



Structural features of nanocrystalline holmium oxide prepared by the thermal decomposition of organic precursors



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ABSTRACT

Powders of nanostructured holmium oxide ($C-Ho_2O_3$) with the crystallite sizes ranging from 6 to 16 nm have been prepared in bulk from the thermal decomposition of holmium acetate and carbamide-containing complex of holmium as precursors at 600 and 700 °C. The powders obtained have been investigated by X-ray diffraction, TEM, thermogravimetry, IR- and Raman spectroscopy. A comparison has been drawn between these and powdered holmium oxide with micron-sized crystallites prepared from the thermal decomposition of holmium chloride. The bcc lattice parameter of the oxides has been found to increase when the crystallite size decreases. It has been noted that the surface of air-exposed powders of holmium oxides is covered by products formed due to the chemisorption of atmospheric CO_2 and H_2O molecules.

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1. Introduction

Like other lanthanide sesquioxides (Ln_2O_3), holmium oxide, Ho_2O_3 , finds its use in various optical, ceramic, and chemical applications, including glasses to transmit radiation for wavelength-calibration instruments [1] and pyrolysis catalysts, where holmium oxide has been reported to exhibit surface bifunctional, acid-base properties [2]. Nanocrystalline microstructure in this solid is of particular interest, since we may expect that when the crystallite size decreases down to nanometer scale, the ratio of surface to bulk atoms increases substantially to endow materials based on holmium oxide with novel features.

For the preparation of nanocrystalline lanthanide oxides a variety of techniques, both physical and chemical ones, have been developed (see for example [3–5] and references therein). Among the latter those that involve the thermal decomposition of precursors of the metal oxides as a part of the synthesis process are

especially versatile (sol–gel technique, for example), because these techniques enable the controlled production of a relatively large amount of the target material. Furthermore, low decomposition temperatures are favorable for the formation of nanocrystalline metal oxides, which can be pivotal to diverse practical applications of these compounds [6–8].

While there have been a number of suitable precursors for the formation of Ln_2O_3 from the thermal decomposition of their salts, including both inorganic such as nitrates, chlorides, sulfates, fluorides and hydroxides, and organic such as carbonates, oxalates, and acetates [9,10], for the preparation of Ho_2O_3 , however, only nitrate at 660 °C [11], carbonate at 700 °C [12,13], and oxalate at 740 °C [11] or 735 °C [14,15] have been so far reported to be decomposed.

In the present study, nanocrystalline powders of holmium oxide have been prepared in bulk from the thermal decomposition of organic precursors, such as holmium acetate and carbamide-containing complex of holmium at temperatures comparable to those mentioned above. The materials obtained have been characterized and investigated with respect to their phase composition, morphology and particle size by means of X-ray diffraction (XRD), IR- and Raman spectroscopy, elemental and thermal analysis, and high-resolution transmission electron microscopy (HRTEM). In this

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Table 1
Synthesis conditions for the powdered samples of holmium oxide under study.

Sample number	Precursor	$T_{\text{synthesis}}$ (°C)
1	Holmium acetate	600
2	Holmium acetate	700
3	Carbamide-containing complex of Holmium	700
4	Holmium chloride	600

paper we also report some observations relating to a crystallite size effect in the samples of holmium oxide.

There is an interesting effect of the crystallite size in nanocrystalline solids, namely these materials exhibit a significant change in the lattice parameter with a reduction of the crystallite size from the micro- to the nanometer scale. There have been a number of studies addressing this effect [16–21]. Regarding to binary metal oxides, earlier, for instance, we reported the dependence of the lattice parameter on the crystallite size of titanium dioxide [22]. In this respect, rare earth oxides and, in particular, holmium oxide, have been given the lack of attention from researchers. Thus, another aim of this paper is to attempt a correlation between the crystallite size and the lattice parameter of holmium oxide.

2. Experimental

Nanocrystalline powders of holmium oxide were synthesized by two methods. Method 1 (acetate route): 2 g of commercially obtained 99.99% purity holmium oxide were added to 15 ml of nitric acid, 63.2% and 15 ml of acetic acid, 70%, stirred until completely dissolved, and evaporated dry in air. The obtained precipitate was air-calcined for 1 h at 600 and 700 °C (samples denoted as 1 and 2, respectively, in Table 1). Method 2 (carbamide route) differs from the Method 1 by that the starting holmium oxide was dissolved in 30 ml of concentrated nitric acid added with 4 g of carbamide. The calcination was carried out in air at 700 °C (sample 3 in Table 1).

For reference purposes an additional sample (4) was prepared by using holmium chloride as precursor. The starting hydrolysis mixture was obtained according to the reaction $2\text{HoCl}_3 + \text{H}_2\text{O} = \text{Ho}_2\text{O}_3 + 6\text{HCl}$ with the following neutralization by NaOH to bring pH to 3.6–3.8, in a cooled flask at a temperature no higher than 60 °C. The obtained slurry was placed in a glassy carbon crucible and evaporated dry on a stove with constant stirring. The resulting mass after being air-calcined at 600 °C for 1 h was washed on a Büchner funnel until NaCl had been completely removed.

All the four powdered samples had yellowish-white appearance in daylight. They were additionally examined for purity by X-ray fluorescent analysis on a COMITA X-Art M energy dispersive spectrometer. The spectrometer was equipped with a silver anode X-ray tube as the source of exciting radiation and with a lithium drifted silicon, Si(Li), detector. To attribute the observed peaks to the corresponding characteristic X-ray transitions we referred to X-ray spectroscopy handbooks [23,24]. The X-ray fluorescence spectrum of holmium oxide synthesized via the acetate route (Fig. 1) indicates that, except for holmium, the mass content of metals with atomic number more or equal than that of magnesium is no more than 0.1% for every element. The precedently described synthesis procedures for the samples of holmium oxide suggest that the X-ray fluorescence data obtained for the sample 2 are applicable to the three others.

Elemental C, H, N (by combustion method) and O (by pyrolysis method) analysis was conducted with the use of an Elementar CHNS/O Vario Micro cube analyzer. Thermal gravimetry and differential scanning calorimetry were carried out on a Netzsch STA 409 LUX thermal analyzer at a heating rate of 10 °C/min in argon or air flow.

X-ray diffraction patterns were obtained at room temperature using a powder θ - θ Bragg–Brentano diffractometer ARL X'TRA with Cu radiation. The diffractometer was equipped with a solid-state X-ray Peltier detector enabling substantially increased peak to background ratio and optimized angular and energy resolution without using β -filters and monochromators.

The average crystallite size of holmium oxides was assumed to be equal to the mean coherent scattering domain size along the crystallographic axis [111] in holmium oxide, which, in turn, was estimated by employing the Scherrer equation, using the (222) peak in the X-ray diffraction patterns of holmium oxides:

$$d = k\lambda/\beta \cos \Theta$$

where d – the average crystallite size, λ – wavelength ($\text{Cu K}\alpha$) = 1.54051 Å, β – the full width at half maximum (FWHM) of the peak (222), Θ – diffraction angle, $k = 1$. The value of β was calculated taking into account instrumental diffraction line broadening which was determined using Si standard powder. It is noteworthy that for the purposes of the estimation we considered the microstrain contribution to the broadening to be small as compared with the crystallite size effect.

IR spectra were registered in the range of wavelengths 4000–675 cm^{-1} on a Perkin-Elmer Spectrum 100 spectrometer with UATR accessory. Raman spectra were recorded using a NXT FT-Raman 9650 spectrometer with an excitation laser wavelength of 976 nm. The spectral resolution was 4 cm^{-1} for the both techniques.

The microstructure of the samples was studied with the use of high resolution transmission electron microscope Jeol JEM-2100 operating at an accelerating voltage of 200 keV. All the specimens for TEM/HRTEM observations were prepared as follows. The powders of holmium oxide were thoroughly ground by hand in an agate mortar with a pestle, then the powder particles were dispersed in ethanol by ultrasonic treatment, drops of the suspension were deposited onto a holey carbon film supported on a copper TEM grid and allowed to dry in air.

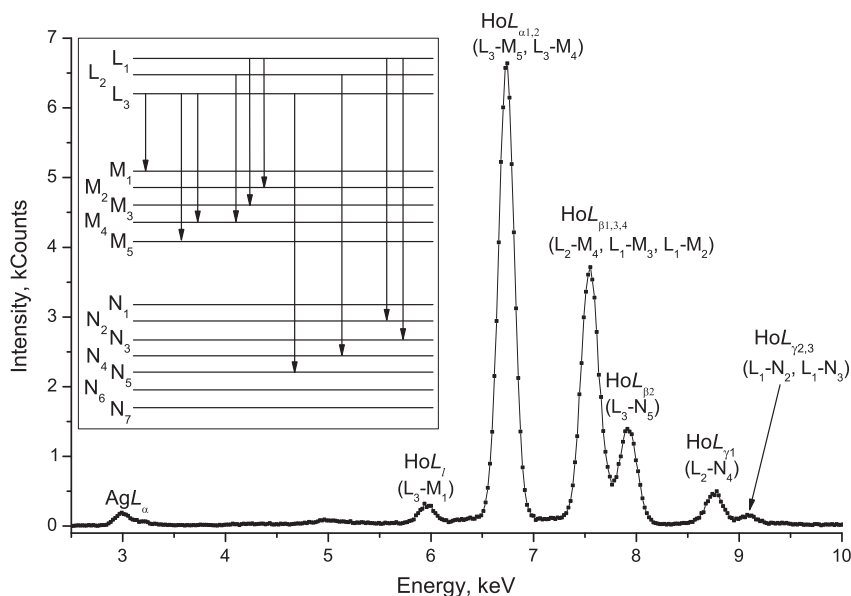


Fig. 1. X-ray fluorescence spectrum of holmium oxide (sample 2, Table 1). The observed characteristic X-ray dipole transitions of holmium are also schematically represented in the inset (as a part of the Grotrian diagram). Peaks in the spectra and the transitions are labeled according to the IUPAC and Siegbahn's notations. The correspondence between them can be found elsewhere [44]. $\text{AgL}(\alpha)$ peak occurs due to the partial elastic scattering of the incident X-ray beam from the sample.

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