

Abstract

Magnetic Properties of CMR Manganese Oxides

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The recent renaissance of interest in $\text{La}_{1-x}\text{D}_x\text{MnO}_3$ ($\text{D} = \text{Ca}, \text{Sr}, \text{Ba}$ etc.) of perovskite structure has focused on the new materials of magnetoresistance(MR) sensor. For the study of magnetic properties for perovskite manganese oxides, the $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{}^{57}\text{Fe}_x\text{O}_3$ ($x = 0, 0.01, 0.03, \text{ and } 0.05$) powders have been prepared by the sol-gel processing method. The Fe ion has a similar electronic configurations and ionic radius of the Mn. A small amount of ^{57}Fe have been doped with the aim of investigating the elucidate the role and magnetic properties of manganese ion in the colossal magnetoresistance effect by the influence of the presence of a metal, which favours an antiferromagnetic coupling in the Mn-O layer. The compound samples have been studied with x-ray diffraction patterns, magnetization and MR curve by vibrating sample magnetometer (VSM) and Mössbauer spectroscopy.

The values of the isomer shifts show that all the iron ions are in the ferric (Fe^{3+}) state. The line width broadening of Mössbauer spectrum increased as doped ^{57}Fe increased and more pronounced near the Curie temperature. Analysis of ^{57}Fe Mössbauer spectrum data has considered nearest-neighbor interactions of Fe ion and average particle size by x-ray

pattern analysis. And then the line width broadening corresponding to asymmetry, as temperature increased, can be explained in terms of the anisotropic hyperfine field fluctuation. For the $x=0.01$ doped ^{57}Fe , the fluctuation frequency at the Curie temperature has $21.7 \text{ \AA/\text{Å}}$ and the anisotropy energy shows a maximum value of 453 erg/cm^3 at 100 K. The temperature dependence of fluctuation frequency and anisotropy energy rapidly increased as doped ^{57}Fe increased. The Curie temperature of the $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}^{57}\text{Fe}_x\text{O}_3$ ($x = 0, 0.01, 0.03, \text{ and } 0.05$) powders decreased from 282 to 180 K proportional to the doped ^{57}Fe increasing and the saturation magnetization at 77 K largely decreased from 84 to 40 emu/g. The decreasing of the saturation magnetization at 77 K is interpreted as increasing of the anisotropy energy by doped ^{57}Fe increasing. The maximum relative magnetoresistance with doped ^{57}Fe is about 45 % at the $T_{\text{SC-M}}=200 \text{ K}$ for the $x=0.03$ doped ^{57}Fe . When the doping ratio was more than $x=0.1$, magnetic ordering in these systems was changed from ferromagnetic to antiferromagnetic and the magnetoresistance effect was not observed.

For the study of the magnetoresistance effect and magnetic properties by changing the ratio of the Mn^{3+} and Mn^{4+} ions for perovskite manganese oxides, $\text{La}_{1-x}\text{MnO}_3$ ($x = 0.0 \sim 0.33$) has been prepared by the sol-gel processing method. For the $x=0.0$ sample, the magnetoresistance effect was not showed by reason of the nonconducting substance under the room temperature. However, in La defected sample, the Curie temperature was increased about 100 K compared to the $x=0.0$ samples and the metal-semiconductor transition was observed near the Curie temperature. Also the magnetoresistance effects show the value more than 20 % at the applied magnetic field of 15 kOe. It was interpreted as the double exchange inaction due to creation of the Mn^{4+} ion. For the $x=0.1$, the cation ratio for Mn^{3+} and Mn^{4+} was 2 : 1, the saturation magnetization at 77 K and the magnetoresistance ratio shown maximum value.

In order to study the magnetic properties of the thin film for the perovskite manganese

oxide, the films have been prepared by the rf-magnetron sputtering and sol-gel spin coating method. For the deposited film by the sputtering method, it was confirmed that the composition of the Ca and Sr were defected comparing with the sputtering target. All the deposited films have been studied with the magnetic properties as a function of the deposited composition and thickness. The LaAlO_3 (100) and SiO_2/Si (100) substrate were used to study the difference in magnetic properties which were arising from the surface state and crystalline structure. In the $\text{La}_{0.89}\text{Sr}_{0.11}\text{MnO}_3/\text{LaAlO}_3$ (100) film, the semiconductor-metal transition occurred at 242 K and the magnetoresistance effect has a value 273 % at the applied magnetic field of 15 kOe. Comparing the magnetoresistance property as a function of the substrate, the film grown on LaAlO_3 (100) has better quality than that on SiO_2/Si (100). It was due to the crystalline shape of film grown on substrate. The semiconductor-metal transition temperature for the epitaxial films on LaAlO_3 (100) increased and the magnetoresistance ratio decreased as the amount of Sr was increased. When the thickness of films was about 1000 Å, the semiconductor-metal transition temperature occurred at highest temperature, but the surface state effect of film had not appreciable difference.

Also for the deposited film, which was prepared by the sol-gel spin coating method, the effect of the substrate class and the annealing time were studied systematically. The result of the substrate class had similar values with the sputtered film. The substrate property as a function of the deposition method has little differences. As a different annealing time of film, the semiconductor-metal transition temperature has smaller change and the resistivity at the semiconductor-metal transition temperature was increased as an annealing time increased. Generally for the film of spin coating, the surface state of substrate and crystalline growth were worse than the sputtered film, but a composition of deposited film was controlled easily.