MceCa16-003

Crystallization, properties, and computational studies of a new Tutton salt based on (NH4)2Fe0.5Ni0.5(SO4)2(H2O)6 for thermochemical systems

Oliveira Neto, J.G.(1); Domingos, F.N.B.(1); Marques, J.V.(1); Viana, J.R.(1); Lang, R.(2); Santos, A.O.(1); Simplicio, J.F.(1);
(1) UFMA; (2) UNIFESP;

Nowadays, the search for promising materials to store energy absorbed by solar devices has received significant attention. For domestic heating and hot water supply, this energy can be stored regularly in reversible reactions, thermally in phase changes, or temperature increases of the storage materials. In this context, hydrated salts emerge as potential candidates due to their low thermal stability, cyclability, and high dehydration enthalpies. In this scenario, we have synthesized a new hydrated salt with the chemical composition (NH4)2Fe0.5Ni0.5(SO4)2(H2O)6 and characterize its structural, geometric, thermal, and electronic properties. Furthermore, a computational study was conducted using Hirshfeld surfaces, crystal voids, and density functional theory (DFT). The structure, solved by powder X-ray diffraction, showed that the sample crystallizes in the monoclinic symmetry of P21/a space group, containing two formulas per unit cell. These characteristics confirm that the crystal belongs to the family of mixed Tutton salts with the simultaneous occupation of Fe2+ and Ni2+ ions in the bivalent site of the lattice. The geometric parameters of bond lengths and experimental bond angles showed a good correlation with theoretical data estimated via DFT, indicating that the local density approximation parameterized by the Perdew and Zunger functionals are suitable computational tools for analyzing the physicochemical properties of this type of material. Thermoanalytical analyses showed that the material is stable up to around 95 °C, followed by a dehydration process. The energy involved in this process corresponds to 431.65 kJ/mol, equivalent to 71.94 kJ per 1 mol of water. Moreover, it was possible to estimate an energy density for the salt of 2.08 GJ/m3, which characterizes it as a promising material for energy storage via thermochemical reactions. Additionally, band structure calculations revealed a band gap characteristic of a broadband semiconductor at approximately 2.80 eV. Finally, it was determined from the Hirshfeld surfaces that the contacts stabilizing the lattice are H...O/O...H, H...H, and O...O. Furthermore, it was found that the unit cell of this mixed Tutton salt has a void space of 50.75 Å3 (7.42%), which is considered small and indicates that the molecular fragments are stabilized by high lattice energy.