



# Luminescence properties of lanthanide-containing layered double hydroxides



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## ABSTRACT

A series of layered double hydroxides with the hydroxalite structure containing Mg<sup>2+</sup> and Al<sup>3+</sup> cations in the brucite-like layers and carbonate in the interlayer have been prepared, with different lanthanide cations (4% loading) in the brucite-like layers. The solids have been characterized by element chemical analysis, powder X-ray diffraction, thermal analysis, particle size distribution, FT-IR and UV–Vis spectroscopies and surface texture by adsorption–desorption of nitrogen at – 196 °C. The color and luminescent properties have been also studied. The results confirmed the hydroxalite-type structure, without any sort of contaminating phases. The solids have been calcined at 1000 °C forming homogeneously dispersed mixed oxides, where the rock-salt structure of MgO and the MgAl<sub>2</sub>O<sub>4</sub> spinel have been identified by powder X-ray diffraction, without any differentiated phase containing lanthanide ions. The samples (original and calcined) containing Tb<sup>3+</sup> exhibited green fluorescence, detected under irradiation of 254 and 365 nm. The emission spectra showed a series of narrow lines ascribed to the Tb<sup>3+</sup> <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>6–2</sub> transitions. The decay curves monitored at 543 nm indicated the presence of a single local Tb<sup>3+</sup> environment in the parent and calcined samples. For the calcined samples, the photoluminescence evidence supports the insertion of Tb<sup>3+</sup> in MgAl<sub>2</sub>O<sub>4</sub> rather than in MgO.

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## 1. Introduction

Layered double hydroxides, LDH, are a sort of layered materials which can be described with the formula [M<sup>2+</sup><sub>1-x</sub>M<sup>3+</sup><sub>x</sub>(OH)<sub>2</sub>]<sup>n-</sup><sub>(x/n)</sub>·mH<sub>2</sub>O. The structure is derived from that of brucite, Mg(OH)<sub>2</sub>, i. e., an hexagonal close packing of hydroxyl groups where all octahedral sites every two interlayers are occupied by Mg<sup>2+</sup> cations. A partial isomorphous M<sup>2+</sup>/M<sup>3+</sup> substitution gives rise to a formal positive charge in the layers, which is balanced by anions located, together with water molecules, in the originally empty interlayers; with the formula above, the square brackets would correspond to the composition of the layers [1]. The most widely known mineral with this structure is hydroxalite, [Mg<sub>0.75</sub>Al<sub>0.25</sub>(OH)<sub>2</sub>](CO<sub>3</sub>)<sub>0.125</sub>·0.5H<sub>2</sub>O, and sometimes LDH are known as hydroxalite-like or hydroxalite-type materials. The value of x usually ranges between 0.2 and 0.33 and the nature of the layer

cations, as well as of the interlayer anion, can be changed in very broad ranges [1–6]. The layer–interlayer interactions are mainly electrostatic and the thickness of the interlayer depends on the precise nature of the interlayer anion, its orientation (if it is not spherical) and the hydration degree. These materials have found applications [1,3,4,7–12] as adsorbents, catalysts, catalyst supports, carriers for controlled delivery of drugs, antacids, anion exchangers and scavengers, composite fillers, etc. On heating they decompose forming initially mostly amorphous species and when the calcination temperature is increased, crystallization of M<sup>2+</sup>O is first observed and at higher temperatures segregation of M<sup>2+</sup>M<sup>3+</sup><sub>2</sub>O<sub>4</sub> spinel takes place (if the interlayer anion contains metal cations, such as in the case of polyoxometalates, the process is somewhat different). These mixed oxides have found also applications as catalysts, catalyst supports and, if they contain transition metal cations, as ceramic pigments [13–19].

LDH can be prepared following different methods [20], although coprecipitation starting from soluble salts of the metal cations to be located in the brucite like layers is the easiest one; the pH can be increased by addition of an alkaline cation hydroxide, sodium

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carbonate, hydrolysis of urea, etc. The mixed oxides obtained upon their mild calcination below ca. 400–500 °C are able to reconstruct the layered structure by immersing the powder in an aqueous solution containing the anion to be inserted between the layers [21,22]. Once prepared the solid, it is usually submitted to ageing in suspension at ambient pressure, or under hydrothermal conditions [23], sometimes applying also microwaves [24], enhancing the speed of the crystallization process.

As mentioned above, the nature of the layer cations can be chosen in a wide range; however, their ionic radii should not be too different from that of  $\text{Mg}^{2+}$ , in order to avoid strong distortions in the structure. For instance, a Mg–Y hydroxalite is structurally unstable, but Y can be incorporated in Mg–Al–Y systems, where the molar fraction of yttrium is kept below a given threshold value, above which segregation of other phases usually takes place [25]. Yttrium has been also incorporated in small amounts in Mg, Al-LDH containing  $\text{Cr}^{3+}$  [15].  $\text{Eu}^{3+}$  can be incorporated up to 2.7% (atomic percentage) without decreasing its luminescence properties, although the spectral position is somewhat changed; maximum loadings of  $\text{Yb}^{3+}$  up to 10% have been also reported [26]. Nevertheless, some degree of symmetry lowering cannot be fully avoided in most of the cases, although the luminescent properties are usually maintained [27].

To avoid such distortions, similar compounds can be prepared using  $\text{Ca}^{2+}$  instead of  $\text{Mg}^{2+}$  as the divalent cation; the structure corresponds to hydrocalumite,  $\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$  (or  $[\text{Ca}_{0.67}\text{Al}_{0.33}(\text{OH})_2\text{Cl}_{0.33}\cdot 0.67\text{H}_2\text{O}]$ , to highlight the relationship to hydroxalite) where  $\text{Ca}^{2+}$  cations are octahedrally coordinated by six hydroxyl groups and by the interlayer chloride, in a  $\text{C}_{3v}$  symmetry. Solids structurally related to hydrocalumite (or its calcined product, mayenite  $\text{Ca}_{12}\text{Al}_4\text{O}_{33}$ ) and hydroxalite (or the mixed oxides formed upon its calcination) have been also used to support lanthanide cations, because of their luminescence properties [28].

Despite photoluminescence has been reported for colloids of Zn, Al LDH [29], such an effect results much more enhanced upon incorporation of lanthanide cations to the LDH structure. The subject has been recently reviewed by Sasaki et al. [30]. Stumpf et al. [31] have prepared Mg–Al–Eu hydroxalites in the chloride form by coprecipitation with  $\text{NaOH}(\text{aq})$ ; EXAFS studies have revealed incorporation of  $\text{Eu}^{3+}$  in the octahedral positions of the brucite-like layers, although when the Al/Eu molar ratio was equal to or lower than 4/1 cocrystallization of  $\text{Eu}(\text{OH})_3$  was observed. The same method was followed by Zhang et al. [32] to prepare a Tb-containing Mg, Al-LDH; as these authors started from  $\text{Tb}_4\text{O}_7$ , addition of hydrazine was necessary to reduce  $\text{Tb}^{4+}$  to  $\text{Tb}^{3+}$ ; acetylacetonate and 1,10-phenanthroline were intercalated in the interlayer and the solid showed a characteristic green light (545 nm) and a fluorescence lifetime and quantum yield larger than that of the  $[\text{Tb}(\text{acac})_3(\text{o-phen})]$  complex.

Musumeci et al. [33] have also used the coprecipitation method to prepare Mg, Al, Tb LDH with Tb/Al molar ratios ranging between 0 and 0.25 and aging under hydrothermal conditions at 100 °C for 4 h. As expected, the increase in the Tb content led to a broadening of the XRD signals, as well to a threefold decrease in the crystallite thickness and increase in the lateral platelet width, due to a distortion of the structure and stacking because of the different ionic radii of the cations (ionic radii of  $\text{Tb}^{3+}$  is 0.923 Å, vs. 0.72 for  $\text{Mg}^{2+}$  and 0.535 Å for  $\text{Al}^{3+}$ ). The green fluorescence shown by these solids showed a rather low quantum yield, 4% (55% for a reference quinine sulfate solution).

In some cases it has been shown that intercalation of active species in the interlayer permits energy transfer to lanthanide cations located in the layers. Xu et al. [34] have reported an efficient energy transfer from the excited state of 4-biphenylacetate intercalated in the interlayers of a  $\text{Tb}^{3+}$ -containing Mg, Al LDH; actually,

the green luminescence is higher than when the same solid, but without the organic photosensitizer, was used.

Systems containing more than one lanthanide cation have been also prepared. Ling et al. [35] have prepared Mg, Al-LDH containing minor amounts of Zn, Eu and Tb in the layers and with different organic species (acac, o-phen, salicylate) in the interlayer space after pre swelling with stearate; synthesis was carried out by coprecipitation and the suspensions aged at 70 °C for 2 days. Upon UV excitation (370 nm) four narrow emission peaks were recorded at 614, 591, 545, and 491 nm, responsible for the characteristic red, green, and blue colored emission of the complexes formed between the cations and the interlayer anions (namely, Eu-acac, Tb-o-phen, and Zn-salicylate), producing a pure white emission.

An alternative route to prepare luminescent materials containing lanthanide cations based on LDH has been to form coordination compounds between the lanthanide species and organic ligands previously inserted between the LDH layers; in this way the lattice distortions arising from the different, large, radii of the lanthanide cations is avoided. Pillinger et al. [36] have reported the incorporation of  $\text{Eu}^{3+}$  and  $\text{Gd}^{3+}$  into Zn, Al LDH where 2,2'-bipyridine-5,5'-dicarboxylate had been previously intercalated. The typical red emission of  $\text{Eu}^{3+}$  was observed, together with a broad band around 460 nm due to non-coordinated ligand species.

Concerning mayenite, it has been prepared by calcination of a hydrocalumite precursor containing  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ , and  $\text{Eu}^{3+}$  by coprecipitation, and calcination at 1350 °C [37]; it was observed that when it is doped with  $\text{Eu}^{3+}$ , an increase in its concentration decreases the average  $\text{Eu}^{3+}$ – $\text{Eu}^{3+}$  distance, increasing the interaction and quenching. When  $\text{Eu}^{3+}$  and  $\text{Nd}^{3+}$  were simultaneously incorporated into hydrocalumite [28], the luminescence spectra showed bands due to intra-4f transitions in the visible ( $\text{Eu}^{3+}$ ) and NIR ( $\text{Nd}^{3+}$ ) regions; the quantum efficiency and lifetime decreased in these codoped samples if compared to that containing only  $\text{Eu}^{3+}$ , probably because  $\text{Nd}^{3+}$  induces nonradiative channels for depopulation of the  $^5\text{D}_0$  level. On calcining at 1300 °C a mixture of lime and mayenite phases was formed, giving rise to two  $\text{Eu}^{3+}$  local environments, as deduced from the emission spectra.

In this paper we report the preparation and characterization of Mg, Al LDH doped with  $\text{Tb}^{3+}$ ,  $\text{Er}^{3+}$ , and  $\text{Yb}^{3+}$ , as well as the materials obtained after their thermal decomposition at high temperatures. The aim is to insight in the properties of the luminescent cations in the LDH matrix and in that of the mixed oxides produced upon their calcination. We have tested the three cations separately, also a mixture of two of them, but always maintaining the same doping level; in addition, some samples where the molar fraction of the luminescent agent has been changed have been also prepared.

## 2. Materials and procedures

### 2.1. Reactants

Magnesium chloride,  $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ , aluminum chloride,  $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$  and sodium hydroxide were from Panreac; terbium, erbium and ytterbium chlorides ( $\text{TbCl}_3\cdot 6\text{H}_2\text{O}$ ,  $\text{ErCl}_3\cdot 6\text{H}_2\text{O}$ , and  $\text{YbCl}_3\cdot 6\text{H}_2\text{O}$ ) were from Aldrich Chemistry, and sodium carbonate from Fluka Chemika. Oxygen (99.999%) for thermal studies, and nitrogen (99.999%) and helium (99.995%) for specific surface area and porosity measurements were from L'Air Liquide.

### 2.2. Characterization techniques

Element chemical analyses for metals were carried out at Servicio General de Análisis Químico Aplicado, University of Salamanca, by atomic absorption in a Mark II ELL-240 instrument, after dissolving the samples in concentrated  $\text{HNO}_3$ .

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