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materials letters
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Materials Letters 96 (2013) 82–84

Contents lists available at SciVerse ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Fluctuations of structural transformations in $La_{0.95}Ba_{0.05}Mn_{0.98}{}^{57}Fe_{0.02}O_{3+\delta}$ under heat treatment

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ARTICLE INFO

Article history:
Received 22 November 2012
Accepted 10 January 2013
Available online 20 January 2013

Keywords:
Perovskites
Crystal structure
X-ray techniques
Mössbauer spectroscopy

ABSTRACT

The structural transformations in polycrystalline Ba-doped lanthanum manganite $La_{0.95}Ba_{0.05}Mn_{0.98}Fe_{0.02}O_{3+\delta}$ under heat treatment in a vacuum have been studied by Mössbauer spectroscopy and X-ray diffraction analysis. It has been experimentally shown that the unusual fluctuation behavior of structural transformations in the compound annealed in a vacuum versus annealing time and/or temperature. We suppose that this behavior is related to stochastic processes.

1. Introduction

The lanthanum manganite compounds doped with divalent impurity (like Ca, Sr, and Ba) are the materials with colossal magnetoresistance and they are of great interest to many researchers.

Manganese in those compounds has a mixed valence: Mn^{3+} and Mn^{4+}. Mn^{3+} is the Jahn–Teller ion with a degenerated orbital state of electrons, while Mn^{4+} is not. Compounds with Jahn–Teller ions are usually characterized by strong lattice distortions and strong correlations between lattice and electron subsystems [1]. Changes in their structure result in significant changes in their electronic and magnetic properties.

Lanthanum manganite compounds can be obtained in different structural modifications depending on heat treatment conditions (temperature and oxygen concentration in ambient atmosphere during annealing) that can reversibly transform into each other [2]. So, by varying the heat treatment conditions it is possible to obtain one or another structural phases independently of the phase in which the sample was initially synthesized. The main crystal structure states are three orthorhombic *PnmaI*, *PnmaII**, and *PnmaII* (common space group *Pnma*) and one rhombohedral (space group *R-3c*) phases [3]. Each phase corresponds to a definite range of the ratio of Mn^{4+} to Mn^{3+} ion concentration.

In our work, Mössbauer spectroscopy in combination with X-ray diffraction (XRD) is used to investigate some features of structural transformations in Ba-doped lanthanum manganite $La_{0.95}Ba_{0.05}Mn_{0.98}Fe_{0.02}O_{3+\delta}$ caused by annealing of the samples in vacuum.

2. Experimental

Polycrystalline powder $La_{0.95}Ba_{0.05}Mn_{0.98}Fe_{0.02}O_{3+\delta}$ was prepared by a sol–gel method using lanthanum and barium nitrates and manganese acetate: $La(NO_3)_3 \cdot 6H_2O$, $Ba(NO_3)_2$, and $Mn(CH_3COO)_2 \cdot 4H_2O$. For Mössbauer investigations a small amount of Mössbauer isotope ^{57}Fe (2 at%) was introduced into the sample during its synthesis in the form of ^{57}Fe nitrate aqueous solution. The synthesis is described in detail in Ref. [4]. The ratio of concentrations of Mn^{3+} to Mn^{4+} was determined by iodometric titration.

Three vacuum annealing conditions were used. The first one was isothermal continuous annealing (ICVA), when each sample was one-time annealed at 650 °C for a definite duration t_{an} (t_{an} was from 4 to 12 h). The second condition was isothermal step-by-step annealing (ISbSVA), when a single sample was used: this sample was annealed at 650 °C for 1 h, cooled, and its structure investigated at room temperature, then this cycle was repeated many times, and the total annealing time was 20 h. The third condition was isochronous vacuum annealing (IVA), when each sample was annealed at a definite temperature for 8 h in the temperature range 645–705 °C. After vacuum annealing, all the samples were fast cooled down to room temperature under continuous pumping out (10^{-3} Torr) of the reactor with the sample.

XRD analysis was performed using a diffractometer SIEMENS D500 (Cu-Kα radiation). The lattice parameters were calculated by the Program PowderCell (Werner Kraus and Gert Nolze, BAM Berlin). The ^{57}Fe Mössbauer spectra were measured at room

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http://dx.doi.org/10.1016/j.matlet.2013.01.031

temperature using a conventional Mössbauer spectrometer MS1101 operating in a constant acceleration mode.

3. Results and discussion

According to the X-ray data the as-prepared $La_{0.95}Ba_{0.05}Mn_{0.98}Fe_{0.02}O_{3+\delta}$ powder sample was single-phase with a rhombohedral structure. Under vacuum annealing, a rhombohedral phase transforms into a mixture of orthorhombic phases: the *PnmaI* phase for ISbSVA and the *PnmaI* and *PnmaII** phases for ICVA and IVA. The titration data show that the quantity of Mn^{4+} ions is about equal to that of Ba ions (5%), i.e., the compound with orthorhombic phases has a stoichiometric oxygen composition ($\delta=0$) after vacuum annealing. The values of lattice parameters and the volume of unit cell for the Ba-doped compound ($a=5.531$ Å, $c=13.369$ Å, and $V=354.2$ Å^3 for the rhombohedral phase and $a=5.541$ Å, $b=7.798$ Å, $c=5.556$ Å, and $V=240.1$ Å^3 for the orthorhombic *PnmaI* phase) are slightly larger than that of the parent $LaMnO_{3+d}$ compound [3], since the Ba ion radius (1.35 Å) is significantly larger than the La one (1.15 Å). Since the lattice parameters of orthorhombic phases are very close, it is quite difficult to distinguish one phase from another by X-ray diffraction and to determine the contribution of each phase. Nevertheless, according to XRD, the lattice parameters and the partial ratio of orthorhombic phases vary significantly depending on annealing time (for ICVA and ISBSVA) and/or temperature (for IVA) and these variations have fluctuating characters.

To identify each phase and to estimate its contribution, Mössbauer spectroscopy was used.

The line width of Mössbauer spectrum for the as-synthesized rhombohedral phase is rather narrow and the spectrum was fitted by a single doublet, $\Delta=0.32$ mm/s, IS$=0.36$ mm/s, $\Gamma=0.33$ mm/s (Δ is a QS value; IS, an isomer shift).

After vacuum annealing, the Mössbauer spectra have strongly broadened quadruple-split (QS) doublets. It means that each spectrum is a superposition of several doublets with different values of quadruple-splitting (Δ) (for example, the spectra for parent compound $LaMnO_{3+d}$ were previously fitted by us using three doublets [5]). Since the shape of spectra is smooth, it is more correct to determine the Δ distribution $P(\Delta)$. We use the computer program DISTRI from the software MSTools [6] for the refinement of the Mössbauer spectra. As an example, Fig. 1 shows several room-temperature ^{57}Fe Mössbauer spectra and the corresponding $P(\Delta)$ for $La_{0.95}Ba_{0.05}Mn_{0.98}Fe_{0.02}O_3$ after ICVA at 650 °C for different annealing durations. This figure clearly shows the presence of three maxima in $P(\Delta)$ for all annealing conditions. We have previously shown that the first maximum with the largest Δ corresponds to the *PnmaII* phase with maximal distortions of the lattice due to the Jahn–Teller effect [7]. The third maximum with the smallest Δ corresponds to the *PnmaI* phase in which the Jahn–Teller effect is suppressed and which therefore is most symmetrical. The second maximum is related to the so-called intermediate phase *PnmaII** [5]. This phase is not independent and can accompany any other orthorhombic phase. So, each maximum in $P(\Delta)$ corresponds to the definite orthorhombic structural phase. The IS values for orthorhombic phases are virtually identical (0.37 ± 0.01 mm/s).Thus, it follows from the Mossbauer investigations that a mixture of three orthorhombic phases is formed after all vacuum annealing conditions rather than one or two orthorhombic phases as follows from XRD.

On vacuum annealing, when a system comes to a stoichiometric oxygen composition ($\Delta=0$), no changes must occur in this system. However it follows from Fig. 1 that the relative intensities of three maxima in $P(\Delta)$ for $La_{0.95}Ba_{0.05}Mn_{0.98}Fe_{0.02}O_3$ strongly fluctuate with annealing time and/or temperature. The position of each maximum does not change after any vacuum annealing conditions (Fig. 2). It means that the local environment around ^{57}Fe ions is virtually constant in each phase and does not depend on heat treatment conditions, but the quantity of each phase fluctuates. The dependences of the intensities of maxima for each orthorhombic phase on the annealing time and temperature for all the used annealing conditions are shown in Fig. 3. It should be noted here that the absolute QS values for ICVA and ISbSVA notably differ from each other (Fig. 2a and b). In addition, it follows from Fig. 3(a) that the amplitude of fluctuations for ICVA increases with annealing duration and is larger as compared to that for ISbSVA. Based on these results one can suppose that rather long time is necessary to “rock” a lattice and to displace ions from their positions under heat treatment for structural transitions. In this case distortions of a lattice may slightly increase and result in an increase in the QS values for ICVA.

It should be noted that so unusual fluctuation character in phase relation has been never observed in any oxide including lanthanum manganite compounds [5]. They have kept the structural state with a stoichiometric composition without change during vacuum annealing until they decomposed.

Very similar phenomena of phase fluctuations were observed by Katsnelson et al. [8]; they observed hydrogen-induced nonmonotonic structural evolution of the Pd-Mo and Pd-Ta deformed alloys in time and explained this behavior by stochastic processes of the structural transformations. The reasons of the fluctuations observed in our work are still not known but we suppose that they are due to stochastic processes as well although the reasons may be different.

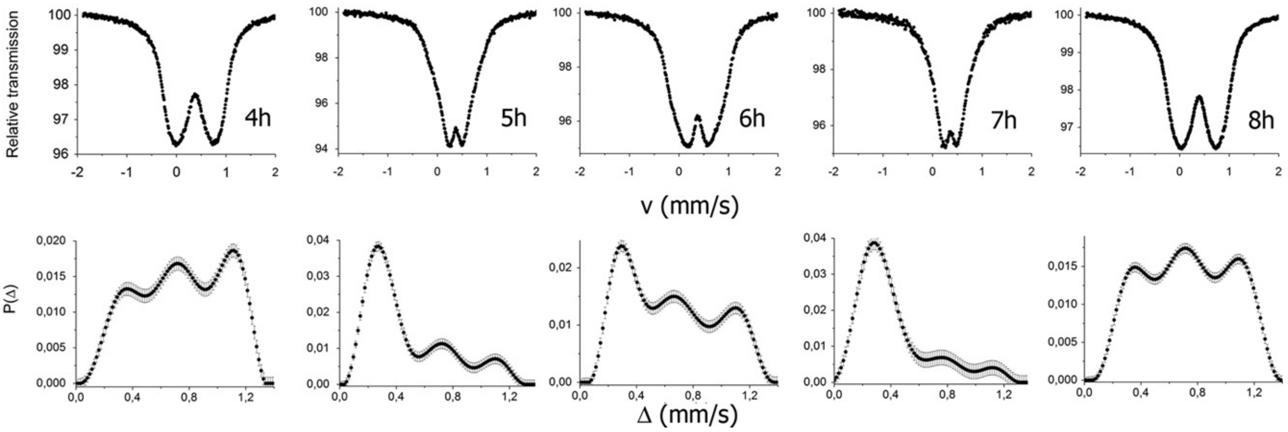

Fig. 1. Examples of room temperature ^{57}Fe Mössbauer spectra and corresponding $P(\Delta)$ for the mixture of orthorhombic phases in $La_{0.95}Ba_{0.05}Mn_{0.98}Fe_{0.02}O_3$ after continuous vacuum annealing at 650 °C for different annealing durations.

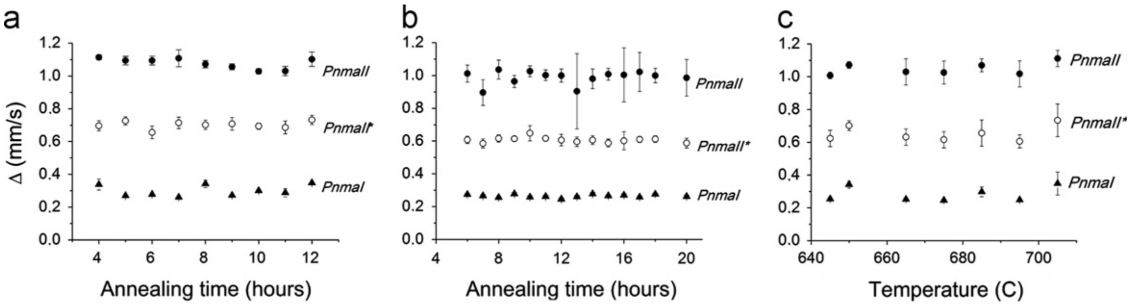

Fig. 2. Value of quadruple splitting (Δ) in $P(\Delta)$ as a function of annealing time t_{an} for isothermal (a) continuous and (b) step-by-step vacuum annealing and of annealing temperature T_{an} for (c) isochronous vacuum annealing.

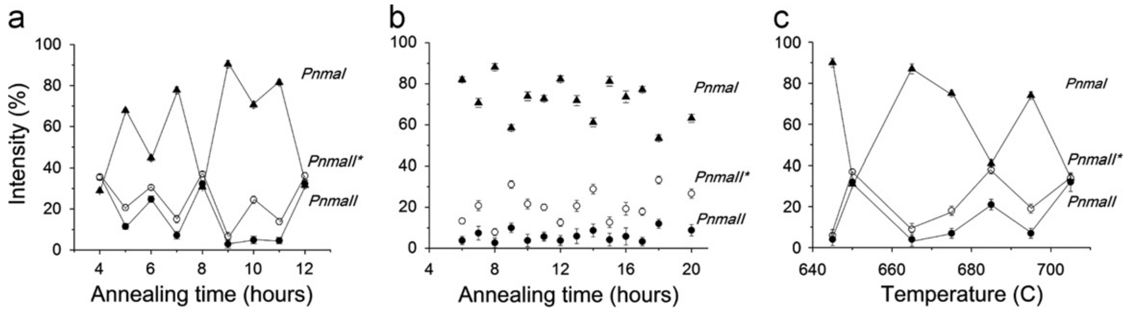

Fig. 3. Intensity of each maximum in $P(\Delta)$ as a function of annealing time t_{an} for isothermal (a) continuous and (b) step-by-step vacuum annealing and of annealing temperature T_{an} for (c) isochronous vacuum annealing.

We have some assumptions concerning the reasons of this observed unusual behavior in the $La_{0.95}Ba_{0.05}Mn_{0.98}Fe_{0.02}O_3$ compound. First, only tilting modes (octahedron rotations) participate in the formation of the *PnmaI* structure [9]. In the *PnmaII* phase the Jahn–Teller modes are present and their contribution is larger than that of tilting modes. Phase transition from *PnmaII* to *PnmaI* means virtually a significant quantitative change in the Jahn–Teller contribution only. Second, the presence of the intermediate *PnmaII** phase can facilitate the phase transitions between *PnmaI* and *PnmaII* phases in energy. Third, a unit cell volume of Ba-doped compound is larger than that of a parent compound. It means that a bond length increases while binding energy decreases, which can lead to a decrease in the energy difference of the structural phase states [10]. Forth, fast cooling of the samples after vacuum annealing can result in nonequilibrium states. These reasons we suppose may give rise to stochastic processes in the Ba-doped $La_{0.95}Ba_{0.05}Mn_{0.98}Fe_{0.02}O_3$ compound.

Note that it is only assumptions based on the presented experimental results, further investigations are inevitable and they are in progress.

4. Conclusions

The fluctuation character of structural transformations has been experimentally obtained for Ba-doped lanthanum manganite $La_{0.95}Ba_{0.05}Mn_{0.98}Fe_{0.02}O_3$ of a stoichiometric oxygen composition after different conditions of vacuum annealing.

The reasons of such unusual behavior in the compound are currently unknown and still open for discussion. This problem is under investigation now.

Acknowledgments

The authors are grateful to I.M. Shmyt'ko, B.S. Bokshtein, and V.E. Antonov for fruitful discussions of the results. This work was made in part under the financial support of RFBR grant 12-02-00303.

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