Enhancement of ordering temperatures of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ thin films by adding Ho atoms

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A series of $\text{Ho}_x\text{-La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ thin films with $x = 0.0, 0.2, 0.4, 0.6$, and 1.0 mol percent have been deposited on $\text{SrTiO}_3(100)$ substrates with the substrate temperature controlled at 600°C by dc magnetron sputtering. The magnetic ordering (T_c) and metal-insulator transition temperature (T_{MI}) were enhanced about $25\text{--}60$ K for $\text{Ho}_x\text{-La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ films. At $x = 0.4$ the ordering temperature has been increased above 280 K. The variation of the ordering temperature is simply ascribed to the presence of Ho. The results of magnetoresistance measurements indicated that the samples exhibited colossal magnetoresistance effect (CMR) and a maximum was observed at a temperature T_p . It was noted that the variation of T_p with x displayed the same trend as that of T_{MI} . Although the CMR was suppressed with the addition of Ho, a sizeable CMR $\approx 20\%$ was still detected at 270 K in the sample with 0.4 mol % Ho due to much higher T_p .

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1 Introduction

The Perovskite-type manganese oxides have attracted considerable interest in recent years because of their usefulness in various fields of research [1]. The strong interplay among structures, electrical characteristics and magnetic behaviors, causes the mixed-valence manganese oxides ($\text{R}_{1-x}\text{A}_x\text{MnO}_3$ (R = rare-earth cation, A = alkali cation)) to exhibit a wide variety of crystallographic, electronic and magnetic phases [2]. An increasing number of studies on such materials have followed the discovery of a colossal magnetoresistance (CMR), near the Curie temperature (T_c). In particular, the tunneling magnetoresistance (TMR) junction, using the perovskite-structured manganite as electrodes, has great potential for the future applications of magneto-electronic devices.

One of the common studied mixed-valence CMR oxides is the calcium-doped LaMnO_3 . However, the Curie temperature of the LaCaMnO_3 (LCMO) thin film is well below 260 K [3] and a large CMR effect appears only at low temperatures. Therefore, utilizing LCMO-based devices at or above room temperatures is difficult. Continuous efforts are being made to achieve CMR at room temperature. One of the approach is to vary processing parameters which in turn affect the microstructural aspects and so the properties. Another approach is suitable addition of trivalent metal ion. Various studies on the substitution effect on magneto-transport have been reported [4, 5]. However, most of them are dedicated to the bulk LCMO. In this work, we have investigated the effect of Ho addition on the magneto-transport properties of $\text{Ho}_x\text{-LCMO}$ ($x=0.0, 0.2, 0.4, 0.6, 1.0$) thin films. It has been found that suitable addition of Ho into LCMO films enhances the metal-insulator transition temperature (T_{MI}) and ferromagnetic ordering temperatures (T_c).

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2 Experiments

$\text{Ho}_x\text{-La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ films with $x = 0, 0.2, 0.4, 0.6$ and 1 mol % were prepared with dc magnetron sputtering. Targets of stoichiometric composition were made by a standard solid-state-reaction technique from a mixture of La_2O_3 , CaCO_3 and MnCO_3 with a purity of 99.9 %, followed by a repeated grinding and then an annealing in flowing O_2 atmosphere. The nominal composition of LCMO was $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$. The final steps in the preparation of the target were the addition of Ho_2O_3 powder and the calcination of the mixed powders in air at 1500°C for 12 hours. The thin films were grown on $\text{SrTiO}_3(100)$ substrates at 600°C in O_2 partial pressure of 60 mtorr. The as-deposited films were post-annealed at 900°C for 1 hr in O_2 atmosphere. The thickness of the films determined by an atomic force microscope (AFM) was about 30 nm. The crystalline phase was examined by X-ray powder diffraction (XRD). The resistivity and magnetoresistance of the films were investigated as a function of temperature (T) and magnetic field (H) using the four-probe technique. Temperature dependent magnetization was measured using a vibrating sample magnetometer (VSM).

3 Results and discussion

Figure 1 displays the representative XRD patterns of $\text{Ho}_x\text{-LCMO}$ films for $x=0$ and 0.6 mole %, grown on STO substrate. Only peaks from substrate plane are visible. However, narrow angle XRD plots (shown as insets) shows the LCMO peak from (004) plane. This indicates that films are of single phase with pseudo-cubic structure and epitaxially grown on STO substrate [6]. It was observed that peak position of LCMO ($2\theta = 46.78^\circ$) did not shift till $x = 0.4$ mol % Ho addition. Further increasing to $x=0.6$ mol %, the LCMO peak was moved toward higher angle ($2\theta = 46.85^\circ$) side. This peak shift suggests that Ho is also substituting into lattice sites. It is worth to mention that the ionic radii of Ho^{3+} ($0.97 \text{ \AA}$) is approximately 20% less than La^{3+} ($1.22 \text{ \AA}$). Therefore, during the deposition and subsequent annealing it is quite probable that some amount of Ho^{3+} is substituting La^{3+} . On other hand, no peak shift below $x=0.6$ mol % also ascertain the possibility of some free Ho in the LCMO matrix with the initial addition. Furthermore, our XPS studies of Ho 4d for $x = 0.6$ mol % Ho-added samples indicated that the peak has been shifted from its original value 159.6 eV to higher binding energy of 161.7 eV . This finding suggests that the Ho 4d peak of Ho added sample is identical to the Ho 4d peak of Ho_2O_3 , confirming the presence of Ho in the lattice sites surrounded by oxygen ions.

In Fig. 2 is plotted the temperature (T) dependence of resistivity under magnetic fields $H = 0$ and 0.5 T for various x . All samples have undergone from metal to insulator transition at the metal-insulator transition temperature (T_{MI}). However, samples with $x = 0$ and 1 mol % exhibited a sharp transition, whereas larger transition width was observed for $x = 0.2, 0.4$ and 0.6 mol % of Ho. The lower value of resistivity under magnetic field was caused by the field-induced spin ordering. Figure 3 displays variation of T_{MI} and T_{C} with Ho content. Notably, T_{MI} initially increases with increasing x , and reaches a maximum for $x = 0.4$ mol % at $T_{\text{MI}} \approx 290 \text{ K}$, which is $\approx 70 \text{ K}$ higher than that of the Ho-free sample. The ferromagnetic transition temperature T_{C} determined from the M - T curves also agrees well with T_{MI} and also has a maximum at $\approx 275 \text{ K}$ for the same sample. Variation of ordering temperatures could be possibly explained by the mechanism of Ho^{3+} substitution for La^{3+} or a nano-scaled distribution of Ho in the LCMO matrix. As suggested by aforementioned XRD results no peak shift was observed with the addition of 0.4 mol % Ho. Furthermore, the shifted XRD peaks for the sample with 0.6 mol % Ho implied that above a certain level of addition, Ho was also going to lattice sites along with LCMO matrix. Based on these results, the enhancement in the ordering temperature is attributed to presence of nano-size Ho in the LCMO matrix, which will act as conduction channels between grain boundaries [7, 8]. Above 0.40 , the decrease in T_{MI} is due to the substitutional effects. Since Ho^{3+} has 20% lower ionic radii than La^{3+} , the presence of Ho^{3+} at La^{3+} site decreases the tolerance factor causing the magnetic scattering due to chemical pressure effect. Consequently a decrease in ordering temperature is expected [9]. Our results are consistent with previously studied Ho-doping and Ho-addition effects on bulk LCMO, where a higher

Fig. 1 XRD patterns of $\text{Ho}_x\text{-LCMO}$ films, (a) $x = 0$ and (b) $x = 0.6$.

Fig. 2 Temperature dependence of the resistivity for $\text{Ho}_x\text{-LCMO}$ films at $H = 0$ and $H = 0.5$ T magnetic field.

Fig. 3 Variation of transition temperatures T_{MI} and T_{C} with Ho addition.

ordering temperature has been realized for Ho added samples [7, 10]. However, a highest ordering temperature was found at $x = 0.4$ mol % in thin films as compared to 1 mol % in the bulk LCMO. Figure 4 depicts the temperature dependence of magnetoresistance (MR). MR is defined as $\text{MR} = \{R(H = 0.5 \text{ T}) - R(H = 0)\}/R(H = 0)$ and the MR value has been found to be always negative. T_p is defined to be the temperature where the magnitude of MR is a maximum. The maximum MR $\approx 120\%$ was observed at $T_p \approx 190$ K for LCMO film. The striking feature is that MR collapse above 230 K in LCMO films, whereas the observed MR for the films with 0.4 mol % Ho is $\approx 20\%$ even at 270 K. The presence of MR at higher temperatures is due to the magnetic inhomogeneity arising from nanoscaled Ho distribution in LCMO matrix. The stress induced effect caused by the Ho addition will produce magnetic scatterings, and does not allow to drop MR at higher temperatures [11]. Moreover the decrease in MR for Ho-added films with increasing temperature is not so sharp as for LCMO film, which provides an added advantage to operate over a wider temperature range with a substantial MR. The compositional dependence of T_p is plotted in Fig. 5. T_p shows the similar behavior as T_{MI} and T_{C} and within the region of metallic

Fig. 4 Temperature dependence of MR.

Fig. 5 Composition dependence of T_p .

behavior. Besides, a maximum of T_p was also obtained for the sample with 0.4 mol% Ho. Further increase in Ho content above 0.4 mole % decreases T_p .

4 Summary

In summary, high-quality $\text{Ho}_x\text{-LCMO}$ films have been successfully synthesized with enhanced metal-insulator transition and ferromagnetic temperatures. The presence of Ho in lattice site and in the LCMO matrix is verified by XRD and XPS studies. An increase in $T_C \approx 70$ K was recorded for the films with 0.4 mol % Ho. This enhancement of ordering temperature is ascribed to the presence of nano-scaled Ho clusters that open new conduction channels. The Ho-LCMO film with a sizable MR at higher temperatures could be used as the electrode material for the future device application.

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