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Magnetic Properties of the Nanocrystalline $DyMnO_3$ Compound

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We report on the X-ray powder diffraction and magnetic measurements of the polycrystalline and the two nanocrystalline samples of $DyMnO_3$ compound synthesized at temperatures of 800 and 850 °C. All samples at room temperature crystallize in the orthorhombic crystal structure (space group *Pnma*). The crystal structure parameters determined change only slightly with preparation methods but the average grains size of the nanoparticles determined from X-ray data increases significantly with increasing annealing temperature. Temperature dependence of the magnetic susceptibility indicates the antiferromagnetic order in Dy sublattice at low temperatures.

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1. Introduction

Physical properties of manganites were shown to depend on doping as well as on the grains size [1, 2]. Usually, the nanocrystalline samples exhibit properties which are different from those of the bulk material. An important factor is increasing surface-to-volume ratio of the grains as the particle size is reduced to the nanoscale. As a result, the small size effect and the surface effect perturb the properties of nanoparticle samples. In these samples the magnetic behaviour of nanoparticles is additionally modified by the interparticle interactions which can be both of the exchange and magnetostatic origins. The main motivation for these studies was to obtain the data concerning the evolution of magnetic properties as a function of grain size.

$RMnO_3$ compounds have been attracting a lot of attention in the last years due to strong coupling between ferroelectricity and magnetism [3]. These compounds crystallize in the orthorhombic crystal structure (space group *Pnma*).

In $DyMnO_3$ below 6.5 K, the Dy magnetic moments order in a commensurate structure with the propagation vector $\boldsymbol{k} = (0, 1/2, 0)$, while the Mn moments order below 39 K. At $T_{\mathrm{t}} = 18$ K the change of the magnetic structure connected with the Mn sublattice is observed. Below T_{t} this order is collinear while above T_{t} it is sine modulated [4].

This work reports the results of the X-ray diffraction and magnetometric macroscopic measurements of the $DyMnO_3$ polycrystalline and nanocrystalline samples with the different average grain size.

2. Experimental and results

The polycrystalline manganite $DyMnO_3$ (denoted hereafter as S_1 sample) was prepared by the solid-state reaction. The final sintering treatment was performed at 1150 °C for 15 h.

For the preparation of nanosize manganite $DyMnO_3$ the sol-gel method has been used. The mixture of stoichiometric amounts of high purity Mn_3O_4 and Dy_2O_3 oxides was dissolved in acetic acid with added hydrogen peroxide. The solution of urea was added to the obtained solution. This mixture was evaporated to dryness. The dry remainder was decomposed at 250–450 °C. Then, the powder was thoroughly grinded into pellets and was annealed at temperatures of 800 and 850 °C for 20 h in air, followed by a slow cooling down to the room temperature. The samples of the nanopowders obtained after annealing at 800 and 850 °C are denoted hereafter as S_2 and S_3, respectively.

The quality of the products was checked by X-ray powder diffraction at room temperature using a Philips PW-3710 X'PERT diffractometer with Cu K_α radiation. The obtained data were analyzed with the Rietveld-type refinement software FullProf program [5]. For all samples the following dc magnetic measurements of nanosize samples using a commercial MPMS SQUID magnetometer have been carried out: magnetic susceptibility measurements in a magnetic field of 1 kOe over a temperature range 2–300 K (from these data the effective magnetic moment μ_{eff} and the paramagnetic Curie temperature θ_{p} were obtained) and magnetization measurements in magnetic fields up to 50 kOe and at temperatures down to 2 K (in order to get the value of the pseudosaturated magnetic moment and character of the magnetization curve).

Additional magnetization vs. temperature measurements of the polycrystalline sample S_1 in the temperature range of 4.2–120 K and in the external field from 50 Oe to 5 kOe and the external field up to 15 kOe were performed using PAR Model 4500 vibrating sample magnetometer.

The X-ray diffraction data indicate that all the samples studied have orthorhombic crystal structure described by the space group $Pnma$. In this structure the respective atoms occupy the following atoms: R and O1 in 4c site: (x, y, 1/4), O2 in 8l site: (x, y, z) and Mn in 4b site: (1/2, 0, 0). All fitted structural parameters: lattice constants and positional parameters x_i, y_i and z_i are listed in Table I. The obtained data indicate that the crystal structure parameters slightly change with the nanostructuration of the samples.

TABLE I

Structural parameters of $DyMnO_3$ at room temperature derived from X-ray diffraction data (S_1 — polycrystalline sample, S_2 and S_3 — the nanocrystalline samples annealed at 800 and 850 °C, respectively).

Samples	S_1	S_2	S_3
a [Å]	5.8385(2)	5.8334(1)	5.8306(1)
b [Å]	7.3792(2)	7.3794(2)	7.3806(1)
c [Å]	5.2789(1)	5.2742(1)	5.2738(1)
V [Å^3]	227.433(19)	227.04(1)	226.95(1)
R x	0.0819(2)	0.0820(1)	0.0822(1)
y	−0.0139(4)	−0.0156(2)	−0.0185(2)
O1 x	0.473(2)	0.462(2)	0.463(1)
y	0.102(3)	0.104(2)	0.105(1)
O2 x	0.324(2)	0.327(1)	0.323(1)
y	0.049(1)	0.054(1)	0.052(1)
z	0.705(2)	0.699(1)	0.704(1)
R_{Bragg} [%]	8.1	6.6	6.6
R_{prof}	10.0	9.3	6.3

In the next step, the grain sizes were determined using the Scherrer relation $d = (\lambda/B)\cos\theta_{\mathrm{B}}$, where d is the grain size, $\lambda = 0.154178$ nm — the X-ray wavelength, θ_{B} — the corresponding angle of Bragg diffraction and B the difference between half-widths of the Bragg reflex of the nanopowder and the standard sample (Si powder with the size 10 μm [6]). The grains sizes were calculated using the experimental X-ray data and the following three relations:

1. $B_1 = \beta - \beta_0$, where β is the half-widths of the Bragg reflex of the investigated sample and β_0 the similar value for the standard sample of Si powder,
2. $B_2 = \sqrt{\beta^2 - \beta_0^2}$,
3. $B_3 = \sqrt{(\beta - \beta_0)\sqrt{\beta^2 - \beta_0^2}}$.

The grain size values d_i $(i = 1, 2, 3)$ determined from these relations are listed in Table II. Presented data indicate that the grain size increases with increasing annealing temperature.

TABLE II

Particle size values, $d(S_i)$ (in nm), of $DyMnO_3$ nanopowder prepared at 800 °C (S_2) and 850 °C (S_3) calculated by the different methods (see text).

$DyMnO_3$	B_1	B_2	B_3
$d(S_2)$	31.6	25.2	28.2
$d(S_3)$	57.2	40.0	47.8

Temperature dependences of magnetization for the polycrystalline sample S_1 measured at different external magnetic field are shown in Fig. 1. The $M(T)$ maximum at $T = 8$ K, which is near the reported value $T_{\mathrm{N}}(Dy) = 6.5$ K [5], indicates the antiferromagnetic order of the Dy moments. The $M(T)$ maximum temperature is seen to be not dependent on magnetic field up to 5 kOe.

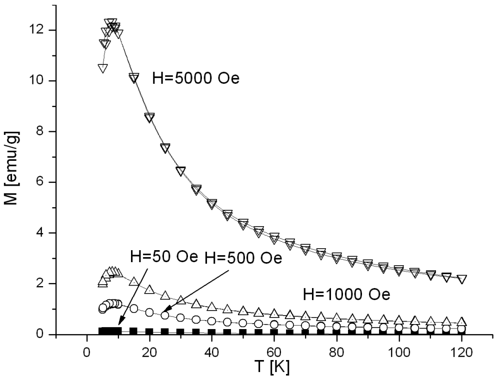

Fig. 1. Temperature dependences of magnetization for the polycrystalline sample $DyMnO_3$ (S_1) measured at different magnetic fields.

The temperature dependences of reciprocal magnetic susceptibility and dc magnetic susceptibility for three samples S_1, S_2 and S_3 at low temperatures are shown in Fig. 2. Above 50 K, the reciprocal magnetic susceptibility follows the Curie–Weiss law with the negative values of the paramagnetic Curie temperature θ_{p} and the effective magnetic moment equal 11.8, 11.3 and 11.5 μ_{eff} for S_1, S_2 and S_3 samples, respectively, and larger than that of the free Dy^{3+} ion value (10.65 μ_{B}) (see Table III). This indicates that also on the Mn atoms is localized magnetic moment. The sign θ_{p} indicates that antiferromagnetic interactions between the magnetic moments are dominant.

The temperature dependence of the magnetic susceptibility for the all samples (see inset in Fig. 2) shows

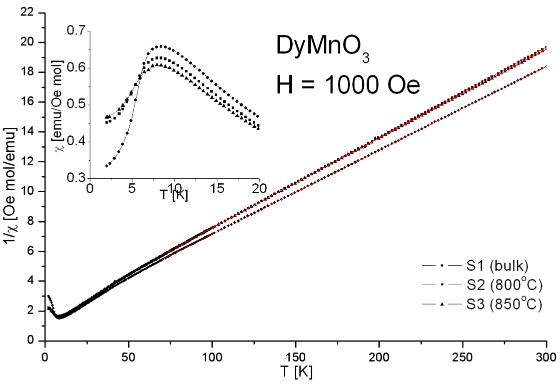

Fig. 2. Temperature dependences of the reciprocal magnetic susceptibility of polycrystalline and nanosized DyMnO$_3$ samples. Inset shows the low temperature part of magnetic susceptibility. The data for S_2(■) and S_3(▲) coincide in the large temperature region.

TABLE III

Magnetic data for DyMnO$_3$ (S_1 — polycrystalline sample, S_2 and S_3 — samples annealed at 800 and 850 °C, respectively), T_N, (Dy) — Nèel temperature, θ_p — paramagnetic Curie temperature, μ_{eff} — effective magnetic moment in paramagnetic state, μ — magnetic moment at $T = 2$ K and magnetic field $H = 50$ kOe.

Sample	$T_{N,Dy}$ [K]	θ_p [K]	μ_{eff} [μ_B]	μ [μ_B]
S_1	8.5	−26.6	11.8	4.8
S_2	8.1	−24.8	11.3	4.4
S_3	8.3	−24.0	11.5	4.5

maximum at temperature of for example $T_N^{Dy} = 8.5$ K for S_1 corresponding to the antiferromagnetic ordering of the Dy moments. Similar values are observed for the S_2 and S_3 samples (see Table III).

Figure 3 shows the magnetization vs. field curves for the S_1 sample measured at temperatures of 5, 42 and 100 K in the external fields up to 15 kOe for the increase and decrease of the magnetic field. These dependence are linear for $T = 42$ and 100 K. For $T = 5$ K a deviation from linear dependence above $H = 5$ K is observed. All curves do not exhibit the hysteresis.

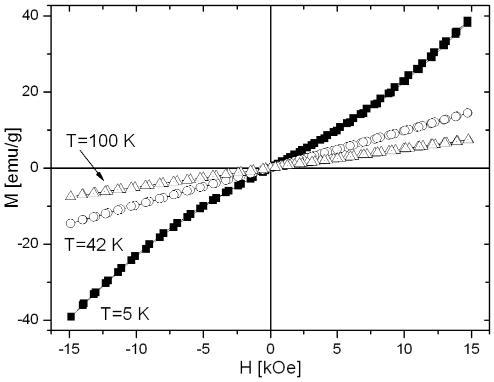

Fig. 3. Magnetization curves for the polycrystalline sample DyMnO$_3$ (S_1) measured in the field of ±15 kOe at $T = 5$, 42 and 100 K.

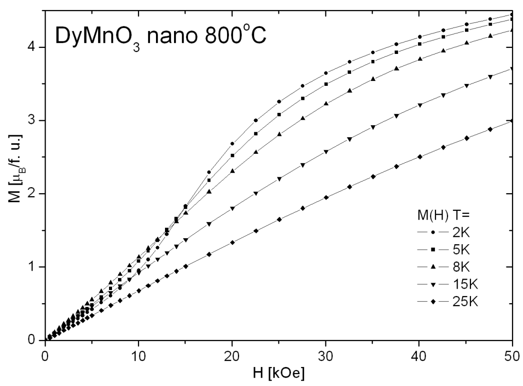

Fig. 4. Magnetization vs external magnetic field for the nanosized DyMnO$_3$ (S_2 sample) at 2, 5, 8.0, 15 and 25 K.

In Fig. 4, the magnetization isotherm for the S_2 sample measured at $T = 2$, 5, 8, 15 and 25 K in the magnetic field up to 50 kOe is present. The $M(H)$ curve at 2 K shows the magnetic field-induced magnetic transition in the rare earth sublattice near 5 kOe, thus proving an essentially antiferromagnetic nature of the ground state. The magnetization curves are not saturated in the magnetic field equal to 50 kOe. The magnetic moment value at $T = 2$ K and $H = 50$ kOe are smaller than that for free Dy^{3+} ion value (10 μ_B) (see Table III).

3. Conclusions

In this paper, the results of the X-ray diffraction and magnetometric measurements of the DyMnO$_3$ prepared by the various methods are presented. All investigated samples have the orthorhombic crystal structure described by the space group *Pnma*. The crystal structure parameters change insignificantly with the preparation method. The grains size increases with increasing annealing temperature.

Magnetic data indicate that all the samples are antiferromagnets. The $M(T)$ dependences presented clearly show the anomalies at low temperatures corresponding to the Dy magnetic moment ordering. The values of effective magnetic moment suggest the localization of the magnetic moment on the dysprosium and manganese atoms. The values of the magnetic parameters: the Nèel and paramagnetic Curie temperatures and effective magnetic field magnetic moments do not change with the magnitude of the grains size.

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