INFLUENCE OF THE PARTICLE SIZE REDUCTION ON MAGNETIC PROPERTIES OF ELECTRON-DOPED $Ca_{1-x}Y_xMnO_3$

by

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The electron-doped magnetic nanoparticles of $Ca_{1-x}Y_xMnO_3$ (x = 0, 0.05, 0.10, 0.15, 0.20, and 0.30) manganite with an average particle size of 50 nm are analyzed and discussed in relation to their bulk counterparts. Nanoparticle samples show dominant anti-ferromagnetic ordering with a significant increase of coercivity, with the maximum value of 0.9 T for x = 0. Particle size reduction in $Ca_{1-x}Y_xMnO_3$ retains the bulk-like magnetic behavior of samples having up to 15% of Y^{3+}, with the small ferromagnetic contribution from disordered surface spins. Suppression of charge ordering state and enhancement of saturation magnetization were found in samples with higher Y^{3+} concentration (x = 0.2, 0.3), indicating high ferromagnetic contribution in these samples.

Key words: electron-doped manganite, nanostructure, magnetic property

INTRODUCTION

The application potentials of materials known as rare earth (RE) manganites are multiple, ranging from magnetic data storage technology to cathode materials in high temperature solid oxide fuel cells [1, 2]. Less known is that manganites have recently came under considerations as bolometric radiation detectors, where they can be used as sensors for various forms of radiation from infrared to high energy synchrotron radiation [3, 4], and as a shielding blocks from low frequency electromagnetic interference in sensitive measuring devices [5]. Bolometric application of manganites is based on a strong coupling between magnetic ordering and conductance that becomes steeply sensitive to temperature change near the phase transition point. Their main advantage over standard bolometric sensors is in the possibility to tailor magneto resistive properties by manipulating their chemical composition, thus enabling their use in a wide temperature range, from above room temperature down to 70 K and lower.

Among $RE_xCa_{1-x}MnO_3$ RE manganites, most of scientific attention has been dedicated to hole-doped or half-doped materials (x 0.5). Nevertheless, interest in electron-doped systems is also significantly enhanced during the last decade, due to the complex role that doped electrons appear to have in magnetic and transport properties, particularly within the 0 x 0.3 concentration range. Recent comparative research on transport and magnetic properties of $CaMnO_3$ doped with non-magnetic RE ions (La, Y, Ce) revealed that, unlike conductivity, magnetic behavior is not entirely dominated by carrier concentration, but the structure factor also plays an important role [6]. It is, therefore, of specific interest to investigate the influence of particle size reduction on magnetic properties of these materials. Yet, in contrast to bulk material, systematic studies on magnetic properties of nanoparticle electron-doped manganites in a wider doping range are exceptionally scarce. Only recently, Wang and Fan [7] have reported such study on lanthanum-doped nanoparticle $Ca_{1-x}La_xMnO_3$ (0 x 0.25).

This work represents the continuation of research on nanoparticle $Ca_{1-x}Y_xMnO_3$ (average particle size of 50 nm, 0 x 0.30), for which the detailed structure, microstructure and morphology study is reported in [1]. In contrast to nanoparticle $Ca_{1-x}La_xMnO_3$, yttrium-doped compounds $Ca_{1-x}Y_xMnO_3$ are so far studied exclusively in their bulk form [8-11] and, to the best of our knowledge this is the first such study regarding magnetic properties of their nanoparticle counterparts.

METHODS AND PROCEDURES

The preparation of $Ca_{1-x}Y_xMnO_3$ samples with nominal yttrium concentration x = 0, 0.05, 0.10, 0.15, 0.20, and 0.30 was done by modified glycine-nitrate

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method (MGNP). The detailed synthesis procedure for these samples, their morphology and structural characterization has been previously described elsewhere [1]. The samples were found to be single phase solid solutions with the average crystallite size of 50 nm and large effective surface [1].

The characterization of magnetic properties in this work was done by Quantum Design XL-5 SQUID-based magnetometer. The magnetization was measured in constant (DC) magnetic field and in alternating (AC) magnetic field, in the temperature range between 5 K and 300 K. DC magnetization measurements were done in magnetic fields 20-1000 Oe (1 Oe = 10^{-4} T), while AC measurements were performed in alternating field of 2 Oe amplitude (in the zero DC field) and at frequencies of ν = 0.1 Hz, 1 Hz, and 1000 Hz. The magnetic hysteresis measurements were carried out in the –5 T < H < 5 T field range, at 10 K.

RESULTS AND DISCUSSION

Magnetization *vs*. field measurements $M(H)$ of nanoparticle samples recorded at 10 K (fig. 1) reveal strong dependence of coercivity, saturation and remnant magnetization on Y^{3+} concentration. The basic characteristic of recorded hysteresis loops is the absence of magnetic saturation up to 5 T and almost linear $M(H)$ dependence above 3 T, which point to the dominant anti-ferromagnetic (AFM) interaction in all samples.

The coercivity H_C of nanoparticle samples (fig. 1, upper inset) shows large values compared to the bulk counterpart, and also reveals the sharp dependence on electron concentration. Though the enhancement of magnetic anisotropy is frequently found in nanoparticle materials, in the case of nanoparticle $Ca_{1-x}Y_xMnO_3$ this increment is exceptionally large, contrary to what was observed in nanoparticle $Ca_{1-x}La_xMnO_3$ [7]. The largest coercivity found in this study was for sample with x = 0 and its value is 9000 Oe, and the smallest value of 2500 Oe was measured for x = 0.3.

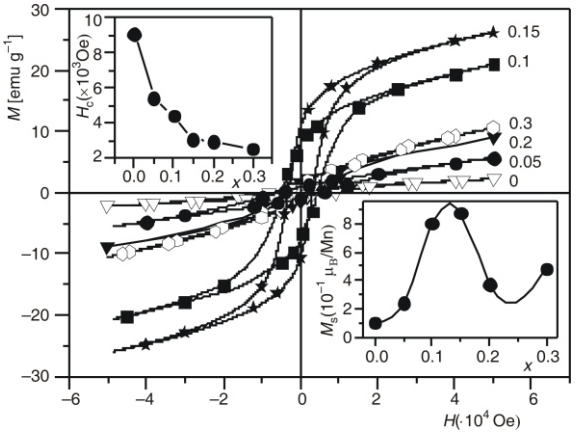

Figure 1. Magnetization *vs*. magnetic field at T = 10 K, with the concentration dependence of coercivity (upper inset) and saturation magnetization M_s (lower inset)*

* Magnetization is expressed in emu (electromagnetic unit) per gram, 1 emu = 10^{-3} Am^2

The concentration dependence of saturation magnetization $M_S(x)$ (fig. 1, lower inset) displays the slope that approximately resembles the one found in bulk $Ca_{1-x}Y_xMnO_3$ or in bulk $Ca_{1-x}La_xMnO_3$ compounds [8-13]. When compared to bulk, a mild enhancement of M_S was noticed for lower concentrations (x = 0.15). This is similar to observations made for nanoparticle $Ca_{1-x}La_xMnO_3$ [7], and suggests that intrinsic magnetic behavior in this concentration range is similar to that of the bulks, but with the addition of small ferromagnetic (FM) contribution originating from partially disordered surface spins, which are believed to form FM clusters [7, 12, 13]. In the bulk material FM clusters disappear at higher doping concentration and are suppressed by charge ordering (CO) state, observable as characteristic peak in field cooled (FC) measurements of M (T) dependence [9]. Our M (T) measurements in FC regime demonstrate the absence of CO state in samples with x > 0.15 (fig. 2), these samples also show notable (3-4 times) larger M_S values in respect to their bulk counterparts. Analog suppression of CO state in nanoparticle $Ca_{1-x}La_xMnO_3$ was also observed [7]. However, unlike the $Ca_{1-x}La_xMnO_3$ case, our observations show that, while still being significantly larger than in bulks, M_S value of nanoparticle $Ca_{1-x}Y_xMnO_3$ decrease for x > 0.15. Since no CO is observed, reduction of FM contribution should be caused by factors other than CO and needs further investigation.

M (T) dependence represents another interesting feature in the low temperature region of zero-field

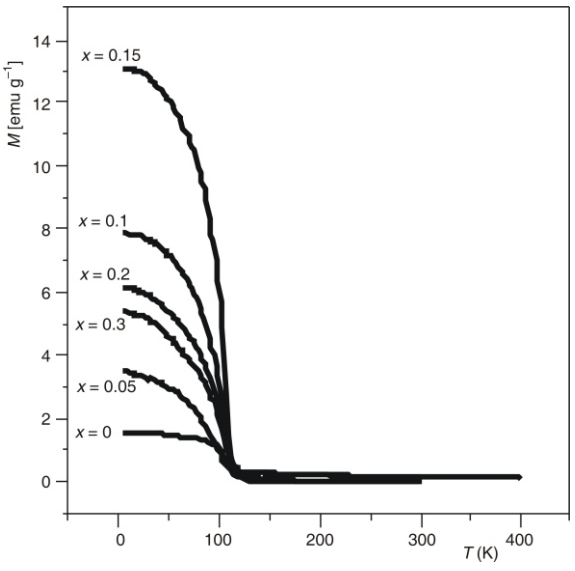

Figure 2. FC magnetization measurements *vs*. temperature. For better visibility, data for x = 0.1 and x = 0.15 are divided by 6 and 9, respectively

cooled (ZFC) magnetization measurements. Instead of expected blocking, freezing or spin-glass like nanoparticle behavior below AFM transition temperature, we have observed the appearance of a broad, field-dependent maximum around 30 K that is present in M (T) of all samples, whereas no change in FC curves was detected in that temperature range.

As an illustration, fig. 3(a) represents the temperature dependence of ZFC magnetization in different magnetic fields for $x = 0.15$ sample. While ZFC curves recorded at 20 Oe show only monotonic increase up to the Néel temperature T_N, additional magnetization maxima below 35 K appear in stronger fields. AC magnetization measurements were performed to check the nature of this low-temperature maximum, but no frequency dependence of the maximum position was observed up to 1000 Hz, fig. 3(b). Thus, the nature of the field-dependent maxima in magnetization below 35 K deserves further investigation, but we can speculate that it resembles the characteristics of a canted-AF (weak-FM) rather than FM behavior, and its breadth as well as its independence on electron concentration points to the influence of a particles' shell region.

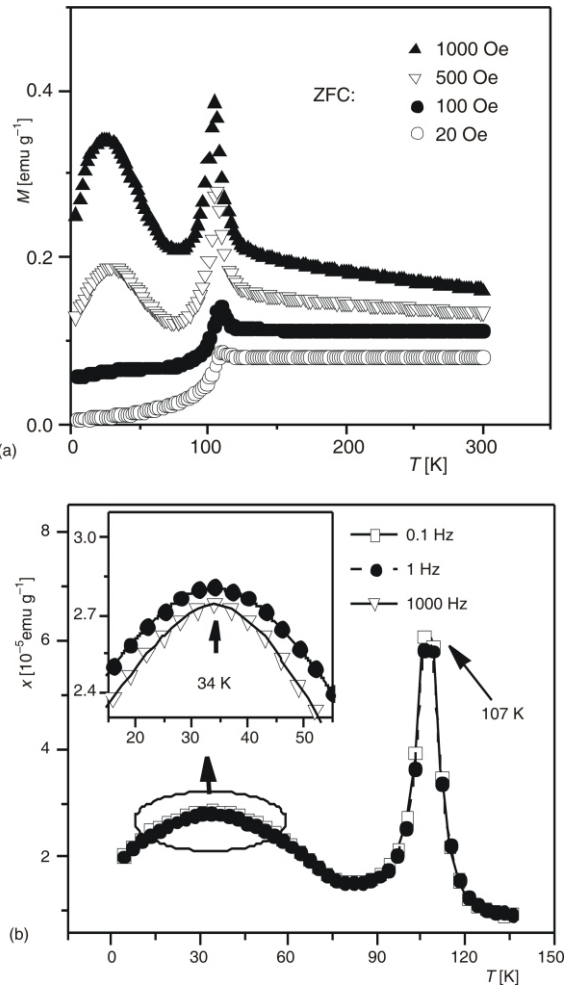

Figure 3. (a) The temperature dependence of ZFC magnetization in different magnetic fields for $x = 0.15$; (b) AC magnetization measurements for the same sample

CONCLUSIONS

The presented results support the standpoint that in addition to electron concentration, other factors like structure, microstructure and sample morphology can play a decisive role in magnetic behavior of electron-doped nanoparticle manganites. Particle size reduction down to 50 nm in $Ca_{1-x}Y_xMnO_3$ retains the bulk-like magnetic behavior of samples having up to 15% of Y^{3+}, with the exception of small FM contribution from disordered surface spins. The surface effects are also responsible for exceptionally enlarged coercivity, which is about 4 times larger than in corresponding samples of bulk material. The effects of size reduction in samples containing 20% and 30% of Y^{3+} are considerably more pronounced. Strong FM contribution in this samples was found through both suppression of CO state and enhancement of saturation magnetization.

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AUTHOR CONTRIBUTIONS

The samples were synthesized by S. Bošković and A. Alqat. The experiments were carried out by V. Spasojević and V. Kusigerski. Analysis of the results and disscussion were made by A. Alqat, Z. Gebrel, and J. Blanuša. The figures were prepared by Z. Gebrel. The manuscript was written by J. Blanuša and A. Alqat.

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УТИЦАЈ СМАЊЕЊА ВЕЛИЧИНЕ ЧЕСТИЦА НА МАГНЕТНЕ ОСОБИНЕ ЕЛЕКТРОНСКИ ДОПИРАНОГ $Ca_{1-x}Y_xMnO_3$

Електронски допирани наночестични манганити $Ca_{1-x}Y_xMnO_3$ (x = 0, 0.05, 0.10, 0.15, 0.20, 0.30) са средњом величином честица од 50 nm, испитивани су са становишта магнетних особина, у односу на особине волуминозних материјала истог састава. Показано је да у наночестичним узорцима доминира антиферомагнетна интеракција, уз изузетно повећану коерцитивност која достиже максималну вредност од 9000 Oe (0.9 T) за недопирани узорак (x = 0). При мањим концентрацијама Y^{3+}, смањење димензије честица $Ca_{1-x}Y_xMnO_3$ не доводи до значајније промене магнетизације у односу на волуминозни материјал, али је примећен њен благи пораст услед феромагнетног доприноса разуређених спинских момената на површини честице. Значајно повећање магнетизације уз истовремено урушавање стања уређеног наелектрисања примећено је код узорака са већом концентрацијом електрона (x = 0.2, 0.3), што указује на јак утицај феромагнетних интеракција у овим узорцима.

Кључне речи: електронски допирани магнетит, наноструктура, магнетна особина