Li1.43[Fe II 4.43Fe III 0.57(HPO3)6] 3 1.5H2O: A Phosphite Oxoanion-Based Compound with Lithium Exchange Capability and Spin-Glass Magnetic Behavior

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Li1.43[Fe II 4.43Fe III 0.57(HPO3)6] 3 1.5H2O has been synthesized by mild hydrothermal techniques. This phase exhibits a crystal structure formed by the [Fe II 4.43Fe III 0.57(HPO3)6]1.43 inorganic framework with Li+ cations as counterions. The anionic inorganic skeleton is based on layers of FeO6 octahedra linked along the c-axis through (HPO3)2− oxoanions. The sheets are constructed using 12-membered rings of FeO6 octahedra that repeat in the ab plane, giving rise to channels ca. 3 Å in diameter along the [100] direction in which the water molecules and Li+ cations are located showing positional disorder. The limit of the thermal stability is ∼285 °C. The IR spectrum shows the vibrational bands belonging to the phosphite groups. From the fit of the Mössbauer spectrum, in the paramagnetic state, characteristic values of the isomer shift and quadrupolar splitting for the simultaneous presence of Fe(II) and (III) cations have been obtained. From the ac-magnetic measurements, spin glass behavior was inferred, which can be attributed to the presence of both Fe(II) (S = 2) and Fe(III) (S = 5/2) cations. The spin-glass-like state was confirmed by specific-heat experiments, with this phase being the first ordered transition-metal phosphite exhibiting this magnetic behavior. The existence of mobile lithium cations in the channels of Li1.43[Fe II 4.43Fe III 0.57(HPO3)6] 3 1.5H2O was studied by impedance spectroscopy at different temperatures. The obtained Nyquist diagrams reveal two conduction processes. Electrochemical characterization was completed by cyclic voltammetry experiments and galvanostatic measurements. A reversible exchange of lithium is also observed for this compound for more than 100 galvanostatic cycles, equivalent to 12 mAh g−1 of sample.