Synthesis, characterization and effect of dopant on magnetic hyperthermic efficacy of Gd$_2$O$_3$ nanoparticles

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Abstract

Rare-earth oxides are paramagnetic materials and their high magnetic susceptibility in the bulk makes them potentially promising materials, but the magnetic properties of their nanoparticles remain incompletely characterized. We explore the effect of dopant (Tb$^{3+}$ and Eu$^{3+}$) in Gd$_2$O$_3$ host lattice as a heating agent for magnetic hyperthermia application. The structural, optical, and magnetic properties of the pristine, Gd$_2$O$_3$:Tb$^{3+}$ and Gd$_2$O$_3$:Eu$^{3+}$ nanocrystals were studied by XRD, HR-TEM, FTIR, and VSM. XRD analysis revealed the presence of mixed-phase (cubic and monoclinic) in pristine, and doped Gd$_2$O$_3$ nanoparticles. The morphological information has been observed with the help of HRTEM and the calculated inter-planar spacing is in well agreement with JCPDS data. Particles are nearly spherical and diameter ~15 nm, estimated from HRTEM image. FTIR spectroscopic analysis confirms the presence of Gd-O-Gd stretching at 583cm$^{-1}$. We confirmed the paramagnetic nature for all samples using VSM analysis. The self-heating capability of prepared samples are investigated by performing the induction heating experiment and it is assessed through calculated SAR and ILP values with help of Box-Lucas fitting model where 10% Tb$^{3+}$ doped Gd$_2$O$_3$ has maximum values.

1. Introduction

Rare-earth oxide (RE$_2$O$_3$) nanocrystal emerged in recent years with their attractive properties and their versatile alternative applications in different fields [1]. Rare-earth (RE) oxide have high value susceptibility ($\chi$), and RE$^{3+}$ magnetic moment ($\mu$) resulting in high saturation magnetization (Ms) [2]. However, gadolinium oxide is typically studied oxide phosphor matrix at nanoscale among all oxides of lanthanides [3]. The characteristic properties like optical, electrical, dimensional, magnetic and physico-chemical response of 4f electrons are influenced by their chemical composition and dimensionality [4]. These properties are making RE oxide based phosphor (e.g. gadolinium oxide host) a promising material in various implements like catalysis, luminescence, bio-medical and other functional devices [4, 5]. The use of magnetic nanomaterial in the diverse area of nanotechnology has created a broad platform for gadolinium oxide [6, 7]. The dual characteristics of Gd$_2$O$_3$ magnetic nanocrystal have been proved as a potential candidate with its versatile applications; as a positive contrast agent in magnetic resonance imaging (MRI) to enhance the quality of cell images, X-ray computed tomography (CT) and neutron captured therapy for cancers in bio-medical field [8–10]. Gadolinium oxide (Gd$_2$O$_3$) is an efficient material to use as an exogenous imaging contrast agent for SS-OCT (Swept source optical coherence tomography) applications in the field of advanced health care [11]. Especially at cryogenic temperature, the Gd$_2$O$_3$ nanotubes of 100 nm size can be considered as a potential candidate for magnetic refrigerators due to their large magneto-caloric effect [12]. The phase transition of Gd$_2$O$_3$ with respect to temperature and pressure at its nanoscale is different from its bulk[13, 14]. So, the characteristic temperature responsive paramagnetic Gd$_2$O$_3$ nanoparticles have the ability to replace the toxic super-paramagnetic iron oxide magnetic nanoparticle in hyperthermia applications [8]. The recent studies revealed that the lanthanide ions doped gadolinium oxide is an effective dual-model candidate for MR imaging and multicolour upconversion luminescence [15]. The great fluorescence and high longitudinal relaxivity due to extrinsic dopant...
and negligible cytotoxic effects are shown by the Gd₂O₃ matric host material [16]. Magnetic hyperthermia is an adjuvant model of therapy to conventional chemotherapy and radiation therapy treatment for cancer; based on the fact that magnetic nanoparticles can generate heat from an external field of appropriate frequency. It is considered as a co-adjuvant of other cancer treatments. It also aims to produce local heating effects with minimum side effects in comparison to chemo and radiotherapy to treat the cancers cell [17, 18]. Due to the low toxicity, the high thermal and mechanical stability of Tb³⁺ doped Gd₂O₃ nanomagnet could meet desired hyperthermic application [8]. The therapeutic need, such as the minimum concentration of nanomagnet should exhibit a high inductive specific absorption rate (SAR) [19, 20]. Gadolinium oxide is a good paramagnetic material with 7 unpaired electrons in its f-orbital. So, the knowledge of collective properties along with induction heating phenomena could help in the study of desired application of this material [21–23]. Although extensive research has been done in the field of hyperthermia using different magnetic nanoparticles, a few literatures are available for RE based nanoparticles in the field of hyperthermia. In this work, we present a simple synthesis method for Tb and Eu doped Gd₂O₃ nanoparticles and their hyperthermic application studies of the temperature responsive nanoparticles. The main aim of this work is that to explore the possible in-vivo application of this material in various biomedical application fields such as hyperthermia, as an exogenous contrast agent in OCTs and in targeted drug delivery, etc.

2. Sample Preparation

2.1. Synthesis of pristine, Tb³⁺ and Eu³⁺ [1%, 5%, and 10%] doped Gd₂O₃ nanoparticles

Analytical grade gadolinium (III) acetate hydrate [Gd(CH₃CO₂)₃·H₂O] (GdAc, CDH, 99.9% pure), terbium (III) acetate [Tb(CH₃CO₂)₃·H₂O] (TbAc, CDH, 99.9% pure), and citric acid [C₆H₈O₇·H₂O] (99% pure, CDH) were purchased and used as precursors. Pristine, Tb³⁺ and Eu³⁺ [1%, 5%, and 10%] doped Gd₂O₃ nanoparticles were prepared by using simple phyico-chemical method with top down approach. In this method, 1:1 molar aqueous solution of gadolinium (III) acetate hydrate and citric acid were prepared under vigorous stirring for 30 min at 3000 rpm at room temperature. Later the resultant white precipitated of Gd(OH)₃ was filtered and washed several times with deionized water and ethanol to remove the unwanted impurities. The filtrate was dried in a hot air flow oven at 70 °C and further, the obtained powder product was calcined at 600 °C for 4 h to obtain Gd₂O₃ nanopowder. For the synthesis of Tb³⁺ and Eu³⁺ [1%, 5%, and 10%] doped Gd₂O₃ powder nanoparticles, terbium (III) acetate or europium acetate were mixed into the reaction mixture in, the initial stage of the reaction respectively, whereas the rest of the reaction steps were kept similar to the aforementioned procedure. The schematic representation of synthesis procedure is given in figure 1.

Figure 1. Schematic representation of synthesis procedure.
2.2. Characterization techniques

Structural characterization of all the synthesized samples was carried out with the help of X-ray diffractometer (Rigaku Ultima IV) employing Cu Kα incident radiation (λ = 1.54 Å). To study the morphological features of the synthesized sample transmission electron microscopy (JEOL JSM100 CX and HRTEM: JEM-2100 and FEI, Tecnai Swin) working at different accelerating voltages (80 kV for TEM and 60–200 kV for HRTEM) was employed. The compositional studies like the presence of functional groups and bond stretching were carried out with the help of Fourier transformed infrared spectrometer with ATR (model: carry 360 FTIR, Agilent Technologies India Pvt. Ltd) Optical characterization like absorption features were revealed by computer interfaced double beam UV-Visible spectrophotometer (model: Cary 100 series UV-vis spectrophotometer). Magnetic characterization of synthesized samples were carried out by vibrating sample magnetometer (VSM), (model: 7410 series).

2.3. Induction heating

The induction heating response of the nanoparticles was tested by Easy Heat AMBREL 8310, UK. The induction heating set-up consists of a helical coil with eight numbers of turn. The calorimetric approach is the most commonly adopted method in evaluating the magnetic hyperthermia properties of magnetic NPs. For our study, we measured the hyperthermic efficacy with a calorimetric approach. In this method, the temperature increase in the sample is recorded over a period of time as the magnetic NPs are exposed to an AC field of a particular amplitude and frequency. A fibre optic temperature probe is typically used in conjunction with a magnetic induction heating system consisting of a water-cooled coil that is connected to a high power generator. Samples are placed in a thermally insulated container to avoid heat loss to the environment during measurement. And using the initial slope method, SAR value was calculated.

To perform induction heating study of pristine, Tb³⁺ and Eu³⁺ [1%, 5%, and 10%] doped Gd₂O₃ nanoparticles was dispersed in Milli-Q water (1 mg ml⁻¹) and placed at the center of a coil. Induction heating data were recorded in the AC magnetic field with frequency 336 kHz and current I = 300 A for the time period of 900 s. The magnetic field intensity in the coil can be tuned by the current through the coil and it is calculated by the well-known relation reported elsewhere [19].

3. Results and discussion

3.1. Structural and morphological analysis

(Note: C* - cubic, M* - monoclinic).
Figures 2 (a) and (b) represents the XRD patterns of pristine Tb$^{3+}$ and Eu$^{3+}$ [1%, 5%, and 10%] doped Gd$_2$O$_3$ powder respectively. The XRD results are in good agreement with standard JCPDS (CAS Number: 12-0474 and 86-2477) which confirms the presence of mixed-phase (cubic and monoclinic) in Gd$_2$O$_3$ powder [13]. According to the references [24, 25], the heat treatment conditions, as well as the addition of dopant, can induce phase variations in the host materials. It is anticipated that the low calcination temperature ($\sim$600 °C) is responsible for the formation of mixed-phase of Gd$_2$O$_3$. One can achieve a pure cubic phase at a higher calcination temperature ($\sim$800 °C) [13]. The preferred crystallographic growth was observed along (222) plane position at 2$\theta$ $\sim$28.6° and (−402) plane at 2$\theta$ $\sim$30.1° for pristine and Tb$^{3+}$ and Eu$^{3+}$ [1%, 5%, and 10%] doped Gd$_2$O$_3$ powder samples respectively. This might be due to the inclusion of foreign atoms (i.e., Tb$^{3+}$/Eu$^{3+}$ atoms) into the host material. It is also reported that the dopant element has a fundamental role in the growth of crystal host lattice [25]. In figures 2 (a) and (b), it is clearly observed from the diffractograms, Tb$^{3+}$ and Eu$^{3+}$ [1%, 5%, and 10%] doped samples exhibit sharper peaks in comparison to pristine sample, signifying an improved crystallinity.

Table 1 Average crystallite size and corresponding microstrain of pristine Tb$^{3+}$ and Eu$^{3+}$ [1%, 5%, and 10%] doped Gd$_2$O$_3$ powder nanocrystals.

| S.No. | Sample name         | Average crystallite size (nm) | Microstrain   |
|-------|---------------------|------------------------------|---------------|
| 1     | pristine Gd$_2$O$_3$ | 10.78                        | 0.012 ± 0.0028|
| 2     | 1%Tb:Gd$_2$O$_3$    | 30.1                         | 0.027 ± 0.013 |
| 3     | 5%Tb:Gd$_2$O$_3$    | 53.9                         | 0.016 ± 0.0028|
| 4     | 10%Tb:Gd$_2$O$_3$   | 75.4                         | 0.031 ± 0.0162|
| 5     | 1%Eu:Gd$_2$O$_3$    | 11.61                        | 0.012 ± 0.0084|
| 6     | 5%Eu:Gd$_2$O$_3$    | 25.1                         | 0.0154 ± 0.0028|
| 7     | 10%Eu:Gd$_2$O$_3$   | 43.01                        | 0.019 ± 0.0217|

Figure 3. HRTEM micrographs of pristine, 5% Tb$^{3+}$ and Eu$^{3+}$ doped Gd$_2$O$_3$ nanoparticles [(a), (c) and (i) HRTEM micrographs (c), (g) and (k) crystal planes (d), (h) and (l) SAED graphs of pristine, 5%Tb$^{3+}$ and Eu$^{3+}$ doped Gd$_2$O$_3$ nanoparticles respectively].

Figures 2 (a) and (b) represents the XRD patterns of pristine and Tb$^{3+}$ [1, 5, 10, and pristine and Eu3+ doped Gd$_2$O$_3$ powder respectively. The XRD results are in good agreement with standard JCPDS (CAS Number: 12-0474 and 86-2477) which confirms the presence of mixed-phase (cubic and monoclinic) in Gd$_2$O$_3$ powder [13]. According to the references [24, 25], the heat treatment conditions, as well as the addition of dopant, can induce phase variations in the host materials. It is anticipated that the low calcination temperature (600 °C) is responsible for the formation of mixedphase of Gd$_2$O$_3$. One can achieve a pure cubic phase at a higher calcination temperature (800 °C) [13]. The preferred crystallographic growth was observed along (222) plane position at 2$\theta$ 28.6° and (−402) plane at 2$\theta$ 30.1° for pristine and Tb$^{3+}$ and Eu$^{3+}$ [1, 5 and 10%] doped Gd$_2$O$_3$ powder samples respectively. This might be due to the inclusion of foreign atoms (i.e., Tb$^{3+}$/Eu$^{3+}$ atoms) into the host material. It is also reported that the dopant element has a fundamental role in the growth of crystal host lattice [25]. In figures 2 (a) and (b), it is clearly observed from the diffractograms, Tb$^{3+}$ and Eu$^{3+}$ (1, 5, and 10%) doped samples exhibit sharper peaks in comparison to pristine sample, signifying an improved crystallinity.
Evidently, an increment in the average crystallite size of Tb$^{3+}$ doped samples can be observed in table 1. The relative broad peaks of the synthesized nanopowder suggest, a crystallinity with nano dimension nature of the rare earth oxides. No other crystalline impurity peaks apart from rare earth oxide were detected in the XRD pattern. The crystallite size and microstrain information were determined by using Williamson hall equation [26].

$$\beta \cos \theta = \varepsilon (4 \sin \theta) + \lambda D$$

Where, \(\beta\) = Full Width Half Maxima (FWHM)  
\(\varepsilon\) = Micro strain  
\(\lambda\) = Wavelength  
\(D\) = Grain size

The average crystallite size for pristine Gd$_2$O$_3$ is found to be \(\sim 10.7\) nm (table 1). It is very much evident from table 1, there is a rapid increment in the crystallite size along with microstrain for all the doped samples. We speculated it to the manifestation of distortion with increased dopant concentration in the host matrix [25].

HRTEM micrographs along with crystal plans and SAED pattern of pristine and 5% (Tb$^{3+}$, Eu$^{3+}$) doped Gd$_2$O$_3$ nanoparticles are depicted in figure 3 (a-l). In the distributed view, the individual nanoparticles are marked by red circles and is very much evident from the image, the nanoparticles are nearly spherical with a diameter of \(\sim 15\) nm (figure 3(a)). Figure 3(c) shows the enlarged view of the lattice fringe pattern of an isolated well-grown nanoparticle. The lattice fringes are distinct, well-separated lattice plane (shown by short parallel red lines) measuring a spacing of 3.15 Å, and 2.96 Å; depicting the high crystalline nature of the nanoparticles with preferential growth occurring along (222) and (−402) planes in case of pristine and doped Gd$_2$O$_3$ specimen respectively (figures 3 (c), (g) and (k)). The evaluated \(d\)-spacing of the image is quite consistent with the diffraction data. On the other hand, a cluster of nearly spherical particles of 5% Tb and Eu$^{3+}$ doped Gd$_2$O$_3$ system is depicted in figures 3(e) and (i) respectively. A film-like substance on the image could be due to leftover surfactant on the final product. Figures 3(d), (h) and (l), depict a selected area electron diffraction (SAED) pattern of the pristine and 5% (Tb, Eu) doped Gd$_2$O$_3$ samples respectively. Apart from distinct bright spots making up a ring, a few weak, diffused rings can be observed in the pattern. The above characteristics signify the polynanocrystalline nature of the specimens. While the central ring consisting corresponded to (222) plane, other outer rings are indexed as (−402) and (622), crystallographic planes of the investigated Gd$_2$O$_3$ system. The index of SAED patterns and inter planar spacing distance (figures 3 (c), (g) and (k) of crystalline plans are in good agreement with XRD results in JCPDS data which confirms the presence of mix phase in the nanocrystals.

3.2. FTIR spectroscopic analysis

Figure 4 illustrates the FTIR spectra of pure and doped Gd$_2$O$_3$ nanoparticles respectively within the range of 4000–500 cm$^{-1}$. The peak observed at 583 cm$^{-1}$ corresponds to the characteristic vibration of Gd–O–Gd [17]. The conventional peaks appearing at \(\sim 1407.4\) and 1487.6 cm$^{-1}$ represent the respective signatures of O–H stretching and C–O stretching of atmospheric water and CO$_2$ molecules [17]. Moreover, the peaks at 1487 cm$^{-1}$ and 858 cm$^{-1}$ correspond to the C–H bending vibrations of the alkyl group [17]. Different peaks that are assigned to various components of pristine and Tb doped Gd$_2$O$_3$ are listed in table 2.
3.3. UV–vis spectra analysis

The absorption spectra of pristine, Tb$^{3+}$ and Eu$^{3+}$ doped Gd$_2$O$_3$ samples with different dopant concentrations are presented in figure 5. There exists a broad absorption edge in the visible region, for all the cases. The extent of broadening in the spectra increases with increasing Tb concentration. Gd$^{3+}$ ions have 7 half-filled electrons with ground state half-filled shell $^8S_7/2$ and electronic configuration Xe [$^4f^7$] $^27$]. The process of energy absorption in the host element (Gd$^{3+}$) will be mediated via transition of electrons from 4$f$ level to 5$d$ level and followed by reorganization of 4$f$ electrons into various multiplets [8]. Among all 3432 multiplets; $^6P_{7/2}$ is the low lying multiplet which is situated just above the ground state $^8S_7/2$ [5, 6]. Two absorption peaks of the synthesized samples can be clearly observed in all the spectra, centered at $\sim$220 nm and $\sim$270 nm. The typical absorption peak at 270 nm is a characteristic feature of Gd$_2$O$_3$ which is attributed due to the transition $^8S_7/2 \rightarrow ^6I_{7/2}$ transition, which is present in all the spectra (figures 5(a) and (b)) [21, 28, 29]. And a peak at 220 nm can be assigned to $^7F_6$ ($^4f^8$) $\rightarrow$ 7$D$ ($^4f^5$5$d$) transition of Tb$^{3+}$ ion in the host Gd$_2$O$_3$ lattice; are very much dependent upon the crystal field of the lattice. It is very much evident that the relative intensity ratio between the two peaks ($\sim$220 and 270 nm peak) significantly increases with dopant concentration (figure 5(a)).

3.4. Magnetic property analysis

Figures 6 (a)–(g) shows the room temperature M–H loops of pristine, Tb$^{3+}$ and Eu$^{3+}$ (1, 5 and 10%) doped Gd$_2$O$_3$ nanoparticles representing strong paramagnetic characteristics. In the paramagnetic region, the total magnetic field $H_{\text{Total}} = H + H_M$ ($H$ is the external applied magnetic field and $H_M$ is generated by the magnetization of the medium itself) tends to line up the magnetic moments along $H_{\text{Total}}$ while the thermal energy tends to randomize the motion. Among lanthanides, Gd$_2$O$_3$ is a typical paramagnetic host because of its seven unpaired parallel electrons in 4$f$ orbital. The magnetic moment of Gd$^{3+}$ ions arises from seven unpaired inner 4$f$ electrons summing up to 7.94 $\mu_B$. Moreover, these electrons are closely bound to the nucleus and effectively shielded by the outer closed shell electrons 5$s^2$5$p^6$ from the crystal field hence belonging to weak crystal field materials [27]. Among various paramagnetic RE ions, Gd$^{3+}$ ions possess a high magnetic moment.
Figure 6. Room temperature M–H loop of pristine, 1% Tb$^{3+}$, 5% Tb$^{3+}$, 10% Tb$^{3+}$, 1% Eu$^{3+}$, 5% Eu$^{3+}$, 10% Eu$^{3+}$ doped Gd$_2$O$_3$ nanoparticles are shown (a)–(g) respectively.
due to isotropic electronic ground state\( ^8S_{7/2} \) \cite{5}. To explore further, we zoomed the \( M \sim H \) response near zero field (not shown here). Small hysteresis in \( M-H \) loops of synthesized nanocrystal signifies a small amount of energy dissipated due to repeated reversal of the magnetization which causes the quick magnetization and demagnetization. The obtained values of the coercivity of all the samples are presented in table 3. The average coercivity values of the synthesized samples are in the range of 25–40 Oe. The obtained coercivity values of synthesized samples signify that the samples are very much suitable for hyperthermia applications. The above phenomenon is very much relevant for said applications \cite{1}.

### 4. Induction heating

In magnetic hyperthermia, magnetic nanoparticles are employed to raise the temperature in a range of 42 °C to 46 °C, by using an external magnetic field, tempers cell growth and proliferation rate by denaturation of membrane and cytoplasmic protein which might finally cause apoptosis \cite{30}. To investigate the heat generation capability of pristine, \( \text{Tb}^{3+} \) and \( \text{Eu}^{3+} \) \cite{1,5 and 10%} doped \( \text{Gd}_2\text{O}_3 \) nanoparticles, each of a minimal concentration of 1 mg ml\(^{-1}\) in aqueous media has been placed under magnetic field amplitude of 12.89 kAm\(^{-1}\) (\( H_1 \)) and frequency 336 kHz (\( f \)), for a time interval of 900 s following biological safety limit; where \( H.\text{f} < 5 \times 10^8 \text{Am}^{-1}\text{s}^{-1} \), defined by Hertz \cite{17}. It is very much visible (figure 7(a)), each of the samples reaches a maximum temperature \(~ 44 \) °C from 25 °C within a time interval 900 s. To investigate the self-heating ability of the synthesized nanoparticles under an external ac magnetic field, the dissipated power per unit mass is expressed by a quantity called specific absorption rate (SAR) is being reported in our earlier work \cite{20}. Considering the non-adiabatic experimental condition, the specific absorption rate (SAR) value is calculated from Box-Lucas fit \cite{31,32} as shown in figure 7(b).

\[
\Delta T = l(1 - e^{-m\Delta t})
\]

Where \( l \) and \( m \) are fitting parameters,
Using the above parameter, SAR value is calculated using

\[
SAR = \frac{\text{Im} \cdot C_v \cdot M_i}{M_s}
\]

Where 'C_v' is the specific heat capacity of the sample (4.186 Jg\(^{-1}\)°C\(^{-1}\)), 'M_s' and 'M_i' are the total mass of suspension and magnetic mass (mass of pristine, Tb\(^{3+}\) and Eu\(^{3+}\) [1, 5 and 10%] doped Gd\(_2\)O\(_3\)) the sample solution; respectively. To make a direct comparison of heating efficacy of different hyperthermic agents, intrinsic loss power (ILP) for all the induction heating curves were measured normalizing respective SAR value with respect to field amplitude and field frequency using the following equation [20]

\[
\text{ILP} = \frac{SAR}{H^2f}
\]

Calculated SAR and ILP values of pristine, Tb\(^{3+}\) and Eu\(^{3+}\) [1, 5 and 10%] doped Gd\(_2\)O\(_3\) nanoparticles are enclosed in the table 4. The SAR values show an increasing trend with an increase in dopant concentration, whereas an anomaly has been observed in the case of 5% Eu: Gd\(_2\)O\(_3\) sample. Such anomalous behavior is ascribed to the intrinsic magnetic properties of the material. Highest SAR (142.7 Wg\(^{-1}\)) value has been recorded for 10% Tb: Gd\(_2\)O\(_3\) in contrast to a minimum value for pristine Gd\(_2\)O\(_3\) (57.4 Wg\(^{-1}\)). The effective magnetic moment of trivalent Tb positive ion (9.72) is higher than Gd (7.94), magnetic mass content increases with the increase in the concentration Tb ion resulting from the above behaviour. We speculate Tb\(^{3+}\) ion as a dopant into the Gd\(_2\)O\(_3\) host material will be a better choice for an effective candidate for a hyperthermic agent.

### 5. Conclusion

We have successfully synthesized pristine, Tb\(^{3+}\) and Eu\(^{3+}\) [1, 5 and 10%] doped Gd\(_2\)O\(_3\) nanoparticles. The synthesized samples have attained a mixed crystal phase (monoclinic and cubic). Nanoparticles with spherical shape is very much evident from HRTEM images and preferred crystallographic orientation is in good agreement with XRD results. FTIR studies reveal the presence of Gd-O-Gd stretching. The characteristic absorption peak has been observed for all the synthesized samples ~270 nm. The magnetic properties of the pristine and the doped Gd\(_2\)O\(_3\) were investigated, with the magnetic responses consistent with paramagnetic nature with a small hysteresis near-zero field region. Doped particles display superior SAR values over pristine Gd\(_2\)O\(_3\). Rare earth ion doping has its particular advantages for its hyperthermic applications and for this purpose it has been intensively studied. Looking ahead, the right concentration of dopant in the Gd\(_2\)O\(_3\) host likely to advance in the field of magnetic hyperthermia to magnetic imaging.

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### Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.
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References

[1] Dutta R K and Pandey A C 2013 Nanoscience & technology: open access fluorescent magnetic gadolinium oxide nanoparticles for biomedical applications J. Nanosci. Technol. 21–6
[2] Trepka K, Hauert R, Cancellieri C and Tao Y 2020 A robust metal oxide thin film with cryogenic saturation magnetization exceeding 2 Tesla Mater. 31–12
[3] Goetzte T, Gansu C, Ruske N, Roeder M, Gornert P and Bahr M 2002 Biocompatible magnetic core/shell nanoparticles J. Magn. Magn. Mater. 252 399–402
[4] Goldys E M et al 2006 Optical characterization of Eu-doped and undoped Gd2O3 nanoparticles synthesized by the hydrogen flame pyrolysis method J. Am. Chem. Soc. 128 14498–505
[5] Anishur Rahman A T M, Vasilev K and Majewski P 2011 Ultra small Gd2O3 nanoparticles: Absorption and emission properties J. Colloid Interface Sci. 354 592–6
[6] Ray R, Biswas S, Das S and Patra M 2012 Magnetic properties of sol-gel derived Gd2O3 nanoparticles AIP Conf. Proc. 1447 319–20
[7] Correa E I et al 2016 Properties of Gd2O3 nanoparticles studied by hyperfine interactions and magnetization measurements AIP Adv. 6 5
[8] Paul N, Borah JP, Mohanta D, Paul N, Borah JP and Mohanta D 2017 Temperature Responsive Gadolinium Oxide Nanoparticles for Hyperthermia Application 050125 1–4
[9] Ahmad M W et al 2015 Potential dual imaging nanoparticle: Gd2O3 nanoparticle Sci. Rep. 5 1–11
[10] Yue H et al 2020 Carbon-coated ultrasmall gadolinium oxide (Gd2O3@C) nanoparticles: application to magnetic resonance imaging and fluorescence properties Colloids Surfaces A Physicochem. Eng. Asp. 586 124261
[11] Dhar D, Mohan M and Poddar R 2020 Assessment of Gd2O3 nanoparticles as exogenous imaging contrast agent for swept source optical coherence tomography Laser Phys. 30 1
[12] Paul R, Sen P and Das I 2016 Effect of morphology on the magnetic properties of Gd2O3 nanotubes Phys. E Low-Dimensional Syst. Nanostructures, 80 149–54
[13] Jamnezhad H and Jafari M 2016 Structure of Gd2O3 nanoparticles at high temperature J. Magn. Magn. Mater. 408 164–7
[14] Zhang F X, Lang M, Wang J W, Becker U and Ewing R C 2008 Structural phase transitions of cubic Gd2O3 at high pressures Phys. Rev. B - Condens. Matter Mater. Phys. 78 1–9
[15] Zhou L et al 2012 Size-tunable synthesis of lanthanide-doped Gd2O3 nanoparticles and their applications for optical and magnetic resonance imaging J. Mater. Chem. 22 966–74
[16] Chen Fei et al 2015 Terbium-doped gadolinium oxide nanoparticles prepared by laser ablation in liquid for use as a fluorescence and magnetic resonance imaging dual-modal contrast agent Physical Chemistry Chemical Physics 17 1189–96
[17] Kossatz S et al 2014 High Therapeutic Efficiency of Magnetic Hyperthermia in Xenograft Models Achieved with Moderate Temperature Dosages in the Tumor Area Pharm. Res. 31 3274–88
[18] Thiesen B and Jordan A 2008 Clinical applications of magnetic nanoparticles for hyperthermia Int. J. Hypertherm. 24 467–74
[19] Hulshof M C C M et al 2004 A feasibility study of interstitial hyperthermia plus external beam radiotherapy in glioblastoma multiforme using the Multi Electrode Current Source (MECS) system Int. J. Hypertherm. 20 451–63
[20] Seal P, Paul N, Babu P D and Borah J P 2019 Hyperthermic efficacy of suitably functionalized MWCNT decorated with MnFe2O4 nanocomposite Applied Physics A, 195 290–9
[21] Fuhai L, Hai L J, Shulin W E L, Wei S U N and Lixin Y U 2013 Photosensitive properties of Eu 3+ and Tb 3+ co-doped Gd2O3 nanowires and bulk materials J. Rare Earths 31 1063–8
[22] Petoral R M et al 2009 Synthesis and characterization of Tb3+ doped Gd2O3 nanocrystals: a bifunctional material with combined fluorescent labeling and MRI contrast agent properties J. Phys. Chem. C 113 6913–20
[23] Mutelet B et al 2011 Suppression of luminescence quenching at the nanometer scale in Gd2O3 doped with Eu3+ or Tb3+: Systematic comparison between nanometric and macroscopic samples of life-time, quantum yield, radiative and non-radiative decay rates J. Appl. Phys. 110 9
[24] Sahu P and Das D 2020 Synthesis and characterization of silica encapsulated magnetite nanoparticles AIP Conf. Proc. 2265 030127
[25] Qin L et al 2009 Effects of doping Lu2O3 into Gd2O3 on phase transformation and luminescence IEEE Trans. Nucl. Sci. 56 2979–82
[26] Mote V, Purushotham Y and Dole B 2012 Williamson–Hall analysis of distortion in lattice strain in nanometer-sized ZnO particles J. Theor. Appl. Phys. 6 2–9
[27] Rahman A T M A, Vasilev K and Majewski P 2011 Ultra small Gd2O3 nanoparticles: Absorption and emission properties Journal of Colloid and Interface Science 354 592–6
[28] Mutelet B et al 2011 Suppression of luminescence quenching at the nanometer scale in Gd2O3 doped with Eu3+ or Tb3+: Systematic comparison between nanometric and macroscopic samples of life-time, quantum yield, radiative and non-radiative decay rates J. Appl. Phys. 110 9
[29] Stagi L, Chiriui D, Ardua A, Cannas C, Carbonaro C M and Ricci P C 2015 Luminescence Enhancement by Energy Transfer in Melamine–Y2O3: Tb3+: Nanohybrids Journal of Applied Physics 125502 2–9
[30] Seal P, Hazarika M, Paul N and Borah J P 2018 MWCNT-MnFe2O4 nanocomposite for efficient hyperthermia applications AIP Conf. Proc. 1942 050083
[31] Teran F J et al 2012 Accurate determination of the specific absorption rate in superparamagnetic nanoparticles under non-adiabatic conditions Appl. Phys. Lett. 101 2010–4
[32] Jonak S and Borah JP 2020 Correlation between cation distribution and heating efficiency of annealed Fe3O4 nanoparticles Mater. Today Commun. 26 101789