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Lu-induced orthorhombic phase in polycrystalline $La_{0.7}Sr_{0.3}MnO_3$

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Abstract

Polycrystalline $La_{0.5}Lu_{0.2}Sr_{0.3}MnO_3$ samples prepared by thermal decomposition are investigated by means of electron diffraction and high-resolution transmission electron microscopy. Besides rhombohedral $La_{0.7}Sr_{0.3}MnO_3$ phase (R-phase) and hexagonal $LuMnO_3$ 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 $a_o = 5.44\,\text{Å}$, $b_o = 7.65\,\text{Å}$ and $c_o = 5.48\,\text{Å}$. The formation of O-phase results from $a^-b^+a^-$ type orthorhombic distortion of MnO_6 octahedra induced by partial substitution of Lu^{3+} for La^{3+}. Meanwhile, based on image simulation of the interface between R and O-phases, the atomic bonding on the interface is particularly discussed.

Keywords: Orthorhombic lattice; Octahedral; Substitution; Atomic bonding

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 Mn^{3+} is converted to Mn^{4+} by substitution of Sr^{2+} for La^{3+}. Therefore, by substituting other trivalent lanthanide ions for La^{3+} and keeping Mn^{3+}/Mn^{4+} 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 $La_{0.7-x}Re_xSr_{0.3}MnO_3$, 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 $La_{0.7-x}Lu_xSr_{0.3}MnO_3$ 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 ($La_{0.7}Sr_{0.3}MnO_3$), hexagonal ($LuMnO_3$) and cubic ($SrMnO_3$) phases in polycrystalline $La_{0.7-x}Lu_xSr_{0.3}MnO_3$ series. However, little work has been done on fine microstructure and composition examinations in the interior of grains. In this paper, with substitution of Lu^{3+} for La^{3+}, 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 °C for 2 h. The obtained powders were ground, pelletized and sintered at 1000 °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 $\lambda\ K_\alpha = 1.54\,Å$). The thin foils for TEM observation were prepared, firstly by mechanical thinning to 40 μm, and then by dimpling to 10 μm 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 $La_{0.7}Sr_{0.3}MnO_3$ doped with Lu. According to the XRD pattern (an inset of Fig. 1), the bulk product is composed of $La_{0.7}Sr_{0.3}MnO_3$ rhombohedral perovskite-based phase (R-phase) and $LuMnO_3$ hexagonal phase (H-phase), a non-perovskite structure with MnO_5 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 $(\bar{1}\,1\,0\,0)$ 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 $[1\,1\,\bar{2}\,0]_R$ zone axis. Different from the typical $[2\,\bar{2}\,0\,1]$ SAED patterns from R-phase (Fig. 2b), these weak diffraction spots in the $[1\,1\,\bar{2}\,0]$