Effect of morphology on the magnetic properties of Gd$_2$O$_3$ nanotubes

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HIGHLIGHTS
- Gd$_2$O$_3$ nanotubes of diameter ~100 nm synthesized through electrochemical technique.
- At cryogenic temperature, the nanotubes exhibit large magnetocaloric effect.
- These are promising candidates for magnetic refrigeration at cryogenic temperature.

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ABSTRACT
Gadolinium oxide (Gd$_2$O$_3$) nanotubes of micron length and average diameter 100 nm have been synthesized by a controlled template-assisted electrochemical deposition technique. Structure and morphology of the synthesized nanotubes have been well characterized by using microscopy and spectroscopy analyses. HRTEM and XRD analysis revealed the crystalline planes of Gd$_2$O$_3$ nanotubes. Magnetic measurements of the aligned Gd$_2$O$_3$ nanotubes have been performed for both parallel and perpendicular orientations of the magnetic field with respect to the axis of the Gd$_2$O$_3$ nanotube array. Large bifurcation in ZFC–FC over the regime of 2–320 K without any signature of long range magnetic ordering confirms the presence of SPM clusters in Gd$_2$O$_3$ nanotubes. Also, large magnetocaloric effect is observed in the cryogenic temperature regime. No anisotropy is seen at the low temperature region but is found to evolve with temperature and becomes significant ~300 K. These nanotubes can be considered as promising candidates for magnetic refrigeration at cryogenic temperature.

1. Introduction
A rise in global warming at an alarming rate necessitates the replacement of the conventional gas compression refrigeration by magnetic cooling technology. By virtue of its environment-friendly energy-efficient refrigeration mechanism, magnetic refrigeration is likely to become the future cooling technology. Magnetocaloric effect (MCE) forms the basis of magnetic refrigeration and hence research on materials with large MCE is in demand [1,2]. Gd-based alloys and compounds have been continuously drawing the attention of the researchers for decades due to their remarkable magnetocaloric properties [3,4]. Bulk Gd exhibits ferromagnetism and demonstrates large MCE at around 293 K. Alloys of Gd viz., Gd$_{85}$Er$_{15}$ and Gd$_5$(Si$_2$Ge$_2$) are also known to show MCE at considerably low temperature [5,6]. Gd metal has a great affinity towards oxygen and forms oxides easily, having fascinating qualities such as low toxicity, thermal and chemical stability, high magnetic susceptibility and interesting optical properties making Gd$_2$O$_3$ attractive for its use in the field of medical science [7–10] viz., in magnetic resonance imaging (MRI), as drug carriers, in various fields of technology as sensors, catalysts, and in magnetic and optoelectronic devices [11]. Gd$_2$O$_3$ also possesses high-k, which can lead to the replacement of conventional silicon-based oxide material used in gate dielectrics [12]. With the advent of micro- and nanoscale electronic devices, [13] miniaturization of the cooling techniques has become a necessity for Micro Electro Mechanical Systems (MEMS) and Nano Electro Mechanical Systems (NEMS) applications. As a result, quest for developing technologies by using nanoclusters [4,14,15], nanocapsules [16], nanoscaled thin-films [17] etc. made of Gd-based materials are emerging worldwide. As nanostructured superparamagnetic materials are very attractive for cryogenic refrigeration [18,19], we attempted to synthesize nanotubes of Gd$_2$O$_3$ through a unique cost effective electrochemical technique to explore their magnetic properties and hence magnetocaloric effect.
In the present article we have reported the preparation of Gd$_2$O$_3$ nanotubes of average diameter 100 nm by controlled template-assisted electrochemical deposition technique [20]. The formation of Gd$_2$O$_3$ nanotubes has been elucidated by field emission scanning electron microscopy (FESEM), High resolution transmission electron microscopy (HRTEM), energy dispersive X-ray spectroscopy (EDS), selected area electron diffraction (SAED) pattern analyses, X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The magnetic behavior of the aligned Gd$_2$O$_3$ nanotubes embedded within the nanoporous alumina template have been studied in a temperature range of 2–320 K, for both parallel and perpendicular orientations of the magnetic field with respect to the axis of the nanotube arrays.

2. Experimental section

Whatman alumina membrane of thickness 60 μm and average pore diameter 100 nm has been procured and chosen as a template for the synthesis of Gd$_2$O$_3$ nanotubes through electrochemical deposition technique. Metrohm AUTOLAB-30 potentiostat having a conventional three-electrode cell of 20 cm$^3$ capacity was used for the deposition of gadolinium oxide nanotubes. To use the membrane as an electrode, one side of the membrane was coated with a conductive gold layer by thermal evaporation technique. The gold-coated membrane served the purpose of a working electrode, a platinum foil as the counter electrode and Ag/AgCl as a reference electrode. Electrodeposition of Gd$_2$O$_3$ was carried out at room temperature from an aqueous electrolyte containing gadolinium nitrate hexahydrate (Gd(NO$_3$)$_3$·6H$_2$O, Alfa Aesar, purity 99.9%) and boric acid (H$_3$BO$_3$, Merck, Assay 99.5%). Addition of boric acid was done to stabilize the pH (2.24) of the solution. On the basis of the linear sweep voltammetry studies, the electrodeposition potential had been considered to be $-0.85$ V. Characterization of the prepared Gd$_2$O$_3$ nanotubes was done using FESEM (FEI INSPECT F50), HRTEM (Tecnai G$^2$ F30, S-Twin), EDS (Bruker), X-ray Diffractrometer (D8 Advance, Bruker) and FTIR (Spectrum Two, Perkin Elmer). In order to perform the microscopy analyses, the alumina template was dissolved in 2 M NaOH (aq) to release the nanotubes from it. XRD and FTIR were performed with nanotubes embedded alumina template. Superconducting quantum interference device

![Image](image_url)
(Quantum Design, SQUID-VSM) magnetometer was used to study the thermo-magnetic properties of the prepared sample. To make an elaborate study of the magnetic properties of the Gd2O3 nanotube array embedded within the alumina template, magnetization as a function of field at different constant temperatures and magnetization as a function of temperature at a constant magnetic field were performed. The weight of the Gd2O3 deposited has been evaluated using Faraday’s law of electrolysis.

3. Results and discussion

Fig. 1(a) shows the FESEM micrograph of arrays of Gd2O3 nanotubes. The tubes are perfectly aligned and are almost uniform in diameter and height. The nanotubes are of micron length and have an average diameter of 100 nm. As shown in the FESEM micrograph the nanotubes are capped. The chunks that appear onto the top surface of the nanotubes are the residue of the undissolved alumina template. However, the tubular nature of Gd2O3 is confirmed from the TEM micrograph as shown in Fig. 1(b). The inset of Fig. 1(b) shows the selected area electron diffraction (SAED) pattern from a nanotube. The SAED pattern indicates the crystalline nature of the nanotubes and the reflections from (611) and (842) planes matches with that of the cubic phase of Gd2O3 (JCPDS-43-1014). In Fig. 1(c) the HRTEM micrograph also shows the crystalline planes of the synthesized Gd2O3 nanotubes.

Fig. 1(d) shows the EDS pattern of the sample prepared. The presence of gadolinium and oxygen is confirmed by the EDS analysis. The presence of Al is due to the alumina template, whereas the sources of Au and Na are the gold coated electrode, essential for electrochemical synthesis and an alkaline NaOH solution, required for etching the template respectively. Image J [21] software has been employed to estimate the average thickness and diameter of the nanotubes and found to be 12 nm and 100 nm respectively.

Fig. 2 shows the XRD pattern of the nanotubes embedded gold coated alumina template. The peaks centered at around 37°, 64° and 81° correspond to the reflections from (420), (642) and (842) planes of the cubic phase of Gd2O3 (JCPDS# 43-1014). However, these planes overlap with (111), (220) and (222) planes of Au (JCPDS# 89-3697), which was used to make the template conducting. The (842) plane of Gd2O3 is revealed from the electron diffraction pattern as discussed earlier and hence the analyses agree well with each other.

Fig. 3 shows the FTIR spectra of Gd2O3 nanotubes. The stretch in the region 400–800 cm\(^{-1}\) is due to Al–O–Al band [22] of Al2O3 template in which the Gd2O3 nanotubes are embedded. The bands near 1384 cm\(^{-1}\) and 1630 cm\(^{-1}\) are the characteristic bands of Al2O3. The band at 545 cm\(^{-1}\) due to Gd–O bond vibrations of Gd2O3 [23] is suppressed here due to higher concentration of Al2O3. However, on making Gaussian multi-peak fit of the FTIR spectra from 400–1000 cm\(^{-1}\) (as shown in the inset of Fig. 3), the band ~545 cm\(^{-1}\) is revealed. The band around 3468 cm\(^{-1}\) is due to the absorption of atmospheric moisture by the pellet containing KBr. Thus the formation of Gd2O3 nanotubes is well established from the analyses undertaken.

The zero field cooled (ZFC) and field cooled (FC) magnetization dependence on temperature have been studied in the presence of 100 Oe external magnetic field applied in both parallel and perpendicular direction with respect to the axis of the nanotube. There is a bifurcation between ZFC and FC, which increases with the decrease in temperature till 50 K and afterwards, the magnetization value increases abruptly. The temperature dependence of magnetization in a typical representation of perpendicular orientation has been shown in Fig. 4. No long range magnetic ordering has been observed in the M(T) data in the measured temperature range of 2–320 K. The inverse susceptibility also shows continuous curvature and deviation from the Curie–Weiss behavior. Large negative θ values in the χ\(^{-1}\) Vs T plots are obtained for the linear extrapolation of the high temperature region, as reported by earlier researchers in the case of Gd2O3 nanospheres [7].

The magnetization hysteresis curves of the prepared Gd2O3 nanotubes measured at 2 K, 10 K and 55 K are shown in Fig. 5. The magnetization measurements have been done with the nanotubes embedded within the alumina template and the diamagnetic signals have been eliminated from the raw data.

To measure the magnetization as a function of external magnetic field at a particular temperature, the sample was at first warmed up to \(T=385\) K. Temperature was then lowered to the required temperature in the absence of any external magnetic field (ZFC Cooling) to remove the magnetic history of the previous measurement, if present. The M–H curves appear in typical S-shape having negligible coercivity as well as hysteresis loss, indicating superparamagnetic (SPM) domains within Gd2O3 nanotubes.
The field-dependent magnetization measured at different fixed temperatures ranging from 2 K to 320 K is presented in Fig. 6. The $M-H$ curves show non-saturating behavior with gradual curvature even for the application of magnetic field above 5 T. This nature of the magnetization isotherms of Gd$_2$O$_3$ nanotubes are very much similar and are well fitted with the Langevin function as expressed by Eq. (1).

\[
M(H) = 2pL\left(\frac{\mu H}{K_BT}\right) + \chi H
\]

where, \(L(x)\) is the standard Langevin function \([L(x) = \cot h(x) - 1/x]\), \(z\) is the number density of the magnetic clusters, \(\mu\) is the average moment of the magnetic clusters and \(\chi\) is the susceptibility [24]. Such fittings indicate that the nanotubes comprise of magnetic clusters of same average magnetic moment and the magnetization of these clusters follow a Langevin function [25].

This $M-H$ relation together with the absence of hysteresis even at lowest temperatures measured, large bifurcation in the FC–ZFC plot from high temperature region without any signature of long range magnetic ordering, and the deviation from linearity in the

\[\chi^{-1} \text{ vs } T\] plots confirm the presence of SPM clusters in Gd$_2$O$_3$ nanotubes [26].

In Fig. 7 the anisotropy between the parallel and perpendicular orientation of the nanotubes has been shown. At a temperature of 2 K, the arrays of 100 nm Gd$_2$O$_3$ nanotubes show no anisotropy but on increasing the temperature, the anisotropy increases gradually. At this stage, the physical origin of such nontrivial behavior of anisotropy at low temperature (2 K) for 100 nm Gd$_2$O$_3$ nanotubes when compared with 200 nm amorphous Gd$_2$O$_3$ nanotubes (Fig. 7(a) and (c)) is not clear. However, the growth of crystalline phase in 100 nm Gd$_2$O$_3$ nanotubes along the axis of nanotube may be responsible for the orientation of the magnetic domains in the direction of the applied field and it is reflected in the higher values of anisotropy at 300 K (Fig. 7(b)) compared to 200 nm Gd$_2$O$_3$ nanotubes (Fig. 7(d)). Such a mechanism of growth may be due to synthesis of Gd$_2$O$_3$ within smaller pore diameter of the alumina template.

The magnetocaloric effect of a magnetic material relies on the temperature dependence of the magnetic entropy change ($-\Delta S_m$) due to the change of applied magnetic field.

The temperature variation of $-\Delta S_m$ for different magnetic field change up to 7 T has been shown in Fig. 8. With the lowering of temperature the value of $-\Delta S_m$ increases slowly and below 50 K there is a sharp rise in $-\Delta S_m$ value. Also, $-\Delta S_m$ increases with the increase in applied magnetic field. The maximum value of $-\Delta S_m$ for 7 T magnetic field change at 3.5 K is 23.21 J kg$^{-1}$ K$^{-1}$, which is quite larger than what we observed for Gd$_2$O$_3$ nanotubes (16.07 J kg$^{-1}$ K$^{-1}$) of average diameter 200 nm. [27] This value of $-\Delta S_m$ is even larger than that of known single crystals TbMnO$_3$ [28] and HoMn$_2$O$_5$ [29], which are most attractive materials for low temperature magnetic refrigeration and are reported to show $-\Delta S_m = 18.0 J kg^{-1} K^{-1}$ and $-\Delta S_m = 12.43 J kg^{-1} K^{-1}$ respectively for 7 T magnetic field change.

It is worthwhile to mention that here we did not observe any remarkable anisotropy in MCE at 2 K unlike what we obtained in the case of 200 nm Gd$_2$O$_3$ nanotubes. Even at 5 T magnetic field change, Gd$_2$O$_3$ nanotubes show better MCE ($-\Delta S_m = 19.44 J kg^{-1} K^{-1}$) in comparison to that of our synthesized Gd$_2$O$_3$ nanotubes ($\sim 14.92 J kg^{-1} K^{-1}$) of 200 nm diameter [27].
The higher value of $-\Delta S_m$ in 100 nm Gd$_2$O$_3$ nanotubes may be possibly due to the growth mechanism of the crystalline phase along the axis of nanotube during the synthesis of Gd$_2$O$_3$ within smaller pore diameter of the alumina template. Such super-paramagnetic Gd$_2$O$_3$ nanotubes of 100 nm diameter can be considered as a promising candidate for magnetic refrigeration at cryogenic temperature.

4. Conclusions

Gd$_2$O$_3$ nanotubes of average diameter 100 nm were synthesized through a unique cost effective electrochemical technique. HRTEM and XRD analyses show the signature of crystalline planes in 100 nm Gd$_2$O$_3$ nanotubes unlike 200 nm Gd$_2$O$_3$ nanotubes synthesized under similar electrochemical environment. Large bifurcation in ZFC–FC over the regime of 2–320 K without any signature of long range magnetic ordering together with the absence of hysteresis even at lowest temperature (2 K), confirm the presence of SPM clusters in the Gd$_2$O$_3$ nanotubes. Large magneto-caloric effect with insignificant anisotropy behavior especially at cryogenic temperature can thus affirm 100 nm Gd$_2$O$_3$ nanotubes to be considered as a promising candidate for magnetic refrigeration.

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Fig. 7. Anisotropy in magnetization in parallel and perpendicular orientation of the Gd$_2$O$_3$ nanotubes of average diameter (a–b) 100 nm and (c–d) 200 nm.

Fig. 8. Magnetic entropy change ($-\Delta S_m$) as a function of temperature of Gd$_2$O$_3$ nanotubes for a magnetic field change up to 7 T.
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