Research Article

Phosphor Dysprosium-Doped Layered Double Hydroxides Exchanged with Different Organic Functional Groups

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Received 3 May 2013; Revised 25 September 2013; Accepted 26 September 2013

Academic Editor: Tifeng Jiao

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The layers of a Zn/Al layered double hydroxide (LDH) were doped with Dy³⁺ cations. Among some compositions, the Zn²⁺ : Al³⁺ : Dy³⁺ molar ratio equal to 30 : 9 : 1 presented a single crystalline phase. Organic anions with carboxylic, amino, sulfate, or phosphate functional groups were intercalated as single layers between LDH layers as confirmed by X-ray diffraction and infrared spectroscopy. Photoluminescence spectra of the nitrate intercalated LDH showed a wide emission band with strong intensity in the yellow region (around 574 nm), originated due to symmetry distortion of the octahedral coordination in dysprosium centers. Moreover, a broad red band emission was also detected apparently due to the presence of zinc oxide. The distorted symmetry of the dysprosium coordination environment, also confirmed by X-ray photoelectron spectroscopy analysis, was modified after the intercalation with phenyl phosphonate (PP), aspartate (Asp), adipate (Adip), and serinate (Ser) anions; the emission as measured from PL spectra of these LDH was more intense in the blue region (ca. 486 nm), thus indicating an increase in symmetry of dysprosium octahedrons. The red emission band from zinc oxide kept the same intensity after intercalation of dodecyl sulfate (DDS). An additional emission of unknown origin at λ = 767 nm was present in all LDHs.

1. Introduction

Layered double hydroxides (LDHs) are crystalline materials whose layers are composed by octahedral units either occupied by divalent or trivalent cations in coordination with hydroxyl groups. Since the electrostatic charge of trivalent cations in such coordination is not completely neutralized, additional anions intercalated between the layers are required. The chemical composition of LDHs is then represented by the general formula: [M²⁺₁₋ₓM³⁺ₓ(OH)₂]ˣ⁺ Aᵐ⁻ₓ/m⁻ nH₂O, where M²⁺ and M³⁺ are the cations in octahedral sites and A is the interlayer anion of charge m⁻ [1–3].

One of the conditions to successfully synthesize these layered structures is the radius size of M²⁺ and M³⁺ cations, which must be close to that of Mg²⁺ (0.86 Å) [1, 4]. If the cationic radius is lower than 0.60 Å, the layers could be distorted and the quality of crystals is reduced [3], while if the radii are larger than 0.93 Å, the most probable product
is a mixture of LDH crystalline phases with single metal hydroxides.

Recently, the synthesis of LDHs doped with Eu$^{3+}$ occupying the M$^{3+}$ sites was achieved [5–8] despite its large cationic radius of 1.08 Å in octahedral coordination [9], thus demonstrating the possibility to introduce large cations in the layers. The introduction of europium led to obtain LDHs with fluorescent properties [6–8, 10, 11]. The fluorescence due to europium in LDHs has also been introduced by intercalating anionic europium complexes in the interlayer space represented by A$^{m-}$ in the general formula [10, 12, 13]; however, the first approach to produce fluorescent LDH is more attractive since the interlayer space is available for further exchange reactions [11]. This combination of fluorescence and intercalation properties in LDH structures has been proposed as an alternative to design drug delivery systems [6, 8] that could be monitored through light emission techniques [14]. This strategy seems feasible owing to the chemical and thermal stability of the LDHs modified with molecules for medical or biological applications [15, 16].

Another interesting application proposed for an europium-doped LDH is as a probe for phenylalanine detection considering that the light emission of europium into the layers shifts from the red to the blue region of the visible spectrum after the amino acid intercalation [8]. Even when this result did not correspond to a single crystalline phase compound, the change in luminescence induced by the substitution of ligands coordinating the europium centers was a novelty [8] considering that the electronic internal transitions in lanthanides should not be affected by ligands [17].

A possible way to confirm the influence of ligands on the lanthanide luminescence is by testing variety of organic ligands introduced in the interlayer space (A$^{m-}$ site) of lanthanide-doped LDHs considering that some organic ions intercalated into LDHs can be grafted to the layers [18, 19]; that is, they could directly coordinate the lanthanide center.

The objective of this work was to synthesize LDH structures containing Dy$^{3+}$ cations in the octahedral sites of the layers to verify whether the layered structure is stable with this large cation, whose ionic radii (1.05 Å) is close to that of europium [9], and to study the emission spectrum of dysprosium after the intercalation of organic ions with carboxylate, amino, phosphonate, and sulfate functional groups in order to confirm the influence of ligands on the emission of the lanthanide in a single crystalline phase compound.

Finally, the paper demonstrated that the introduction of dysprosium is an advantage due to a weak emission near to the red light which opens the possibility to design biological probes since the light with this energy is able to cross biological tissues.

2. Experimental Part

The chemicals used in this work were Zn(NO$_3$)$_2$·6H$_2$O (Analytyka, Mexico, 98%), Al(NO$_3$)$_3$·6H$_2$O (Analytyka, Mexico, 98%), Dy(NO$_3$)$_3$ (Sigma-Aldrich, USA, 99%), L-serine, Ser, (Sigma-Aldrich, USA 99%), L-aspartic acid, Asp, (Sigma-Aldrich, USA, 99%), sodium dodecylsulfate, DDS (Jalmex, Mexico, 99%), adipic acid, Adip, (Meyer, Mexico, 99%), and phenyl phosphonic acid (PP) (Sigma-Aldrich, USA, 99%). All of these materials were used as received without further purification. To avoid the co-intercalation of carbonate, decarbonated distilled water was used to prepare all the solutions and the syntheses were performed under flow of nitrogen.

2.1. Layered Double Hydroxides. The LDHs were prepared with the Zn$^{2+}$ : Al$^{3+}$ : Dy$^{3+}$ molar ratios of 30:10:0, 30:9:1, and 30:0:10, and these values were used as labels to identify the LDHs. All the compositions maintain the constant Zn$^{2+}$ : M$^{3+}$ molar ratio equal to 3:1.

As example, the LDH with the ratio 30:9:1 was prepared by dissolving 4.4709 g of Zn(NO$_3$)$_2$·6H$_2$O (2.36 × 10$^{-2}$ mol of Zn$^{2+}$), 2.6671 g of Al(NO$_3$)$_3$·9H$_2$O (7.1 × 10$^{-3}$ mol of Al$^{3+}$), and 0.2741 g of Dy(NO$_3$)$_3$ (7.8 × 10$^{-4}$ mol of Dy$^{3+}$) in 250 mL of decarbonated distilled water in a sealed vessel and purged with nitrogen. The solution was titrated with 4% ammonia solution up to pH 9. The white powder was recovered by decantation, washed with distilled water three times, and dried at 60°C to constant weight.

2.2. Intercalation of Organic Anions. The coprecipitation method was followed to obtain the LDH because this is more efficient for intercalation of amino acids [20]. The metal cations solution with the Zn$^{2+}$ : Al$^{3+}$ : Dy$^{3+}$ molar ratio of 30 : 9 : 1 was prepared according to the procedure described previously for the LDH. A second solution containing 0.0106 mol of Asp, Ser, PP or DDS, or 0.0053 mol of Adip in 100 mL of water was adjusted to pH = 9, with 4% ammonia solution, and then was added to the metal cations solution under vigorous stirring. The final pH was adjusted to pH = 9 and the stirring was kept for 18–24 h. The powders were recovered by filtration, washed with water, and dried at 60°C to constant weight.

2.3. Characterization. The X-ray diffraction patterns were collected with a Shimadzu diffractometer (XDR-6000) using CuK$_α$ radiation (0.15418 nm) with 30 mA and 40 kV and graphite crystal as monochromator; the scan step was 0.02 degrees. Fourier transform infrared (FTIR) spectra were collected in the transmission mode with a Perkin-Elmer spectrometer model Spectrum One using a resolution of 4 cm$^{-1}$. Photoluminescence (PL) spectra were obtained with a fluorescence spectrometer (Hitachi FL-7000) operated with a 5 nm slit and 500 V at room temperature. A series of excitation measurements were conducted in order to determine the optimum excitation energy. X-ray photoelectron spectra (XPS) were collected with an AES-XPS PHI 548 system with Al anode. An energy step of 100 eV was used for the generation of survey spectra, which was scanned from 0 to 1200 eV. For high-resolution spectra, an energy step of 50 eV was used with 0.8 eV resolution. The C1s binding energy was used to compensate surface charge effects. The electronic paramagnetic resonance (EPR) analyses were done in quartz tubes containing powdered samples which were placed in
3. Results and Discussion

3.1. Dysprosium Doped LDHs. The XRD patterns of the 30:10:0 LDH presented a basal distance of 9.3 Å, similar to that in the 30:9:1 LDH, whereas the distance decreased to 8.3 Å in the 30:0:10 LDH. These different values have been observed earlier and demonstrated to depend on the perpendicular or parallel orientation of nitrate ions with respect to the layers, respectively [21]. The orientation becomes important to define the ion-exchange capability in LDHs once parallel nitrate ions are more difficult to be exchanged [21]; then the 30:0:10 LDH would not be a suitable matrix for exchange experiments; furthermore, this compound presented a second phase of ZnO whose reflections are identified with asterisks in Figure 1. Therefore, the selected LDH for the intercalation study was 30:9:1 because it presented a single phase; additionally, the basal distance of 9.3 Å related to perpendicular nitrate anions would facilitate the ion-exchange in future works.

The FTIR analysis of the three LDH presented the typical wide band around 3500 cm\(^{-1}\) of O–H vibrations [5, 7, 22] and the intense signal at 1384 cm\(^{-1}\) of the stretching mode in the nitrate ion with D\(_{3h}\) symmetry (Figure 2); that is, nitrate is free in the interlayer space [18] of 30:10:0 and 30:9:1 LDHs, which are the same structures whose XRD pattern suggested nitrate with perpendicular orientation in the interlayer space. The 30:0:10 LDH presented an additional band at 1515 cm\(^{-1}\), which clearly appears when nitrate ions are bonded to the layers [18], contributing to reducing the basal space in addition to the parallel orientation. The bands below 550 cm\(^{-1}\) indicate the presence of metal-oxygen stretching and bending modes [23], which are associated with metals in the octahedral sites for the structures whose XRD pattern indicated a layered structure; in the case of the 30:0:10 LDH, the metal-oxygen vibrations belong also to zinc oxide.

3.2. Intercalation in Dysprosium-Doped LDH. The coprecipitated LDHs with organic anions were analyzed by XRD (Figure 3). The patterns of the Asp, PP, Adip, and DDS derivatives presented basal spaces of 12.5, 15.0, 14.5, and 29.2 Å, respectively, in agreement with the intercalation of a single organic layer in the interlayer space of the LDH structure [19, 20, 22, 24, 25]. The Ser coprecipitation product did not produce an intercalated compound since the basal space of 8.3 Å corresponded to the 30:0:10 LDH intercalated with nitrate ions, which is plotted in Figure 1; however,
the FTIR spectrum clearly indicated that nitrate anions are free; then the Dy$^{3+}$ cations could only be allocated in the octahedral sites of the layers and surrounded by hydroxide anions, thus remaining the different degrees of distortion in the dysprosium sites as a feasible explanation to the wide band observed by XPS. The Dy spectrum in the Asp derivative was not detected since the co-precipitation products of layered matrices also contain organic anions covering the outer crystallites surface [29] and this type of shell reduces the efficiency for the X-rays to reach the inorganic layers; even if some beams do, the content of dysprosium is low and the photoemission is not detected by the equipment. On the other hand, the Zn 2p 3/2 spectrum in both samples presented the same symmetry with FWHM of 2.1 eV (Figure 5), suggesting that the zinc sites were not affected with the intercalation of Asp anions.

Therefore, the incorporation of Dy$^{3+}$ cations into the layers of the LDH was possible despite the large ionic radii, but the octahedral sites allocating this lanthanide are distorted.

Owing to the difficulty to analyze dysprosium by XPS, the EPR spectroscopy was conducted to all the organic intercalated samples (Figure 6). To collect an EPR spectrum of the paramagnetic Dy$^{3+}$ cation ($I = 5/2$) is a difficult task since the unpaired electron in the 4f shell can be shielded with outer 5 s electrons. Maybe, due to this difficulty several EPR studies on materials doped with dysprosium do not report the spectra [30–32].

However, other authors have detected a signal with $g = 2.007$ in stronitum aluminates and sulfides doped with Dy$^{3+}$ [33, 34], whose hyperfine splitting is coherent with $I = 5/2$ [33]. In these reports, an additional absorption appeared in regions of $g$ values around 11, 7, and 4, associated with low field resonance of Dy$^{3+}$ [35]. These last signals fall within the range expected for Dy$^{3+}$ [36]; then the absorptions with $g = 4.2$ in Figure 6 probably are originated from dysprosium cations. Since the signals are wide, it is only possible to confirm the paramagnetic properties in the 30:9:1 LDH and the Ser, PP, and Adip derivatives. The absorption near to $g = 2.0$ appeared in the Ser and Asp derivatives. Since these are not present in the 30:9:1 LDH, then the absorption probably corresponds to radicals formed in the serine and adipate anions. In the literature, the $g = 2.0$ signal has been observed in solid samples of calcium sulfate doped with dysprosium, and it was assigned to sulfate oxides radical but not to dysprosium [31].

3.3. Photoluminescence

3.3.1. Dysprosium Doped LDHs. The PL spectra of nitrate intercalated LDHs with different content of dysprosium are presented in Figure 7. The main emission of dysprosium atoms dispersed in inorganic matrices are found in the blue and yellow region when excited with photons in the range of $\lambda = 350–387$ nm [37–39]. The spectra of the two LDHs are formed by a wide band around 620 nm, which could be considered as inhomogeneous broadening resulting from changes in the crystal field of the phosphorescent cation [17], but such situation is limited for our compounds since.

Figure 4: FTIR spectra of the 30:9:1 LDH coprecipitated with L-aspartic acid (Asp), L-serine (Ser), phenylphosphonic acid (PP), adipic acid (Adip), and sodium dodecylsulfate (SDS).
the Dy\textsuperscript{3+} cations are restricted to occupy octahedral sites surrounded by hydroxide anions or eventually by nitrate anions; otherwise, the XRD profiles in Figure 1 would not correspond to LDH structures. Thus, one probable fact changing the chemical environment is distortions in the octahedral sites allocating dysprosium, as it was also inferred from the XPS spectrum. The changes in the crystal field are known to contribute to the broadening of the 620 nm emission [17]. A second possible reason for this widening effect, which has not been well understood, is the contribution of the LDH lattice from ZnO defect centers [40, 41] or from Zn–OH moieties [41]; this factor is likely contributing considering that the 30:0:10 LDH, which presented ZnO reflection in the XRD pattern presents the band centered at $\lambda = 620$ nm with higher relative intensity than the 30:9:1 LDH.

With respect to the dysprosium emission in the blue region (468 nm), the low intensity indicates a low contribution of the magnetic dipole ($^4F_{9/2}$ to $^6H_{15/2}$ transition) because the Dy\textsuperscript{3+} cations are delocalized from the inversion center [37] in the two compounds. However, the relative intensity of the blue emission was higher in the 30:9:1 LDH suggesting that dysprosium cations achieved higher symmetry in comparison with the structure with higher dysprosium content (30:0:10), whose red band at 620 nm
Figure 7: Emission spectra of LDH with different Zn : Al : Dy molar ratios. Excitation at 363 nm.

Figure 8: Emission spectra of the 30 : 9 : 1 LDH coprecipitated with L-aspartic acid (Asp), L-serine (Ser), phenyl phosphonic acid (PP), adipic acid (Adip), and sodium dodecylsulfate (DDS). Excitation at 363 nm.

3.3.2. LDHs Intercalated with Organic Molecules. PL spectra of the organic intercalated LDHs (Figure 8) show narrower band emissions and a clear absence of the broad orange emission (except for the DDS). All compounds presented blue emission peaks between 468 and 480 nm (characteristic magnetic dipole transition $^4F_{9/2} \rightarrow {}^6H_{15/2}$ in Dy), which appeared with higher relative intensity than the transitions of the electric dipole in the Asp, Adip PP, and Ser derivatives. Knowing that magnetic dipole transition depends on the crystal symmetry, the increased intensity indicates an improvement in crystallinity after the organic anion intercalation, which probably occurred because the organic species separate the inorganic layers allowing a rearrangement of the dysprosium octahedrons to increase the symmetry and the formation of inversion centers uniformly coordinated by hydroxyl groups.

Regarding the PP derivative, the intensity of the blue band (486 nm) is higher than the yellow emission (574 nm), but this spectrum contains a new peak at 546 nm. The new band can be assigned to the interaction of Dy$^{3+}$ with PP as ligand, since this anion has the capability to substitute some hydroxyl groups in LDHs [42]. In fact, a recent report described the lost of the common red emission (620 nm) of europium ions after the functionalization with phenylalanine, while a blue band (445 nm) rose; the new band was explained due to the ligand-metal charge transference formed with functionalization [8]. For our case, the effect caused PP could be an explanation if functionalization did occurred; that is, the PP anions substituted some hydroxyl sites of the inorganic layers, thus changing the crystal field of Dy$^{3+}$ ions. The consequence of the new crystal field was also reflected in the weak band at 620 nm.

The PL spectrum of the DDS derivative presented a weak blue emission (468 nm) and a broad yellow emission from dysprosium centers overlapped with the 620 nm emission coming from Zn–O regions. The activation mechanism of the band involving Zn needs further studies, since its presence occurred only in nitrate intercalated LDHs and in the PP and DDS derivatives. Similarly, studies are required for the anomalous emission observed at 546 nm in the PP, DDS, and Ser derivatives. This band has not been reported for dysprosium, zinc oxide/hydroxides, or aluminate, neither can be associated with the organic anions, since the band was present in the nitrate intercalated samples contributing to enlarge the main emission band, but it raises monochromatized when the inorganic layer interacts with PP, DDS, and Ser.

On the other hand, the yellow emission of dysprosium at 574 nm becomes narrower in the derivatives where carboxylate anions are present like Asp, Adip, and Ser. In the last case of Ser, as the effect does not seem to depend on intercalation, then a probable effect of ligands is present.

Finally, the weak band at 767 nm of unknown origin was present in all LDHs samples. Since this emission is independent of the functional groups in the organic anion, this could be useful for monitoring dysprosium-doped LDH as biological probes; additionally, the energy of this emission is near to that of the IR light, which is able to pass through cell walls and tissues.

4. Conclusions

The precipitation of the LDHs with different Zn$^{2+}$ : Al$^{3+}$ : Dy$^{3+}$ molar ratio was conducted. The 30 : 9 : 1 LDH comprised
a single crystal phase with free nitrate ions intercalated. Wide PL spectrum of the yellow emission of dysprosium (574 nm) suggested that the coordination environment of Dy$^{3+}$ has different degrees of distortion, matching with the information obtained by XPS. Along the yellow emission, a red emission (620 nm) from zinc centers was detected, which was retained in the DDS derivative in contrast with the LDHs intercalated with PP, Asp, Adip, and Ser anions where the yellow dysprosium emission became narrow, while the broad red contribution from zinc centers disappeared. Then, the emission of Dy$^{3+}$ is influenced by ligands. The emission of unknown origin at 767 nm in all LDHs samples could be useful for optical probes once this type of light is able to transverse cell walls.

Acknowledgments

This work was supported by PROMEP (UDG-PTC-1055). Authors are grateful to J. A. Diaz Hernandez and Professor Wencel de la Cruz for providing the access to the XPS spectrometer at CNyN-UNAM and indebted to Professor A. S. Mangrich for his helpful assistance in the EPR measurements. Gustavo A. Hirata acknowledges the support from DGAPA-UNAM (Grant IN-109913).

References


[37] K. N. Shinde, S. J. Dhoble, and A. Kumar, “Combustion synthesis of Ce\text{\textsuperscript{3+}}, Eu\text{\textsuperscript{3+}} and Dy\text{\textsuperscript{3+}} activated NaCaPO\text{\_4} phosphors,” *Journal of Rare Earths*, vol. 29, no. 6, pp. 527–535, 2011.


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