

# Structural evolution of non-isothermally formed dysprosium sesquioxide nanoparticles and their optical and electrical conductivity properties



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## ABSTRACT

This paper describes the utilization of dysprosium acetate non-isothermal decomposition as a route for Dy<sub>2</sub>O<sub>3</sub> nanoparticles preparation. Thermal events emerging during the heat treatment of dysprosium acetate was monitored using thermogravimetric analysis (TGA). The structural properties of the various solids obtained at the temperature range of 200–900 °C were investigated using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR). It was found that 700 °C adequate for both the complete precursor decomposition and the crystallization process of the desired Dy<sub>2</sub>O<sub>3</sub> nanoparticles. The morphology of the obtained Dy<sub>2</sub>O<sub>3</sub> nanoparticles was examined by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Photo Luminescence (PL) was used for investigating the optical features of the obtained Dy<sub>2</sub>O<sub>3</sub> nanoparticles. Moreover, the electrical conductivity of these nanoparticles has been investigated in the temperature range of 200–500 °C.

## 1. Introduction

Dysprosium sesquioxide, Dy<sub>2</sub>O<sub>3</sub>, is an insoluble rare earth (RE) oxide with high thermal and chemical stabilities. Dy<sub>2</sub>O<sub>3</sub> is characterized by a wide band gap (4.8–5.46 eV) and a high dielectric constant (14–18) [1–4]. Based on CO<sub>2</sub> adsorption, Sato et al. [5] reported a weak basicity of Dy<sub>2</sub>O<sub>3</sub>. Moreover, they showed that it transforms from monoclinic to cubic structure as a result of rising its calcination temperature from 900 to 1000 °C. Jaques and Butt [2] demonstrated that Dy<sub>2</sub>O<sub>3</sub> acts as a p-type semiconductor at temperatures < 750 °C and n-type at higher temperatures. Phase transitions of cubic Dy<sub>2</sub>O<sub>3</sub> were, also, reported on compression [6]. In this way, cubic to a monoclinic phase transition, which starts at 7.7 GPa and completed at 18.8 GPa, and monoclinic to hexagonal phase transition, which starts at around 10.9 GPa, have been reported [6]. Hexagonal Dy<sub>2</sub>O<sub>3</sub> phase becomes predominant at 26.6 GPa and persists at pressures as high as 49.0 GPa [6]. Releasing the pressure has led to the persistence of the monoclinic phase.

Recently, Dy<sub>2</sub>O<sub>3</sub> and Dy<sub>2</sub>O<sub>3</sub>-containing materials has gained increased attention due to their various fascinating applications. It has been investigated as complementary metal-oxide-semiconductor (CMOS) devices [3]. Dy<sub>2</sub>O<sub>3</sub> has been widely used in magnetic resonance imaging (MRI) as a high field single-phase contrast agents [7,8].

It has been also as a component in cermet anodes for the intermediate-temperature solid oxide fuel cells application [9]. The Ru/Dy<sub>2</sub>O<sub>3</sub>/TaN memory device has shown excellent resistive switching for nonvolatile memory applications [10]. Singh et al. [11] fabricated pelletized Dy<sub>2</sub>O<sub>3</sub> and showed that it is a promising candidate to be used in the central rod in advance heavy water reactor. Furthermore, Dy<sub>2</sub>O<sub>3</sub>-based catalysts showed high photocatalytic activity in malachite green and Orange-G dyes degradation [1,12]. The activity of these catalysts was ascribed to the f-shells in the Dy<sub>2</sub>O<sub>3</sub> that traps the excited electrons and retards the process of recombination of electron–hole pair [1,12].

Most of the aforementioned properties and applications strongly depend on the preparation and pretreatment conditions utilized, which in turn influence the texture and particle size of the prepared Dy<sub>2</sub>O<sub>3</sub>. If the Dy<sub>2</sub>O<sub>3</sub> is made-up within the nanometer regime, while keeping its chemical composition unchanged, its properties will be fundamentally enhanced. Accordingly, various methods have been employed for the synthesis of Dy<sub>2</sub>O<sub>3</sub> nanostructures. For instance, Salavati-Niasari et al. [13] synthesized Dy<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·1.7H<sub>2</sub>O nanoparticles and Dy(OH)<sub>3</sub> nanotubes employing a sonochemical route and obtained Dy<sub>2</sub>O<sub>3</sub> nanoparticles via the subsequent calcination. Kang et al. [14] synthesized Dy<sub>2</sub>O<sub>3</sub> nanorods and nanosheets by the calcination at 700 °C of Dy(III) complexes, which are synthesized using the hydrothermal method at 120 °C. Concurrently, Chandrasekhar et al. [15] prepared Dy<sub>2</sub>O<sub>3</sub>

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nanorods by calcining, at 750 °C for 2 h, Dy(OH)<sub>3</sub> nanorods, which was prepared by the hydrothermal method. Dy<sub>2</sub>O<sub>3</sub> nanophosphors have been prepared using the solution combustion method at relatively low temperature (500 °C) employing two different fuels (sugar and oxalyl dihydrazine). XRD estimated crystallite sizes of the obtained Dy<sub>2</sub>O<sub>3</sub> nanoparticles were be 26 and 78 nm, respectively. Sphere-like Dy<sub>2</sub>O<sub>3</sub> nanoparticles were obtained via the precipitation method, using NaOH and hexamethylenetetramine as precipitants, and subsequent calcination at the temperature range of 500–700 °C [16,17].

The thermal degradation of various RE-carboxylic acid salts, especially RE-acetates, -formates -oxalates, and propionate as precursors for the rare earth oxides has been investigated extensively [18–23]. With respect to dysprosium acetate, only few reports were published addressing their thermal decomposition behavior [19,23]. In both papers, it was shown that dysprosium acetate decomposes to dysprosium oxide throughout the formation of carbonate intermediates. Hussein et al. [19] focus on the decomposition course of dysprosium acetate and characterization of the isothermally formed decomposition products. Mahfouz et al. [23] performed a kinetic study on the un-irradiated and pre-γ-irradiated dysprosium acetate. In both papers there are a lack of information about the nanocrystalline nature of the formed Dy<sub>2</sub>O<sub>3</sub> and its particles size. Therefore, we report herein a detailed investigation on the thermal decomposition of dysprosium acetate, which would be useful in gaining information of optimizing the process parameters used for the manufacture of nanocrystalline Dy<sub>2</sub>O<sub>3</sub> via the thermal decomposition of its acetate salt. The parent salt was pretreated non-isothermally using the same heating rate utilized in the TGA measurement, 5 °C min<sup>-1</sup>, in the temperature range 200–900 °C. The obtained solids were characterized using various techniques including XRD, FT-IR, SEM, TEM and XPS. In addition, the PL and electrical conductivity properties of some selected solids obtained in the range 400–900 °C have been measured.

## 2. Experimental

Dy(CH<sub>3</sub>COO)<sub>3</sub>·4H<sub>2</sub>O, abbreviated as DyAc, was a 99.9% pure material (Alfa Aesar) and was used as received. The decomposition products of DyAc were obtained by heating portions of this salt, heating rate 5 °C min<sup>-1</sup>, in the temperature range of 200–900 °C. This range was chosen based on the decomposition pathway of the DyAc as indicated by the TGA results. After reaching the desired temperature, the obtained solids were quenched to room temperature. For simplicity the various pretreated solids will be denoted as Dy-x, where x indicates the pretreatment temperature.

TGA measurement was performed using TA (model TGA-Q500) instrument using a sample weight of 5 mg at heating rate of 5 °C min<sup>-1</sup> in nitrogen flow (40 ml min<sup>-1</sup>). XRD patterns were recorded with a Thermo-Scientific (model ARL X'TRA) powder diffractometer operated with copper Kα radiation (λ = 1.5418 Å). The scanning rate 0.02° s<sup>-1</sup> was in the 2θ range from 10 to 80°. The average crystallite size of the obtained Dy<sub>2</sub>O<sub>3</sub> was estimated by using the Scherer equation;  $D = 0.9\lambda / \beta \cos \theta$ , where λ is wavelength of the incident X-rays, β is the FWHM of the given diffraction peak and θ is diffraction angle. Williamson-Hall (W-H) equation was used for the calculation of the crystallite size and the lattice strain of the prepared Dy<sub>2</sub>O<sub>3</sub>. The equation is given by;  $\beta \cos \theta = (0.9 \lambda / D) + 4\epsilon \sin \theta$ , where ε is the strain associated with the Dy<sub>2</sub>O<sub>3</sub> nanoparticles. FT-IR spectra of the various Dy-x samples were obtained in the wavelength range of 4000–400 cm<sup>-1</sup> using ATR technique on the Nicolet iS50 FT-IR spectrometer. Electron microscopic examinations of some selected Dy-x samples were performed by (i) scanning electron microscope (JEOL, model JSM-7600F) and (ii) transmission electron microscopy (TEM, model JEM1011). The chemical composition bonding in Dy-900 samples was analyzed using SPECS GmbH X-ray photoelectron spectrometer with a monochromatic Al-Kα (1486.6 eV) radiation, which operated at 13.5 kV and 5 × 10<sup>-1</sup> mbar. Room temperature photoluminescence spectra were recorded using a

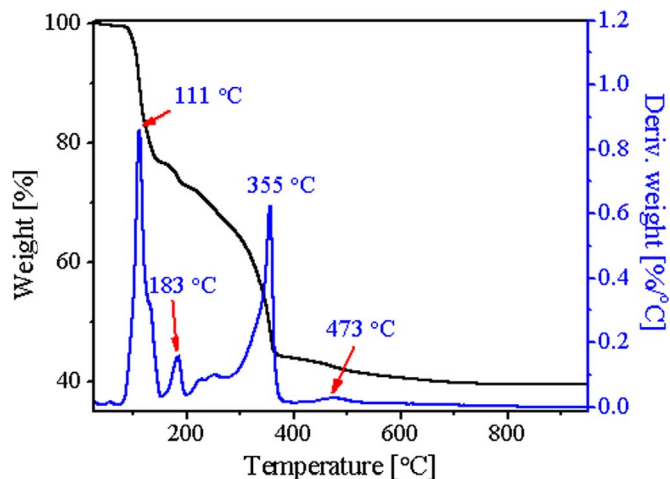


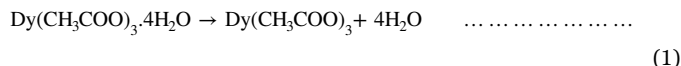
Fig. 1. Typical TGA/DTG curves of as received dysprosium acetate.

Shimadzu RF 5300 fluorescence spectrophotometer. The electrical conductivity measurements were performed Pyrex glass cell placed inside a tubular furnace. The resistance of the samples was measured using a Keithley 6517A electrometer.

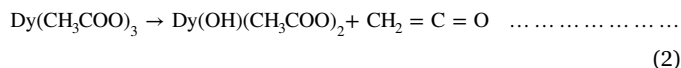
## 3. Results and discussion

### 3.1. Thermal analysis and in situ electrical conductivity

Fig. 1 shows the TGA-DTG curves obtained upon heating Dy(CH<sub>3</sub>COO)<sub>3</sub>·4H<sub>2</sub>O from ambient to 950 °C in N<sub>2</sub> flow. Inspection of this Figure reveals that DyAc decomposes in several weight loss steps. The first step, which extends from ambient to 122 °C, results in a 17.27% loss. This value is close to that anticipated to the complete dehydration of DyAc according to:



The anhydrous salt decomposes in a consecutive steps; the first one ends at around 190 °C and leads to a loss of 10.13%. This value is close to that (10.21%) expected for the formation of hydroxy acetate intermediate as follows:



In this respect, the formation of ketene (CH<sub>2</sub>=C=O) was proved by Hussein et al. [19]. The major decomposition step is a composite one, which maximized at 355 °C and is accompanied by the formation of a residue value of 44.6%. This value is close to that (45.3%) ascribed for the formation of Dy<sub>2</sub>O<sub>3</sub>. In this context, it was shown that the hydroxy-acetate phase decomposes, in air flow, into Dy<sub>2</sub>O<sub>3</sub> via the formation of DyO(CH<sub>3</sub>COO), Dy<sub>2</sub>O(CO<sub>3</sub>)<sub>2</sub> and Dy<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> intermediates and the evolution of CH<sub>3</sub>COOH and CH<sub>3</sub>COCH<sub>3</sub> gases [19]. Taking into account the wide range of temperatures, 190–365 °C, covered by the major decomposition step (Fig. 1), the formation of these intermediates cannot be identified from TGA thermogram. The final decomposition step, which is maximized at 473 °C, results in the formation of residue value of 39.50%. This value agrees well with that (39.47%) assigned for Dy<sup>o</sup> formation.

In situ electrical conductivity measurement was used to follow up the changes in the electrical properties during the thermal decomposition of DyAc. Fig. 2 shows the log σ variation of DyAc with temperature from ambient to 500 °C (the temperature limit of the Pyrex glass cell utilized). Four regions (a)–(d) can be identified upon inspection of this Figure. In region (a), which extends from ambient to 208 °C, the general trend is a conductivity increase in a stair-like manner. TGA

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