Exchange Bias Effect in La$_{1-x}$Ag$_x$MnO$_3$ Nanopowders

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Abstract. Exchange bias (EB) phenomena were first observed in the La$_{1-x}$Ag$_x$MnO$_3$ as prepared and heat treated (300 °C/2 hours) nanopowders (x = 0.10, 0.15, 0.20) which were synthesized by self-combustion glycine-nitrate method. These nanoparticles have an average size of about 25 nm and adopt orthorhombic $Pnma$ crystal structure. Cooling in magnetic field $H_E \neq 0$ through the Curie temperature $T_C$ shifts hysteresis loop in horizontal and vertical direction. The values of exchange bias field $H_E$, coercive field $H_C$, remnant asymmetry $\mu_R$ and coercive magnetization $\mu_c$ increase with increasing value of cooling field $H_E$. In addition the training effect was observed. Basic magnetic properties like the Curie temperature $T_C$ and the saturated magnetization $\mu_s$ increase with increasing value of cooling field $H_E$. Heat treatment at 600 °C/2 hours increases the average size of nanoparticles to about 55 nm, crystal structure changes to rhombohedral structure (space group $R3c$) and EB effect vanishes.

1 Introduction

The exchange bias (EB) was discovered more than 55 years ago, by Meiklejohn and Bean on Co/CoO core–shell nanoparticles [1], and its characteristic signature is the horizontal shift of the centre of magnetic hysteresis loop from its normal position at $H = 0$ to $H_E \neq 0$ and vertical shift which can be characterised by remnant asymmetry $\mu_R$. EB usually occurs in systems which are composed by an antiferromagnet (AFM) that is in atomic contact with a ferromagnet (FM) after the system is cooled, below the respective Néel and Curie temperatures $T_N$ and $T_C$, in an external cooling field $H_E$. EB phenomena were observed in various materials like Laves phases, intermetallic compounds and alloys, binary alloys, Heusler alloys [2] or on layered bulk fluorometallo complex [3] where different aspects of magnetism were focused from the EB effect. The first evidence of the EB effect in mixed-valent manganites having perovskite structure was reported in a spontaneously phase separated system Pr$_{1/3}$Ca$_{2/3}$MnO$_3$ [4] which stimulated new interest for study of the EB effect in structurally single-phase compounds. The EB phenomena attributed to the spontaneous phase separation are very often observed in manganites with different perovskite structures. In the case of a fine particle system the surface to volume ratio becomes significantly large compared to the bulk counterpart. In such a case the surface effect dominates over the core part quite often, leading to a variety of magnetism and core-shell model can provide good interpretation of observed phenomena. Both concepts were frequently used for interpretation of EB effects in the La$_{1-x}$Ca$_x$MnO$_3$ [5-10], Nd$_{0.5}$Ca$_{0.5}$MnO$_3$ [11] and Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ [12] nanoparticles. In our paper we report on EB phenomena which were observed in the La$_{1-x}$Ag$_x$MnO$_3$ nanoparticles with orthorhombic crystal structure. Recent investigations have revealed that replacing the trivalent ion of La by monovalent ion like Ag results in synthesis of room temperature ferromagnetic ceramics [13] or nanoparticles [14] exhibiting colossal magnetoresistance, magnetocaloric effect and similar properties which are typical for manganites where La was partially substituted by the divalent alkali-earth metals.

2 Experimental

Preparation of La$_{1-x}$Ag$_x$MnO$_3$ nanopowders (x = 0.10, 0.15, 0.20) followed the glycine-nitrate method, which use glycine as fuel and nitrates as oxidants [15, 16]. Within this procedure, the aqueous solutions of the starting compounds were stirred and heated to dehydrate. Afterwards the solutions became viscous gel which underwent an auto ignition after some time. After short combustion of only few seconds, black porous ashes of La$_{1-x}$Ag$_x$MnO$_{3-x}$ were formed. Thermal analysis performed by TGDTA analyser Setsys16 on as prepared samples revealed thermal processes at about 270 °C.
which can be attributed to removing of residual material of synthesis. A part of as-cast samples were annealed at 300 °C and 600 °C for 2 hours in air atmosphere by a muffle furnace. The oxygen content (together with mean oxidation state of manganese atoms) in prepared compounds (both as prepared and annealed) was estimated by iodometric titration analysis. The average valence of manganese varies between 3.14 and 3.44 and was estimated by iodometric titration analysis. The average valence of manganese varies between 3.14 and 3.44 and has a tendency of increasing with x and temperature of annealing. The X-ray powder diffraction (XRD) patterns of both samples contain two additional relatively sharp peaks which cannot be attributed to any relevant nitrate or oxides. Traces of segregated silver were observed on all samples. Silver content increases with increasing temperature of annealing. Samples annealed at 600°C adopt rhombohedral structure (space group $R3c$) with lattice parameters close to $a = 0.55035$ nm, $c = 1.33540$ nm (sample with $x = 0.1$) and average size of nanoparticles is about 55 nm. Magnetization measurements were realised in the temperature range between 1.8 K and 400 K and in magnetic fields up to 5T or 9 T by a SQUID and VSM magnetometer in MPMS or PPMS, respectively.

3 Results and discussion

Our measurements revealed that all samples undergo a paramagnetic (PM) to ferromagnetic (FM) transition at the Curie temperature $T_C$. The temperature dependences of magnetization in zero field cooled (ZFC) and field cooled (FC) regimes are shown in Fig.1 for La$_{0.85}$Ag$_{0.15}$MnO$_3$ sample annealed at 600°C/2h. The hysteresis 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

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temperature $T_C$ and even is a little bit higher for as prepared samples. The Curie temperature was determined as a minimum on $d\mu/d(T)$ dependence (see inset of Fig.1.). Substitution of Ag for La and subsequent heat treatment increase $T_C$ reaching the maximal value $307$ K for sample with $x = 0.2$ annealed at $600^\circ$C/2h. Changes of magnetic properties which were induced by increasing of silver content $x$ are much smaller than drastic changes induced by annealing especially performed at $600^\circ$C. Heat treatment induces the increase of $T_C$ from $107$ K to $121$ K and then to $268$ K for as prepared, at $300^\circ$C/2h and $600^\circ$C/2h annealed particles of La$_{0.85}$Ag$_{0.15}$MnO$_3$, respectively. High temperature magnetic susceptibility $\chi$ follows the Curie-Weiss law $\chi = \chi_0/(T - \theta)$ for all samples in temperature region high enough above $T_C$ ($\chi_0$ is the Curie constant and $\theta$ is paramagnetic Curie-Weiss temperature) as it is demonstrated for sample with $x = 0.15$ annealed at $600^\circ$C/2h (Fig.2). The paramagnetic Curie temperature increases with annealing from $\theta = 110$ K to $113$ K and finally to $267$ K on the sample with $x = 0.15$ and is comparable with $T_C$. The same tendency we have found on samples with $x = 0.10$ and $0.20$. The increase of $T_C$ and $\theta$ with annealing we attribute to oxidation generating higher content of Mn$^{4+}$ in samples which interaction ferromagnetic interaction via double exchange interaction. Evidence for enhanced oxidation was provided by iodometric titration and TG measurements. The effective magnetic moment $\mu_{\text{eff}}$ changes by non-monotonic way with annealing; at first $\mu_{\text{eff}}$ decreases from $4.74 \mu_B$ to $4.14 \mu_B$ and then increases to $4.53 \mu_B$ for as prepared, $300^\circ$C/2h and $600^\circ$C/2h annealed samples with $x = 0.15$. The decrease of $\mu_{\text{eff}}$ can be understood assuming oxidation resulting in higher content of Mn$^{4+}$ in samples and smaller moment can be obtained by the combination of magnetic moments of Mn$^{4+}$ (4.90 $\mu_B$), Mn$^{3+}$ (3.87 $\mu_B$). Annealing at $600^\circ$C/2h will again increase Mn$^{3+}$ content in samples but the effective moment is smaller now. Relation between gradual oxidation and decreasing moment is now not so straightforward and seems to be misleading but the change of crystal structure from $Pnma$ to $R3_c$ has to be taken into account.
Two magnetization hysteresis loops which were measured on as prepared sample with \(x = 0.15\) are displayed in Fig. 4. First of them was obtained after cooling down in zero magnetic field. Initial magnetization curve starts from zero remnant magnetization and the hysteresis loop is symmetric in respect to zero point of coordinates. Before measurement of second loop the sample was exposed to static magnetic field \(H_0\) with induction of 1 T and cooled from 120 K through \(T_C\) down to 2K. This procedure gives rise to displacement of the magnetic hysteresis loop, which is the typical manifestation of the EB effect. The loop is pinned on vortex in the region of negative magnetization, is tilted and shifted in horizontal and vertical direction. The horizontal shift of the loop is usually expressed by exchange bias field \(H_E = (H_c - H_{r+})/2\) and vertical shift is described by \(M_E\) which is defined as difference of saturated magnetization \[2]\); \(H_c\) and \(H_{r+}\) is coercive field on positive and negative axes. In the case that hysteresis loops are not very rectangular another parameter, the remnant asymmetry \(\mu_r = (\mu_{r+} - \mu_{r-})/2\), is frequently used \[19\]; \(\mu_r\) and \(\mu_r\) is remnant magnetization on positive or negative axis. The heat treatment at 300°C leads to damping of EB phenomena. Despite of the fact that the coercive magnetization \(\mu_c = (\mu_{c+} + \mu_{c-})/2\) increases from 0.130 \(\mu_B\) to 0.246 \(\mu_B\), horizontal shift of hysteresis loop is reduced and vertical shift is nearly unchanged as it can be seen from Fig.5 on sample with \(x = 0.15\). EB phenomena were observed on all samples which adopt orthorhombic crystal structure and comparison of EB effect for as prepared samples with different content of \(x\) is shown in Fig.6. Saturated magnetization at 5 T decreases with \(x\) and horizontal and vertical shift of hysteresis loops is remarkable. All characteristic parameters of EB effect which were obtained in magnetic fields with induction \(\pm 9\) T are summarised in Fig.7 which shows effect of cooling field \(H_{ci}\) on EB phenomena. All studied parameters have tendency of saturation for relatively low field of about \(\mu_0H_{ci} = 0.1\) T. The heat treatment at 300°C leads to reduction of coercive force \(H_c\) and bias field \(H_{r+}\) on the other hand the coercive magnetization \(\mu_c\) and remnant asymmetry \(\mu_E\) increase. The difference between subsequent magnetization reversal loops which were measured after cooling in \(\mu_0H_{ci} = 1\) T, the training effect, is shown in Fig.8. Measurement of magnetization reversal loop was repeated 7 times at 2.5 K. Both parameters \(H_c\) and \(\mu_E\) describing the horizontal and vertical shift of loop decrease with consecutive number of cycles and reach stable values. In conclusion, EB phenomena were observed on ferromagnetic \(La_{1-x}Ag_xMnO_3\) nanopowders (\(x = 0.10, 0.15\) and 0.20) with average size of about 25 nm which adopt orthorhombic crystal structure (space group \(Pnma\). All parameters describing EB effect have tendency of saturation in relatively low field of about \(\mu_0H_{ci} = 0.1\) T. The heat treatment at 300°C leads to reduction of coercive force \(H_c\) and bias field \(H_{r+}\) on the other hand the coercive magnetization \(\mu_c\) and remnant asymmetry \(\mu_E\) increase. Both parameters \(H_c\) and \(\mu_E\) describing the horizontal and vertical shift of loop decrease with consecutive number of cycles in training effect. Heat treatment at 600 °C/2 hours increases the average size of nanoparticles to 55 nm, crystal structure changes to rhombohedral structure (space group \(R3c\)) and EB effect vanishes. Our results suggest that surface effects and core shell model can explain EB phenomena in this case because it is well known that surface effect is important on particle with average size smaller than 50 nm. On the other hand magnetic phase separation in single crystalline phase cannot be completely excluded, too.

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