
Structural, magnetic and electronic properties of pure crystalline Co/Fe 6/2 ferrite spinel

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Résumé

Ferrite spinels are of technological interest because of their magnetic ordering, which can be ferrimagnetic or antiferromagnetic depending on the structure and the nature of the metal ions.

Pure and crystalline Co/Fe 6/2 ferrite spinel was obtained by High Temperature treatment of Co/Fe-based Layered Double Hydroxide (LDH) nanoparticles. Experiment was conducted operando, using X-Ray Diffraction (XRD), in the range from 25 to 900°C. Co/Fe 6/2 ferrite was also characterized by SEM-EDS, Atomic absorption, Raman, Fourier-transform infrared, Mössbauer and X-ray photoelectron spectroscopies.

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Co/Fe 6/2 ferrite spinel consists of granular sphere-like particles of 200 nm whose thickness ranges between 50 and 100 nm and of fibrous particles of several tens of μm whose diameter varies between 50 nm and 1 μm (Figure 1A); the fibrous structure being a network of the granular sphere-like Co/Fe 6/2 particles.

The ^{57}Fe Mössbauer spectra of the spinel obtained at 300K (Figure 1B, 300K) shows a dominant quadrupolar doublet, in addition to a weak magnetic feature. The corresponding spectrum can be well described by means of a quadrupolar component and two magnetic components: the values of isomer shift are unambiguously attributed to the exclusive presence of High Spin (HS) FeIII species. On the contrary, the magnetic sextet is dominant at 77K (Figure 1B, 77K). The values of the isomer shift confirm those observed at 300K, resulting from the exclusive presence of HS FeIII species. The hyperfine structures observed at 300 and 77K is in agreement with a Co/Fe ferrite spinel composed of HS CoII located in tetrahedral sites, Low Spin (LS) CoIII located in octahedral sites and HS FeIII located in octahedral sites. According to the content of Co and Fe and the absence of FeII species, the global composition can be written as $\text{CoII}_{\text{Tetra}}\text{HS1CoIII}_{\text{octa}}\text{LS1.25FeIII}_{\text{octa}}\text{HS0.75O}_4$. The distribution of FeIII and CoIII in the octahedral originates different cationic surroundings for FeIII positions, hyperfine field distribution with values lower than 50T at 77K and finally the evolution of the hyperfine structure versus temperature with a large quadrupolar component at 300K. Experiments conducted by XPS spectroscopy confirmed the global composition.

Figure 9. A) SEM images of the Co/Fe 6/2 ferrite spinel, B) ^{57}Fe Mössbauer spectra of the spinel obtained at 300K and at 77K.

Mots-Clés: Co/Fe Layered Double Hydroxide, High Temperature treatment, Co/Fe 6/2 ferrite spinel, operando XRD, Mössbauer, XPS