

Study of Lanthanoide Organic Frameworks Properties and Synthesis: Multicomponent Ligands

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Abstract : Coordination polymers, also known as metal-organic frameworks (MOFs) or lanthanoide organic frameworks (LOFs) have been reported due of their promising applications in gas storage, separation, catalysis, luminescence, magnetism, drug delivery, and so on. As a type of organic-inorganic hybrid materials, the properties of coordination polymers could be chosen by deliberately selecting the organic and inorganic components. LOFs have received considerable attention because of their properties such as porosity, luminescence, and magnetism. Methods such as solvothermal synthesis are important as a strategy to control the structural and morphological properties as well as the composition of the target compounds. In this work the first solvothermal synthesis was employed to obtain the compound $[Y_{0.4}Yb_{0.4}Er_{0.2}(dmf)(for)(H_2O)(tft)]$, by using terephthalic acid (tft) and oxalic acid, decomposed in formate (for), as ligands; Yttrium, Ytterbium and Erbium as metal centers, in DMF and water for 4 days under 160 °C. The semi-rigid terephthalic acid (dicarboxylic) coordinates with Ln^{3+} ions and also is possible to form a polyfunctional bridge. On the other hand, oxalate anion has no high-energy vibrational groups, which benefits the excitation of Yb^{3+} in upconversion process. It was observed that the compounds with water molecules in the coordination sphere of the lanthanoide ions cause lower crystalline properties and change the structure of the LOF (1D, 2D, 3D). In the FTIR, the bands at 1589 and 1500 cm^{-1} correspond to the asymmetric stretching vibration of $-COO$. The band at 1383 cm^{-1} is assigned to the symmetric stretching vibration of $-COO$. Single crystal X-ray diffraction study reveals an infinite 3D coordination framework that crystallizes in space group $P21/c$. The other three products, $[TR(chel)(ofd)_0,5(H_2O)_2]$, where $TR = Eu^{3+}$, Y^{3+} , and Yb^{3+}/Er^{3+} were obtained by using 1, 2-phenylenedioxydiacetic acid (ofd) and chelidonic acid (chel) as organic ligands. Thermal analysis shows that the lanthanoide organic frameworks do not collapse at temperatures below 250 °C. By the polycrystalline X-ray diffraction patterns (PXRD) it was observed that the compounds with Eu^{3+} , Y^{3+} , and Yb^{3+}/Er^{3+} ions are isostructural. From PXRD patterns, high crystallinity can be noticed for the complexes. The final products were characterized by single X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), energy dispersive spectroscopy (EDS) and thermogravimetric analysis (TGA). The X-ray diffraction (XRD) is an effective method to investigate crystalline properties of synthesized materials. The solid crystal obtained in the synthesis show peaks at $2\theta < 10^\circ$, indicating the MOF formation. The chemical composition of LOFs was also confirmed by EDS.

Keywords : isostructural, lanthanoids, lanthanoids organic frameworks (LOFs), metal organic frameworks (MOFs), thermogravimetry, X-Ray diffraction

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