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Fabrication and Study of $GdMnO_3$ Multiferroic Thin Films

N. Andreev, N. Abramov, V. Chichkov, A. Pestun, T. Sviridova and Ya. Mukovskii*

Moscow State Steel and Alloys Institute, Leninskii prosp. 4, 119049 Moscow, Russia

Laboratory technology of $GdMnO_3$ thin film fabrication was elaborated. Samples of $GdMnO_3$ were fabricated at $NdGaO_3$ substrate by magnetron sputtering using off-axis scheme. Structure and phase content of the samples obtained were studied as well as their magnetic properties. The surface topography of the films was observed by atomic force microscopy. Presence of peculiarities at the temperature dependences of magnetic susceptibility points at magnetic phase transitions in $GdMnO_3$, which were found before in the single crystals. This fact jointly with X-ray data shows that at definite fabrication regimes one can obtain the multiferroics thin film $GdMnO_3$ modification, and the film quality permits to carry out accurate study of the compound in question.

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1. Introduction

In the last years the great interest was directed to the physics of multiferroics. Discovered in the 70's, these rare materials exhibit simultaneously ferroelectric and magnetic orderings. These two order parameters are strongly entangled by a magnetoelectric coupling, allowing the reversal of the ferroelectric polarization by applying a magnetic field, or the control of the magnetic order parameter by an electric field. Together with recent unprecedented progress in epitaxial thin film growth, this unique property makes these materials promising candidates in designing tunable multifunctional spintronic devices [1].

Some years ago coexistence of ferroelectricity and magnetic order was found in rare-earth manganites $RMnO_3$. These materials represent strongly correlated systems in which charge, spin, orbital, and lattice subsystems are linked very tightly. The very nature of the interplay between magnetic ordering and ferroelectricity in these compounds is at the moment one of the puzzling fundamental questions in condensed matter physics. However, a large number of publications in this field tend to show that these materials are the crossroads of two key ingredients: the magnetic frustration and a very large spin–lattice coupling [1–5].

The multiferroic behaviour of rare-earth manganites emerges as one moves along the $4f$ series, decreasing the R element size. This decrease induces a crystallographic change from an orthorhombic (R = Pr, Nd, Sm, Eu, Gd, and Tb) to a hexagonal (R = Ho, Er, Tm, Yb, Lu, Y, Sc, and In) structure. The hexagonal compounds show both ferroelectric and antiferromagnetic order, but the $T_{FE} \approx 1000$ K and $T_N \approx 100$ K differ by an order. In contrast, orthorhombic multiferroic manganites (with R = Gd, Tb and Dy) have comparable transition temperatures for the magnetic and the ferroelectric ordering, indicating that there might be direct coupling between them. The multiferroic transition in the orthorhombic case is currently understood with the help of two key aspects: (1) magnetic frustration due to competing exchange integrals between successive neighbours stabilizes a spiral magnetic phase below the Néel temperature T_N; (2) to lower the spin–lattice coupling, namely due to the Dzyaloshinskii–Moriya interaction, oxygen atoms are pushed off the Mn–Mn bond, driving an electric polarization at T_N [2]. As a result, this particular spin–lattice coupling mixes polar phonon and spin waves involving deviations out of the spiral magnetic plane.

The $GdMnO_3$ compound belongs to the orthorhombic rare-earth manganite family and it is multiferroic one. It has orthorhombically distorted perovskite lattice structure. Magnetoelectric properties of bulk $GdMnO_3$ single crystals were studied systematically in [4, 5]. At room temperature the compound is dielectric and paramagnetic. At $T_N \approx 42$ K the first magnetic phase transition takes place, the Mn^{3+} magnetic moments order into the incommensurate sinusoidal antiferromagnetic structure. At $T_{lock} \approx 23$ K the second phase transition takes place. On the base of X-ray data and magnetization study [3, 4] it was suggested that below T_{lock} the incommensurate sinusoidal antiferromagnetic structure turns into the canted antiferromagnetic one of A-type. Below $T \approx 6.5$ K magnetic moments of Gd^{3+} order antiferromagnetically. Below T_{lock} in magnetic field, the compound turns into ferroelectric phase [4].

2. Experimental

The single-phased $GdMnO_3$ targets were prepared by solid-state synthesis using stoichiometric Gd_2O_3 and MnO_2 powders as the starting materials. Then, $GdMnO_3$ thin films were grown on $NdGaO_3(001)$ substrates by

* corresponding author; e-mail: yakovm@list.ru

magnetron sputtering using RF power and off-axis sputtering scheme with double cathodes. Such scheme allows to transfer the elements from a target to the substrate without element content changing. The substrate temperature $T_{\rm sub}$ was changed in the range from 650 ℃ to 900 ℃. The mixture of Ar and O_2 was used as working atmosphere. The mixture pressure during the growth process was 1–2 mTorr. The thickness of the films obtained was 100–200 nm. The structural characteristics of the grown $GdMnO_3$ thin films were studied by X-ray diffraction (XRD), using X-ray DRON-4.0 diffractometer with monochromatized CuK_{α_1} radiation by off-site Θ-2Θ method. The surface topography of the films was observed by atomic force microscopy (AFM). The temperature-dependent magnetic susceptibility was measured by SQUID magnetometer (Quantum Design MPMS-5XL).

3. Results and discussion

In the X-ray spectra obtained for the samples grown at $T_{\rm sub}$ = 650–700 ℃ (Fig. 1a) in addition to the substrates lines one can see the lines that evidence the films have $GdMnO_3$ structure of *o*P20 type and they are single crystal (or strongly textured) ones. Presence of only (001) reflexes shows that the growth was epitaxial one with *c*-axis normal to the substrate plane. For the samples grown at $T_{\rm sub}$ = 750–900 ℃ (Fig. 1b) one can see two lines close to the substrate line, one of them corresponds to (001) orientation of the $GdMnO_3$ phase, and the other to (110).

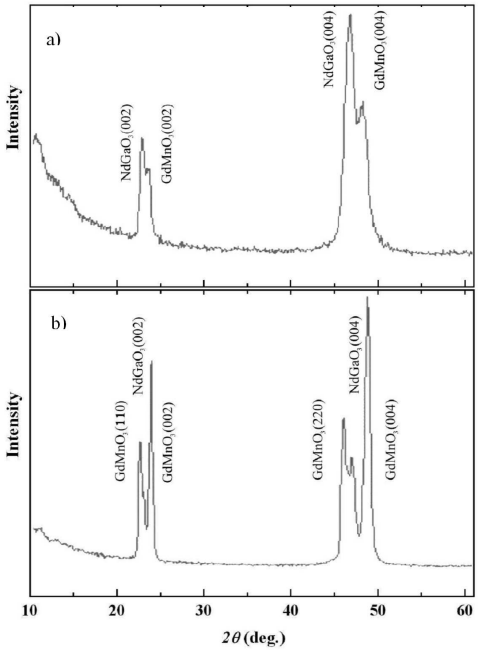

Fig. 1. X-ray diffraction patterns of $GdMnO_3$ thin films on $NdGaO_3$(001) substrates. The substrate temperatures are (a) $T_{\rm sub}$ = 650−700 ℃ and (b) $T_{\rm sub}$ = 750−900 ℃.

Study of magnetic properties of $GdMnO_3$ film is embarrassed by the case that $NdGaO_3$ is paramagnetic at $T > 1$ K [6] with a large value of the Nd magnetic moment (3.5 $\mu_{\rm B}$/atom), so the substrate makes the main input into the sample (film + substrate) magnetization. In Fig. 2 it is shown the temperature dependence of the inverse magnetic susceptibility $1/\chi$ for the sample grown at $T_{\rm sub}$ = 700 ℃. The dependence is linear in the temperature interval from ≈ 330 K to ≈ 40 K and drastically falls below 40 K. Since $NdGaO_3$ is paramagnetic at $T > 1$ K with good Curie–Weiss dependence (linear $1/\chi(T)$), so the deflection is caused by the film. The value of $T \approx 40$ K is in accordance with $T_{\rm N}$ for bulk $GdMnO_3$.

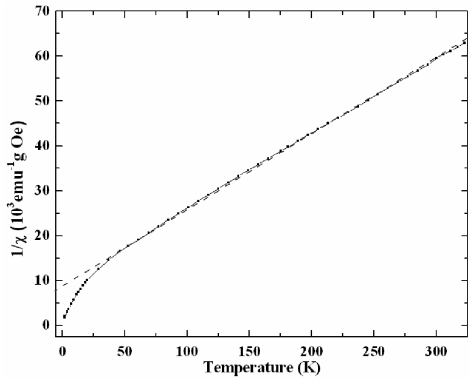

Fig. 2. Temperature dependence of the inverse susceptibility $1/\chi$ for $GdMnO_3$ film grown at $T_{\rm sub}$ = 700 ℃ on $NdGaO_3$ substrate.

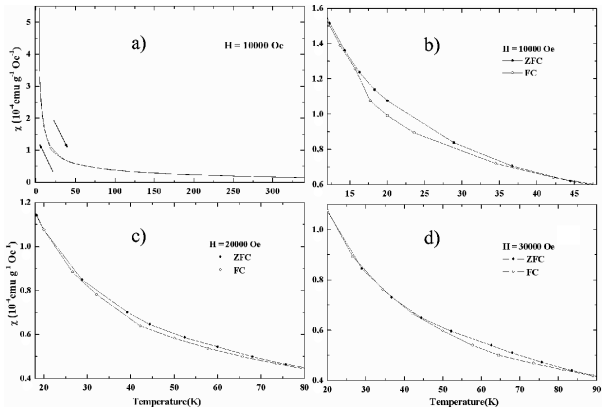

Fig. 3. Temperature dependence of the magnetic susceptibility $\chi(T)$ in different magnetic fields H for $GdMnO_3$ film grown at $T_{\rm sub}$ = 700 ℃ on $NdGaO_3$ substrate.

In Fig. 3, for the sample fabricated at $T_{\rm sub}$ = 700 ℃, are shown $\chi(T)$ curves obtained for cooling the sample in different magnetic fields (FC) and for cooling the sample without the field (ZFC). One can see the hysteresis for the samples fabricated at lower temperature so this hysteresis can be attributed to the $GdMnO_3$ film. The

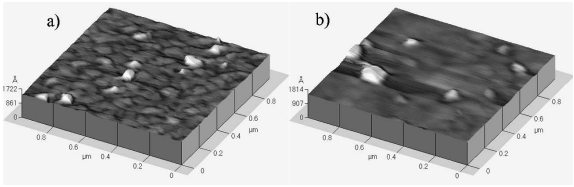

Fig. 4. The AFM images of $GdMnO_3$ thin film. The substrate temperatures are (a) $T_{sub} = 650-700\,^{\circ}C$ and (b) $T_{sub} = 750-900\,^{\circ}C$.

hysteresis range is shifting to a higher temperature as the field is increasing (Fig. 3b–d). In the field of $H = 10$ kOe at cooling, one can see obvious jump at $T \approx 16$ K in $\chi(T)$. Similar behaviour was observed at $\chi(T)$ for single crystal [4]. At this temperature the phase transition of $GdMnO_3$ film occurs from the incommensurate sinusoidal antiferromagnetic structure to the canted one. In the higher field, the jump makes smoother and shifts to higher temperature. Such behaviour is in accordance with magnetic phase diagram for bulk $GdMnO_3$ [4, 5].

The AFM has shown (Fig. 4) a smooth surface film with roughness of 1.4–2.0 nm, with inclusions of uncertain nature. For two groups of films (with $T_{sub} \leq 700\,^{\circ}C$ and $T_{sub} > 700\,^{\circ}C$) one can see different surface morphology (Fig. 4a, b), so the films with single orientation are smoother.

4. Conclusions

Laboratory technology of $GdMnO_3$ thin film fabrication was elaborated. Films obtained at $NdGaO_3$ substrate by magnetron sputtering at 650–700 °C were $GdMnO_3$ single-phased and have single orientation. The film quality permits to carry out accurate study of the compound in question.

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References

[1] R. Ramesh, N.A. Spaldin, *Nature Mater.* **6**, 21 (2007).

[2] S.-W. Cheong, M. Mostovoy, *Nature Mater.* **6**, 13 (2007).

[3] T. Arima, T. Goto, Y. Yamasaki, S. Miyasaka, K. Ishii, M. Tsubota, T. Inami, Y. Murakami, Y. Tokura, *Phys. Rev. B* **72**, 100102 (2005).

[4] T. Kimura, G. Lawes, T. Goto, Y. Tokura, A.P. Ramirez, *Phys. Rev. B* **71**, 224425 (2005).

[5] J. Baier, D. Meier, K. Berggold, J. Hemberger, A. Balbashov, J.A. Mydosh, T. Lorenz, *Phys. Rev. B* **73**, 100402 (2006).

[6] F. Luis, M.D. Kuzmin, F. Bartolomé, V.M. Orera, J. Bartolome, M. Artigas, J. Rubin, *Phys. Rev. B* **58**, 798 (1998).