Electric and structural properties of single crystal $La_{0.95}Sr_{2.05}Mn_2O_7$

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Abstract

We have grown the single crystal of the bi-layered manganaites $La_{2-2x}Sr_{1+2x}Mn_2O_7$ for x=0.525 by the optical floating zone furnace. The quality of obtained sample was evaluated by X-ray diffraction measurement. The electric and magnetic properties were also evaluated by the resistivity (ρ) and magnetic susceptibility (χ) measurements, respectively. A clear anomaly was observed around 210 K in both ρ and χ measurements. These results are compared with previous studies done by other groups, from the view of the oxygen concentration.

Key words: M-I transition; Single crystal; the oxygen content;

Rudlesden-Popper compounds with general formula $(La,Sr)_{n+1}Mn_nO_{3n+1}$ (n=1, 2, ∞) is intensively studied because of their unique properties, such as colossal magnetroresistance (CMR), Jahn-Teller effect and metal-insulator transition and so on[1,2]. These amazing phenomena are considered to originate from the strongly correlation between charge, spin and orbital degrees of freedom and is balanced very perilously on Mn atom which locates on center of a perovskite structure. Furthermore, it enables us to control the ionic covalent of Mn atoms, lattice effects and orbital degree of freedom between $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ by substituted La^{3+} for Sr^{2+} which has larger ionic radius than La^{3+}. Here, $La_{2-2x}Sr_{1+2x}Mn_2O_7$ (n=2) has bi-layered structure along c-axis; the natural stacking of $(La,Sr)MnO_3$ perovskite bi-layered is separated by (La,Sr)O. In other words, this material owns superlattice as it is. Therefore, it shows great anisotropy in some physical properties.

It has already been reported that charge-ordered(CO) and A-type Antiferromagnetic phase appear below $T_{CO,N}$=210 K[3] and CE-type AFM phase is also observed below T_{CE}=145 K in $LaSr_2Mn_2O_7$[4], which is 50% half-doped system. This suggests that CO phase induces CE-type AFM phase and the competition between CO and A-type AFM phase can occur in the crystal and this temperature region. Actually, it has recently reported that the phase competition between CO phase and A-type AFM phase below T_{CO} become strongest for x=0.525 in hole doped region x=0.5∼0.6[5]. However, there is few investigation reported so far, and their clear physical picture and systematic studies has not been well estimated, due to the difficulty to control the hole concentration.

In this paper, we will report the crystal growth of $La_{2-2x}Sr_{1+2x}Mn_2O_7$($x$=0.525) and their evaluation by means of ρ and χ. The single crystals have grown by the optical floating-zone method under the condition; at the growing rate 1 mm/hour, the amount of supplied O_2, 2 lit/min. The structural property was evaluated by X-ray diffraction owned four-goniometers ATX-G by RIGAKU at room temperature. A resistivity measurement was performed by standard ac four-probe technique down to the temperature 4.2 K. The magnetic susceptibility measurement was made by SQUID.

Fig.1 shows the result of X-ray diffraction of $La_{2-2x}Sr_{1+2x}Mn_2O_7$ (x=0.525) at room temperature. Four significant peaks represent the Bragg diffraction [0 1 5] and symmetrical planes [1 0 5], [0 1 -5], [1 0 -5], respectively. $La_{2-2x}Sr_{1+2x}Mn_2O_7$ classifies parent

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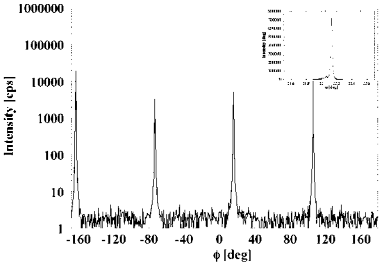

Fig. 1. The profile of X-ray diffraction measured at room temperature corresponding to the plane [0 1 5] and symmetrical plane {0 1 5}. Inset: the result of rocking curve on [0 0 10].

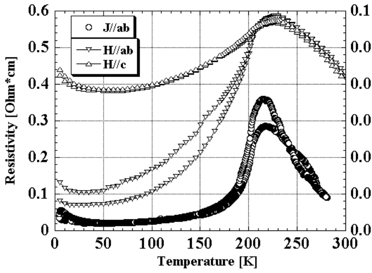

Fig. 2. Temperature dependence of resistivity supplied current with ab-plane ($J \| ab$; circle line) and that of magnetic susceptibility in magnetic field of 0.1T parallel to *ab*-plane and *c*-axis ($H \| ab$; opposite triangle line, $H \| c$; triangle line).

symmetry *I4/mmm* in space group, as well known. If this crystal consisted of lots of crystal domains, diffracted peaks satisfied Bragg's law (corresponded to {0 1 5}) must inevitably turn out more than four. Thus this suggests that the crystal clearly orientates along *c*-axis and has only single domain. Secondly, inset in Fig.1 shows the result of the rocking curve measurement corresponded to the plane [0 0 10] at room temperature. It shows only one peak and proves that this crystal consists of only single domain. The angle of $2\theta/\theta$ on [0 0 10] is good agreement with that of powder X-ray diffraction. The half-value width is estimated to be 0.023 deg. For these results, it can be determined that this crystal is single crystal.

Fig.2 shows the result of temperature dependence of the resistivity supplied current with the *ab*-plane ($J \| ab$) (corresponding to left Y-axis), and the magnetic susceptibility χ in magnetic field 0.1T parallel to *ab*-plane and *c*-axis ($H \| ab$, $H \| c$) (corresponding to right Y-axis). With decreasing temperature, the resistivity exhibits semiconductor-like behavior above $T_{CO,N}$=210 K and then abrupt decrease below $T_{CO,N}$. At lower temperatures, the value almost keeps constant implying metallic behavior. Furthermore, hysteresis was observed in the temperature region 200∼250 K. These results indicate that the metal-insulator transition may occur at 210 K and not only due to CO phase but also A-type AFM phase. If the phase includes charge-ordering, the resistivity curve must be non continuous and rise more and more below $T_{CO,N}$, because CO phase belongs to the same category as Mott insulator.

χ for $H \| c$ has maximum at $T_{CO,N}$ and decrease fluently in further low temperature. But, χ for $H \| ab$ decreases intensively below $T_{CO,N}$. It implies that AFM phase ordering occurs with parallel to *ab*-plane at lower temperature; in short, it's A-type AFM.

Here, let us discuss the present results. The obtained results didn't exhibits CO phase compared to those reported by other group[5]. Probably, this difference is ascribed to a surplus of the oxygen content. If the oxygen content excesses over stoichiometric amounts in this system, the hole concentration (Mn with tetravalent) is higher than x=0.525 under the condition that this crystal includes stoichiometric amounts of La and Sr. From the result of quantity analysis by Electron Probe Micro Analyzer (EPMA), we can confirm no difference of compositions La, Sr and Mn in this obtained crystal. On the other hand, resistivities and magnetic susceptibilities $La_{2-2x}Sr_{1+2x}Mn_2O_7$ x=0.50∼0.6 have been performed previously[5]. Compared with these results, resistivities and magnetic susceptibilities resemble closely to that of x=0.55 or x=0.6. This is to say, the obtained sample may contain a little more career concentration.

As conclusion, we have grown $La_{0.95}Sr_{2.05}Mn_2O_7$ single crystal and measured follwing properties. By X-ray diffraction measurement, it confirmed that the crystal structure has ideal symmetry. But the resistivity shows abrupt decrease at $T_{CO,N}$ and the magnetic susceptibility shows a clear anomaly at the same temperatures. These results predict that no or few CO phase exists in the obtained crystal, and it may own discrepancies in compositions to stoichiometric amounts, especially the oxygen content. In order to clarify this situation, the examination of the oxygen content by means of iodmetry method is currently in progress.

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