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XAS of Hydrothermally Grown Fe-Doped ZnO Nanorods

B. Magallanes[1,4], M. Uy-Apostol[2], H. Abe[2,3,4], M. Kimura[2,3], A. Nueva[1], V. Samson[4], T. Matsuoka[1], B. Singidas[1], R. Sarmago[1*]

[1]National Institute of Physics, University of the Philippines-Diliman
[2]Institute of Materials Structure Science (IMSS), KEK
[3]Department of Materials Structure Science, School of High Energy Accelerator Science, The Graduate University for Advanced Science (SOKENDAI)
[3]Graduate School of Science and Engineering, Ibaraki University
[4]DOST-Philippine Nuclear Research Institute

Fe K-edge X-ray absorption spectroscopy was used to evaluate the oxidation state and local coordination of hydrothermally grown Fe-doped ZnO nanorods with nominal Fe concentrations of x = 0.01, 0.03, and 0.05 after annealing from 200 C to 600 C. XANES shows that Fe is predominantly oxidized, with edge positions above metallic Fe and trending toward $FeCl_3$-like behavior at higher annealing temperatures. EXAFS radial-distance spectra show a strong first-shell Fe-O environment and concentration-dependent second-shell features associated with Fe-Zn and Fe-Fe correlations. Together, the data indicate that annealing stabilizes Fe^{3+}-rich local environments and improves Fe-O structural ordering, while higher Fe loading promotes Fe-rich clustering or secondary-phase-like behavior.

XAS experiments were performed to ascertain the state of Fe upon substitution and its occupied site in the ZnO lattice.

Fe-doped ZnO samples show absorption edges significantly above Fe foil and approaching the $FeCl_3$ reference, indicating that Fe is present predominantly in an oxidized state rather than as metallic Fe. Across all doping levels, the edge shifts positively with increasing annealing temperature, consistent with progressive oxidation from Fe^{2+} toward Fe^{3+} as oxygen diffusion and lattice equilibration improve during thermal treatment. A weak but visible pre-edge feature between about 7114 eV and 7115 eV is present in all samples. This feature is consistent with partial site-symmetry distortion and suggests that Fe occupies slightly distorted tetrahedral or octahedral environments compatible with substitution into Zn lattice sites in wurtzite ZnO. The white line near 7130 eV becomes stronger and broader with increasing Fe concentration and annealing temperature, implying increased Fe^{3+} character, stronger Fe-O hybridization, and at 5% Fe, the emergence of Fe^{3+}-rich environments or Fe-O clustering.

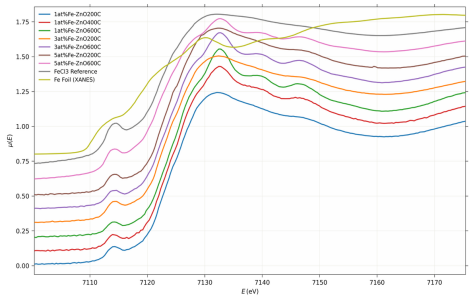

Figure 1. Fe K-edge XANES spectra of Fe-doped ZnO nanorods annealed at different temperatures.

Fourier-transformed EXAFS spectra show the expected coordination features for Fe incorporated into an oxide lattice. A prominent first-shell peak at about R = 1.0 - 1.2 A (uncorrected) corresponds to Fe-O bonding. This peak becomes stronger and sharper with increasing annealing temperature and Fe concentration, indicating higher effective coordination and reduced structural disorder. Samples annealed at 600 C display the most well-defined Fe-O environment, consistent with improved local ordering and stronger bonding. The second major peak, around R = 2.4-2.8 A, reflects contributions from Fe-Zn and Fe-Fe interactions. At 1% Fe, this feature is weak and broad, consistent with mostly isolated substitutional Fe. At 3% Fe, the second-shell amplitude increases, suggesting stronger Fe-Zn coordination and the onset of Fe-Fe interactions. At 5% Fe, the stronger and occasionally split second-shell structure points to substantial Fe-Fe correlation and possible Fe-rich clusters or secondary-phase-like environments, such as Fe_2O_3-like local ordering.

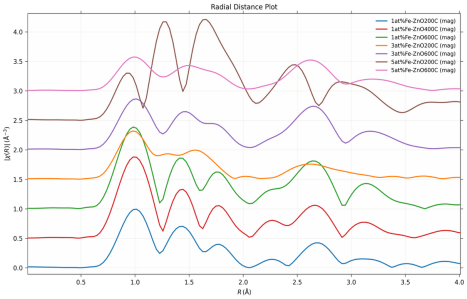

Figure 2. Fourier-transformed EXAFS radial-distance spectra for Fe-doped ZnO nanorods.

The combined XANES and EXAFS support substitutional incorporation of Fe into ZnO at low to moderate doping, with annealing enhancing oxidation toward Fe^{3+} and improving local Fe-O ordering. At higher Fe content, the spectral evolution indicates increasing Fe-Fe correlation and a tendency toward Fe-rich clustering or secondary-phase formation. The thermal treatment therefore plays a dual role: it stabilizes the oxidized Fe environment and improves short-range order, but it may also accentuate dopant aggregation at the highest Fe concentration.

*rvsarmago@up.edu.ph