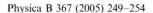


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Lu-induced orthorhombic phase in polycrystalline La_{0.7}Sr_{0.3}MnO₃

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Abstract

Polycrystalline La_{0.5}Lu_{0.2}Sr_{0.3}MnO₃ samples prepared by thermal decomposition are investigated by means of electron diffraction and high-resolution transmission electron microscopy. Besides rhombohedral La_{0.7}Sr_{0.3}MnO₃ phase (R-phase) and hexagonal LuMnO₃ phase (H-phase) reported by Huang, unexpectedly, an orthorhombic lattice (O-phase) with space group Pnma is observed in the interior of R-phase grain. The lattice parameters of the orthorhombic unit cell are $a_0 = 5.44 \,\text{Å}$, $b_0 = 7.65 \,\text{Å}$ and $c_0 = 5.48 \,\text{Å}$. The formation of O-phase results from $a^-b^+a^-$ type orthorhombic distortion of MnO₆ octahedra induced by partial substitution of Lu³⁺ for La³⁺. Meanwhile, based on image simulation of the interface between R and O-phases, the atomic bonding on the interface is particularly discussed.

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1. Introduction

The manganites perovskites $La_{1-x}Sr_xMnO_3$ have attracted considerable interest [1–5] due to their remarkable magnetic/transport properties and colossal magnetoresistance (CMR) effect. Several different

studies [6,7] have shown that CMR effect can be optimized when 30% of the Mn³⁺ is converted to Mn⁴⁺ by substitution of Sr²⁺ for La³⁺. Therefore, by substituting other trivalent lanthanide ions for La³⁺ and keeping Mn³⁺/Mn⁴⁺ ratio unchanged, some researchers have attempted to further improve the microstructure, magnetic and transport properties by means of La-site cation size effect. The type of compound can be characterized as La_{0.7-x}Re_xSr_{0.3} MnO₃, where Re stands for other trivalent lanthanide ions such as Lu. Ho or Pr.

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As the light rare earth element, substitution of Pr for La gives rise to a decrease in T_c , an increase in resistivity at T_c , and an increase in the magnitude of the magnetoresistance with decrease in average ionic radius of the La-site [8,9]. When La is replaced by Ho or Dy, a gradual increase of antiferromagnetic interaction can be observed with increasing holmium or dysprosium concentration, ultimately leading to a spin-glass-like state [10–12]. Huang et al. [13] proposed that Lu doping leads to phase separation and coexistence of rhombohedral and hexagonal phases in polycrystalline La_{0.7-x} Lu_xSr_{0.3}MnO₃ samples. The magnetic inhomogeneity also can be determined by the competition between two phases. Although La-site doping resulted in the variations of properties, the microstructure and the element distribution is not very clear due to the lack of systematic energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM) which provides direct observation of microstructure.

In an earlier study [14], the authors reported multiphase separation with rhombohedral (La_{0.7}Sr_{0.3} MnO₃), hexagonal (LuMnO₃) and cubic (SrMnO₃) phases in polycrystalline La_{0.7-x}Lu_xSr_{0.3}MnO₃ series. However, little work has been done on fine microstructure and composition examinations in the interior of grains. In this paper, with substitution of Lu³⁺ for La³⁺, coexistence of orthorhombic and rhombohedral lattice symmetry in the same grain is investigated using high-resolution transmission electron microscopy (HRTEM). The atomic bonding on the interface between both phases is interpreted according to projected model and image simulation.

2. Experimental procedure

Ceramic sample of $La_{0.5}Lu_{0.2}Sr_{0.3}MnO_3$ was prepared by thermal decomposition of the complex precursor, as described elsewhere [15]. Stoichiometric $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$, $Mn(CH_3COO)_2 \cdot 4H_2O$ and $Lu(NO_3)_3$ were used as the corresponding starting materials. The initial powders were presintered at $600\,^{\circ}C$ for 2 h. The obtained powders were ground, pelletized and sintered at $1000\,^{\circ}C$ for 12 h, and then the products were reground, pressed into pellets with a diameter of 6 mm, and finally sintered

at 1200 °C for 18 h. X-ray diffraction (XRD) analysis of sample was carried out on a Rigaku D/max 2400 X-ray diffractometer (12 kW) with Cu K_{α} radiation (wavelength λ $K_{\alpha}=1.54$ Å). The thin foils for TEM observation were prepared, firstly by mechanical thinning to 40 μ m, and then by dimpling to 10 μ m and lastly by ion milling. The sample was examined in JEOL-2010 HRTEM with a point-to-point resolution of 0.19 nm, operated in 200 kV. Composition analyses were performed on the FEI TECNAI G^2 F30 with EDX.

For the image simulation of interface, multislice calculations [16] were performed using the NCEMSS (version 1.8) software for running under linux platform. The microscope parameters used in the image simulations were the spherical aberration coefficient of the lens $C_s = 0.5$ mm, the convergent angle of the beam $\alpha = 0.5$ mrad and $\Delta f_{\text{scherzer}} = -43.0$ nm.

3. Results and discussion

Fig. 1 is the low-magnification TEM image, showing typical morphology of polycrystalline La_{0.7}Sr_{0.3}MnO₃ doped with Lu. According to the XRD pattern (an inset of Fig. 1), the bulk product is composed of La_{0.7}Sr_{0.3}MnO₃ rhombohedral perovskite-based phase (R-phase) and LuMnO₃ hexagonal phase (H-phase), a non-perovskite structure with MnO₅ trigonal bipyramids. Two selected area electron diffraction (SAED) patterns have demonstrated the coexistence of R-phase and H-phase, which agrees well with those reported previously [14].

Fig. 2 displays a TEM image of R-phase grain, size of which is about 300 nm. A SAED pattern from A region, as marked by black circle and arrowhead, can be assigned to be ($\overline{1}\,1\,0\,0$) reciprocal plane of R-phase. However, when the selected-area aperture is utilized in B region, the additional weak reflections in the middle of the main diffraction spots of R-phase can be observed from the obtained SAED pattern. Meanwhile, another pair of SAED patterns from both regions were obtained by titling the sample around the $[1\,1\,\overline{2}\,0]_R$ zone axis. Different from the typical $[2\,\overline{2}\,0\,1]$ SAED patterns from R-phase (Fig. 2b), these weak diffraction spots in the $[1\,1\,\overline{2}\,0]$

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