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Luminescence enhancement in nanocrystalline Eu_2O_3 nanorods – Microwave hydrothermal crystallization and thermal degradation of cubic phase

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ABSTRACT

Thermally induced crystallization of cubic Eu_2O_3 obtained with the microwave hydrothermal method has been investigated. The starting material crystallized in the form of needle-shaped agglomerates of nanocrystalline hexagonal $Eu(OH)_3$. Thermal treatment up to 800 °C induced the crystallization of cubic Eu_2O_3, after further calcination at 1200 °C in the air a monoclinic phase appeared. The phase transformation caused abnormal reduction of Eu^{3+} ions, related to the oxygen vacancy creation during sintering of the oxide crystallites. The crystallization process of cubic Eu_2O_3 occurred within the agglomerates without change of their shapes. The cubic form exhibited bright emission of Eu^{3+} related luminescence with intensity increasing with the size of crystallites.

1. Introduction

Europium sesquioxide (Eu_2O_3) exhibits complicated phase relations. Five polymorphic forms were discriminated [1]: C, B, A, H and X. The first one is stable at room temperature to 1100 °C. The temperatures of the respective phase transformations are: 2040 °C, 2140 °C, 2280 °C, and the oxide melts at 2340 °C. Europium sesquioxide was used as a component in the cathode ray tube television phosphors for years [2]. It was also used in catalysis [3], scintillators [4] and luminescent materials [5]. The most common use of Eu_2O_3 in optically active materials is as the source compound of europium ions in solid state reactions.

Calcination process, as a thermally induced reaction, is commonly performed in the oxidative atmosphere of the air. However, a number of publications reported the anomalous Eu^{3+} ions reduction in such conditions. This phenomenon was related to the substitution by Eu^{3+} of a differently charged cation in compounds with the structure containing tetrahedral anion groups [6]. The application of nanoparticulate precursors enhances the rates and decreases the temperature of solid state reactions. A large number of nanocrystalline oxides preparation methods have been developed. The hydrothermal technique utilizes the properties of high temperature water in nanomaterials synthesis [7]. Application of microwaves as a heating agent ensures uniform and rapid temperature increase, not limited by the heat inertia of the reactor [8]. It allows crystallization of very small nanoparticles with narrow distribution of sizes [9]. The size and shapes may be controlled by the synthesis conditions. Additionally, the products exhibit high purity, since there is no contact of heating elements with the reaction mixture.

In present work we report on the crystallization process of cubic Eu_2O_3 nanorods starting with the microwave hydrothermal step, their luminescent properties, and issues related to the thermal degradation of the material.

2. Experimental

Nanocrystals of cubic Eu_2O_3 were prepared using microwave driven hydrothermal method. The procedure was conducted as follows. 12.16 g of europium(III) nitrate pentahydrate (99.9%, Aldrich) was dissolved in 200 ml of distilled water to obtain 5 g of Eu_2O_3. The solution was then alkalized to pH = 10 by addition of aqueous ammonia solution (25%, Carl Roth). The obtained white residue was suction filtered, washed with distilled water, and then placed in a Teflon vessel of the microwave hydrothermal reactor (Ertec).

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The reaction was conducted at the pressure of 6 MPa by 20 min, then the reactor was cooled down and the wet product was collected. The resulting powder was dried overnight at 40 °C in the air. The product was calcined at 400, 800, and 1200 °C.

The samples were analyzed using the following instrumentation. Scanning electron microscopy (SEM) measurements were conducted with high resolution (1 nm) Hitachi SU-70 microscope, equipped with characteristic radiation detector (EDX) and cathodoluminescence system GATAN Mono CL3. The photoluminescence (PL) emission and excitation spectra were taken using Horiba/Jobin-Yvon Fluorolog-3 spectrofluorimeter, equipped with a xenon lamp as excitation source and Hamamatsu R928P photomultiplier. The EPR spectra were taken with a Bruker spectrometer operating at X-band. The X-ray diffraction measurements were performed with Phillips X'Pert powder diffractometer. The measurements were conducted in the 2Θ range from 15° to 90° with a step of 0.05° and at counting time of 3 s. The CuK_α radiation (1.54 Å) was used in the latter experiments. The morphology of the samples was examined with transmission electron microscopy (TEM, FEI Tecnai F20).

3. Results and discussion

3.1. Structure

Diffraction patterns of prepared nanocrystals are shown in Fig. 1A. The as crystallized – in the microwave hydrothermal process – sample (bottom pattern) contains only the hexagonal $Eu(OH)_3$ phase (PDF database code: 83-2305, ICSD code: 200488, Fig. 1B). The crystallization method includes a wet chemistry step only for this sample. As the sample is prepared in water environment it is not surprising, that the hydroxide phase was obtained. However, some of the previously reported syntheses resulted in the oxide phase crystallization, as for example zirconium [10] and zinc [11] oxides. The calcination in the air atmosphere led to a variety of products depending on the temperature of treatment. After heating at 400 °C cubic Eu_2O_3 is obtained (PDF code: 86-2476, ICSD code: 040472), however, the reflexes are strongly broadened suggesting low crystallinity or small crystallite sizes. Also, a halo is seen at angles below 20°, peaking in the region close to that of the (1 0 0) reflex of the hexagonal $Eu(OH)_3$ phase, suggesting that the hydroxide has undergone thermal decomposition. Removing the water caused hydroxide structure damage and further decrease of the phase crystallinity. In its place a new phase appeared, also poorly crystallized, indicating a transformation from the decomposed hydroxide phase. Calcination at 800 °C results in growth of cubic europia phase crystallites with sizes ranging from 7 to 49 nm (calculated by Scherrer's method). The only phase occurring in the sample is cubic Eu_2O_3. However, after calcination at 1200 °C a full transformation has taken place to form the pure monoclinic Eu_2O_3 phase (PDF code: 71-0589, ICSD code: 008056) with the mean crystallite sizes of 108 nm. Therefore, in the range of calcination temperatures up to 1200 °C hydroxide transforms into oxide, then phase transformation occurs to form monoclinic Eu_2O_3.

SEM images are shown in Fig. 2. The samples crystallize in the form of needles and remain in that form after heating up to 800 °C. Needle-like structures are 1–3 μm long and 50–80 nm wide in as crystallized sample. Calcination causes the structures to shorten to maximum of a few hundred nanometers, but does not influence the width. Needles are crystallites of europium compounds or agglomerates of nanoparticles. The material calcined at the highest temperature is different as it contains sintered structures with porous morphology. Typical pore sizes are in the range of hundreds of nanometers, and the structure sizes vary from 500 nm (single grains) to a few μm (whole sinter).

TEM images are found in Fig. 3. The intrinsic crystallization mechanism is shown. The initial needle shaped structures are agglomerates of europium hydroxide crystallites placed along the agglomerate longer side axis (Fig. 3A). Crystallites are elongated

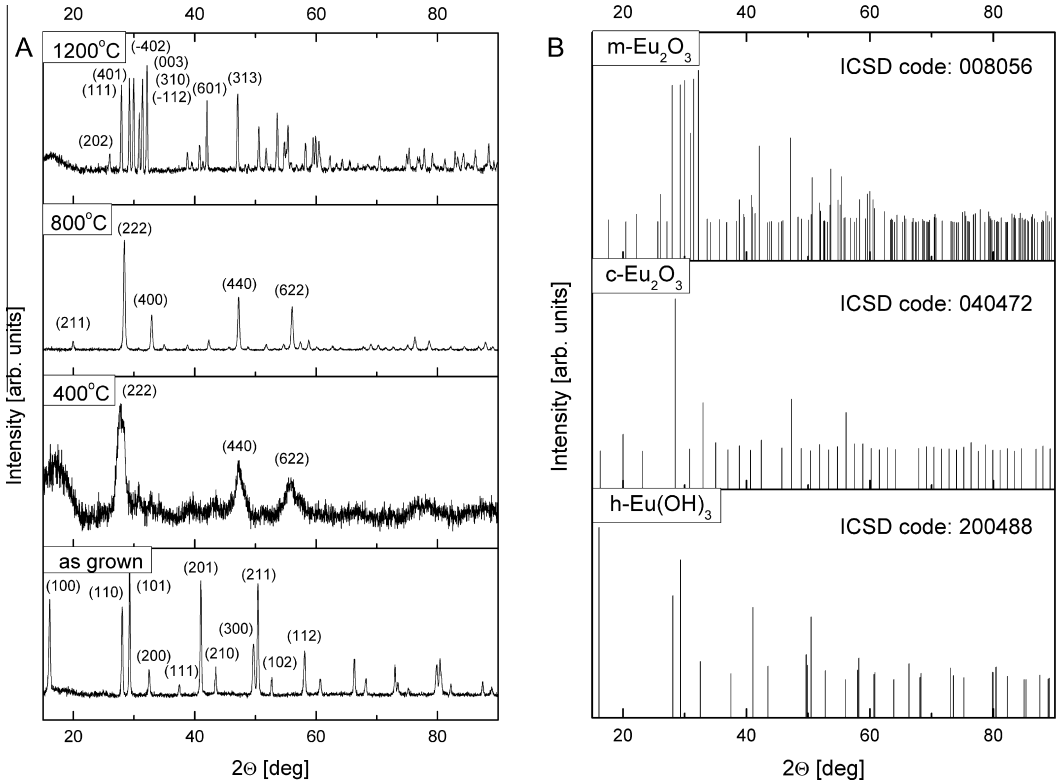

Fig. 1. X-ray diffraction patterns of obtained europium compounds (A), reference patterns of h-$Eu(OH)_3$, c-Eu_2O_3, m-Eu_2O_3 phases and corresponding ICSD numbers (B).