

Investigation of cation distribution in single crystalline $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$ microspheres based on Mössbauer spectroscopy

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Monodispersed $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$ ($x = 0, 0.25, 0.5, 0.75,$ and 1.0) microspheres were prepared by a solvothermal reaction method. Field emission scanning electron microscope (FESEM) and high resolution transmission electron microscope (HRTEM) measurements showed that the size of the monodispersed particles was around $200 \sim 400$ nm, with single crystalline spots in the selected-area electron diffraction (SAED) patterns. From the detailed Rietveld refinement analysis, the crystal structure was determined to be cubic spinel with lattice constant a_0 , linearly increasing from 8.3956 to 8.4319 Å with the Mn concentration. Also, with Mn concentration, saturation magnetization decreased from 76.9 to 60.3 emu/g at 295 K and 99.5 to 78.4 emu/g at 4.2 K, while coercivity decreased from 66 to 36 Oe at 295 K and 271 to 185 Oe at 4.2 K. We have analyzed the recorded Mössbauer spectra as 3 sets with six lines of tetrahedral A site and octahedral B_1 and B_2 sites at 295 K and 4.2 K. From the isomer shift values, the valence state of the A and B_1 site was determined to be ferric, while the B_2 site was ferrous. The corresponding area ratio of the A site increased from 40 to 50%, while that of the B site decreased from 60 to 50% as the Mn concentration changed from $x = 0$ to 1.0. Here, the changes in the area ratios of A and B sites are due to the changes in the cation distributions at the A and B sites, originating from the randomly substituted Mn ions in $\text{Fe}_{3-x}\text{Mn}_x\text{O}_4$ microspheres. © 2012 American Institute of Physics.

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