Available online at www.sciencedirect.com
SCIENCE DIRECT®

ELSEVIER

Physica C 433 (2006) 189–194

PHYSICA C

www.elsevier.com/locate/physc

Reversibility of structure phase transitions in $LaMnO_{3+\delta}$ manganite under heat treatment

V. Sedykh *, V.Sh. Shekhtman, I.I. Zverkova, A.V. Dubovitskii, V.I. Kulakov

Institute of Solid State Physics, Russian Academy of Sciences, Institute Street 2, Chernogolovka,
Moscow Region 142432, Russia

Received 26 October 2005; received in revised form 27 October 2005; accepted 27 October 2005
Available online 6 December 2005

Abstract

The effect of heat treatment on the formation and mutual transitions of the structure modifications in the ^{57}Fe-doped $LaMnO_{3+\delta}$ manganite has been experimentally investigated by X-ray diffraction analysis and Mössbauer spectroscopy. It has been found out that the successive heat treatments in vacuum and in air provide controlled reversible structural transformations between rhombohedral and two orthorhombic modifications. Variations in the oxygen environment configuration of cations and in crystal-chemical packing have been analyzed at reversible phase transitions. The experimental evidences confirming the presence of extra oxygen in the structure modifications of lanthanum manganite have been obtained.

PACS: 75.30.Vn; 75.90.+w; 74.62.Bf; 61.10.−i; 64.70.Kb

Keywords: $LaMnO_{3+\delta}$; X-ray diffraction analysis; Mössbauer spectroscopy; Phase transitions; Perovskite manganites

1. Introduction

Structure polymorphism of the compositions based on lanthanum manganite has been repeatedly discussed in literature [1,2]. The different conditions of synthesis make it possible to prepare a set of the structure modifications of $LaMnO_3$: a rhombohedral phase of space group $R\bar{3}c$, two orthorhombic phases (named *Pnma I* and *Pnma II*) of space group *Pnma* and a monoclinic phase of space group $P112_1/a$.

Peculiarity of the structure processes in the oxide family (as compared to ordinary metallic systems) is the combined influence of the temperature and controlled oxygen factor on the formation of the specific modification. According to

---

* Corresponding author. Tel.: +7 095 993 27 55; fax: +7 095 52 49 701.
E-mail address: sedykh@issp.ac.ru (V. Sedykh).

0921-4534/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.physc.2005.10.013

one of the viewpoints [3,4] there is no excess of oxygen. It is considered that the orthorhombic phase *Pnma II* has the standard stoichiometric composition ABO_3, and the phases *Pnma I* and $R\bar{3}c$ have the non-stoichiometric compositions: in the La and Mn positions there are the cation vacancies (the formula should be written as $A_{1-x}B_{1-x}O_3$). In this case when transiting from *Pnma I* to $R\bar{3}c$ the ion concentration correlates with the total number of cation vacancies. In our opinion the transition of a part of Mn^{3+} ions to Mn^{4+} in the phases *Pnma I* and $R\bar{3}c$ under oxidation is accompanied by the appearance of the fixed concentration of an excess of oxygen, i.e. the formula should be written as $ABO_{3+\delta}$. In this consideration the rhombohedral phase, in which the quantity of Mn^{4+} ions is maximal, has the maximum concentration of an excess of oxygen.

In the present work, the influence of different heat treatment conditions on the phase transitions between the structure modifications of the ^{57}Fe-doped $LaMnO_{3+\delta}$ compound has been investigated by X-ray diffraction analysis and Mössbauer spectroscopy to clear up the real picture of crystal-chemical packing.

2. Experimental

To synthesize the ^{57}Fe-doped $LaMnO_{3+\delta}$ compound a lanthanum oxide or carbonate (La_2O_3, $La_2(CO_3)_3\ 6H_2O$), manganese oxides Mn_2O_3 or MnO_2 and 4%^{57}Fe dissolved in HNO_3 have been used. Chemical analysis has shown that the oxide content in the specimens of the original compound was 99.5%. The specimens of the original compound taken in a stoichiometric ratio were ground and mixed in a ball micromill. Then the mixture was preliminary annealed in air at 900 °C for 10 h. After annealing the mixture was again ground. The final synthesis was made in air at 1100 °C for 20 h.

The orthorhombic phase *Pnma I* was synthesized when quenching a specimen at 1100 °C.

A sequential series of annealing at $T = 650$ °C in air and in vacuum (10^{-3} Torr) was performed on the same both non-doped and Fe-doped specimens with the original orthorhombic phase *Pnma I* to investigate the phase transitions.

A quantity of oxygen excess δ (or relation between the Mn^{3+} and Mn^{4+} ions) was determined by a direct weight method or potassium iodide titration. The compositions were $LaMn_{0.96}Fe_{0.04}O_{3.08}$ (Mn^{4+}—17%) for the phase *Pnma I* and $LaMn_{0.96}Fe_{0.04}O_{3.15}$ (Mn^{4+}—30%) for the phase $R\bar{3}c$.

X-ray diffraction measurements were carried out on the polycrystalline specimens at a diffractometer SIEMENS D500 (Cu Kα-radiation).

The ^{57}Fe Mössbauer measurements were carried out on the polycrystalline specimens at room temperature by using a conventional Mössbauer spectrometer operating in the constant acceleration mode. To analyze the absorption spectra, the thin-foil approximation was used and a least-square fit was performed assuming a sum of Lorentz functions.

3. Results and their discussion

X-ray diffraction measurements have shown that the original orthorhombic phase *Pnma I* of the ^{57}Fe-doped $LaMnO_{3+\delta}$ compound transforms to the rhombohedral modification $R\bar{3}c$ under annealing in air at $T = 650$ °C then to the orthorhombic phase *Pnma II* under annealing in vacuum at the same temperature. The next annealing in air specifies the following series of transformations: *Pnma II* to *Pnma I* to $R\bar{3}c$. It means that when varying the successive annealing conditions in vacuum and in air it is possible to obtain the mutual transitions of the indicated phases at the same specimen. X-ray diffraction patterns for different phases of the ^{57}Fe-doped $LaMnO_{3+\delta}$ specimen obtained after a series of heat treatments are shown in Fig. 1. The obtained data testify that the phase transitions at different heat treatments are reversible. The lattice parameters of the obtained phases are presented in Table 1.

To gain a better understanding of the occurring processes under heat treatment the Mössbauer investigations providing information of the nearest environment of the Mössbauer atom have been carried out. The peculiarities of oxygen environment of the Fe atoms replaced the Mn ones are mainly reflected in the considered case. Cation vacancies (if they exist), which are more distant