PRESSURE-INDUCED PHASE TRANSITION IN NANOSTRUCTURED CATION-DEFICIENT $ZN_{0.34}FE_{2.53}\square_{0.13}O_4$ FERRITE

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Cation-deficient spinel ferrite nanoparticles are of strong interest because point defects and nanoscale strain can markedly tune electronic, magnetic, and transport properties. In particular, cation vacancies modify local bonding and the compressibility of oxygen polyhedra, potentially altering pressure-induced transformation pathways compared with stoichiometric $ZnFe_2O_4$, whose high-pressure behavior is better established [1,2].

Nanostructured cation-deficient zinc ferrite $Zn_{0.34}Fe_{0.53}\square_{0.13}O_4$ (□ - denotes cation vacancies) with mean particle size ~14 nm were prepared by thermal decomposition of metal acetylacetonates in a high-boiling solvent under inert atmosphere. High-pressure measurements including X-ray diffraction (XRD) up to 34 GPa and Raman spectroscopy up to ~29 GPa were conducted in a diamond anvil cell using an alcohol-based pressure medium.

At ambient conditions the sample crystallizes in the cubic spinel structure (space group Fd–3m) with lattice parameter a ≈ 8.331 Å. With increasing pressure, cubic reflections shift smoothly up to ~18 GPa. Above ~18 GPa, new diffraction features appear and characteristic cubic peak intensities are suppressed, indicating the onset of a structural transformation. Among tested post-spinel models, an orthorhombic Bbmm ($CaTi_2O_4$-type) phase provides the best fit to high-pressure XRD patterns. The transformation is strongly broadened: the orthorhombic fraction is already detectable near the onset (~12% at ~18 GPa) and rises to ~43% at ~32–34 GPa, consistent with extended phase coexistence typical for nanomaterials with internal strain and defect-related local distortions.

Equation-of-state analysis yields a bulk modulus $B_0 \approx 185$ GPa for the cubic phase (with fixed $B' \approx 4$) and $B_0 \approx 210$ GPa for the orthorhombic phase, consistent with densification in the post-spinel structure. The orthorhombic lattice compresses anisotropically (the b axis is more compressible than a and c). In the spinel phase, octahedral (B-site) Fe–O bonds contract more strongly than tetrahedral (A-site) Fe–O bonds, consistent with vacancies predominantly affecting octahedral environments.

Raman spectra show the expected spinel modes ($A_{1g} + E_g + 3F_{2g}$). Above ~18 GPa, a clear splitting/restructuring of the A_{1g} band (~ 620–675 cm^{-1}) is observed, in agreement with XRD evidence for the emergence of the orthorhombic component and indicating modified local coordination/force constants, similar in spirit to high-pressure Raman signatures in $ZnFe_2O_4$ [2].

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[2] Z. Wang, et al. (2003). High pressure Raman spectroscopy of spinel-type ferrite $ZnFe_2O_4$. Journal of Physics and Chemistry of Solids. 64(12), 2517-2523.