

Study of Site Occupancy in $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ Microspheres Based on Mössbauer Analysis

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The crystal structure of $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ ($x = 0, 0.05, 0.1, 0.2, 0.4$), prepared by a solvothermal reaction technique, showed cubic spinel structure with space group $Fd-3m$ based on Rietveld refinement. The lattice constant a_0 increased linearly with the Zn contents from $x = 0$ to 0.4. Field emission scanning electron microscope (FESEM) and high resolution transmission electron microscope (HRTEM) measurements showed that the size of the monodispersed particles was around 300 ~ 500 nm. With increasing Zn contents M_s and H_c values at 295 K increase with x up to 0.05 and then decrease monotonously as x increases above 0.4, respectively. We have analyzed the Mössbauer spectra as 4 set with tetrahedral A site and octahedral B_1 , B_2 , and B_3 sites at 295 K and 4.2 K. From the isomer shift values, the valence states of A , B_1 and B_3 sites were determined to be ferric (Fe^{3+}), while that at B_2 site to be ferrous (Fe^{2+}). The corresponding area ratio of A and B_2 sites decreased by 40 ~ 25 and 20 ~ 8%, while that of B_1 , B_3 sites increased by 40 ~ 52 and 0 ~ 15%, with increasing the Zn contents. This site preference, depending on the amount of Zn^{2+} ion substituted in A and B sites, affects the electron hopping between $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions, and changed the super-exchange interaction $A-O-B$ and $B-O-B$ between A and B sites.

Index Terms—Cation distribution, magnetism, Mössbauer spectroscopy, $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ microspheres.