

Luminescent LDH: study of $[\text{Zn}_2\text{Al}_{0.999}\text{Eu}_{0.001}(\text{OH})_6]\text{NO}_3$, $[\text{Zn}_2\text{Al}_{0.999}\text{Eu}_{0.001}(\text{OH})_6]\text{bca}$ and $[\text{Zn}_2\text{Al}(\text{OH})_6][\text{Eu}(\text{bca})_4]$ systems and their properties.

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The challenge of chemistry in the twenty-first century is the study for obtaining promising materials for applications and innovative perspectives. A great example is the synthesis of two-dimensional luminescent materials. Among the available structures, it can be highlighted Layered Double Hydroxides (LDH) synthesized in the laboratory by simple route and low cost. LDH have the general formula $[\text{M}^{2+}_{(1-x)}\text{M}'^{3+}_x(\text{OH})_2](\text{A}^{n-})_{x/n} \cdot z\text{H}_2\text{O}$ (M, M' = layer metal ions, and Aⁿ⁻ = interlayer anion)¹. This work consists of three experimental steps. In the first step it was prepared and studied Eu³⁺-doped LDH with small concentration of dopant and in the interlayer spaces containing NO₃⁻ anions, $[\text{Zn}_2\text{Al}_{0.999}\text{Eu}_{0.001}(\text{OH})_6]\text{NO}_3$ -LDH (sample a), obtained by co-precipitation method with pH = 6.5. In the second step, it was intercalated the 4-biphenylcarboxylic anion (bca) by ion exchange method in the sample obtained previously in the first stage thereby obtaining, $[\text{Zn}_2\text{Al}_{0.999}\text{Eu}_{0.001}(\text{OH})_6]\text{bca}$ -LDH (sample b). Finally, in the last step, it was obtained pure LDH by co-precipitation method and intercalated with an anionic complex, $[\text{Eu}(\text{bca})_4]^-$, containing the same ligand used in the second stage by ion exchange method, $[\text{Zn}_2\text{Al}(\text{OH})_6][\text{Eu}(\text{bca})_4]$ -LDH (sample c). The samples were characterized by XRD, FTIR, SEM, Zeta Potential, Photoluminescence Spectroscopy (PL) and X-Ray Excited Optical Luminescence (XEOL). Within the technique detection limits, it can be seen that the compounds were successfully achieved without the formation of spurious phases. The intercalation of anionic species (bca or $[\text{Eu}(\text{bca})_4]^-$) in the LDH interlayer domain is evidenced by the increase in the basal spacing, meaning that this increase is directly related to the displacement of the basal plans for smaller angles when compared to the reference array². The interlayer spacing are 0.38, 0.99 and 0.41 nm for samples a, b and c, respectively. From FTIR results, the coordination between Eu³⁺ and bca is chelating bidentate and small changes in conformation and consequent modifications of the M-O complex bond intercalation. In excitation spectra, $\lambda_{\text{em}} = 615$ nm, there is a broad band between 285 and 305 nm assigned to the charge transfer (CT) $\text{O}^{2-} \rightarrow \text{M}$ (M = Eu³⁺ or Zn²⁺). In the region between 350 and 490 nm the lines were attribute to intraconfigurational transitions (f → f). When bca is present, besides these bands a new one at 313 nm appears and it is assigned to the $\pi-\pi^*$ of bca. Emission spectra were obtained by setting the excitation wavelength λ_{ex} at 296 nm (CT band). It is observed $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition (0-2) is more intense than the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition (0-1) that indicates the Eu³⁺ sites are not centrosymmetric. The doping distorts the aluminum sites due to difference in radii, probable increasing the number of coordinated water molecules surrounding of cluster formation³. The red emission is observed in the absence of sensitizer. However, with the intercalation of organic ligands emission spectra change: as (splitting transitions and increasing bands intensities. Under X-ray excitation, the emission is not intense and probably suppressed by the formation of defects that promote non-radiative transitions and/or the sample decomposition.

References

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