Controlling Phase Separation in Manganite Thin Films

A Antonakos[1*], D. Lampakis, D. Palles, E Liarokapis[1], M Filippi[2], W Prellier[2], G. H. Aydogdu[3] and H-U Habermeier[3]

[1]*Department of Physics, National Technical University of Athens, GR-15780 Athens, Greece*
[2]*Laboratoire CRISMAT, CNRS UMR 6508, ENSICAEN, 6 Bd Marechal Juin, F-14050 Caen Cedex, France*
[3]*Max-Planck-Institute for Solid State Research, Stuttgart, D-70569, Germany}*

**tantonak@central.ntua.gr*

The very interesting complex physics, the discovery of colossal magnetoresistance (CMR) effect [1] and the possible applications [2] of the rare-earth manganites $R_{1-x}Ca_xMnO_3$ (R: a trivalent rare-earth ion; A: a divalent alkaline-earth ion) [3], have attracted much attention during past decades. The complex phase diagram of the manganites with doping can be described by a Jahn-Teller (JT) induced charge-localization competing with the magnetic interactions (double exchange-DE model [4]), charge, orbital and spin ordering [5]. The control of the transport and magnetic properties is crucial for the application of manganites to devices.

We have investigated methods for tuning the charge ordered state and controlling the phase separation in manganite [$R_{1-x}Ca_xMnO_3$ (R = La, Pr)] thin films grown on different substrates ($SrTiO_3$ (STO), $LaAlO_3$ (LAO), $SrLaGaO_4$ (SLGO) and $SrLaAlO_4$ (SLAO)). By our systematic Raman and IR studies under varying external (temperature, pressure and magnetic field) and internal (interfacial strains and doping) conditions, we have analyzed certain phonon modes and extracted direct information about the amount of the Jahn-Teller distortions, the charge ordered state, and the strain or the pressure induced phase separation in the manganite thin films.

A full assignment of the observed modes in LCMO and PCMO has been achieved and the results obtained by several perturbations were combined with polarization-dependent scattering [6, 7] and compared with previously published theoretical and experimental works on manganites.

The effect of epitaxial strains on the Raman and IR spectra were studied at room temperature for the $Pr_{1-x}Ca_xMnO_3$ and $La_{0.5}Ca_{0.5}MnO_3$ thin films of varying thickness deposited on different substrates that induce tensile or compressive strains. The Raman scattering scanning of the cross section area of the film demonstrates that the $A_g(2)$ tilting mode, which is related with the rotation of the MnO_6 octahedra, is highly sensitive to local changes and distortions in the lattice caused by the variations in epitaxial strains and can be used as a measure of strains [7].

The low temperature phase diagram of the $Pr_{1-x}Ca_xMnO_3$ thin films has been studied systematically as a function of doping and epitaxial strains. It appears that both doping and the strains from the substrate can alter the charge ordered state, as detected by the JT modes, and tune the electrical properties of the compound. The distortion of the structure can be measured by the shift of the $A_g(2)$ titling mode frequency, which is a soft mode and couples with the structural and the phase transitions [7]. The compounds were also studied under hydrostatic pressure [8] and the application of a magnetic field for various doping levels in order to induce a delocalization of the carriers and destroy the charge ordered state [9]. Based on the spectral analysis and the coexistence of modes and the characteristics of the metallic phase with others attributed to the Jahn-Teller distortions that identify an insulating charge-ordered behavior, we conclude that the compound has undergone a phase separation into metallic and insulating domains.

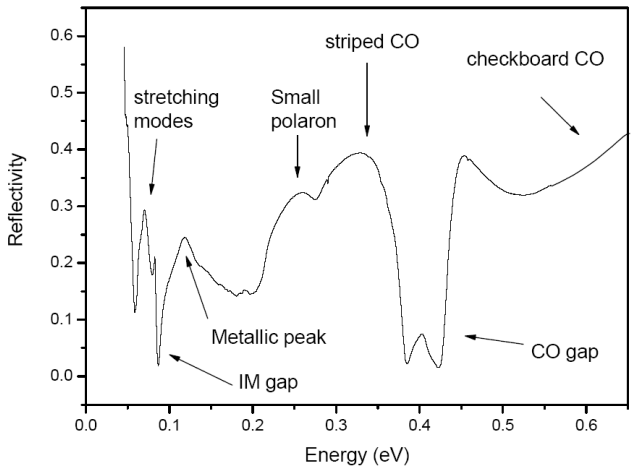

Fig. 1. The assignment of the MIR reflectivity features to several phases. Reproduced from [11].

The strain effects on the low temperature optical spectra of $La_{0.5}Ca_{0.5}MnO_3$ thin films were also investigated [6, 10]. It is demonstrated that different substrates can be exploited as a tool to obtain thin films with adjustable electronic and magnetic properties even if chemical compositions and thicknesses of the films remain unchanged [10]. The differences between the Raman spectra of the bulk and the strained thin films compounds are analyzed in terms of a phase separation scenario. The appearance of new modes in superposition with several broad bands in the reflectivity IR spectra (Fig. 1) are correlated with the magnetotrasport results and strongly suggest that phase separation between coexisting charge/orbitally ordered/disordered phases is an intrinsic property of the $R_{1-x}Ca_xMnO_3$ manganite compounds [11]. We have identified distinct phases, namely the insulating or the metallic one and two or more charge ordered phases (checkerboard and stripes). The strain effects on the LCMO/STO(100) thin film destroy the ferromagnetic phase and the charge ordered phase is more robust than in the bulk compound, leading to the charge/orbital ordered insulating phase at LT. On the contrary, the ferromagnetic metallic clusters grow and start to coalesce until the percolation limit is reached on the LCMO/SLGO, LCMO/STO(111) and the LCMO/SLAO thin films, and the system behaves as a metal due to the strain effect [12].

These findings provide important information for a comprehensive theoretical model that will understand the complex physics of the orthorhombic manganite thin films. Furthermore, they demonstrate that the proper selection of film thickness, substrate, and orientation can manipulate the film properties. These results contribute to the control of phase separation and the creation of functional materials with selected subphases for technological applications.

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