Crystal Structure and Magnetocaloric Effect of La$_{0.80}$Ag$_{0.15}$MnO$_3$ Nanoparticles

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Abstact: Annealing of non stoichiometric La$_{0.80}$Ag$_{0.15}$MnO$_3$ nanoparticles leads to the change of the crystal symmetry from $Pnma$ to $R3c$ and to almost doubling of its Curie temperature from 117 K to 317 K. This effect is due to the releasing of lattice distortions and strengthening of double exchange interaction. The large values of the magnetocaloric entropy of the order of $\Delta S = 6.19$ J/(kg K) were observed at $\Delta T = 5$ T and $T = 315$ K.

DOI: 10.12693/APhysPolA.137.900

PACS/topics: manganites, nanoparticles, magnetic properties, magnetocaloric effect

1. Introduction

Magnetic cooling based on magnetocaloric effect (MCE) is a simple, convenient, and more promising attractive cooling technology than the classical one used in the vapour compression refrigerators [1]. MCE is an intrinsic property for all magnetic materials. Materials exhibiting the large MCE are actively sought and investigated [2]. Large values of the MCE are observed in rare earth elements [1, 2]. Perovskite lanthanum hole doped manganites with a general formula of La$_{1-x}$Ag$_x$MnO$_3$ have arisen as potential candidates in magnetic refrigeration at various temperature ranges [3–5]. Recently, it was shown on La$_{0.80}$Ag$_{0.15}$MnO$_3$ ceramic that the magnetic entropy change is 5.6 J/(kg K) for the field change of 2.6 T at 270 K, which corresponds to 6 J/(kg K) for Gd [3]. A significant advantage of these materials is the possibility of controlling the temperature of phase transitions in a wide range including room temperature, by varying the concentrations of the constituent chemical elements and conditions of synthesis [5, 6]. Nowadays, the interest shifts from classical ceramic materials [3–5] towards nanosized materials [7]. This work is continuation of our previous research of nanosized La$_{1-x}$Ag$_x$MnO$_3$ materials [8]. In our study we modify magnetic properties of La$_{0.80}$Ag$_{0.15}$MnO$_3$ nanosized off stoichiometric material by heat treatment in order to reach magnetic transition above the room temperature.

Nanosized powder La$_{0.80}$Ag$_{0.15}$MnO$_3$ was prepared by the glycine-nitrate method, which is advantageous due to series of simple steps and the ability to achieve greater efficiency compared to other methods [9].

2. Experimental procedure

A molar ratio between glycine and nitrate was equal 1. Formation of agglomerates was suppressed by additional oxidant (NH$_4$)NO$_3$, which was added to solution with the same weight as glycine. The as-prepared samples were afterwards annealed at 800 °C for 1, 12 and 48 hours in the air. We use labels $a_0$, 1h, 12h and 48h when referring to these four samples in the main text. Powder X-ray diffraction (XRPD) measurements at room temperature were carried out on the Rigaku Ultima IV diffractometer. The diffraction patterns were analyzed by the FullProf program that is based on the full-profile Rietveld method [10]. The basic parameters of crystal structure are summarised in Table I. The as-prepared sample adopts orthorhombic crystal structure ($Pnma$). The building blocks MnO$_6$ of the crystal structure were deformed by Jahn Teller (JT) distortion, and were tilted. We expected that the degree of JT distortion is large [11]. The annealed samples crystallized in rhombohedral structure ($R3c$). The size of nanoparticles increased with annealing time, and then the amount of precipitated Ag was reduced. Scanning electron microscopy (SEM) was performed on Mira III FE (Tescan). The SEM analysis confirmed our previous results [8], namely that the prepared samples in the form of fine powder form agglomerates and the size of nanoparticles scales the size determined by XPRD (Table I). The mixed-valence state was determined with iodometric titration. The average oxidative state increased with heating due to incorporation of Ag into the lattice, and was close to 3.30. Such result implies the presence of 70% of Mn$^{3+}$ and 30% of Mn$^{4+}$ in samples.

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3. Results and discussion

Magnetization and AC susceptibility measurements were done by the Quantum Design MPMS XL-5 SQUID magnetometer. Our measurements revealed that all samples undergo paramagnetic (PM) to ferromagnetic (FM) transition at the Curie temperature \(T_C\). The examples of the temperature dependences of magnetization in zero field cooled (ZFC) and field cooled (FC) regimes and DC susceptibility are shown in Fig. 1. The hysteric behaviour between magnetization measurements performed in ZFC and FC regimes for low applied magnetic fields is typical feature of all samples. Bifurcation temperature \(T_b\) is comparable with the Curie temperature \(T_C\), which was determined as a minimum on \(d\mu/dT(T)\) and \(d\chi'/dT(T)\) dependence or from Arrot's plots. The value of \(T_C\) increases from 117 K for sample \(a0\) to 310 K, 316 K and 317 K for annealed samples 1h, 12h and 48h, respectively, as shown in Fig. 1a. Doubling of \(T_C\) is mainly due to reduction of JT distortions and to the increase of bonding angle Mn–O–Mn induced by crystal structure transformation from \(Pnma\) to \(R3c\) (Table I). It was shown theoretically that the JT coupling drastically reduces the Anderson-Hasegawa double exchange (DE) due to reduction of mobility of electrons, which is required by mechanism of this interaction [12].

XRPD measurements in analogy with our study performed on \(La_{1-x}Ca_xMnO_3\) system of nanoparticles [11], indicate that the JT distortion of crystal lattice is enhanced on as-prepared sample. The pressure effect on \(T_C\) causes that due to very low mobility of 3d electrons the dominant exchange interaction in the case of as-prepared sample is superexchange [13, 14]. The releasing of JT distortion by the heat treatment leads to enhanced \(T_C = 225 \text{ K}\) preserving \(Pnma\) structure, as was shown for ceramic sample with stoichiometric composition \(La_{0.85}Ag_{0.15}MnO_3\) [4]. Additional rise of \(T_C\) is attributed to the increase of bonding angle Mn–O–Mn due to the structure phase transformation, because the strength of (DE) ferromagnetic interactions and the corresponding value of \(T_C\) are proportional to a bandwidth of the conduction \(e_g\) electrons, given by \(W = \nu \cos(\phi) \cos(\theta_{ij}/2)\), where \(\nu\) is the covalent mixing parameter, \(\phi\) is the bond-bending angle (\(\phi = 180^\circ - \beta\)), \(\beta\) is Mn–O–Mn bond angle, and \(\theta_{ij}\) is the angle between the two spin directions of the neighbouring manganese ions [15].

High temperature magnetic inverse susceptibility \(1/\chi\) (insert of Fig. 1b) indicates the validity of the Curie-Weiss law, i.e., \(\chi = C/(T - \theta)\), for all samples in temperature region enough high above \(T_C\) (\(C\) is the Curie constant, \(\theta\) is the paramagnetic Curie-Weiss temperature). Therefore, for \(a0\), 1h, 12h and 48h samples we have \(\theta = 116 \text{ K}, 310 \text{ K}, 318.4 \text{ K}, \text{ and } 318 \text{ K}\) and \(\mu_{eff} = 4.99\mu_B\), \(\mu_{eff} = 5.17\mu_B\), \(\mu_{eff} = 4.64\mu_B\), and \(\mu_{eff} = 5.32\mu_B\), respectively. The experimental values of \(\mu_{eff}\) are very close, especially for sample 12h, to theoretical predictions \(\mu_{eff} = 4.62\mu_B\). In fact, this assumes the presence of 70% of Mn\(^{3+}\) (4.90\(\mu_B\)) and 30% of Mn\(^{4+}\) (3.87\(\mu_B\)) in samples.

The transition from ferromagnetic (FM) to paramagnetic (PM) phase on rhombohedral sample 48h is accompanied by the presence of distinguished maxima in both in-phase \(\chi'(T)\) at 301 K and out-of-phase \(\chi''(T)\) at 305 K components of AC susceptibility (Fig. 2a). The temperature dependence of \(\chi'(T)\) corresponds very well to measurements of magnetic moment in ZFC regime.

![Fig. 1. Temperature dependence of (a) magnetization in ZFC and FC regimes for annealed sample 48h (and for sample \(a0\) in insert), (b) susceptibility (and inverse susceptibility in insert) for annealed sample 48h.](image)

**Summary of basic crystal parameters for as prepared sample and annealed samples at 800 °C**

| Sample | Crystal structure | \(a [\text{Å}]\) | \(b [\text{Å}]\) | \(c [\text{Å}]\) | \(V [\text{Å}^3]\) | Mn–O1–Mn angle \(\beta_1\) | Mn–O2–Mn angle \(\beta_2\) | Particle size [nm] | Ag content [%] | Oxidative state |
|--------|------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| \(a0\) | \(Pnma\)         | 5.5791         | 7.7615         | 5.5342         | 239.64         | 155.799        | 136.686        | 22.614         | 4.33           | —              |
| 1h     | \(R3c\)          | 5.4986         | 5.4986         | 13.3596        | 349.81         | 165.518        | —              | 36.740         | 0.22           | —              |
| 12h    | \(R3c\)          | 3.4970         | 5.4976         | 13.3618        | 349.74         | 165.520        | —              | 39.766         | 0.48           | 3.30           |
| 48h    | \(R3c\)          | 3.5001         | 5.5001         | 13.3604        | 350.02         | 165.517        | —              | 48.099         | 0.33           | —              |

**TABLE I**
Change of slope in $\chi'(T)$ and a dull maximum in $\chi''(T)$, which start to develop below 55 K, can indicate a creation of short range antiferromagnetic correlations, or can be attributed to freezing of magnetic moments. The mentioned anomaly is weaker than in orthorhombic La$_{0.85}$Ag$_{0.15}$MnO$_3$ sample [4]. Figure 2b demonstrates frequency dependence of maxima in $\chi'(T)$ and $\chi''(T)$, which are reduced by the frequency increase, but do not change their position.

The ferromagnetic character of samples is evident from magnetic hysteresis loops taken at 5 K (Fig. 3a). The coercive force decreases from 156.65 mT for $as0$ to 16.2 mT for 48h with annealing (insert Fig. 3a), and for rhombohedral samples is negligible at room temperature. The magnetization of $as0$ sample does not completely saturate at 5 T, and both remnant and saturated magnetization increases with annealing.

Figure 3b shows a dependence of $B/\mu$ vs. $\mu^2$, which is known as the Arrott plots for sample 48h which was constructed from magnetic isotherms in the vicinity of $T_C$. The positive slope in almost the whole temperature range indicates the second order magnetic transition. The same conclusion can be made from the Arrott plots constructed for $as0$ sample. The magnetocaloric properties of La$_{0.80}$Ag$_{0.15}$MnO$_3$ nanoparticles, orthorhombic sample $as0$ and rhombohedral sample 48h, have been investigated by indirect method based on determination of the magnetic entropy change $\Delta S$ from measurements of magnetic isotherms in a given temperature range. For sample $as0$ the range varies from 95 K to 170 K, and for sample 48h is from 280 K to 345 K. The temperature dependence of $-\Delta S(T)$ in respect with applied magnetic field which is shown in Fig.4. The highest values $-\Delta S \approx 1.22$ J/(kg K) ($\Delta\mu_0H = 5$ T) for $as0$ sample ($Pnma$) are typical for temperature range near $T_C$ between 112 K and 123 K, which corresponds to very broad transition to ferromagnetic state. The determined value is much smaller than $-\Delta S = 5.16$ J/(kg K) ($\Delta\mu_0H = 5$ T, $T = 270$ K) for
crystal structure with the same crystal structure where the degree of JT distortion was partially released by annealing [4]. The maximal value of \( -\Delta S = 6.19 \text{ J/(kg K)} \) \((-\Delta \mu_0 H = 5 \text{ T}, T = 315 \text{ K})\) for \(a\text{48}\) sample (\(R\bar{3}c\)) is higher than for orthorhombic sample [4], and the value \(-\Delta S = 4.08 \text{ J/(kg K)} \) \((-\Delta \mu_0 H = 2.79 \text{ T}, T = 315 \text{ K}, a\text{48}\) is comparable with \(-\Delta S = 5.6 \text{ J/(kg K)} \) \((-\Delta \mu_0 H = 2.7 \text{ T}, T = 265 \text{ K})\) of a ceramic sample with the same chemical composition and \(R\bar{3}c\) structure [3]. In addition \(-\Delta S = 3.58 \text{ J/(kg K)} \) \((-\Delta \mu_0 H = 2.21 \text{ T}, T = 315 \text{ K}, a\text{48}\) is much larger than \(-\Delta S = 0.96 \text{ J/(kg K)} \) \((-\Delta \mu_0 H = 2 \text{ T}, T = 306 \text{ K})\) of a nanosized sample with similar composition, and prepared by sol gel method [7].

Conclusions

To summary, the self combustion method in combination with heat treatment is powerful method for a preparation of magnetic nanoparticles with the Curie temperature above the room temperature, e.g., with \(T_C = 315 \text{ K}\) and large values of the MCE with \(-\Delta S = 6.19 \text{ J/(kg K)} \) at \(\Delta \mu_0 H = 5 \text{ T}\) and \(T = 315 \text{ K}\), which have large potential for practical application. Our study underlines the dominant effect of JT distortion of the crystal lattice on magnetic properties of hole-doped manganites, which is stronger than the change of crystal structure itself.

Acknowledgments

This research was financed by projects VEGA 2/0137/19, SK-SRB-18-0066 and ITMS: 26220220186.

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