Structural transitions in $La_{0.95}Ba_{0.05}Mn_{0.98}{}^{57}Fe_{0.02}O_3$ under heat treatment

V. Sedykh · V. Rusakov

Abstract Structural transitions in polycrystalline Ba-doped lanthanum manganite $La_{0.95}Ba_{0.05}Mn_{0.98}Fe_{0.02}O_{3+\delta}$ have been investigated under different cooling conditions after vacuum annealing (fast and slow cooling) by Mössbauer spectroscopy and X-ray diffraction (XRD) analysis. A rhombohedral structure of the synthesized $La_{0.95}Ba_{0.05}Mn_{0.98}Fe_{0.02}O_{3+\delta}$ sample transfers into a mixture of the orthorhombic *PnmaI*, *PnmaII** and *PnmaII* phases (common space group *Pnma*) with a stoichiometric oxygen composition under vacuum annealing. The further vacuum annealing leads to fluctuations in a partial relation of the orthorhombic phases on fast cooling. This unusual behavior of the structural transitions are discussed.

Keywords Mössbauer spectroscopy · XRD analysis · Lanthanum manganites

1 Introduction

Polycrystalline Ba-doped lanthanum manganite $La_{0.95}Ba_{0.05}MnO_{3+\ddot{o}}$ with a rhombohedral structure synthesized by sol-gel method has been shown by us in [1] to transfer to a mixture of orthorhombic phases with a stoichiometric composition under vacuum annealing condition. The further vacuum annealing results in an unusual fluctuation change in a partial relation of orthorhombic phases after fast cooling of the samples down to room temperature.

V. Sedykh (✉)
Institute of Solid State Physics, Russian Academy of Sciences,
Academician Ossipyan Str.2, Chernogolovka, 142432, Russia
e-mail: sedykh@issp.ac.ru

V. Rusakov
Faculty of Physics, Lomonosov Moscow State University,
Leninskie gory, Moscow, 119991, Russia

🌱 Springer

In the present work the structural changes in the Ba doped lanthanum manganite $La_{0.95}Ba_{0.05}Mn_{0.98}Fe_{0.02}O_{3+\delta}$ have been investigated depending on cooling conditions of the samples (fast and slow cooling down to room temperature)) after vacuum annealing by Mossbauer spectroscopy and X-ray diffraction (XRD) analysis.

2 Experimental detail

Polycrystalline powder sample $La_{0.95}Ba_{0.05}Mn_{0.98}Fe_{0.02}O_{3+\delta}$ was synthesized by sol-gel method. Synthesis of the sample was described in details in [2]. Mossbauer isotope ^{57}Fe (2 at.%) was introduced into the sample during its synthesis for Mossbauer investigations.

The samples were annealed in a vacuum for different annealing time. Two cooling conditions were used. The first one was fast cooling when a reactor with a sample was taken out from a furnace after annealing and cooled down to room temperature under continuous pumping out. The second one was slow cooling in a vacuum down to room temperature with a cooling rate of about 50°/h.

Relation of valence states of Mn^{3+} and Mn^{4+} was determined by iodometric titration.

The ^{57}Fe Mössbauer spectra were measured at room temperature using a conventional Mössbauer spectrometer MS1101 operating in a constant acceleration mode. XRD analysis was performed using a diffractometer SIEMENS D500 (Cu-Kα -radiation). The lattice parameters were calculated by the Program PowderCell (Werner Kraus & Gert Nolze, BAM Berlin).

3 Results and discussion

According to the X-ray data the as-prepared polycrystalline powder $La_{0.95}Ba_{0.05}Mn_{0.98}Fe_{0.02}O_{3+\delta}$ sample has a single-phase composition with a rhombohedral structure (space group $R\overline{3}c$). Since there are reversible structural transitions in lanthanum manganites [3], it does not matter what phase is synthesized; varying heat treatment conditions (annealing in a vacuum or in air) it is possible to obtain one or another phase (rhombohedral or orthorhombic). The orthorhombic phases were obtained by annealing of the synthesized sample with a rhombohedral structure at 650 °C in a vacuum [1].

When a divalent impurity is introduced into the parent $LaMnO_{3+\delta}$ compound that replaces trivalent lanthanum ions, oxygen vacant sites appear in a lattice. Therefore already during synthesis in air a part of Mn^{3+} (Jahn-Teller) ions transfers into Mn^{4+} (non Jahn-Teller) ions, and oxygen coming with Mn^{4+} occupies first of all these vacant oxygen positions in a lattice and after that interstitial sites.

The titration data show that approximately 32 % Mn^{4+} ions are in a rhombohedral structure, and 5 % Mn^{4+} are in a mixture of the orthorhombic structures after vacuum annealing. It means that a quantity of Mn^{4+} ions is equal to that of Ba impurity (5 %), i.e. the sample with the orthorhombic phases has a stoichiometric oxygen composition ($\delta = 0$) after vacuum annealing.

The lattice parameters and the volume of unit cell of the phases in the Ba-doped compound are slightly larger than that of the parent $LaMnO_{3+\delta}$ compound [4]. It is

Table 1 Lattice parameters of the $R\bar{3}c$ phase and a mixture of two orthorhombic *PnmaI* and *PnmaII** phases of La$_{0.95}$Ba$_{0.05}$Mn$_{0.98}$Fe$_{0.02}$O$_{3+\delta}$ for different times of vacuum annealing

%Ba	t_{an}, h	Phase	a, Å	b, Å	c, Å	V, Å^3	%
0		R-3c	5.514(2)		13.298(4)	350.2(3)	
0		PnmaI	5.523(2)	7.788(3)	5.537(2)	238.1(3)	
0		PnmaII	5.736(2)	7.700(3)	5.534(2)	244.4(3)	
0		PnmaI	5.587(2)	7.814(3)	5.484(2)	239.4(3)	
		PnmaII*	5.642(2)	7.730(3)	5.521(2)	240.8(3)	
5	0	R-3c	5.531(2)		13.369(4)	354.2(3)	100
5	4	PnmaI	5.552(2)	7.815(3)	5.577(2)	242.0(3)	58
		PnmaII*	5.641(2)	7.757(3)	5.552(2)	243.0(3)	42
5	5	PnmaI	5.533(2)	7.801(3)	5.552(2)	239.6(3)	81
		PnmaII*	5.631(2)	7.748(3)	5.543(2)	241.8(3)	19
5	6	PnmaI	5.539(2)	7.802(3)	5.555(2)	240.0(3)	81
		PnmaII*	5.637(2)	7.737(3)	5.556(2)	242.0(3)	19
5	7	PnmaI	5.533(2)	7.798(3)	5.550(2)	239.5(3)	100
5	8	PnmaI	5.574(2)	7.818(3)	5.556(2)	242.1(3)	69
		PnmaII*	5.626(2)	7.764(3)	5.559(2)	242.8(3)	31
5	9	PnmaI	5.530(2)	7.803(3)	5.552(2)	239.6(3)	100
5	10	PnmaI	5.544(2)	7.799(3)	5.561(2)	240.4(3)	79
		PnmaII*	5.620(2)	7.745(3)	5.541(2)	241.2(3)	21
5	12	PnmaI	5.579(2)	7.825(3)	5.559(2)	242.7(3)	62
		PnmaII*	5.652(2)	7.746(3)	5.552(2)	243.1(3)	38

For comparison, the data for the parent LaMnO$_{3+\delta}$ compound are listed as well [6]. For two-phase samples a quantity of each phase is listed in the last column

related to the fact that the Ba^{2+} ionic radius (1.35 Å) is significantly larger than that of La^{3+} (1.15 Å) [5].

It follow from the X-ray data that the orthorhombic *PnmaI* phase appears when increasing vacuum annealing time, a quantity of rhombohedral phase decreases and that of *PnmaI* phase increases. After vacuum annealing with further fast cooling the rhombohedral phase disappears and a mixture of orthorhombic *PnmaI* and *PnmaII** phases is formed rather than one *PnmaI* phase; their partial relations significantly vary with annealing time and have a fluctuation character (Table 1). For comparison, the data for the parent LaMnO$_{3+\delta}$ compound are listed in Table 1 as well [6]. This behavior is unusual because the compound has a stoichiometric composition ($\delta = 0$) and nothing changes have to appear in it.

According to X-ray data a mixture of orthorhombic *PnmaI* and *PnmaII** phases is formed after slow cooling, their lattice parameters do not virtually change with annealing time and are a = 5.557 Å, b = 7.787 Å, c = 5.541 Å for *PnmaI* and a = 5.636 Å, b = 7.728 Å, c = 5.531 Å for *PnmaII**.

Since the lattice parameters of the orthorhombic phases are close in value, it is very difficult to separate them by XRD when a mixture of the phases is present. However it is very easy to identify each phase and estimate its contribution by Mössbauer spectroscopy.

For Mössbauer investigations, 2at%^{57}Fe was introduced into the compound. It follows from isomer shifts that iron has a trivalent state in all phases. The Fe^{3+} cation replaces Mn^{3+}. Since Fe^{3+} and Mn^{3+} ions have close ionic radii, this replacement does not introduce any notable distortions into the lattice.

Fig. 1 Mössbauer spectrum of the synthesized rhombohedral phase of the Ba-doped $La_{0.95}Ba_{0.05}Mn_{0.98}Fe_{0.02}O_{3+\delta}$ compound
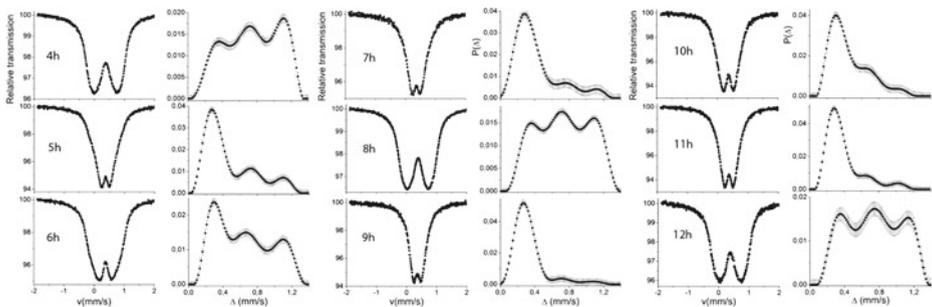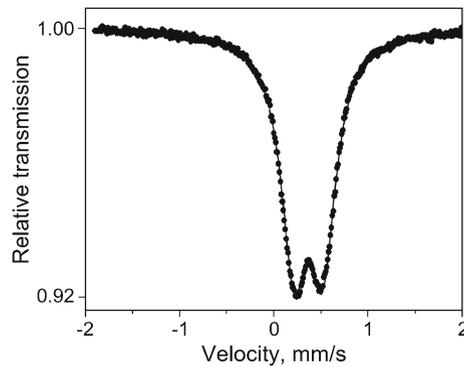
Fig. 2 Room temperature ^{57}Fe Mössbauer spectra and corresponding P(Δ) for the mixture of orthorhombic phases in $La_{0.95}Ba_{0.05}Mn_{0.98}Fe_{0.02}O_3$ after vacuum annealing at 650 °C for different annealing times with further fast cooling

The Mössbauer spectrum of the synthesized rhombohedral phase of the Ba-doped compound has rather narrow lines like in the parent compound [3] and is fitted by a single doublet (Fig. 1) ($\Delta = 0.32$ mm/s, IS = 0.36 mm/s, $\Gamma = 0.33$ mm/s).

The Mössbauer spectra for a mixture of the orthorhombic phases after all heat treatment conditions represent strongly broadened quadruple-splitting doublets that can be due to a superposition of several subspectra with different values of quadruple splitting (Δ). Room-temperature Mössbauer spectra for the samples annealed with different annealing times and fast cooled are shown in Fig. 2.

It is more correct to determine the distribution P(Δ), when it is not possible to describe an experimental Mössbauer spectrum by a small discrete set of partial spectra, or when spectra are smooth, i.e. the shape of lines do not display any specific features. This problem can be solved by one of the methods of incorrect tasks [6]. The quadruple splitting distribution P(Δ) was obtained for each Mössbauer spectrum after all vacuum annealing conditions by the program DISTRI of the complex programs MSTools [Rusakov] and are shown in Fig. 2.

It follows that P(Δ) has three maxima for all Mössbauer spectra for all used vacuum annealing conditions that correspond, as was previously shown by us [7], to three orthorhombic phases rather than two orthorhombic phases, as follows from X-ray data. The first maximum in P(Δ) with a largest Δ value corresponds to the local environment of the *PnmaII* phase with maximal lattice distortions related

Fig. 3 Value of quadruple splitting (Δ) in P(Δ) (Fig. 2) as a function of annealing time under fast cooling condition
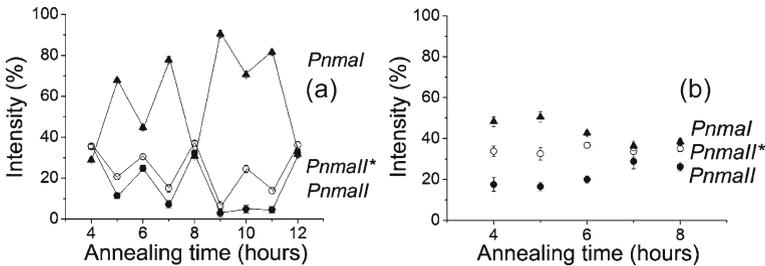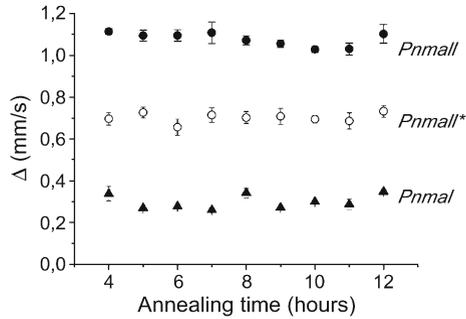
Fig. 4 Intensity of each maximum in P(Δ) (Fig. 2) as a function of annealing time under fast (**a**) and slow cooling (**b**) conditions

to the Jahn-Teller effect. The third maximum in P(Δ) with a smallest Δ value corresponds to the local environment of the *PnmaI* phase with minimal lattice distortions in which the dynamical Jahn-Teller effect is suppressed and which is most symmetrical as compared to *PnmaII*. The second maximum is associated to the so-called intermediate orthorhombic *PnmaII** phase, which is not independent and appears on phase transition from one to another orthorhombic phase [4].

It should be noted that the pure *PnmaII* phase in manganites doped with any divalent impurity cannot be obtained, since already during synthesis in air a part of Mn^{3+} automatically transfers to Mn^{4+}, and in this case its minimal quantity is equal to a quantity of impurity (stoichiometric oxygen composition) [1].

It follows from P(Δ) that the position of each maximum does not change in time within each phase (Fig. 3). It means that the local environment is virtually stable in each phase and does not depend on heat treatment conditions.

It has been previously shown by us that the parent $LaMnO_3$ compound with a stoichiometric oxygen composition (interstitial oxygen is absent) is stable and keeps its structural state without changing during further vacuum annealing until it decomposed [4]. However as it is follows from Fig. 2, in Ba-doped compound $La_{0.95}Ba_{0.05}Mn_{0.98}Fe_{0.02}O_3$ with a stoichiometric oxygen composition the relative intensities of three maxima in P(Δ) strongly fluctuate in time under vacuum annealing with further fast cooling. The annealing time dependence of the intensities of maxima for each orthorhombic phase is shown in Fig. 4a for vacuum annealing with further fast cooling.
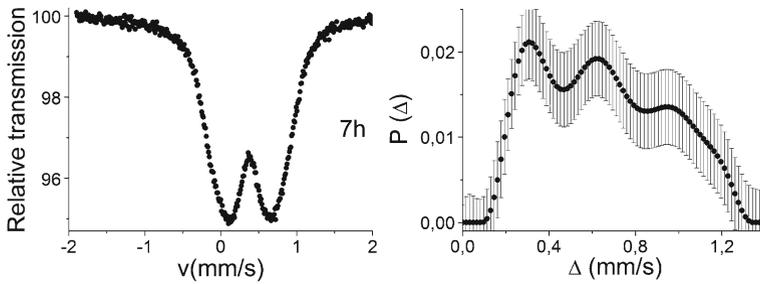
Fig. 5 Typical Mossbauer spectrum and corresponding $P(\Delta)$ of the sample annealed for 7 h and slowly cooled

Mössbauer spectra of the samples annealed with different vacuum annealing time and slowly cooled are virtually identical (Fig. 5). The system becomes equilibrium.

The quantity of the *PnmaI* phase dominates (intensity of doublet D-3) after four-hour vacuum annealing (when a mixture of the orthorhombic phases are initially formed) with further slow cooling (Fig. 4b). After long vacuum annealing the system leads to a virtually equi-probable relation of the phases. It corresponds to a minimal quantity of the *PnmaI* phase and maximal one of the *PnmaII* and *PnmaII** phases. Fluctuations are absent.

One may suppose that an orbital ordering must break down at a certain high temperature and a quantity of the *PnmaI* phase will tend to a maximal value. It means that two extreme states will exist in the Ba-doped $La_{0.95}Ba_{0.05}Mn_{0.98}Fe_{0.02}O_3$ compound. The first one is equilibrium with a maximal quantity of the *PnmaII* and *PnmaII** phases due to the Jahn-Teller effect and with a minimal quantity of the *PnmaI* phase. The second one can appear under vacuum annealing at a certain high temperature when an orbital ordering breaks down and only the *PnmaI* phase exists. It means that the definite corridor of the limiting quantities exists for each orthorhombic phase.

As it follows from Fig. 4, when fluctuation character of the variation in a partial ratio of the orthorhombic phases is observed under fast cooling, these fluctuations exist within these limiting quantities for each orthorhombic phase.

It was noted in [8], if the difference in energies of possible phase states is small, their simultaneous formation is possible, but this system is nonequilibrium. Since the Ba ion radius is smaller than that of La, the lattice parameters and bond lengths in the Ba-doped compound increase as compared to the parent compound [9] that can lead to a decrease in an energy difference of structural phase states. One can suppose that the system consisting of three orthorhombic phases with close energies is thermodynamically nonequilibrium.

Very similar phenomena of phase fluctuations were observed by Katsnelson et al. [10]; they observed hydrogen-induced nonmonotonic structural evolution in the Pd-Mo and Pd-Ta deformed alloys in time and explained this behavior by stochastic processes of the structural transformations.

It is necessary the further investigations to find out the reason of so unusual phenomenon observed by us in the Ba-doped $La_{0.95}Ba_{0.05}Mn_{0.98}Fe_{0.02}O_3$ compound. Nevertheless one can suppose that the fluctuations observed in the present work are due to stochastic processes in thermodynamically nonequilibrium systems as well in

spite of the fact that the reasons of fluctuations observed by us and Katsnelson may be different.

4 Conclusions

The structural transitions in the Ba-doped La$_{0.95}$Ba$_{0.05}$Mn$_{0.98}$Fe$_{0.02}$O$_{3+\delta}$ compound annealed at T$_{an}$ = 650 °C in vacuum and cooled under different cooling conditions (fast and slow cooling down to room temperature) have been investigated by Mössbauer spectroscopy and X-ray diffraction analysis. Polycrystalline sample synthesized by sol-gel method has a rhombohedral structure. A mixture of the orthorhombic *PnmaI*, *PnmaII**, and *PnmaII* phases with a stoichiometric oxygen composition (δ = 0) is formed under vacuum annealing conditions. The further vacuum annealing and fast cooling down to room temperature leads to unusual fluctuation changes in partial relation of the orthorhombic phases in the Ba-doped La$_{0.95}$Ba$_{0.05}$Mn$_{0.98}$Fe$_{0.02}$O$_{3+\delta}$ compound. Fluctuations disappear in the samples cooled slowly.

We suppose that the investigated system consisting of three orthorhombic phases is thermodynamically nonequilibrium and the observed fluctuations are due to stochastic processes.

References

1. Sedykh, V., Rusakov, V.S., Kveder, V.V., Zver'kova, I.I., Kulakov, V.I.: Mater. Lett. **96**, 82 (2013)
2. Sedykh, V.D., Shekhtman, V.Sh., Dubovitskii, A.V., Zverkova, I.I., Kulakov, V.I.: Phys. Solid State **51**(2), 373 (2009)
3. Sedykh, V., Shekhtman, V.Sh., Zverkova, I.I., Dubovitskii, A.V., Kulakov, V.I.: Physica C **433**, 189 (2006)
4. Sedykh, V., Abrosimova, G.E., Shekhtman, V.Sh., Zver'kova, I.I., Dubovitskii, A.V., Kulakov V.I.: Physica C **418**(3–4), 144 (2005)
5. Mishchenko, K.P., Ravdel', A.A. (eds.): Handbook of Physical Chemical Values. Chemistry, Leningrad (1974) (in Russian)
6. Rusakov, V.S., Kadyrzhanov, K.K.: Hyperfine Interact. **164**, 87 (2005)
7. Sedykh, V., Rusakov, V.S.: AIP Conf. Proceedings **1258**, 108 (2010)
8. Shmyt'ko, I.M., Kudrenko, E.A., Strukova, G.K.: Phys. Solid State **51**(9), 1947 (2009)
9. Chukalkin , Yu.G., Teplykh, A.E.: Phys. Metals & Metallography **104**(1), 99 (2007)
10. Katsnelson, A.A, Avdjukhina, V.M., Kolesova, N.S., Revkevich, G.P.: J. Surface Investigation (Poverkhnost') **12**, 835 (1997) (in Russian)