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New experimental and theoretical approach in Eu_2O_3 microspheres: From synthesis to a study of the energy transfer

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ABSTRACT

We have prepared porous microspheres of Eu_2O_3 using a simple, two-step procedure. In the first step, hydrothermal conditions were used to prepare the precursor spheres from $EuCl_3{\cdot}6H_2O$ and 6-aminonicotinic acid. Then, a heat treatment under inert atmosphere yielded the final material. Its structure and purity were confirmed by XRD, while SEM images showed the widespread spherical morphology. Excitation and emission spectra allowed us to infer details about the local symmetry of the Eu^{3+} and correlate them with what is known from the oxide. In addition, the Eu_2O_3 structure was accurately predicted for the first time by applying the combination of the Sparkle/PM3 model with a semiempirical approach to simulate solid state structures to a set containing more than 600 atoms. The full optimized structure was used to study the energy transfer channels between two europium trivalent ions. The results suggest that the $Eu^{3+} \longrightarrow Eu^{3+}$ energy transfer channels herein investigated are predominantly governed by quadrupole–quadrupole mechanism.

1. Introduction

In recent years, studies aimed at developing novel organic–inorganic hybrid materials have attracted great interest in the scientific and technological communities due to their useful mechanical, optical and thermal properties [1]. In this sense great efforts are being made to obtain compounds with nano- and microscale morphologies due to the ample potential for applications in multifunctional devices [2,3].

Mesoporous materials, according to IUPAC, comprise a class of solids that present pore sizes within the 2–50 nm diameter range [4]. These solids have a wide range of applications such as photovoltaic cells [5], batteries [6], catalysts [7], adsorbents [8], and others. Several papers have reported methodologies for obtaining these mesoporous materials with morphologies as diverse as tubes [9], flowers [10] and spheres [11,12], among others. These morphologies often modify the physical and chemical behavior of the functional compound.

Rare earth oxides are used in various applications such as photonic devices [13], catalysts [14], and electrochemical applications [15]. Due to the large interestin obtaining various forms of these compounds, several synthesis routes are described in the literature, such as the hydro- and solvothermal methods [16], dissolution of lanthanide salts in polyalcohols [17], ultrasonic [18], microemulsion [19] and Pechini method [20]. Among these oxides, the Eu_2O_3 is one of the most important because the Eu^{3+} ion has a maximum emission band at ~610 nm (red), one of the three primary colors. As stated before, a precise morphologic control may bring forth new applications and/or improve the material's performance in existing ones [21]. For example, Yue Li et al. [22] have obtained mesoporous Eu_2O_3 microspheres by calcining a europium precursor synthesized hydrothermally.

The use of quantum chemical models for calculating solid phase structures is currently carried out with the density functional theory (DFT) [23]. In these calculations, simple potentials are used to enable the calculations of systems with a great number of atoms. In addition, translation vectors are included in order to consider periodicity conditions. Stewart has recently published a similar procedure aiming at performing solid phase calculations using PM6 semiempirical methods [24]. Translation vectors are also used in this procedure to treat the solid structure's periodicity. Even though the procedure was proposed for the PM6 model [25], similar models such as AM1 [26], PM3 [27], or RM1 [28] are also suitable since they preserve the accuracy level. As far as we know, only two previous works have used this procedure associated to the Sparkle model for studying solids containing trivalent lanthanide ions. The first one, published in 2012 [29], dealt with the energy transfer between Eu^{3+}

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and Tb^{3+} in the coordination polymer $_{\infty}[(Tb_{1-x}Eu_x)(DPA)(HDPA)]$. The second work was published in 2013 [30] and reported two new MOFs containing Tm^{3+}, which were studied from both the theoretical and the experimental fronts. Despite the interesting results presented in these works, in which the computational results compared very well with the experimental ones, further investigations are warranted in order to validate the methodology.

In this paper we reported a new methodology using two-step synthetic route that involved a hydrothermal step and a heat treatment and a theoretical different approach applied to the europium oxide spheres. In the first step of the synthetic methodology, hydrothermal conditions were used to prepare the precursor spheres from $EuCl_3{\cdot}6H_2O$ and commercially available 6-aminonicotinic acid. Then, a heat treatment under inert atmosphere yielded the final material, which exhibited a spherical morphology and a seemingly well-defined mesoporous structure. Moreover, this is the first time the Sparkle theoretical model is used to study an inorganic solid, and we are therefore comparing the quality of the structural predictions of the models Sparkle/AM1, Sparkle/PM3, and Sparkle/PM6 to the available crystallographic data. The most accurate calculated structure was selected for the study of the spectroscopic properties of the Eu_2O_3 system.

2. Materials and methods

2.1. Preparation of material

In a typical synthetic procedure, 6-aminonicotinic acid (0.2 g, 1.5 mmol; Sigma–Aldrich or Alfa-Aesar) and $EuCl_3{\cdot}6H_2O$ (0.1 g, 0.5 mmol; prepared from Eu_2O_3, Sigma–Aldrich) were dispersed in 12 mL of distilled water in a metal-encased Teflon reactor. Reaction was carried out at 200 °C for 72 h. After cooling undisturbed, the orange precipitate (MS-1, for the pristine, as-synthesized samples) was filtered, rinsed with acetone, and dried in air. In order to obtain the Eu_2O_3 microspheres (MS-HT, for the high temperature treatment), the solid was transferred to an alumina boat, carefully placed inside a EDG FT-HI tube furnace, and heated to 800 °C at 10 °C min^{-1}, under an atmosphere of argon. The heat treatment lasted 4 h, after which the sample was cooled under Ar and retrieved.

2.2. Characterization

The morphology of the samples was studied using a Shimadzu SS550 scanning electron microscope with an EDS attachment. The samples were degassed at room temperature for several hours and then gold-coated (~20 nm-thick) prior to insertion in the SEM chamber. The parameters for image acquisition were: acceleration voltage of 10–15 kV, working distance of 12–17–18 mm, and probe size of 3 or 4 mm. Larger probe sizes and a standard working distance of 17 mm were used for EDS analysis. TGA data under an N_2 atmosphere were obtained with a Shimadzu TGA 50-H thermogravimetric analyser, up to a temperature of 900 °C, at a heating rate of 10 °C min^{-1}.

XRD analysis of well-ground samples was carried out with a Bruker D8 Advance diffractometer (Cu Kα radiation, λ = 1.541 Å) equipped with a LynxEye detector. Typical 2θ range was 5–80°, step size of 0.01°, and acquisition time of 1.0 s per step.

Nitrogen adsorption isotherms at 77 K were obtained with a Micromeritics ASAP 2420. Samples were degassed at 250 °C for 4 h prior to measurements.

For the luminescence spectra the samples were excited using a 450 W xenon lamp. The emission and excitation spectra were analyzed using a modular spectrofluorometer Horiba-Jobin Yvon Fluorolog-3 with double excitation, fitted with a 1200 groves/mm grating blazed at 330 nm, and a single emission spectrometer (TRIAX 320) fitted with a 1200 groves/mm grating blazed at 500 nm coupled to a R928P Hamamatsu photomultiplier. All emission spectra were corrected for the spectral response of the monochromators and the detector using typical correction spectra provided by the manufacturer. The lifetime of Eu^{3+} was obtained by monitoring the $^5D_2 \longrightarrow {}^7F_2$ (612 nm) emissions upon excitations at 395 nm.

2.3. Theoretical details

The input structure was obtained from ICSD database (code name cc11399). From this structure, using the program Mercury, the lattice points were duplicated in order to satisfy the calculation requirements. The next step consisted of identifying the atom to be used as atom 1 and other three atoms that atom 1 would become if it was translated; these three atoms were renamed "Tv". All atoms which were not in lattice point (0,0,0) were deleted and the remaining Cartesian coordinates were saved to build the MOPAC input file. The Sparkle/AM1 [31–33], Sparkle/PM3 [34] and Sparkle/PM6 [35] models associated to semiempirical approach to simulated solid state structures proposed by Stewart in 2008 [24] were used to predict the Eu_2O_3 solid state structure.

2.4. Ion–ion energy-transfer rates

To calculate the energy transfer (ET) rate between any two europium ions that compose the solid, we applied the Malta's model [36]. According to this model published in 2008, by using the distance between two metallic centers it is possible to calculate the ET rates considering the contributions of dipole–dipole (W_{d-d}), dipole–quadrupole (W_{d-q}), and quadrupole–quadrupole (W_{q-q}) mechanisms. Eqs (1)–(3) show each one of these contributions.

$$W_{d-d} = \frac{(1-\sigma_1^D)^2(1-\sigma_1^A)^2}{[J_D^*][J_A]}\frac{4\pi}{3\hbar}\frac{e^4}{R^6}\left(\sum_K \Omega_K^D \left\langle \psi_D J_D \left\| U^{(k)} \right\| \psi_D^* J_D^* \right\rangle^2\right) \times \left(\sum_K \Omega_K^A \left\langle \psi_A^* J_A^* \left\| U^{(k)} \right\| \psi_A J_A \right\rangle^2\right) F \quad (1)$$

$$W_{d-q} = \frac{(1-\sigma_1^D)^2(1-\sigma_2^A)^2}{[J_D^*][J_A]}\frac{2\pi}{\hbar}\frac{e^4}{R^8}\left(\sum_K \Omega_K^D \left\langle \psi_D J_D \left\| U^{(k)} \right\| \psi_D^* J_D^* \right\rangle^2\right) \times \langle r^2\rangle_A^2 \langle f||C^{(2)}||f\rangle^2 \langle \psi_A^* J_A^*||U^{(k)}||\psi_A J_A\rangle^2 F \quad (2)$$

$$W_{q-q} = \frac{(1-\sigma_2^D)^2(1-\sigma_2^A)^2}{[J_D^*][J_A]}\frac{28\pi}{5\hbar}\frac{e^4}{R^{10}} \times \langle r^2\rangle_D^2 \langle r^2\rangle_A^2 \langle f||C^{(2)}||f\rangle^4 \times \left\langle \psi_D J_D \left\| U^{(2)} \right\| \psi_D^* J_D^* \right\rangle^2 \times \langle \psi_A^* J_A^*||U^{(2)}||\psi_A J_A\rangle^2 F \quad (3)$$

Malta's method is based on expressions derived by Kushida [37] that do not include the shielding effects for the ET mechanisms. In the three equations showed above, the term A is related with acceptor state ($^5D_0/Eu^{3+}$) while the D index is associated with donor state ($^5D_1/Eu^{3+}$). R is donor–acceptor distance and the quantities $(1-\sigma)$ are shielding factors of the lanthanide ions. The σ's values used in this work were experimentally calculated by Edvardson and Klintenger [38] and their values are equal to $\sigma_2 = 0.502$, $\sigma_4 = 0.0190$ and $\sigma_6 = -0.0308$. The σ_1 value was determined by the following equation proposed by Malta [36]:

$$(1-\sigma_k) = \rho(2\beta)^{k+1} \quad (4)$$