectivity (XRR) and SQUID magnetometry.

2. Experimental methods

The ceramic $Gd_{0.6}Ca_{0.4}MnO_3$ (GCMO) and $Sm_{0.6}Ca_{0.4}MnO_3$ (SCMO) targets for pulsed laser deposition were prepared by the solid state reaction method. First, Gd_2O_3 and Sm_2O_3 oxides were calcined at 1300 °C for 12 h in air and at the same time $CaCO_3$ and MnO_2 were dried at 200 °C in air. Then stoichiometric amounts were thoroughly ground, pressed to a pellet and calcined at 750 °C for 60 h in air. Afterwards the pellets were ground again and sintered at 1300 °C for 24 h in air. The grinding-sintering process was repeated twice. The phase purity of the targets was determined by X-ray diffraction (XRD) using a Philips X'pert PRO diffractometer and FullProf Rietveld analysis suite [17].

The films were made with pulsed laser deposition (PLD) on single crystal $SrTiO_3$ (STO)(100) substrates using a XeCl-laser ($\lambda = 308$ nm) with energy density of 2.0 J/cm^2 and frequency of 5 Hz. The deposition temperature, T_d, was either 500 °C or 700 °C depending on the sample. Details of the deposition setup have been published in [18]. For 10 min after the deposition, the films were kept in atmospheric pressure of oxygen at the annealing temperature, T_a , which was 500 °C or 700 °C depending on the sample. The samples are referred hereafter as material-T_d/T_a (e.g. GCMO-500/700 is deposited at 500 °C and annealed at 700 °C).

The structural characterisation of the thin films was made using a Philips X'pert PRO diffractometer with a Schulz texture goniometer and a PixCel 1D detector. To determine the lattice parameters, $\theta - 2\theta$ scans were measured over $(00l)$ (sample tilt angle $\psi = 0°$), $(0kk)$ ($\psi = 54.7°$) and $(h, 2h, h)$ ($\psi = 45°$) peak sets. The substrate peaks were used as standards using $a = 3.905$ Å as the lattice parameter for STO. Also, two dimensional scans in $2\theta - \phi$ of (242) peaks were measured to estimate the crystalline spread in film plane and in $2\theta - \omega$ for evaluation of the spread in out-of-plane direction.

The thickness of the films was measured using X-ray reflectivity measurements (XRR) with the Philips X'pert PRO equipped with an X-ray mirror and a proportional counter detector. Thicknesses were determined from the positions of the interference minima as in [19].

The magnetic properties of the films were determined with a Quantum Design MPMS SQUID magnetometer. In addition to zero field cooled and field cooled temperature scans in 50 mT, hysteresis loops between −5 T and 5 T were measured at 10 K, 50 K and 300 K. In all the measurements the plane of the film was parallel to the magnetic field. The $I(V)$ curves were measured with a standard two point configuration at room temperature and zero magnetic field with a Keithley 220 current source and HP 34401A multimeter. The contacts to the samples were made by brazing with indium. The films were not patterned for the measurement and the current was along the film plane. The electric fields, E were calculated as the set voltage divided by the distance of the contacts and the current densities, J, as the measured current divided by the cross section of the sample. This was done in order to have comparable $I(V)$ curves from samples of different thickness.

3. Results and discussion

3.1. Structural properties

According to the $\theta - 2\theta$-measurements (Fig. 1), all the films were phase pure and fully textured with $(0k0)$ as the out-of-plane direction. The samples deposited at 700 °C show a clearly stronger (040) peak than the samples made at 500 °C. This indicates a better crystallinity of the higher temperature films. This is in contrast to the results obtained earlier for PCMO films [10], where deposition at 500 °C was found optimal.

The lattice parameters and the unit cell volumes of the films were determined from $\theta - 2\theta$-measurements in different directions and the results are shown in Table 1. The bulk values were determined from the targets using Rietveld refinement [17]. The in-plane unit cell parameters, a and c, have the largest changes compared to the bulk values. The a parameters are larger than bulk in all but the GCMO-500/500 film, where the parameter is at its bulk value. This is natural since the diagonal of the STO substrate is 5.522 Åand the substrate induces tensile strain to the films. In contrast, in all the GCMO films the c parameter is compressed from the bulk value, inducing a more tetragonal unit cell. In the SCMO films, c values may increase or decrease. This difference leads to different signs of the change in unit cell volume. Since the GCMO in-plane unit cell parameters are further from the diagonal of STO than SCMO, it is possible that the films use e.g. dislocations to relieve strain. A similar difference has been observed in Sr_2FeMoO_6 films deposited on different substrates [20].

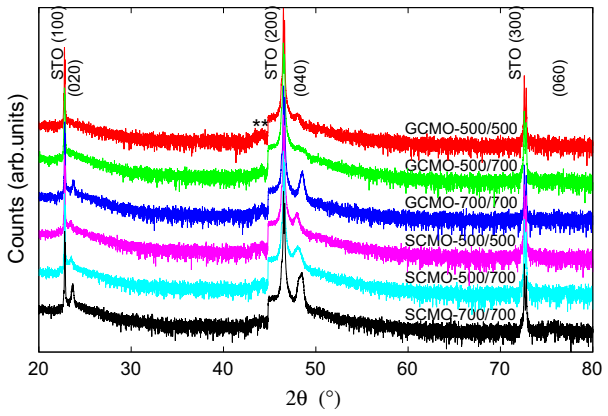

Fig. 1. $\theta - 2\theta$ scans for all the samples. Intensity is given in logarithmic scale and the curves are shifted for clarity. The peaks marked with an asterisk (*) arise from the sample holder.