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# Magnetic and optical properties of multiferroic GdMnO<sub>3</sub> nanoparticles

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# Magnetic and optical properties of multiferroic $\text{GdMnO}_3$ nanoparticles

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The magnetic and optical properties of multiferroic  $\text{GdMnO}_3$  nanoparticles synthesized by a polymerized complex method have been investigated. The  $\text{GdMnO}_3$  nanoparticles crystallized in orthorhombic perovskite-type structure. The zero-field-cooled and field-cooled magnetizations show that complicated magnetic transitions occur in a temperature range from 2 to 60 K, which were confirmed by magnetic hysteresis loops. Three shoulder absorption peaks centered at about 2.0, 2.3, and 2.7 eV are attributed to the Mn (3d)-electronic transitions, while an absorption peak at around 4.1 eV corresponds to the charge-transfer transitions between O (2p) and Mn (3d) states. UV emission at about 396 and 406 nm and blue emission at around 466 nm have been found, which may be attributed to the spin-allowed charge-transfer transitions. © 2010 American Institute of Physics. [doi:10.1063/1.3358007]

## I. INTRODUCTION

Multiferroics with significant magnetoelectric coupling effect have been widely investigated because of their attractive physical mechanism and potential applications in data storage and sensors.<sup>1-4</sup> The single-phase  $\text{RMnO}_3$  ( $\text{R} \equiv$  a trivalent rare-earth ion, such as Tb, Dy, and Gd) perovskite manganites have attracted more attention in recent years because strongly competing magnetic interactions play a very important role in inducing a magnetoelectric effect.<sup>5-10</sup> Bulk  $\text{GdMnO}_3$  has metamagnetic features with a transition from antiferromagnetic to weak-ferromagnetic state upon cooling and the antiferromagnetic alignments of Gd sublattice below 6 K.<sup>11</sup> Investigation on a single crystal  $\text{GdMnO}_3$  shows a significant anisotropy with a strong increase in magnetization along the *c*-axis at about 20 K, indicating a canted state of the spontaneous magnetization.<sup>12</sup> Recently, attention has been focused on optical properties of single crystals and films of the manganites, proving that characteristic energy scales are related to corresponding physical phenomena. The electronic structure of the manganites has a close relationship with their crystal structure, specially the distance between Mn and O atoms.<sup>13-16</sup> It is well known that the nanosized materials may exhibit unique electrical, magnetic, and optical properties far different from those of their bulk counterparts because of low dimensionality and quantum confinement effect.<sup>17</sup> In this work, we study the magnetic and optical properties of  $\text{GdMnO}_3$  nanoparticles.

## II. EXPERIMENTAL PROCEDURE

$\text{GdMnO}_3$  nanoparticles were synthesized by a polymerized complex method described elsewhere.<sup>18</sup> All reagents are commercial ones in analytical purity, which were used with-

out further purification. A solution was prepared by mixing aqueous solution of  $\text{Mn}(\text{NO}_3)_2$  and  $\text{Gd}(\text{NO}_3)_3$  in 1:1 molar ratio and then citric acid was added with stirring. When the solution was adjusted to  $\text{pH} \sim 6$  by adding dilute ammoniacal solution under stirring, the cations of  $\text{Mn}^{2+}$  and  $\text{Gd}^{3+}$  were complexed into their citrates. Then, ethylene glycol was added to make gelation. The molar amounts of citric acid and ethylene glycol were twice that of Gd and Mn cations. Excess citric acid and ethylene glycol can prevent nucleation and inhibit the growth of the nuclei, which can induce a preferable size distribution. The solution was stirred at room temperature for 5 h and heated at 100 °C until a gel was formed. This gel was further dried in oven at 130 °C and grounded into fine black powders. Finally, black precursor powders were calcined in air atmosphere at 700, 800, and 900 °C for 5 h, respectively.

The phase analysis for all the products was performed by using powder x-ray diffraction (XRD) on a D/max-2000 diffractometer with Cu  $K\alpha$  radiation at 56 kV and 182 mA. The averaged grain size of the powder was estimated from the (111) reflection by means of the Scherrer equation. Morphology was investigated by a Supra 35 field-emission scanning electron microscope (SEM) equipped with energy-dispersive spectrum (EDS) operated at an acceleration voltage of 20 kV. Magnetic properties were measured by a superconducting quantum interference device (Quantum Design). UV spectra were recorded with a Hitachi UV-3010 spectrophotometer with a scan speed of 1200 nm/min. Fluorescence spectra were recorded with a Hitachi F-4500 spectrophotometer equipped with a xenon lamp using the excitation wavelength of 270 nm.

## III. RESULTS AND DISCUSSION

Figure 1 exhibits XRD patterns of the  $\text{GdMnO}_3$  precursors calcined at different temperatures. The main phase of

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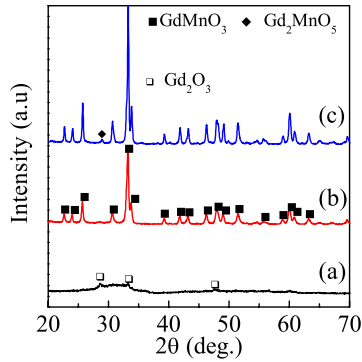


FIG. 1. (Color online) XRD patterns of the GdMnO<sub>3</sub> precursors calcined at (a) 700 °C, (b) 800 °C, and (c) 900 °C for 5 h.

the sample calcined at 700 °C in an amorphous state mixed with a small amount of Gd<sub>2</sub>O<sub>3</sub>. When the precursors are calcined at 800 °C, a single phase GdMnO<sub>3</sub> with orthorhombic structure is obtained. With increasing the calcination temperature up to 900 °C, a small amount of GdMn<sub>2</sub>O<sub>5</sub> appears. The morphology of the GdMnO<sub>3</sub> nanoparticles obtained at 800 °C was observed by SEM, as shown in Fig. 2(a). The averaged particle size of the assembled nanoparticles is estimated to be 52 nm, a little larger than its averaged grain size of 31 nm. In order to determine the chemical composition of the GdMnO<sub>3</sub> nanoparticles, an EDS spectrum was recorded. Figure 2(b) shows that main elements in our sample are Gd, Mn, and O with Gd to Mn molar ratio of about 1:1, close to the nominal concentration. The unmarked peaks C and Cu in Fig. 2(b) are originated from the sample grid.

Figure 3 shows the zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves of GdMnO<sub>3</sub> nanoparticles recorded at an applied field of 100 Oe between 2 and 60 K.

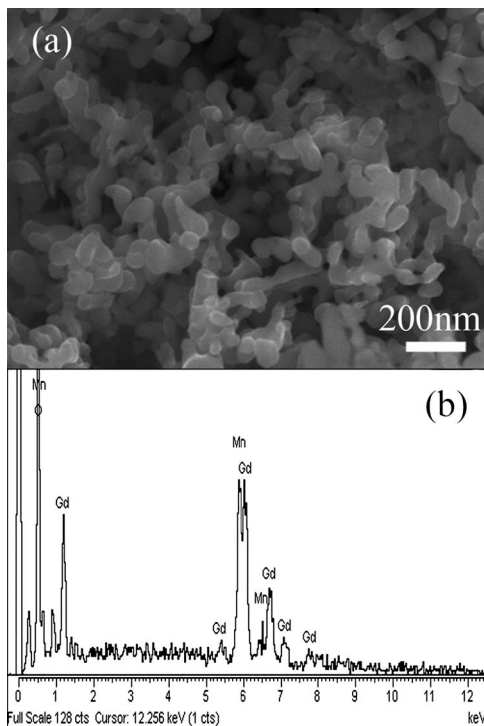


FIG. 2. (a) High-magnification SEM and (b) EDS images of the GdMnO<sub>3</sub> nanoparticles.

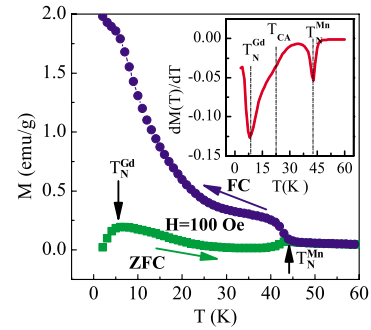


FIG. 3. (Color online) ZFC and FC magnetization curves of the GdMnO<sub>3</sub> nanoparticles at an applied field H=100 Oe between 2 and 60 K. Inset: temperature dependence of the derivative dM(T)/dT.

In the present nanoparticles, complicated magnetic transitions take place in the vicinity of the transition temperatures of the bulk and/or single crystal GdMnO<sub>3</sub>, corresponding to the sine wave ordering of Mn<sup>3+</sup> moments and magnetic ordering of Gd<sup>3+</sup> moments, respectively.<sup>7,11</sup> The transition temperatures are determined by the numerical derivative dM(T)/dT, as shown in the inset of Fig. 3. Neutron diffraction analysis indicated that Néel temperature (T<sub>N</sub><sup>Mn</sup>) in TbMnO<sub>3</sub> is ~40 K.<sup>19</sup> The T<sub>N</sub><sup>Mn</sup> of GdMnO<sub>3</sub> should be larger than that of TbMnO<sub>3</sub> because the T<sub>N</sub><sup>Mn</sup> for rare-earth orthoferrites, vanadates, titanites, and chromites increases with increasing radius of the lanthanon.<sup>11</sup> In Fig. 3, a paramagnetic-antiferromagnetic transition at about 44 K indicates the T<sub>N</sub><sup>Mn</sup> for a configuration of Mn moments in GdMnO<sub>3</sub>. With decreasing the temperature, an increase of magnetization is observed at around 20 K due to an appearance of weak ferromagnetism, which may be contributed by the canting of Mn moments and the polarization of the Gd 4f spins.<sup>12</sup> At 7 K, due to the interaction of the 4f spins, the long-range order of Gd moments appears, resulting in a configuration of a net moment of canted Gd spins antiparallel to that of canted Mn spins.

Figure 4 represents the hysteresis loops of GdMnO<sub>3</sub> nanoparticles recorded at different temperatures after a ZFC process. The paramagnetic behavior of the GdMnO<sub>3</sub> nanoparticles is found in the loops at 50 and 60 K. With decreasing the temperature, an antiferromagnetism is observed at about 30 K in GdMnO<sub>3</sub> nanoparticles, in agreement with the phase transition at T<sub>N</sub><sup>Mn</sup> around 44 K. With further decreasing the temperature, a weak-ferromagnetic behavior is found at

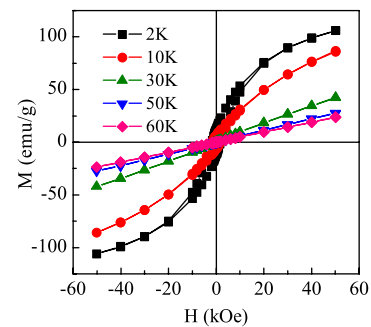


FIG. 4. (Color online) Hysteresis loops of the GdMnO<sub>3</sub> nanoparticles recorded at different temperatures.

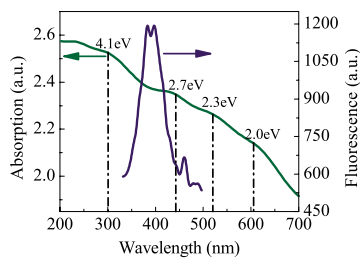


FIG. 5. (Color online) Absorption and fluorescence spectra of the  $\text{GdMnO}_3$  nanoparticles.

about 10 K, due to the spin canting of the Mn moments and the polarization of the Gd 4f spins.<sup>12</sup> At 2 K, the contribution of the net moment of the Gd spins is larger than that of the antiferromagnetically canted state of the Mn spins, giving rise to a ferromagneticlike loop because the external magnetic field aligns the Gd moments.<sup>12</sup>

The absorption and fluorescence spectra of the  $\text{GdMnO}_3$  nanoparticles are shown in Fig. 5. At room temperature, the absorption spectra in a range of wavelength between 400 and 700 nm consist of three shoulder peaks centered at about 2.0, 2.3, and 2.7 eV, which are attributed to the Mn (3d)-electrons' transition.<sup>20–23</sup> On the other hand, the higher energy absorption peak centered around 4.1 eV should be associated with the manifold of charge-transfer transitions between O (2p) and Mn (3d) states.<sup>23–25</sup> The ultraviolet emission with peaks around 396 and 406 nm, as well as a blue band emission with peak around 466 nm are also observed due to the spin-allowed charge transfer transitions.

#### IV. CONCLUSION

In conclusion, the magnetic and optical properties of the multiferroic  $\text{GdMnO}_3$  nanoparticles have been investigated. The magnetization measurements show that complicated magnetic transitions take place in the present nanoparticles, very similar to the case of the bulk (and/or single crystal)  $\text{GdMnO}_3$ , while the saturation magnetization of about 106 emu/g is smaller than the value of 125 emu/g for the bulk  $\text{GdMnO}_3$  at 2 K. Absorption peaks for  $\text{GdMnO}_3$  nanoparticles centered at about 2.0, 2.3, and 2.7 eV originates from the Mn (3d)-electrons' transition, while the absorption peak centered at 4.1 eV is associated with the manifold of charge-transfer transitions between O (2p) and Mn (3d) states. The multiple UV emissions and a blue band emission are attributed to the spin-allowed charge transfer transitions.

#### ACKNOWLEDGMENTS

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