

## Synthesis of Dy<sub>2</sub>O<sub>3</sub> nanoparticles via hydroxide precipitation: effect of calcination temperature

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**Abstract:** This work described the preparation of dysprosium oxide, Dy<sub>2</sub>O<sub>3</sub>, nanoparticles using the homogeneous precipitation method. Dy<sup>3+</sup> ions were precipitated using NaOH solution. The obtained product was filtered, dried, and then calcined for 1 h at the temperature range of 300–700 °C in static air. The calcination temperature of the Dy-precursor was chosen based on its decomposition as indicated by the TGA analysis. The crystalline structure and surface morphology of the calcined solids were studied by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The obtained results revealed that Dy<sub>2</sub>O<sub>3</sub> with crystallites size of 11–21 nm was formed at 500 °C. Such value increased to 25–37 nm for the sample calcined at 700 °C.

**Keywords:** nanocrystalline dysprosium oxide; Dy<sub>2</sub>O<sub>3</sub>; precipitation method; Dy<sub>2</sub>O<sub>3</sub> nanoparticles; rare earths

Dysprosium sesquioxide, Dy<sub>2</sub>O<sub>3</sub>, is a basic, highly insoluble, and thermally stable material<sup>[1]</sup>. In addition, it has high resistivity, large energy band, and high dielectric constant<sup>[2]</sup>. Dy<sub>2</sub>O<sub>3</sub> sesquioxide belongs to the face-centered cubic (fcc) arrangement ( $\alpha$  phase) polymorph of Mn<sub>2</sub>O<sub>3</sub> with cubic lattice parameter  $a=1.06706(7)$  nm<sup>[3]</sup>. Dy<sub>2</sub>O<sub>3</sub> crystallizes in the cubic structure below 1870 °C. At higher temperatures, it exists in the monoclinic and/or hexagonal structures<sup>[1]</sup>. Tang et al.<sup>[4]</sup> reported a cubic to monoclinic phase transition of Dy<sub>2</sub>O<sub>3</sub> upon irradiation, at cryogenic temperature, with Kr<sup>++</sup> ions. This transformation is accompanied by an approximately 9% decrease in its molecular volume. Concurrently, Sun et al.<sup>[5]</sup> reported monoclinic phase fraction associated with a corresponding decrease of the amount of the cubic phase during the inductively coupled radio frequency plasma spraying of Dy<sub>2</sub>O<sub>3</sub>. Dy<sub>2</sub>O<sub>3</sub> suffers from another phase transition, cubic to hexagonal, on increasing the applied pressure from ambient to the range of 14.6–25.5 GPa<sup>[6]</sup>. With the release of the applied pressure, the starting cubic phase is not recovered at total release; instead it ends up in monoclinic structure<sup>[6]</sup>.

Due to its unique properties, arising from their 4f electrons, Dy<sub>2</sub>O<sub>3</sub> as well as numerous functional materials based on dysprosium oxides have been developed in a variety of applications. For instance, Dy<sub>2</sub>O<sub>3</sub> is used as a photoluminescent and thermoluminescent material<sup>[7,8]</sup>. Recently, dysprosium oxide was successfully applied as T<sub>2</sub> magnetic resonance imaging (MRI) contrast agents<sup>[9]</sup>. It was demonstrated that Ni-Dy<sub>2</sub>O<sub>3</sub> cermet exhibit high electrochemical

performance, comparable to the state-of-the-art Ni-samarium doped ceria anodes, for intermediate-temperature solid oxide fuel cells<sup>[10]</sup>. Wang et al.<sup>[11]</sup> showed that Dy<sub>2</sub>O<sub>3</sub> can enhance the nonlinearity and threshold voltage of SnO<sub>2</sub>-based varistors. As a catalyst, Dy<sub>2</sub>O<sub>3</sub> supported on ZrO<sub>2</sub> showed higher selectivity to 3-buten-1-ol during the vapor-phase catalytic dehydration of 1,4-butanediol<sup>[12]</sup>.

Nanocrystalline materials are polycrystalline solids with particle diameters of 1–100 nm. When falling in nano-sized regime, the materials exhibit unique physical and chemical properties that are totally different from their bulk counterparts. Several physical and chemical methods have been reported for the synthesis of nanomaterials. Regarding the synthesis of Dy<sub>2</sub>O<sub>3</sub>, it is usually obtained by the thermal decomposition variety of dysprosium precursors such as Dy(CH<sub>3</sub>COO)<sub>3</sub>·5H<sub>2</sub>O<sup>[13]</sup> and Dy(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O<sup>[14]</sup>. Due to the high temperature applied during the thermal decomposition, which yields highly agglomerated Dy<sub>2</sub>O<sub>3</sub>, it is not possible to obtain nanocrystalline Dy<sub>2</sub>O<sub>3</sub> using this method. Accordingly, other methods were suggested in the open literature which led to different morphologies of Dy<sub>2</sub>O<sub>3</sub>. In this respect, irregular shaped Dy<sub>2</sub>O<sub>3</sub> nanoparticles were recently prepared using the solution combustion synthesis at 500 °C employing sugar and oxalyl dihydrazine as fuels<sup>[8]</sup>. Employing soft chemical route using hexamethylenetetramine as precipitant has led, also, to the formation of irregular shape Dy<sub>2</sub>O<sub>3</sub> nanoparticles<sup>[15]</sup>. Spherical nanocrystalline mesoporous Dy<sub>2</sub>O<sub>3</sub> was prepared using a

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combined sol-gel process with surfactant-assisted templating technique<sup>[1]</sup>. Kattel et al.<sup>[9]</sup> obtained Dy<sub>2</sub>O<sub>3</sub> nanospheres by refluxing, at 200 °C for 24 h, a mixture of Dy(NO<sub>3</sub>)<sub>3</sub> and triethylene glycol in presence of sodium hydroxide. A mixture of porous plate-shaped particles and nano-hollow spheres of Dy<sub>2</sub>O<sub>3</sub> was obtained by the decomposition, at 400 °C, of the product obtained from the reaction of the acetate precursor with 1,2-propanediol at 300 °C<sup>[16]</sup>. Several research groups have successfully prepared Dy<sub>2</sub>O<sub>3</sub> nanorods using the hydrothermal route. In this way, Song et al.<sup>[17]</sup> prepared Dy<sub>2</sub>O<sub>3</sub> nanorods directly from commercial bulk Dy<sub>2</sub>O<sub>3</sub> crystals using hydrothermal process at 210 °C without any alkaline and complexing agents. Chandrasekhar et al.<sup>[7]</sup> and Zhang et al.<sup>[18]</sup> prepared Dy<sub>2</sub>O<sub>3</sub> nanorods by the subsequent heat treatment at 600–750 °C for 2 h of Dy(OH)<sub>3</sub> previously prepared by hydrothermal method.

Homogenous precipitation represents a simple, reproducible, and economically feasible technique for potential large scale production of nanomaterials. Recently, this technique was used in the preparation of nearly spherical cerium doped Dy<sub>2</sub>O<sub>3</sub> nanoparticles<sup>[19]</sup>. Therefore, the present paper was undertaken to investigate the use of the homogeneous precipitation method, using NaOH as precipitant, to prepare nanocrystalline Dy<sub>2</sub>O<sub>3</sub>. The thermal, structural, morphological and electrical properties of the obtained solids were also investigated.

## 1 Experimental

### 1.1 Preparation of Dy<sub>2</sub>O<sub>3</sub> nanoparticles

The reagents used in the present investigation, Dy<sub>2</sub>O<sub>3</sub>, HNO<sub>3</sub>, and NaOH were analytical grade chemicals. First, 1.5 g of Dy<sub>2</sub>O<sub>3</sub> was dissolved in dilute HNO<sub>3</sub> with heating, resulting in the formation of a pale colorless stock solution of Dy(NO<sub>3</sub>)<sub>3</sub>. A solution of NaOH (2 mol/L) was added dropwise to the obtained Dy(NO<sub>3</sub>)<sub>3</sub> solution with vigorous stirring until a pH value of 12.0 was reached. The white colloidal precipitate was stirred for 30 min, filtered using centrifuge, and washed with distilled water several times until a pH value of about 7 was reached then washed with alcohol for one time. The obtained solid was dried at 60 °C overnight. Finally, the white product was calcined for 1 h under a static atmosphere over the temperature range of 300–700 °C. For simplicity, the different samples will be referred to by the abbreviations Dy-*x*, where *x* indicates the calcination temperature.

### 1.2 Characterization

The TGA-DTG curves were obtained with the aid of a Shimadzu DT-60 thermal analyzer using a heating rate of 10 °C/min in air flow (40 mL/min). The FT-IR spectrum of the dried Dy-precipitate was obtained by the KBr disc technique over the wavelength range of

4000–400 cm<sup>-1</sup> using a Thermo-Nicolet-6700 FTIR spectrophotometer. XRD diffractograms of the different Dy-*x* samples were recorded using a Philips diffractometer (model PW 2103/00) with Cu K $\alpha$  radiation ( $\lambda$ =0.15405 nm) at 35 kV and 20 mA with a scanning rate over  $2\theta$  of 0.06 (°)/min. SEM images were performed using a JEOL field-emission scanning electron microscope (model JSM-7600F). Transmission electron images were obtained using a JEOL transmission microscope (model JEMTH-100 II). The composition and chemical bonding of Dy-700 sample were analyzed using a SPECS GmbH X-ray photoelectron spectrometer. The electrical conductivity measurements were carried out using a conductivity Pyrex glass cell. The temperature was controlled with a WEMA temperature controller. The resistance measurements were carried out using a Keithley 610C solid-state electrometer.

## 2 Results and discussion

### 2.1 FT-IR and TGA analyses

The FT-IR spectrum of the dried Dy-precipitate is shown in Fig. 1. The absorption band at 3445 cm<sup>-1</sup> and the shoulder at 1639 cm<sup>-1</sup> are assigned to the  $\nu$ (OH) and  $\delta$ (HOH) modes of vibration of crystalline water, respectively<sup>[13,14]</sup>. The spectrum shows the presence of five absorptions at 671, 852, 1088, 1387, and 1521 cm<sup>-1</sup>. The two absorptions at 1521 and 1387 cm<sup>-1</sup> are attributed to the  $\nu_3$  mode of CO<sub>3</sub><sup>2-</sup> group. The splitting of the 1521 cm<sup>-1</sup> band could be due to the carbonate anions of dysprosium located at a crystallographically non-equivalent site<sup>[20]</sup>. The bands located at 1088, 852, and 671 cm<sup>-1</sup> can be assigned to the  $\nu_1$ ,  $\nu_2$ , and  $\nu_4$  modes of the carbonate ion, respectively<sup>[21]</sup>. Thus, the analysis of the Dy-precipitate indicates that the precursor could be dysprosium hydroxyl carbonate. This result is in agreement with that reported for the formation of dysprosium basic carbonate

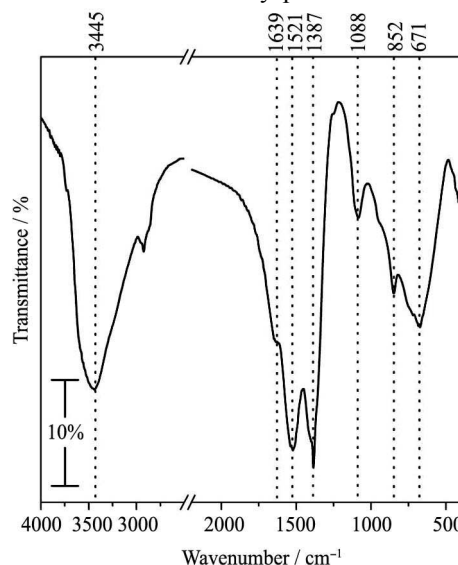


Fig. 1 IR spectra of the Dy-60 sample

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