



Rare earth and zinc layered hydroxide salts intercalated with the 2-aminobenzoate anion as organic luminescent sensitizer

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ABSTRACT

Rare earth (RE = Eu, Y and Tb) and zinc layered hydroxide salts intercalated with nitrate anions were synthesized, followed by exchange with 2-aminobenzoate. The obtained compounds were characterized by powder X-ray diffraction (PXRD), Fourier transform infrared (FTIR) and ultraviolet visible (UV-vis) spectroscopies, fluorescence measurements and thermal analysis (TGA/DTA). The results from FTIR spectroscopy suggest a direct coordination of 2-aminobenzoate to the metal cations of the inorganic layered structure. The organic derivative products from the intercalation reactions absorb a broader range of UV-light in relation to that shown by the parent material; the photoluminescence measurements present a strong violet, blue and green luminescence under UV-light excitation for layered compounds with Zn, Y and Tb, respectively. Rare earth hydroxide salts (RE-LHS) are potential alternative matrices for the immobilization of organic species to produce luminescent materials.

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1. Introduction

Layered compounds such as layered double hydroxides (LDH) and some layered hydroxide salts (LHS) have been found to exchange anions and attract intense interest due to their structural anisotropy, variable chemical composition and the ease to produce intercalated/grafted compounds. LHS have the general formula $M^{2+}(\text{OH})_{2-x}(\text{A}^{n-})_{x/n} \cdot y\text{H}_2\text{O}$, where M^{2+} is a metal cation (e.g., Mg^{2+} , Ni^{2+} , Zn^{2+} , Ca^{2+} , Cd^{2+} , Co^{2+} and Cu^{2+}) and A^{n-} is the intercalated exchangeable anion (e.g., Cl^- , NO_3^- , SO_4^{2-} , CH_3COO^- among others) [1–4].

In 1960s, the first layered lanthanide hydroxide salts were reported, with generic composition represented by $(\text{Ln})_2(\text{OH})_{6-m}(\text{A}^{x-})_{m/x} \cdot n\text{H}_2\text{O}$ (Ln = lanthanide trivalent ion = Ln^{3+} , and A^{x-} = anion). These compounds belong to a new type of layered crystalline materials closely related to LDH, in which the positive charge of the layer is generated by varying the number of hydroxyl groups or water molecules coordinated to the Ln^{3+} cation. These compounds can be divided in two classes ($m = 1$ and $m = 2$ in

the generic formula above), which are based in the chemical composition and structural aspects. In the first class where $m = 1$ ($(\text{Ln})_2(\text{OH})_5(\text{A}^{x-})_{1/x} \cdot n\text{H}_2\text{O}$), the intercalated anions are free to move between the layers and in the second class, where $m = 2$ ($(\text{Ln})_2(\text{OH})_4(\text{A}^{x-})_{2/x} \cdot n\text{H}_2\text{O}$ or $\text{Ln}(\text{OH})_2(\text{A}^{x-})_{1/x} \cdot n\text{H}_2\text{O}$), the anions are covalently bonded to the layers.

Thereafter some other publications appeared where these layered lanthanide salts were the basis of multifunctional materials for diverse applications, such as luminescent materials and biomedical devices [5,6]. Most of the lanthanide cations (Ln^{3+}) display intense luminescence and are good activators in luminescent compounds. These excitations can be improved by using organic sensitizers to capture energy from external light sources followed by internal transfers to excite electrons in Ln^{3+} [7–9].

In a recent paper, Cursino et al. described the intercalation of 2-aminobenzoate, an organic anion with ultraviolet absorption ability, by replacing nitrate anions from layered zinc hydroxide nitrate [10]. Since the intercalated 2-aminobenzoate in the zinc hydroxide nitrate-like compound absorbed a broader range of ultraviolet radiation than its sodium salt, it is expected that the organic anion presents different UV absorption if it is intercalated into a layered inorganic matrix containing rare earth cations.

On this basis, the aim of this work was to use different layered rare-earth (Eu^{3+} , Tb^{3+} and Y^{3+}) hydroxides salts intercalated/grafted with 2-aminobenzoate to explore the properties of the

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resulting material, specially to examine the sensitization or any antenna effect of the rare earth fluorescent matrix by 2-aminobenzoate. The possible future application is to explore these materials as functional luminescent fillers in polymer nanocomposites to produce technologically important flexible sheets devices with a broad range of applications.

2. Materials and methods

2-Aminobenzoic acid (Aldrich, 98%), zinc nitrate hexahydrate (Panreac, 98%), europium chloride hexahydrate (Aldrich, 99.9%), terbium chloride hexahydrate (Aldrich, 99.9%), yttrium chloride hexahydrate (Aldrich, 99%) and sodium hydroxide (Vetec, 99%) were used without any further purification. All the reactions were conducted in distilled water.

2.1. Syntheses of zinc, europium and terbium hydroxide salts

Zinc, europium and terbium layered hydroxides salts intercalated with nitrate anions were synthesized by the slow addition of a NaOH aqueous solution (1 mol L^{-1}) to 70 mL of a solution containing 8 mmol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, respectively, under magnetic stirring; the final pH was adjusted to neutrality. The solids were separated by centrifugation at 3000 rpm for 5 min, followed by extensive washing with distilled water (5 times), dispersion and centrifugation. The resulting layered hydroxide salts (named respectively as LHS-Zn/ NO_3 , LHS-Eu/ NO_3 , and LHS-Tb/ NO_3) were dried under vacuum at room temperature until constant mass.

The synthesis of yttrium hydroxide nitrate (LHS-Y/ NO_3) was performed by a hydrothermal route [11]. A mixture of 7.5 mL of an aqueous solution (0.44 mol L^{-1}) of yttrium nitrate, 2.5 mL of NaNO_3 (1.44 mol L^{-1}) and 2.5 mL of NaOH (2.1 mol L^{-1}) was placed in a sealed teflon vessel. The mixture was stirred and hydrothermally treated at 125°C for 48 h. The resulting white solid was extensively washed with distilled water (5 times), recovered by centrifugation and dried under vacuum at room temperature for 24 h.

2.2. Intercalation of 2-aminobenzoate by anion exchange and coprecipitation

A solution of sodium 2-aminobenzoate (2AB-Na) was prepared by the slow addition of 20 mL of NaOH (1 mol L^{-1}) to 50 mL of a suspension containing 22 mmol of 2-aminobenzoic acid in decarbonated water, then 0.6 g of the solid hydroxide salt (LHS-Zn/ NO_3 , LHS-Y/ NO_3 , or LHS-Tb/ NO_3) was added to this solution, and the suspension was magnetically stirred at room temperature for 40 min, centrifuged and extensively washed with distilled water (5 times). The final white solids LHS-M/2AB (where $M = \text{Zn, Y}$ and Tb) were dried under vacuum at room temperature for 24 h.

Europium matrix intercalated with 2-aminobenzoate was prepared by coprecipitation reaction by dissolving 15 mmol of 2-aminobenzoic acid (2AB-H) in 20 mL of an aqueous solution of NaOH (0.4 mol/L). To this solution, 20 mL of a solution containing 2.5 mmol of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ was slowly added and the final pH was adjusted to around 7 by the addition of a NaOH (1 mol/L) solution. The suspension was magnetically stirred at room temperature for 6 h. Later, this suspension was centrifuged and washed with distilled water four times. The final white solid (LHS-Eu/2AB) was dried under vacuum at 45°C for 24 h.

2.3. Characterization

Powder X-ray diffraction (PXRD) patterns were recorded with a Siemens D-500 instrument using $\text{CuK}\alpha$ radiation ($\lambda = 1.54050 \text{ \AA}$) controlled by the Diffrac AT software. The current and tension were

set respectively to 30 mA and 40 kV and the patterns were collected with dwell time of 2° min^{-1} .

Specific surface area assessment was carried out in a Gemini instrument from Micromeritics. The sample (ca. 50–100 mg) was previously degassed in flowing nitrogen at 110°C for 2 h in a FlowPrep 060 apparatus (Micromeritics) in order to remove physisorbed water, and the data were analyzed using published software [12].

The FTIR spectra were recorded in a PerkinElmer Spectrum-One using approximately 1% of the sample in 100 mg of spectroscopic grade KBr, the pellets being pressed at 10 tons. The measurements were performed in the transmission mode with accumulation of 32 scans and recorded with a nominal resolution of 4 cm^{-1} .

Thermal analyses (TGA/DTA) were performed on SDT Q600 equipment. All measurements were carried out at a heating rate of $10^\circ\text{C min}^{-1}$ under an oxygen flow of 20 mL min^{-1} (Air Liquide, Spain, 99.999%). The TGA/DSC curves were recorded in an equipment of simultaneous thermal analysis STA, NETZSCH, STA 449 F3 Jupiter.

The UV-vis reflectance spectra (DRU-Vis) were recorded at room temperature in the 200–800 nm range, at intervals of 0.5 nm, in a VARIAN Cary 100 spectrophotometer equipped with an integration sphere.

The photoluminescence spectra of powders were collected at room temperature in a PerkinElmer LS55 spectrofluorometer.

3. Results and discussion

3.1. X-ray diffraction

The powder X-ray diffraction pattern of LHS-Zn/ NO_3 shown in Fig. 1 matches with the profile reported in the ICDD card corresponding to $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, which is characterized by a major basal reflection at 9.7 \AA caused by the 200 plane of the monoclinic structure [13,14]. The rare earth (RE) layered hydroxide salts (LHS), presented typical profiles of layered compounds whose signals at the lowest angle indicate basal reflections of 8.6 \AA , 9.3 \AA and 8.2 \AA for LHS-Eu/ NO_3 , LHS-Y/ NO_3 and LHS-Tb/ NO_3 , respectively (Fig. 1). These results suggest the formation of LHS with composition $\text{RE}_2(\text{OH})_5\text{NO}_3 \cdot x\text{H}_2\text{O}$, where $\text{RE} = \text{Eu, Y}$ and Tb [11,15]. From these nitrate LHS, the noisy pattern of LHS-Eu/ NO_3 indicates that the synthesis conditions are not suitable to achieve a high degree of crystallinity, i.e., a different level of energy is required to improve the atoms packing in this particular structure,

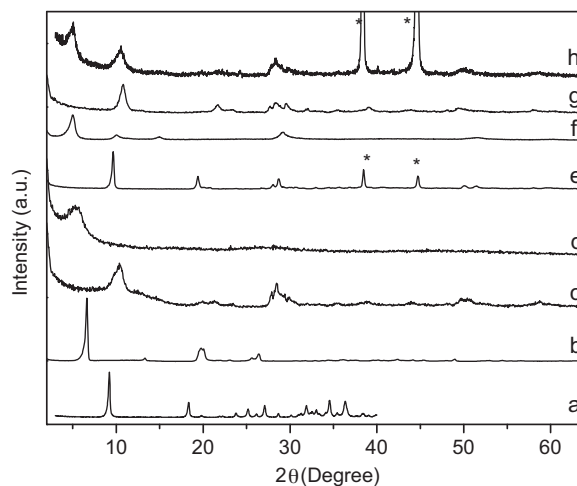


Fig. 1. PXRD patterns of LHS-Zn/ NO_3 (a), LHS-Zn/2AB (b), LHS-Eu/ NO_3 (c), LHS-Eu/2AB (d), LHS-Y/ NO_3 (e), LHS-Y/2AB (f), LHS-Tb/ NO_3 (g), LHS-Tb/2AB (h). * = Aluminium sample holder.

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