

Role of O-La(Ca or Ba) Bond in the Strain Effect on $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ and $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$ Thin Films

The strain effect on $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ and $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$ thin films on SrTiO_3 (001) substrate with different thicknesses has been studied by X-ray absorption near edge spectroscopy (XANES), which can reveal the details of the coupling between cations and anions. The strain may suppress the T_C of LCMO films while enhancing that of LBMO films. The theoretical calculation results suggest the unoccupied states of the third structure of XANES are formed by much more complex hybridization of O 2p to Mn 4sp, La 6s and (Ca 4sp or Ba 6sp) orbitals. The change of the absorption intensity of the second and third structures is compatible to the T_C change of both films due to the strain effect. This strongly suggests that the strain effect on LCMO and LBMO thin films is mainly associated with the bonding situation between O and La(Ca or Ba) ions.

Beamline

20A1 High-Energy SGM

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Colossal

magnetoresistance (CMR) materials with the general formula $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ (Ln = rare-earth, A=divalent ion) reveal interesting electric and magnetic properties, and have attracted a great deal of attention since their discovery in 1950. The most pronounced physical property of CMR is the robust ferromagnetism and accompanying a huge magnetoresistance (MR). The metal-insulator transition temperature (T_p) and the ferromagnetic-paramagnetic transition temperature (T_C) of doped manganite thin films can be altered by the strain effect which originates from the lattice mismatch between the thin film and substrate. The lattice of both $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (LCMO) and $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$ (LBMO) can be reassigned as pseudocubic structures with lattice constant s of 0.386 nm and 0.392 nm, respectively. By comparison to the lattice constant of SrTiO_3 (STO) of 0.395 nm to that of films, shows that the LCMO and LBMO films undergoes tensile and compress strain, respectively. The strain effect suppresses the T_C of LCMO films with the decreasing thickness of films, whereas the T_C of $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ films are found to increase for $x \leq 0.2$ in thinner films. The highest T_C for LBMO films is about 310K for $x = 0.2$ with a thickness of 21 nm.

Up to now, the mechanism of this strain effect has not been fully understood. Since the mechanism of CMR materials depends on the hopping probability of itinerant carriers between two Mn ions which are located inside the Mn-O_6 octahedral, any change of the Mn-O bond length, Mn-O-Mn bond angle or the vibration frequency would influence the electric and magnetic properties. Kanki and Zhang proposed an orbital stability model based on the elongation of the in-plane Mn-O bond length that stabilizes and increases the electron occupancy of the $d_{x^2-y^2}$ orbital in the thinner LBMO films and which results in T_C enhancement. This model can also conclude the suppression of T_C in LCMO thinner films. However, Yuan cited Miniotas's measurements that the in-plane Mn-O bond length of the LCMO thin films does not change with the strain

but is instead fixed. Yuan proposed that the dependence of the normal vibration frequency of oxygen in the Mn-O-Mn bond in response to the tensile strain might be responsible for the T_C enhancement. However, all these models and assumptions remain purely theoretical, and lack direct experimental support.

Since the X-ray absorption near edge spectra (XANES) at the O K-edge is a powerful tool to bring to light the bonding detail around the oxygen and may provide a clue of the mechanism of the unsolved strain effect on CMR films. In this study, we employ XANES measurements at the O K-edge of the LCMO and LBMO films with various thicknesses to try to reveal the possible mechanism behind the strain effect.

The LCMO and LBMO thin films are grown on STO (001) single crystal substrates by an off-axis RF magnetron sputtering system. The LCMO films with thicknesses of 200nm and 20nm and the LBMO films with thicknesses of 150nm and 15nm are deposited at heater temperatures of 750°C for the LCMO film and 800°C for the LBMO film. The substrate temperature was measured by the infrared thermometer and was found to be 50°C lower than the heater's temperature. To ensure that films were not affected by oxygen depletion, the as-grown films were *in-situ* annealed in 500 Torr pure oxygen at 850°C for one to two hours. The crystal structures and transport properties are studied by the X-ray diffraction and a four points probe, respectively. The magnetization is measured by a Quantum Design Superconducting Quantum Interference Device (SQUID). The XANES are taken by using the high-energy spherical grating monochromatic beamline of the Synchrotron Radiation Research Center in Taiwan, operating at 1.5GeV with a maximum stored current of 200mA. The O K-edge XANES is measured utilizing both total electron yield (TEY) and fluorescence yield (FY) methods at room temperature ($T \doteq 300\text{K}$) and at low temperature ($T \doteq 30\text{K}$) in a vacuum lower than $1 \times 10^{-9}\text{Torr}$. Energy resolution of the monochromator is around 0.1eV. The background and the self-absorption effects of spectra were subtracted and cor-

rected by a standard procedure. The final spectra were then normalized to the tabulated standard absorption cross section in the energy range from 600 to 620eV.

The resistivity and magnetization curves of the films exhibit typical ferromagnetic-metal-like to paramagnetic-insulator-like transitions at approximately the Curie temperatures, T_C , and the resistivity-peak temperatures, T_p , respectively. The thick LCMO film experiences strain-relaxation and behaves similar to that of bulks, while the thin LCMO film is affected completely by the tensile strain and exhibits a much lower T_C of 146K. Since the 200nm thick LCMO film is not thick enough to have a complete strain-relaxation, it exhibits a magnetic transition temperature of 242K, 13 degrees lower than that of the bulk value. LCMO films thicker than 300nm may exhibit the same T_C as that of bulk, however, the rough surface morphology makes it not ideal for XANES measurements. LBMO films have the opposite response to the strain, in that their T_C were enhanced by up to 311K for the thinner films. Normalized $R-T$ and $M-T$ curves of 200- and 20-nm-thick LCMO films and 150- and 15-nm-thick LBMO films are plotted in Fig. 1. T_C and T_p of the films are listed in Table 1.

Tab. 1: The T_C and T_p of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ and $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$ thin films with different thickness grown on SrTiO_3 (001) substrates.

| | $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ | | $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$ | |
|----------------|--|-----|--|-----|
| Thickness (nm) | 200 | 20 | 150 | 15 |
| T_C (K) | 242 | 146 | 296 | 311 |
| T_p (K) | 235 | 146 | 312 | 330 |

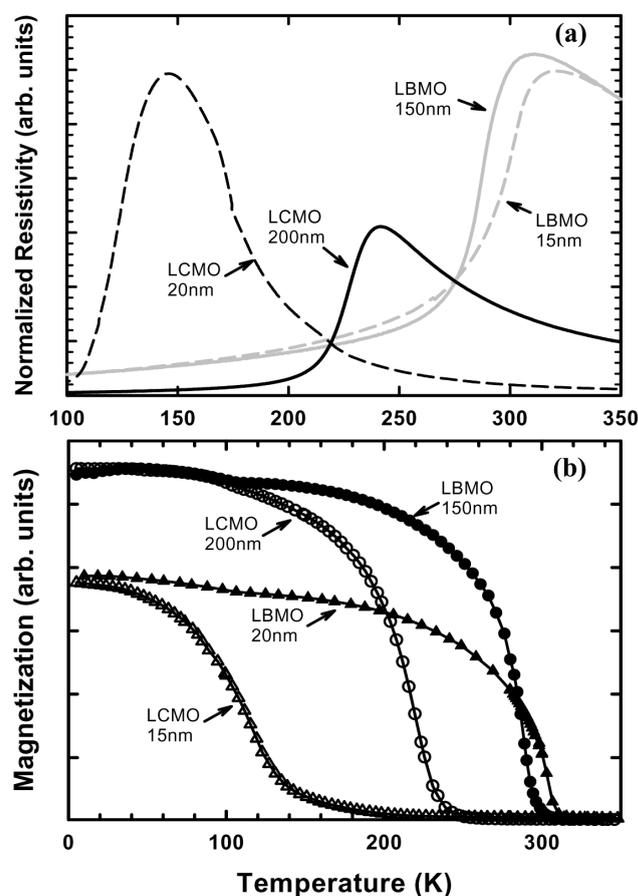


Fig. 1: Normalized $R-T$ (a) and $M-T$ (b) curves of 200- and 20-nm-thick LCMO films and 150- and 15-nm-thick LBMO films.

XANES is a powerful tool in investigating the empty excited states of materials. Once the material interacts with the incident X-ray, the core electrons are excited to the empty excited states, and the following transition to fill the vacancy at the core level will emit correspondent fluorescent, which is collected as the fluorescent yield. All electrons - such as the backscattering electrons, the secondary electrons, the Auger electrons and the conduction electrons are collected as the total electron yield. Both modes qualitatively reflect the spectrum of the empty excited states of materials. Because the excited states also reflect the electronic structure and the contribution of each component of the material, XANES becomes a valuable tool for exploring the bonding states between components. Since fluorescent yield mode in XANES is more bulk-sensitive, the strong substrate signal for an ultra thin film outweighs the film signal. To eliminate the substrate signal, we focus on the total electron yield mode to investigate the electronic status of the top few layers of the films, as shown in Fig. 2. It can be noted that all TEY curves contain three main structures that a number of experiment propose as having been initiated from strong hybridization of O 2p orbital to La(Ca

or Ba) or Mn orbitals. The first structure around 528~532eV, which is usually called the "pre-edge" structure, is composed of the unoccupied O 2p to Mn 3d hybridized orbitals. The Mn 3d orbital can be assigned e_g^\uparrow , t_{2g}^\downarrow and e_g^\downarrow states. Due to the Jahn-Teller distortion effect, these three states experience splitting into many states. The Mn-3d multi-states contribute to a smeared pre-edge structure. The second and third structures at around 532.5~538 eV and 538~550 eV are assigned as the O 2p and La 5d(Ca 3d or Ba 5d) hybridized orbital and the O 2p to Mn 4sp hybridized orbital, respectively. The absorption intensity corresponds to the degree of covalence of the O 2p orbital.

It is obvious that the pre-edges of LCMO and LBMO films are independent of the thickness and of the strain, while the second and the third structures exhibit a large change. The absorption intensity of the second and the third structures of the LCMO thinner film is approximately 40% less than that of the thickest films. The LBMO thinner film, however, exhibits an absorption intensity 5% higher than the LBMO thicker film, as can be seen by carefully comparing the two curves in Fig. 2(b). In addition, the

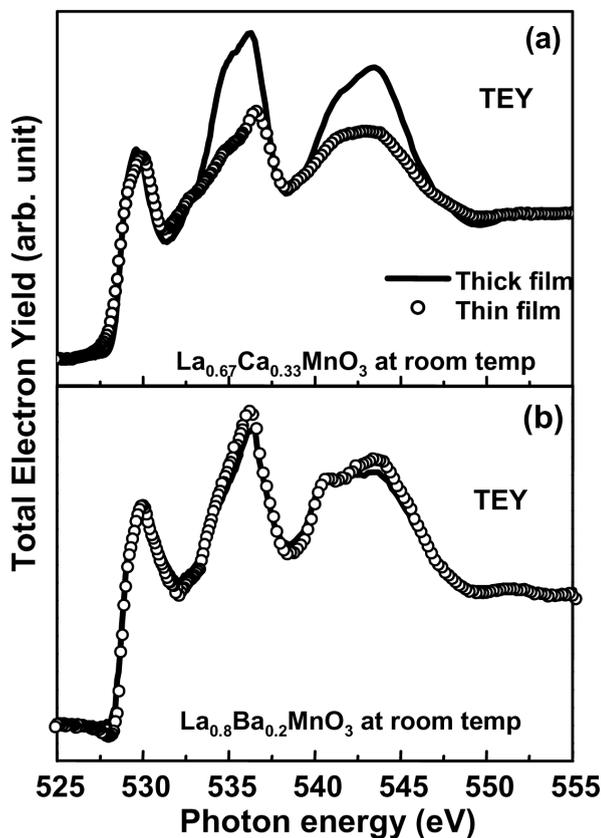


Fig. 2: The O K-edge XANES of (a) $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ and (b) $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$ films taken at room temperature in the total electron yield (TEY) mode for the thick (solid lines) and thinner (circles) films.

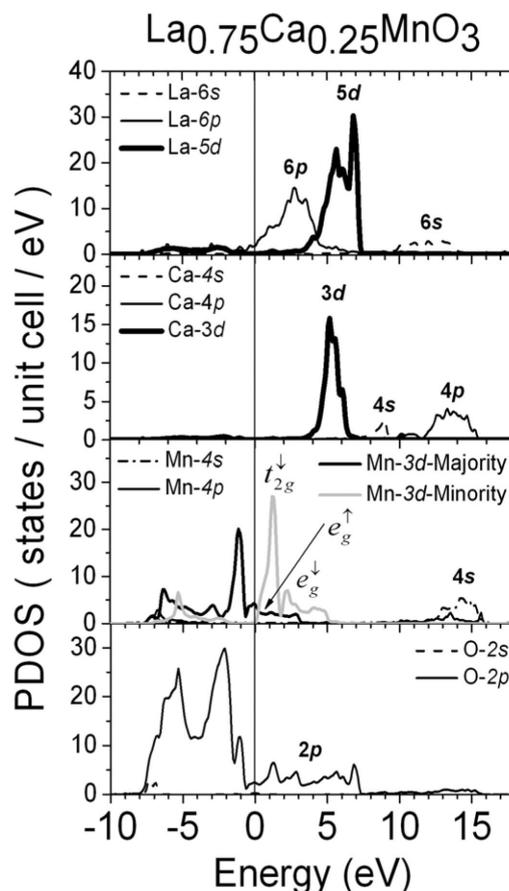


Fig. 3: The partial density of states (PDOS) plots of La, Ca, Mn and O ions of $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$.

two high energy structures are very sensitive to the strain. The scales of the intensity changes under strain are very compatible to the change of T_C .

If the first and third structures are only simply associated with the hybridization of the orbital of O and Mn ions, they should exhibit the same trend under the influence of the strain. However, the first structures of both films in Fig. 2 exhibit nearly the same intensity, while the third structures are in fact changed by the strain. This inconsistent trend indicates that the third structure does not simply reflect the hybridization of O 2p to Mn 4sp orbital alone, but rather other orbitals are involved. To shed some light on the detail of the third structure, the unoccupied states - that can be simulated as the partial density of states (PDOS) of $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ for energy around and higher than the Fermi energy - are calculated by the pseudofunction method, which uses both local-spin-density approximation (LSDA) of von Barth and Hedin and the Andersen's linear theory. The calculation results are plotted in Fig. 3. The theoretical calculation confirms that the second structure is the O 2p and La 5d/(Ca 4d or Ba 6d) hybridized states. The third structure, which spans from 10~22 eV above the Fermi surface, is not only associated with the unoccupied O 2p and Mn 4sp hybridized orbital, but also associated with the that of O 2p and La 6s (Ca 4sp) hybridized orbital. Therefore, the major change of the absorption intensity of the third structure can be attributed to the O 2p and La 6s/Ca 4sp) hybridized states. The absorption intensity change of the second structure is related to O 2p and La 5d/Ca 4d hybridized states. This strongly suggests that the strain effect on LCMO and LBMO thin films is mainly associated with the bonding situation between O and La(Ca or Ba) ions.

The strain effect on LCMO and LBMO films has been studied by the XANES measurements in the TEY mode. The theoretical calculations confirm that the second structure is the O 2p and La 5d/(Ca 4d or Ba 6d) hybridized states, and indicates that the third structure in XANES is the unoccupied state of the p-symmetry projection of Mn 4sp, La 6s and (Ca 4sp or Ba 6sp) states on the O site. The change of the absorption intensity of the second and the third structures is compatible to the T_C change of both films due to the strain effect. This strongly suggests that the strain effect on LCMO and LBMO thin films is mainly associated with the bonding situation between O and La(Ca or Ba) ions.

Experimental Station

Photoabsorption end station

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