

Surface and Size Effects on Magnetic Ordering in Spinel Ferrite Nanoparticles

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Magnesium-substituted copper ferrite nanoparticles with composition $\text{Cu}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ ($0.0 \leq x \leq 1.0$) were synthesized by a polymer-assisted sol-gel self-combustion method using polyethylene glycol (PEG-2000) as both chelating agent and fuel [1]. X-ray diffraction confirms that all compositions crystallize as a single-phase cubic spinel (space group $\text{Fd}\bar{3}\text{m}$) without detectable secondary phases. A systematic lattice expansion is observed with increasing Mg content, with the lattice parameter increasing from $a = 8.3710 \text{ \AA}$ ($x = 0.0$) to $a = 8.3801 \text{ \AA}$ ($x = 0.8$). Williamson–Hall analysis reveals nanocrystalline domains in the range of approximately 8–21 nm, with the largest crystallite size ($\sim 21 \text{ nm}$) and minimum lattice strain occurring at $x = 0.6$.

Room-temperature ^{57}Fe Mössbauer spectra show multiple magnetically split Zeeman sextets coexisting with a paramagnetic doublet, indicating the presence of magnetically ordered cores and superparamagnetic surface-affected regions. The isomer shift values confirm Fe^{3+} ions at both tetrahedral (A) and octahedral (B) sites, while quadrupole splitting reflects local symmetry variations related to cation redistribution and interfacial disorder. The hyperfine magnetic fields indicate that A–O–B superexchange interactions dominate the magnetic coupling, whereas linewidth broadening and reduced internal fields are attributed to superparamagnetic relaxation and surface spin disorder characteristic of nanoscale ferrites [2].

Magnetic hysteresis measurements at 300 K demonstrate a strong correlation between magnetic behavior, particle size, and cation distribution. The saturation magnetization exhibits non-monotonic behavior, reaching a maximum at $x = 0.6$ ($M_S = 26.21 \text{ emu/g}$), followed by a decrease at higher Mg contents. The results highlight the decisive role of nanoscale structure, surface spin disorder, and cation redistribution in the directing of the magnetic properties of $\text{Cu}_{1-x}\text{Mg}_x\text{Fe}_2\text{O}_4$ nanoparticles.

References:

[1] J. Mazurenko, *J. Nano R.* 84 (2024) 95-116

[2] R. Zapukhlyak, *Magn. Magn. Mat.* 587 (2023) 171208

This work was partly supported by Ministry of Education and Science of Ukraine, grants 24BF051-01M (0124U001654), 24BF051-04