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Synthesis, Structural, and Gas Sensing Properties of Rare Earth-Substituted Zinc and Cobalt Ferrites: A Comparative Study

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This study presents a comprehensive comparative analysis of pure and rare earth (RE)-substituted spinel ferrites, including ZnFe_2O_4 , CoFe_2O_4 , $\text{Zn}_{0.05}\text{Co}_{0.05}\text{Fe}_2\text{O}_4$, and their Gd^{3+} - and Nd^{3+} -substituted counterparts, synthesized via the glycothermal method. The substitution of RE ions at Fe^{3+} octahedral sites was employed to investigate their impact on the structural, physicochemical, and gas sensing properties of the materials. XRD confirmed the formation of single-phase cubic spinel structures across all samples. A distinct shift in diffraction peaks toward lower angles upon RE substitution indicated lattice expansion, attributable to the larger ionic radii of Gd^{3+} and Nd^{3+} . The average crystallite sizes, calculated using the Debye-Scherrer equation, were approximately 11.3 nm for ZnFe_2O_4 , 8.2 nm for CoFe_2O_4 , and 22.3 nm for $\text{Zn}_{0.05}\text{Co}_{0.05}\text{Fe}_2\text{O}_4$, with slight variations following rare earth doping. FTIR spectroscopy exhibited characteristic metal-oxygen stretching bands near 540 cm^{-1} and 410 cm^{-1} , corresponding to tetrahedral and octahedral sites, respectively. Shifts and broadening of these peaks in RE-doped samples confirmed modifications in the local bonding environment and cation distribution. HRTEM images revealed partly spherical nanoparticles with uniform size distribution and clearly resolved lattice fringes. Interplanar spacing in RE-substituted samples ($x = 0.10$) was $\sim 0.292\text{ nm}$ for the (220) planes, except for $\text{ZnGd}_{0.10}\text{Fe}_{1.90}\text{O}_4$, which exhibited 0.486 nm spacing in the (111) plane. These values aligned well with XRD data and reflected enhanced surface roughness and boundary strain favourable traits for surface active applications. EPR spectra at room temperature revealed g-values ranging from 2.10 to 2.32. Broader resonance linewidths observed in RE-substituted samples indicated increased magnetic anisotropy and dipolar interactions. Gas sensing tests conducted for NO_2 , H_2S , and CH_4 across a temperature range of $(100 - 300)^\circ\text{C}$ showed promising results. Gd^{3+} -substituted CoFe_2O_4 demonstrated the highest sensitivity toward NO_2 ($\sim 82\%$ at 200°C), attributed to enhanced surface reactivity and elevated oxygen vacancy concentrations. In contrast, Nd^{3+} -substituted ZnFe_2O_4 exhibited high selectivity for H_2S ($\sim 75\%$ response at 150°C), along with rapid response and recovery times, likely due to improved charge carrier mobility and defect-assisted adsorption mechanisms. The co-doped $\text{Zn}_{0.05}\text{Co}_{0.05}\text{Fe}_2\text{O}_4$ displayed a balanced sensing performance across all tested gases, suggesting compositional tunability through dual substitution. This study highlights the significant role of rare earth doping in tuning the structure-property-performance relationship in spinel ferrites. Gas sensing analyses establish a strong foundation for the development of RE-doped ferrites as multifunctional materials suitable for both biomedical and gas sensing applications. Magnetic property measurements are currently underway to further understand the role of RE ions in influencing magnetic ordering and spin dynamics.

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