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^{57}Fe Mössbauer spectroscopy investigation of $La_{0.7}Ca_{0.3}Mn_{0.5}Fe_{0.5}O_3$

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ABSTRACT

A $La_{0.7}Ca_{0.3}Mn_{0.5}Fe_{0.5}O_3$ (LCMFO) ceramic sample was produced using conventional solid-state reactions. According to the X-ray diffraction data, the obtained sample has an orthorhombic space group *Pnma* (a = 5.482(2) Å, b = 7.739(3) Å, c = 5.446(3) Å). Magnetic properties of the obtained sample were studied by ^{57}Fe Mössbauer spectroscopy in the temperature interval of 77–423 K. All spectra recorded at room temperature exhibit the presence of trivalent Fe. Mössbauer spectra of the LCMFO sample show the presence of two intensive components: a paramagnetic doublet and a magnetic sextet, and several weak magnetic sextets. Within the investigated temperature range, phase separation and coexistence of a paramagnetic matrix and a phase of nano-sized antiferromagnetic clusters both below and above T_N were found.

Introduction

The interest to study of mixed-valence $R_{1-x}A_xMnO_3$-type manganites (where R is a rare-earth element, A is a divalent alkaline-earth element) has arisen again due to the colossal magnetoresistance effect (CMR effect) which was observed in these compounds (see reviews [1,2]). The variety of mixed-valence properties in manganites is, in most of cases, connected to the phase separation in these materials. The phase inhomogeneity in manganites is seen as a competition between charge-ordered insulating and ferromagnetic metallic phases. Due to the internal microscopic inhomogeneity in manganites phase separation (PS) occurs. This phase separation covers a wide length scale between 1 and 200 nm and can exhibit static or dynamic character [2,3]. It is well known that the colossal magnetoresistance (CMR) and accompanying properties can be attributed to the double exchange phenomena, which describes the electron jump between Mn^{3+} ($t_{2g}^3e_g^1$, JT ion) and Mn^{4+} ($t_{2g}^3e_g^0$, non-JT ion) ions. At the same time, the aforementioned properties also can be attributed to the ferromagnetic metallic state and paramagnetic insulating state below and above T_c, respectively. In the insulating state, Jahn-Teller distortions bring electrons into the localized state that leads to the charge ordering of Mn^{3+} and Mn^{4+} ions. Competition between charge ordering and double exchange mechanism leads to the antiferromagnetic insulating behavior (AFI) [3]. In ferromagnetic metals (FMM), which exhibit the presence of the CMR effect, charge-ordered clusters exist at low temperatures. The size of these clusters depends on the solid-solution content, carrier concentration, average atom size at the *A*-sites, temperature and some external factors like magnetic and electric fields [2,3]. Also, so-called electron-phase-separation effect can appear when the coexistence between carrier-rich ferromagnetic phase and carrier-poor antiferromagnetic phase takes place. This coexistence is the cause of the microscopic heterogenic electron distribution and influences the appearance of various magnetic structures [4]. The existence of large ferromagnetic clusters with a long life-time, far above T_C in $La_{0.7}Ca_{0.3}Fe_{0.09}Mn_{0.91}O_3$, has been detected [5].

The study of phase separation phenomena is a rather difficult process due to the smoothness of the metal-dielectric transition and the small size of the domains, which are hard to detect by neutron or X-ray diffraction. The electron-phase separation in manganites is the cause of the strong Coulomb interaction. Nano-sized clusters of one phase are included into another. The Coulomb interaction splits the large domains of the phase-separated system into smaller parts. These parts can form drops or bands according to the interaction strength and the competition between double

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exchange and Coulomb interaction, which also defines the cluster size.

Iron doping effects in manganites are also interesting to study because the Fe^{3+} ion has the same radius as Mn^{3+} has, and Fe^{3+} is magnetic but a non-Jahn-Teller cation and does not get involved into the double exchange [5]. Influence of the iron-doping on the magnetic and electric properties was studied for the hole-doped $La_{1-x}Ca_xMn_{1-y}Fe_yO_3$ (x = 0.3 and 0.25) and for the electron-doped manganites. It was shown that, in these materials, Mn^{3+} is replaced by Fe^{3+} and ferromagnetic interaction due to the double exchange in Fe^{3+}–Mn^{4+} couples does not occur [2,3].

Currently, we are not aware of other works, devoted to the investigation of the strong doping of $La_{1-x}Ca_xMn_{1-y}Fe_yO_3$ up to total replacing of Mn^{3+} by Fe^{3+}. In our earlier work [6] a study of 50% Mn/Fe substitution was done. There, it was shown that the 50%-substitution leads to full suppressing of magnetoresistance in the $La_{0.7}Ca_{0.3}Mn_{0.5}Fe_{0.5}O_3$ ceramic samples. A neutron diffraction study of substituted samples has been carried out in the temperature range of 10–300 K. Analysis of the temperature dependence of the average magnetic moment allows detection of the critical temperature (T_N = 350 K) of the transition to the G-type antiferromagnetic state. The magnetic moment of the Mn/Fe ions in LCMFO was obtained as 1.3 μ_B at 10 K. For LCMFO in the G-type AFM state the magnetic moment of each Mn ion has opposite direction as compared to the direction of the magnetic moment of neighboring Mn/Fe ions. On the other hand, the magnetization versus temperature measurements in weak magnetic fields show a irreversibility of the magnetization curves obtained in zero-field (M_{ZFC}) and in non-zero-field (M_{FC}) regimes. This irreversibility can be suppressed by increasing the magnetic field, which is characteristic of spin-glass materials.

In this work the strong doping of LCMO ceramic samples by Fe has been studied. Properties of the sample with iron atoms concentration up to 50% were investigated using ^{57}Fe Mössbauer spectroscopy.

It was shown the advantage that gives Mossbauer spectroscopy in investigation of phase separation in LCMFO in a wide temperature range

Materials and experimental methods

A $La_{0.7}Ca_{0.3}Mn_{0.5}Fe_{0.5}O_3$ ceramic sample was synthesized using the conventional solid-state reaction route. Powders of La_2O_3, $CaCO_3$, MnO_2 and Fe_2O_3 were mixed in stoichiometry quantities and two times fired in air at temperatures of 1320 °C for 35 h with intermediate grinding [6]. The obtained mixture was pressed into a 7 × 7 × 4 mm-size cuboid using 30 MPa hydrostatic compression. The final annealing was made in air at a temperature of 1375 °C for 22 h.

The purity of the obtained sample was checked using X-ray diffraction (Rigaku IV) in the θ -2θ geometry. The angle range was 10–100 deg. (step was 0.04 deg., velocity 2 deg/min., and filter Ni (K_β) CuK_α λ = 1.54056 Å). According to the X-ray diffraction data, the sample belongs to an orthorhombic space group *Pnma* with the lattice parameters of *a* = 5.482(2) Å, *b* = 7.739(3) Å and *c* = 5.446 (3) Å. Neutron diffraction measurements of the LCMFO were also performed [6]. The same structure with an orthorhombic space group *Pnma* was observed.

^{57}Fe Mössbauer spectra were recorded in the temperature interval of 77–423 K in transmission geometry using a maximal Doppler velocity of 10.00 mm/s. A 25 mCi Cyclotron Co. ^{57}Co: Rh source was used for producing of gamma quanta. For measurements at temperatures between RT and 77 K an Oxford continuous-flow cryostat with a liquid N_2 as a cooling agent was used. For measurements above room temperature a home-built resistive heater with the sample placed in a dry N_2 atmosphere was used. The full hamiltonian of combined electric and magnetic interactions was used in the fit program. Fitting model contained the following Mössbauer parameters: line width (was taken the equal for all spectral components), quadrupole splitting (QS = $eQV_{zz}/2$), isomer shift (δ), line intensity (I), and magnetic hyperfine field (B_{eff}) for magnetic sextets. Isomer shift values were taken relative to α-Fe at room temperature.

Mössbauer spectra of the $La_{0.7}Ca_{0.3}Mn_{0.5}Fe_{0.5}O_3$ sample: results and discussion

Mössbauer spectroscopy was used for monitoring the oxidation state of Fe and to check the sample hyperfine properties. The spectra at three selected temperatures are shown in Fig. 1. From Fig. 1, two intensive components: a paramagnetic doublet and a magnetic sextet, as well as two weak magnetic sextets, were used in the fitting model. All spectra exhibit the presence of one paramagnetic component with the isomer shift of $\delta \approx 0.32$ mm/s (at RT), indicating a trivalent state of Fe, and the QS value of 0.39 mm/s (at RT). The dominating sextet with intensive resonance lines has a hyperfine field value of ~50 T and δ = 0.45 mm/s (at RT). This sextet looks very similar to low temperature pictures for $La_{0.5}Ca_{0.5}$-$Mn_{1-x}Fe_xO_3$ manganites with a very small amount of Fe (x = 0.01), which show a full magnetic ordering below 50 K [7]. Connection between the paramagnetic doublet and the dominated magnetic sextet is confirmed by an intensity ratio behavior: the I_{PM}/I_M ratio increases with temperature increasing. According to

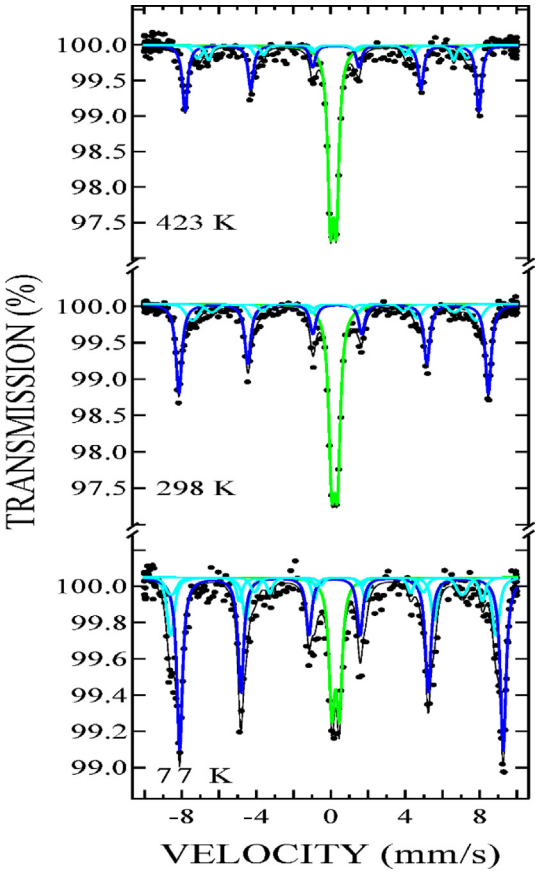

Fig. 1. ^{57}Fe Mössbauer spectra of $La_{0.7}Ca_{0.3}Mn_{0.5}Fe_{0.5}O_3$ recorded at indicated temperatures. Components due to the paramagnetic doublet (green) and the magnetic sextets (blue, cyan) are indicated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

this behavior, magnetic ordering of a part of the sample occurs between 423 K and 77 K. The weaker magnetic sextets in the Mössbauer spectra can possibly be attributed to the small local distortions in surroundings of iron atoms. In contrast to a recent study of manganites, done on samples containing a small iron amount of x = 0.01 [7], in our study the paramagnetic component remains visible in all spectra (77–423 K). Moreover, the line width of this paramagnetic component does not drastically change in the examined temperature range, which indicates a spatial separation of paramagnetic and magnetic phases in our sample.

Mössbauer spectra of the LCMFO sample show the presence of magnetically split components up to 423 K – the highest temperature that was achieved in this study. Thereby, a 50% Mn-by-Fe substitution level in LCMFO ceramics leads to an almost full substitution of Mn^{3+} ions by Fe^{3+} ions, that is accompanied by a double-exchange-process (Mn^{3+}–O^{2-}–Mn^{4+}) interruption and suppression of ferromagnetism at low temperatures. In the studied sample phase separation and coexistence of paramagnetic matrix and the phase constructed from nano-sized AFM clusters are observed both below and above critical temperature of T_N = 350 K, which is the critical temperature for transition to the G-type antiferromagnetic state as can be seen from the spectrum of neutron diffraction obtained from the same sample [6].

Conclusion

In this work a $La_{0.7}Ca_{0.3}Mn_{0.5}Fe_{0.5}O_3$ ceramic sample was produced successfully using a standard solid-state reaction route. According to the X-ray and neutron diffraction data the obtained sample has an orthorhombic space group *Pnma* and the lattice parameters were found to be a = 5.482(2) Å, b = 7.739(3) Å and c = 5.446(3) Å. All Mössbauer spectra recorded in temperature interval of 77–423 K show the presence of an intense magnetically-ordered sextet along with a paramagnetic doublet, that is in contrast with the recent study of LCMFO with a small iron concentration. The observed line-width values at different temperatures indicate a spatial separation of paramagnetic and magnetic phases in the sample. The interruption of double exchange and the suppression of ferromagnetism at low temperatures due to the high level of substitution were observed. And the coexistence of paramagnetic matrix with the nano-sized antiferromagnetic clusters was found below and above T_N = 350 K. The obtained results fulfill the investigation results [6], that were performed using $La_{0.7}Ca_{0.3}Mn_{0.5}Fe_{0.5}O_3$ samples and does not contradict the results [5] and other works, devoted to investigation of LCMFO properties with low iron concentration, and also they help to reveal the dynamic of Fe influence.

Conflict of interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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