Mössbauer Studies of Cation Distribution in Zn_xCo_{0.5-x}Fe_{2.5}O₄ Microspheres

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The crystal structure of $Z_{n_x}C_{0,\mathbf{5}_{-x}}Fe_{2,\mathbf{5}}O_{\mathbf{4}}$ ($\mathbf{x}=0,0.25,0.5$), prepared by a solvothermal reaction method, showed cubic spinel structure with space group Fd-3 m based on Rietveld refinement. The lattice constant $\boldsymbol{\alpha_0}$ increased linearly with the Zn concentration from $\boldsymbol{x}=0$ to 0.5. Field emission scanning electron microscope (FE-SEM) measurements showed that the size of the monodispersed particles was around 300–400 nm. With increasing Zn concentration, the saturation magnetization increased from 80.3 to 109.7 emu/g, while the coercivity at 293 K decreased from 893 to 46 Oe, respectively. The magnetocrystalline anisotropy constants (K_1) were determined as 1.62, 1.32, and 1.16 × 10⁸ erg/cm³ for $\boldsymbol{x}=0$, 0.25, and 0.5, respectively, based on the law of approach to saturations (LAS) method. We have investigated the cation distribution by Mössbauer spectroscopy, closely related to K_1 . We have analyzed the recorded Mössbauer spectra as 3 sets with six-lines of tetrahedral \boldsymbol{A} site, and octahedral $\boldsymbol{B_1}$ and $\boldsymbol{B_2}$ sites both at 4.2 and 293 K. From the isomer shift values, the valence states of \boldsymbol{A} and $\boldsymbol{B_1}$ site were determined to be ferric (Fe³⁺), while that at $\boldsymbol{B_2}$ site to be ferrous (Fe²⁺). The corresponding area ratio of \boldsymbol{A} site decreased from 40 to 30 % while that of \boldsymbol{B} site increased from 60 to 70% as the Zn concentration changed from $\boldsymbol{x}=0$ to 0.5 both at 4.2 and 293 K. Here, the changes in the area ratios of \boldsymbol{A} and \boldsymbol{B} sites are due to the changes in the cation distributions at the \boldsymbol{A} and \boldsymbol{B} sites, being originating from the randomly substituted Zn ions in $Z_{1,2}$ Co_{0.8-x} Fe_{2.5} O₄ microspheres.

Index Terms—Znx Coo, 5-x Fe2.5 O4 microspheres, Mössbauer spectroscopy, cation distribution, magnetocrystalline anisotropy.