Dilution effects on X-ray photoelectron spectra of La$_{0.8}$Sr$_{0.2}$MnO$_3$ with SiO$_2$

SHIGEMI KOHIKI, YOSHIHISA ISHIDA, TAKESHI KUMASHIRO, HIROKAZU SHIMOOKA, TAKAYUKI TAJIRI, HIROYUKI DEGUCHI
Faculty of Engineering, Kyushu Institute of Technology, Kitakyushu 804-8550, Japan
E-mail: kohiki@che.kyutech.ac.jp

MASAOKI OKU
Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Diluted samples of La$_{0.8}$Sr$_{0.2}$MnO$_3$ with SiO$_2$ were prepared by calcination of the MCM-41 molecular sieve soaked in precursor solutions with various concentrations (0.1, 0.05 and 0.005 mol/l). The diluted samples from the 0.1, 0.05 and 0.005 mol/l solutions showed ferromagnetic behavior in temperature dependent magnetic susceptibility below $\approx$300, $\approx$250 and $\approx$100 K, respectively. The electron binding energy of the La 3$d_{5/2}$ main peak of the diluted samples from the 0.1, 0.05 and 0.005 mol/l solutions were 835.7, 836.0 and 837.4 eV, respectively, and were larger than that of La$_{0.8}$Sr$_{0.2}$MnO$_3$ bulk sample (834.2 eV). Reduction in intensity of the La 3$d$ charge-transfer satellite was more pronounced for more diluted sample. The Mn 2$p_{3/2}$ main peak of all the diluted samples remained at 642.2 eV, which is larger by 0.6 eV than that of the bulk sample (641.6 eV). The charge-transfer peak energy in the optical absorption spectra was the same (2.3 eV) for all the diluted samples, and the energy was larger by 0.4 eV than the bulk one (1.9 eV). The dilution caused localization of charge carriers within the La$_{0.8}$Sr$_{0.2}$MnO$_3$ lattices isolated by the insulator. Suppression of charge flow between the isolated La$_{0.8}$Sr$_{0.2}$MnO$_3$ lattices resulted in the enlargement of the La 3$d$ electron binding energy and the decrease of the La 3$d$ charge-transfer satellite peak intensity, and also the lowering of the ferromagnetic ordering temperature.

© 2005 Springer Science + Business Media, Inc.

1. Introduction

Hole-doped manganese oxide La$_{1-x}$Sr$_x$MnO$_3$ has attracted a great interest after discovery of the giant magnetoresistance [1, 2]. Bulk of La$_{1-x}$Sr$_x$MnO$_3$ crystal shows a great variety of magnetic and electric properties with $x$ because of strong coupling between the charge carriers and the local spins [3, 4]. The parent material LaMnO$_3$ belongs to the class of compounds called charge-transfer insulators. Each Mn$^{3+}$ site in the octahedral crystal field has four $d$ electrons with a configuration of $t^2_2 g^2 e^1$. The $t_{2g}$ electrons localized at the Mn site form local spins of $S=3/2$ and couple with the $d_{eg}$ conduction electron. The conduction band consists of the Mn 3$d_{eg}$ states strongly hybridized with the O 2$p$ states. An increase of the nominal hole concentration ($x$) takes place antiferromagnetic-to-ferromagnetic phase transition at around $x=0.1$ and insulator-to-metal phase transition at around $x=0.175$. In the ferromagnetic region, the Curie temperature ($T_C$) rises from $\approx$150 to $\approx$370 K with increasing $x$ from 0.1 to 0.3. At $x=0.2$, $T_C$ of the material reaches $\approx$310 K. The ferromagnetic and metallic phase transition is due to the delocalization of charge carriers (hopping electron) via double exchange interaction between Mn$^{3+}$ and Mn$^{4+}$ [5, 6]. Such a mechanism for magnetism and electron transport of La$_{1-x}$Sr$_x$MnO$_3$ is based on semi-infinite repetition of the octahedral crystal field for the Mn ions in the bulk crystal.

The ground state is described by the configuration interactions of two symmetrized states: $|de_{g}^{1}\rangle$ and $|de_{g}^{1}L\rangle$. Here, $|de_{g}^{1}\rangle$ represents the state with one electron moved from the $2p$ orbitals of surrounding oxygen atoms (ligand) to the Mn $|de_{g}^{1}\rangle$ state, which leaves a hole $L$ in the ligand $p$ orbitals. The energy required to move one electron from the ligand $p$ to Mn $d$ orbitals is called the charge-transfer energy and given by $\Delta = \Delta_{e_{g}^{1}} - \Delta_{e_{g}^{1}} = \langle e_{g}^{1}|H|e_{g}^{1}\rangle - \langle e_{g}^{1}|H|e_{g}^{1}\rangle$, where $H$ is the Hamiltonian [7]. In a solid, a change in the photoelectron binding energy ($BE$) consists of changes in the orbital and electronic relaxation energies. Electronic relaxation is due to flowing negative charge toward the positive charge suddenly created by photon absorption, and lowers the observed $BE$ than that expected from Koopmans’ theorem [8]. For an identical material, we can evaluate variation in the electronic relaxation energy ($RE$) with changes in the physical state. An increase of $BE$ reflects a decrease of $RE$ by enlargement of the bond ionicity. Dilution of La$_{1-x}$Sr$_x$MnO$_3$ in the ferromagnetic metal phase with a nonmagnetic insulator provides a unique opportunity to observe the...
evolving magnetic properties and electronic states of the strongly correlated material growing from molecule to bulk.

2. Experiment
The diluted samples of La$_{0.8}$Sr$_{0.2}$MnO$_3$ were prepared by calcination at 730 °C in air of the MCM-41 molecular sieve soaked in precursor solutions with various concentrations (0.1, 0.05 and 0.005 mol/l). The MCM-41 was synthesized from a mixture of amorphous SiO$_2$ (1:00: C$_{12}$H$_{25}$Ni(CH$_3$)$_3$Cl 0.70: NaOH 0.24: H$_2$O 53.7 in molar ratio. A Rigaku CN2013 diffractometer with Cu K$_\alpha$ radiation was employed for X-ray diffraction (XD) measurement. The MCM-41 showed the XD peaks that can be indexed on a hexagonal unit cell with $a \sim 4.3$ nm ($a = 2d_{100}/\sqrt{3}$ and $d_{100} = 3.7$ nm). The MCM-41 were soaked in precursor solutions with the concentration of 0.1, 0.05 and 0.005 mol/l, which consisted of La(CH$_3$COO)$_3$·1.5H$_2$O, Mn(NO$_3$)$_2$·6H$_2$O, SrC$_2$O$_4$·H$_2$O, and H$_2$O. The nominal $x$ value (the Sr content) of the samples was 0.2, which corresponds to the ferromagnetic metal phase. While La$_{0.8}$Sr$_{0.2}$MnO$_3$ bulk sample prepared from the 0.05 mol/l solution under the same conditions showed the XD pattern with sharp peaks from the crystal, all the diluted samples showed no peaks and a broad bump at around $2\theta = 24^\circ$, as shown in Fig. 1. In the diluted samples, incoherent X-rays due to diffuse scattering by the amorphous SiO$_2$ matrix concealed X-rays reflected from the La$_{0.8}$Sr$_{0.2}$MnO$_3$ lattices dispersed in the matrix.

Temperature dependence of magnetic susceptibility ($\chi$-$T$ curve) was measured with a Quantum Design MPMS-5S superconducting quantum interference device magnetometer in the $dc$ field of 1 kG. We used a Surface Science Laboratories Model SSX-100 spectrometer with monochromatized Al K$_\alpha$ X-ray source for X-ray photoemission spectroscopy. The measurements were performed in a vacuum of $4 \times 10^{-10}$ Torr at room temperature. The spectrometer was calibrated utilizing the Au 4$f_{7/2}$ electrons (83.79 eV). The full width at half-maximum (FWHM) of the Au 4$f_{7/2}$ peak was 1.03 eV. The spectra were taken with the electron flood of about 1 eV. Charge shifts were corrected with the C 1s electrons (285.0 eV). The experimental uncertainty amounted to ±0.15 eV. Ultraviolet-visible (UV-vis) diffuse reflectance spectra were measured with a resolution of 0.002 eV using a JASCO V-550 spectrometer.

3. Results and discussion
Fig. 2 shows $\chi$-$T$ curves of the diluted samples. The samples from the 0.1, 0.05 and 0.005 mol/l solutions showed ferromagnetic behavior below $\approx 300$, $\approx 250$ and $\approx 100$ K, respectively, overlapping the paramagnetic divergence at low temperatures. Such paramagnetic behavior was not observed for the bulk sample, as seen in the inset of Fig. 2. The ferromagnetic ordering of local magnetic moments of the La$_{0.8}$Sr$_{0.2}$MnO$_3$ bulk sample is based on Hund’s-rule coupling of the Mn $d_{3z^2-r^2}$ local spins ($S = 3/2$) with conduction $e_\pi$ electrons [5, 6]. In the bulk sample, the $de_\pi$ electrons are hopping between the Mn sites of continual crystal fields through the Mn 3$d_{e_\pi}$–O 2$p$ conduction band spreading over the bulk crystal. The dilution with insulator isolated the La$_{0.8}$Sr$_{0.2}$MnO$_3$ lattices, and resulted in a suppression of the hopping range of conduction electron. The paramagnetic behavior is due to localized spins at the Mn site in the crystal field within each molecule. Elongation of the effective correlation length of charge carriers from molecule to bulk raised the ferromagnetic ordering temperature higher of the sample with higher concentration.

Overlapping between the filled O 2$p$ orbital and the empty La 4$f$ orbital is quite small since localization of the La 4$f$ orbital is very strong, however, there remains two possible final states with a La 3$d$ core-hole. As shown in Fig. 3, $BE$ of the La 3$d_{5/2}$ main peak of the diluted samples from the 0.1, 0.05 and 0.005 mol/l solutions and that of the bulk sample were 835.7, 836.0, 837.4, and 834.2 eV, respectively. The La 3$d$ spectra shifted systematically toward the higher $BE$ side with decreasing the concentration. The La 3$d$ main peak (lower-$BE$) and the satellite peak (higher-$BE$) correspond to the electron configurations of $|E^{f0}\rangle$ and $|E^{f1/2}\rangle$, respectively [9]. Relative peak intensity of the $|E^{f1/2}\rangle$ to $|E^{f0}\rangle$ states decresed with increasing the

![Figure 1](image1.png)  
**Figure 1** XD patterns of the diluted samples from the 0.005 (a), 0.05 (b) and 0.1 (c) mol/l solutions, and the bulk sample (d).

![Figure 2](image2.png)  
**Figure 2** $\chi$-$T$ curves of the ZFC samples from the 0.005 (a), 0.05 (b) and 0.1 (c) mol/l solutions. Inset: $\chi$-$T$ curve of the bulk sample (d).