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PREPARATION OF NANOCRYSTALLINE LANTHANIDE-BASED METAL-ORGANIC FRAMEWORKS AND THEIR DERIVATIVES

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01 INTRODUCTION

Metal-organic networks (MOFs) are a type of porous materials built from metal cations linked by an organic component (ligands). They can exist in the form of one-, two- and three-dimensional structures, depending on the coordination number of the metal and the type of ligand. Due to their high porosity, MOFs have a large specific surface, which enables their use for catalytic purposes and gas storage. In this work, MOFs based on lanthanides La, Ce and Pr and succinic acid (SA) were synthesized via solvothermal synthesis. Solvothermal synthesis is based on carrying out the reaction at higher temperatures and elevated pressure inside an autoclave, and an organic substance (most often DMF) is used as a solvent. With this method, MOFs of different structures are obtained depending on the reaction conditions. Furthermore, since lanthanoid metals have the ability to release electrons easily, the synthesized MOFs have potential applications in photocatalysis, electrocatalysis and gas storage, but further research in this area is necessary.

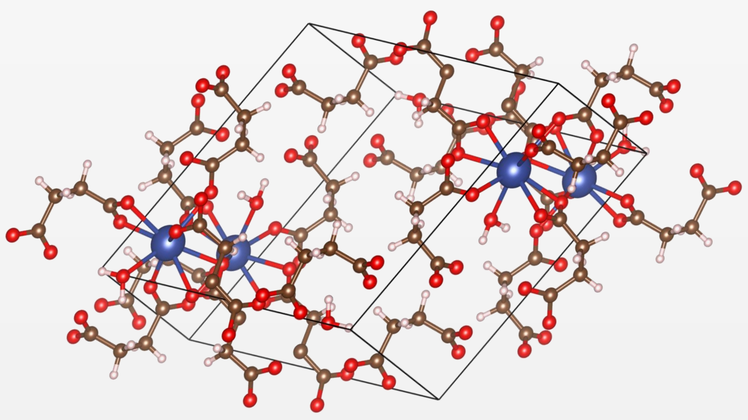

Fig 1. 3D structure of synthesized Ln-succinate MOFs (Ln = La, Ce and Pr).

02 SYNTHESIS

Table 1. List of compounds used in synthesis of Ln-MOFs.

Compound	*n* / mmol
$Ln(NO_3)_3$ x 6 H_2O Ln = La, Ce and Pr	1
Succinic acid	1.5

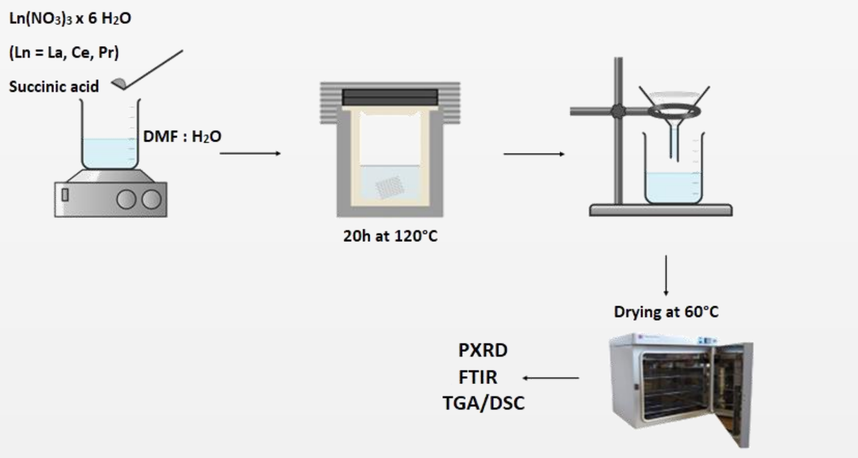

Fig 2. Synthesis pathway for obtaining phase-pure Ln-MOFs.

03 RESULTS

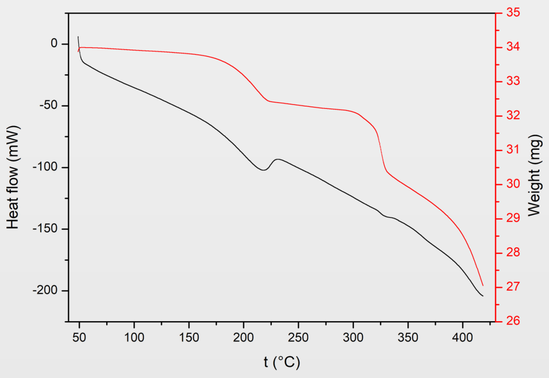

Fig 3. Thermogravimetric analysis (red) and differential scanning calorimetry (black) curves of LaSA in an inert nitrogen atmosphere. The obtained curves indicate the stability of the compound up to 210 °C and the decomposition of the compound in two steps.

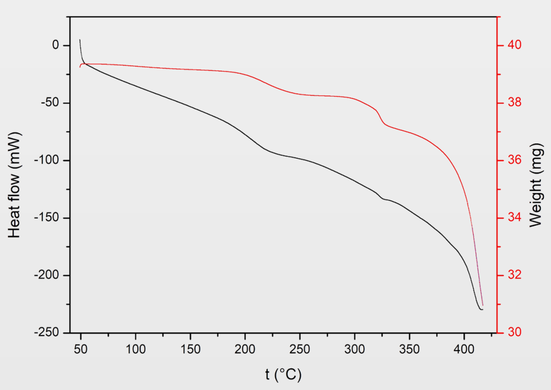

Fig 4. Thermogravimetric analysis (red) and differential scanning calorimetry (black) curves of CeSA in an inert nitrogen atmosphere. The obtained curves indicate the stability of the compound up to 225 °C and the decomposition of the compound in two steps.

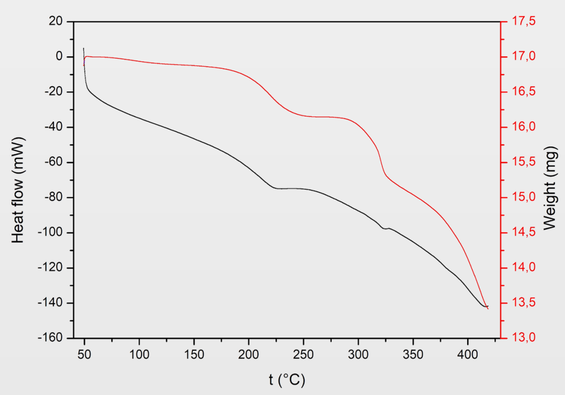

Fig 5. Thermogravimetric analysis (red) and differential scanning calorimetry (black) curves of PrSA in an inert nitrogen atmosphere. The obtained curves indicate the stability of the compound up to 225 °C and the decomposition of the compound in two steps.

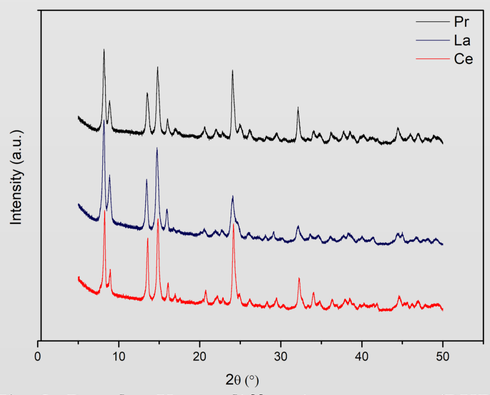

Fig 6. Powder X-ray diffraction patterns (PXRD) of LaSA, CeSA and PrSA. All of the compounds crystallize in low-symmetry triclinic crystal system, space group *P*–1. Wide peaks reveal nanocrystallinity of the synthesizes compounds with average crystallite sizes around 20 nm.

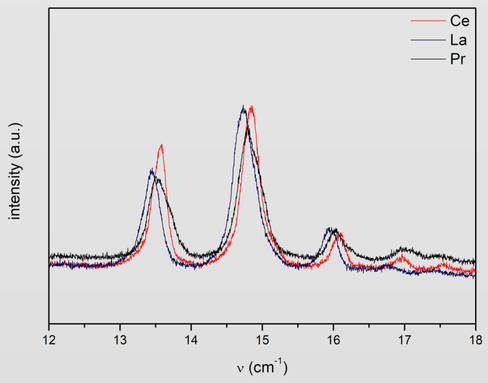

Fig 7. Powder X-Ray pattern of LaSA, CeSA and PrSA visualized from 2θ = 12 – 18° to see the shift in peaks.. Since cation radii of La^{3+}, $Ce^{4+/3+}$ and $Pr^{3+/4+}$ are similar, crystal structures of these compounds are similar, but the small difference leads to change in lattice parameters which is demonstrated by peak shifts.

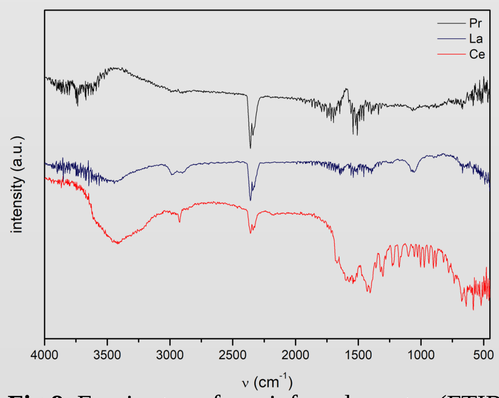

Fig 8. Fourier-transform infrared spectra (FTIR) of LaSA, CeSA and PrSA. Given FTIR patterns show the stretching vibration of -CH groups at 2300 cm^{-1} and the absence of the characteristic stretching vibration of the -OH group for succinic acid at 3000 cm^{-1}.

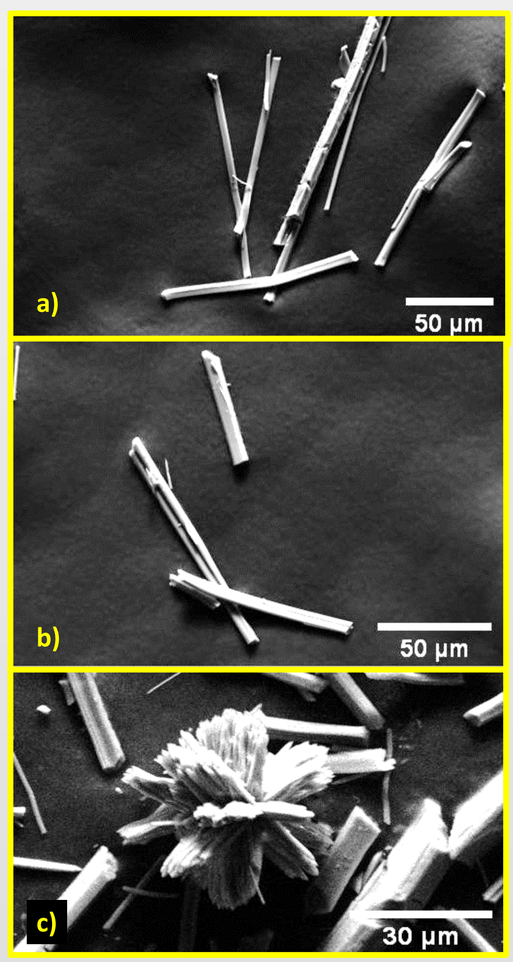

Fig 9. Scanning electron microscopy (SEM) images of LaSA (a), CeSA (b) and PrSA (c) show nanorod-like morphology with lengths around 80 µm. SEM image of PrSA shows flower-like arrangement of nanorods.

04 CONCLUSIONS

Using the solvothermal method, Ln-MOFs based on succinic acid and La, Ce and Pr were synthesized. FTIR analysis indicates the binding of metal centers to the carboxyl ends of the acid due to the lack of stretching vibration of the -OH group. TGA/DSC analysis indicates the stability of the compounds at high temperatures, which enables their potential use as catalysts at high temperatures.