Journal of Magnetism and Magnetic Materials 417 (2016) 182–188

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Magnetocaloric effect at cryogenic temperature in gadolinium oxide nanotubes

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ARTICLE INFO

Article history:
Received 4 June 2015
Received in revised form
10 May 2016
Accepted 18 May 2016
Available online 19 May 2016

Keywords:
Gadolinium oxide
Nanotubes
Electrochemical deposition
Magnetization
Magnetocaloric effect

ABSTRACT

We have synthesized fascinating nano-structure of Gadolinium oxide (Gd_2O_3) using controlled template-assisted electrochemical deposition technique which showed interesting anisotropic magnetic behavior. The nanotubes of Gd_2O_3 with average diameter 200 nm, length 10 μm and wall thickness 20 nm are constituted of nanoclusters with average diameter 7.5 nm. The tubes are aligned and are almost uniform throughout their length. Detailed magnetic measurements of aligned Gd_2O_3 nanotubes have been performed for both parallel and perpendicular magnetic field orientations with respect to the axis of the Gd_2O_3 nanotube array. Significant differences in magnetization values have been observed between the parallel and perpendicular orientations. Experimental results indicate the superparamagnetic nature of the nanomaterial. Large magnetocaloric effect, associated with the sharp change in magnetization of the Gd_2O_3 nanotubes, has been observed in the cryogenic temperature regime that shows anisotropic behavior.

1. Introduction

Present situation of global warming demands environment-friendly technology, which would replace the hazardous technology used worldwide in our day to day life. In this aspect, the conventional gas compression refrigeration technology can be very well replaced by magnetic cooling technology.

Magnetocaloric effect (MCE), which forms the basis of magnetic refrigeration, is advantageous due to its environment-friendly energy-efficient refrigeration mechanism and is anticipated to be the future cooling technology. Hence, a quest for materials with large MCE is in demand [1,2]. Rare earth metal, gadolinium (Gd) and Gd-based alloys and compounds have continuously drawn the attention of the researchers for decades due to its superior magnetocaloric properties [3,4]. Single crystal rare earth [5,6] compounds are also known for their giant anisotropic MCE and are suitable for low temperature magnetic refrigeration. However, nowadays researchers are interested in amorphous materials because they are also probable candidates to show large MCE [7]. Miniaturization of the cooling techniques for Micro Electro Mechanical Systems (MEMS) and Nano Electro Mechanical Systems (NEMS) applications are required with the advent of micro and nanoscale electronic devices [8]. As a result, a desire to develop technologies by using nanoclusters, [4,9,10] nanocapsules [11] etc. made of Gd-based material is growing worldwide. Specially, nanostructured superparamagnetic materials are attractive for cryogenic magnetocaloric refrigeration [7,12]. As far as we know there is no previous report on magnetocaloric effect in tubular oxide nanomaterials. Gadolinium oxide (Gd_2O_3) is a promising material with extensive application in various fields of technology [13–16]. Bulk crystalline Gd_2O_3 is well-known to have three different crystalline phases: hexagonal structure (A phase, space group: $P\bar{3}m1$), monoclinic structure (B phase, space group: $C2/m$), and cubic structure (C phase, space group: $Ia\bar{3}$) [17]. Recently, Yang et al. [17] reported that the cubic phase of Gd_2O_3/Er^{3+} is not stable in high pressure and the Gd_2O_3/Er^{3+} nanorods start to transform into an amorphous phase at 9.4 GPa external pressure. Hanke et al. found that the crystallization into cubic structure of Gd_2O_3 on Si (111) appears after a few monolayer of deposition only [18]. As a result, thin layer of Gd_2O_3, without having any long range crystalline structure may form if allowed to grow specially on some non-crystalline material. Moreover, due to large aspect ratio and shape anisotropy along with the large magnetic moment of Gd, array of Gd_2O_3 nanotubes forms an interesting system for studying different physical properties.

Though cathodic electrodeposition is an attractive technique owing to its powerful control on the structural and morphological properties of metal oxides, [19] electrochemical synthesis of Gd_2O_3 nanostructures still remains a challenging issue [20]. In this article we report the preparation of Gd_2O_3 nanotubes by controlled

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http://dx.doi.org/10.1016/j.jmmm.2016.05.057
0304-8853/

template-assisted electrochemical deposition technique [21]. The template method provides a great control over the parameters which include their diameter, length, and thickness. The formation of Gd_2O_3 nanotubes has been elucidated by field emission scanning electron microscopy (FESEM), high resolution transmission electron microscopy (HRTEM), electron energy loss spectroscopy (EELS) and energy dispersive x-ray spectroscopy (EDS) analysis.

We have studied the magnetic behavior of the aligned Gd_2O_3 nanotubes embedded within the nanoporous alumina template in a temperature range of 2–385 K, for both parallel and perpendicular orientations of the array to the applied field direction. The nanotubes are of average diameter 200 nm, wall thickness 20 nm and length 10 μm. While bulk crystalline Gd_2O_3 [22] is well-known to be antiferromagnetic below the temperature 3.9 K for monoclinic phase and 2.8 K for cubic phase, the synthesized gadolinium oxide nanotubes show superparamagnetic (SPM) behavior down to 2 K. We have also observed the anisotropic giant magnetocaloric effect in Gd_2O_3 nanotubes at cryogenic temperature regime.

Due to low toxicity, high magnetic susceptibility, thermal as well as chemical stability [23] and unique optical properties [24] superparamagnetic Gd_2O_3 nanomaterials are also important for medical diagnosis. Thus, it is obvious that Gd_2O_3 nanotubes may also be used as potential candidates for targeted drug delivery applications as these nanotubes can hold drugs within their cavities.

2. Experimental section

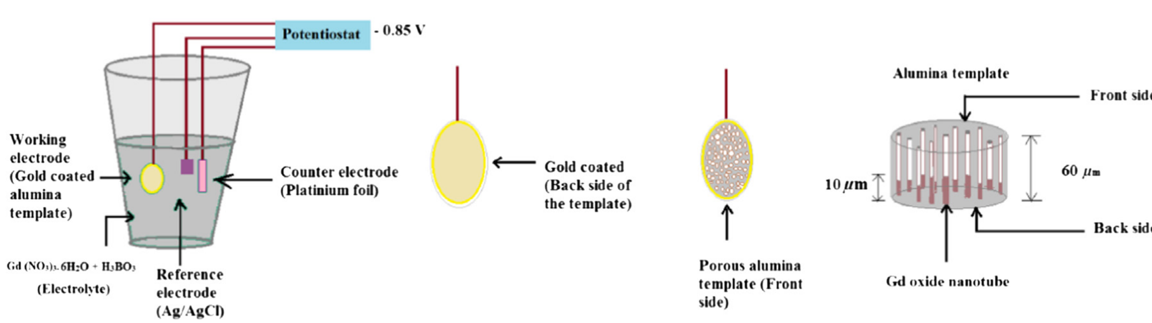
Commercially available Whatman Anodisc alumina membrane of thickness 60 μm and average pore diameter 200 nm has been chosen as a template for the synthesis of Gd_2O_3 nanotubes through electrodeposition technique. The advantage of using alumina membrane as a template is that it has a high pore density (10^9 per square cm) and it dissolves easily in aqueous base. At the very beginning, one side of the membrane was coated with a conductive gold layer by the thermal evaporation technique. Electrochemical deposition of gadolinium oxide nanotubes was carried out using Metrohm AUTOLAB-30 potentiostat, consisting of a conventional three-electrode cell of 20 cm^3 capacity. The gold-coated membrane was used as a working electrode (cathode), a platinum foil as the counter electrode and Ag/AgCl was used as a reference electrode. The schematic diagram of the Electrodeposition technique is shown in Scheme 1. Gd_2O_3 was electrodeposited at room temperature from an aqueous electrolyte containing gadolinium nitrate hexahydrate (Gd $(NO_3)_3.6H_2O$, *Alfa Aesar*, purity 99.9%) and boric acid (H_3BO_3, *Merck*, Assay 99.5%). Boric acid was used as a buffer and the pH of the solution was adjusted to 2.24. The electrochemical deposition was performed in the potentiostat mode to avoid deposition of unwanted chemical species. Based on the linear sweep voltammetry studies [Fig. S1, Supporting Information] over the potential range 0 to −1.00 V at a scan rate of 20 mV/min, the electrodeposition potential had been considered to be −0.85 V.

To perform morphological studies the array of nanotubes were released from the template by dissolving the alumina membrane in 2 M NaOH (aq). The structure and purity of the Gd_2O_3 nanotubes were verified using FESEM (FEI INSPECT F50), HRTEM (Tecnai G^2 F30, S-Twin) which was equipped with high-angle annular dark-field (HAADF) detector (from Fischione, model 3000), a scanning unit, EELS (Gatan imaging filter, Quantum SE, model 963) and EDS (EDAX Inc.) facility and FTIR (Perkin Elmer, Spectrum Two) spectroscopy. A superconducting quantum interference device (Quantum Design, SQUID-VSM) magnetometer was used to study the thermo-magnetic properties of the prepared sample. Magnetization measurements as a function of field at different constant temperatures and as a function of temperature at a constant magnetic field were performed to make an elaborate study of the magnetic properties of the Gd_2O_3 nanotube array embedded within the alumina template. The weight of Gd_2O_3 deposited was evaluated using Faraday's law of electrolysis.

3. Experimental results and discussion

The TEM micrograph of the synthesized Gd_2O_3 nanotubes is shown in Fig. 1(a). The tubular nature of the synthesized material is clearly visible in the figure. The inset (i) of Fig. 1(a) shows the wall thickness of a nanotube which is about 20 nm. Inset (ii) shows the selected area electron diffraction (SAED) pattern from a nanotube. The SAED pattern as well as the HRTEM micrograph (not shown) of the nanotubes do not show any signature of crystallinity of Gd_2O_3 in nanotube form. The presence of gadolinium and oxygen is confirmed from the EDS analysis in scanning TEM (STEM) mode. Here, Cu signal is due to the copper grid used for TEM analysis, Al is due to the alumina template and Na is from NaOH which has been used to release the nanotubes from the template. Si has come from the glass container in which aqueous NaOH solution was stored as glass reacts mildly with aqueous NaOH to form soluble silicates. Fig. 1(c) shows EDS spectrum from area 1 of STEM-HAADF image shown in Fig. 1(b). Spectrum imaging with Gd-L and O-K energy was done from area 2 and is shown in Fig. 1(d). This gadolinium and oxygen mapping of the nanotube indicate the presence of both the elements within the nanotube. Different regions of the nanotubes were further examined by EELS, as shown in Fig. 1(e). The points along the axis of the nanotubes which were probed using EELS are marked by 1 and 2 in Fig. 1(b). On comparing with the standard Gd_2O_3 [25,26] spectrum (as shown in Fig. 1(f)), the EELS spectra confirm the formation of Gd_2O_3 nanostructure. The non-crystalline nature of the Gd_2O_3 nanotubes may possibly be guided by the amorphous nature of the alumina template.

The FESEM micrographs of the nanotubes released from the alumina template are shown in Fig. 1(g) and (h). It is clear from the



Scheme 1. Schematic diagram of the experimental set-up for electrodeposition.