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Optical properties of neodymium oxides at the nanometer scale

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Abstract

The polyol method has been recently developed for preparing concentrated and stable colloids of highly crystallized colloids. Already applied to europium oxide it is used here for synthesizing particles of neodymium oxide as the main constituent or as a 10 mol% doping element in RE_2O_3 (RE = Y, Gd). High-resolution transmission electron microscopy has identified particles with an average grain diameter in the range 3–5 nm crystallized in the cubic phase. The absorption spectra were recorded, from which the Judd–Ofelt analysis was performed. The calculated radiative lifetime of the $^4F_{3/2}$ Nd^{3+} energy level was found to be 144 μs in the Nd_2O_3 nanoparticles, that is to say much longer than the measured lifetime (70 ns), indicating a strong luminescence quenching attributed to nonradiative losses.

Keywords: Luminescent particle

1. Introduction

Over the past few years, there has been considerable interest in the study of compound materials with dimensions of the nanometer scale, in terms of their fundamental and technological importance [1,2]. It is particularly true in the field of optics because of a quantum confinement effect which leads to novel optoelectronic properties. Emission lifetime, luminescence quantum efficiency and quenching concentration were found to strongly depend on the particle-size in the nanometer range [3–5]. High efficiencies [6], ultra-fast recombination times [7], interesting nonlinear optical behaviors [8] and unusual fluorescence were observed in nanometer sized nanocrystals [9]. In this context, rare-earth oxides have been widely studied and a large variety of techniques have been turned out for preparing them at the nanometer scale: chemical vapor deposition, laser ablation, sol–gel processes, microemulsion techniques, hydrothermal methods. However stable colloids were rarely obtained. Colloids of lanthanide sesquioxides Eu_2O_3 [8] and Tb_2O_3 [9] in methanol medium were successfully

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prepared and recently we have presented a new simple approach to synthesize Eu_2O_3, pure or as a doping agent in yttrium or gadolinium oxide, in polyol medium [10,11]. In each case, the presence of a capping agent is essential to prevent agglomeration [12] and achieving electrical passivation; it is trioctylphosphine oxide in the first case and directly the polyol in the second case. The fact that the medium also fulfills the function of capping agent makes this last method very elegant and this is why we chose it in the present paper.

This method, generally called the polyol method, has been successfully used for preparing a large variety of materials including oxides, phosphates [13], sulfides [14] and elemental metals [15,16]. For preparation of rare-earth based sesqui-oxides the choice of the precursors is quite crucial. The use of acetates, alcoholate, halogenide leads to intermediate compounds which require further heating for transformation into oxides [17,18], whereas the use of chlorides permits stable colloidal suspensions of oxide nanoparticles to be obtained. In this paper the preparation of neodymium oxide colloids with the polyol method using chlorides as precursors is reported for the first time. At the nanometer scale Nd_2O_3 is reported to have been elaborated only in the form of agglomerated powders by microemulsion technique [19] hydrogen plasma–metal reaction [20] and sol–gel auto-combustion [21]. Having now particles of Nd_2O_3 as colloids presents a strong interest for fundamental studies since, contrary to aggregates in powders; the interactions between the particles can be neglected. It also permits the simplicity of experiments since, due to the absence of light scattering; the colloids can be investigated with the same spectroscopic techniques as those used for bulk mono-crystals.

2. Experimental procedures

2.1. Nanocrystals synthesis

A typical preparation is as follows. 3 mmol of rare-earth chloride $RECl_3$, $6H_2O$ with RE = Nd, Gd or Y (99.9% Aldrich) was dispersed in 20 ml of diethylene glycol (DEG, 99% Aldrich). After strong stirring for 30 min, 1 ml of aqueous NaOH solution (3 mol/l) was added and the mixture was heated in a silicon oil bath at 140 °C for 1 h. After complete dissolution of the compounds and obtaining of a homogeneous solution, the mixture was carried out at 180 °C for 4 h under vigorous stirring in refluxing diethylene glycol. As a result, transparent suspensions of particles dispersed in organic solvent were obtained; the resulting oxide particles suspension were colloidally stable for weeks. Whatever the Nd content, solid solutions of Nd/Gd and Nd/Y oxides have been obtained so that the nanometer sized particles consist of a unique phase.

The dehydrating properties of DEG and the high temperature of synthesis prevent any hydroxide formation provided that the OH^- concentration of the starting solution is small. The addition of one equivalent of NaOH was then considered to be a good compromise: lower values gave small reaction yields (less than 30% of lanthanide oxides formation) and larger values led to irreversible precipitation of hydroxides.

The obtained transparent colloidal suspensions have been dialyzed against pure diethylene glycol for different durations to achieve purification. Resulting solution containing up to 8 g/l wt% rare earth oxide was obtained without particle agglomeration.

2.2. Nanocrystals characterization

Direct measurements of the size distribution of the nanoparticles suspended in the polyol medium were performed via a Zetasizer 3000 HS PCS (Photon Correlation Spectroscopy).

High-resolution transmission electron microscopy (HRTEM) was used to obtain detailed information about the shape, the composition and the size distribution of colloidal dispersions. The HRTEM measurements were made with a *TOPCON* microscope operating at 200 kV and the energy dispersive X-ray (EDX) analyses with a JEOL-2010 microscope using a spot size of 1.5 nm. All the samples were prepared by depositing a drop of a diluted colloidal solution on a carbon grid.

2.3. Optical properties

The absorption spectra were recorded with a Perkin–Elmer spectrophotometer. The emission