

Structural and vibrational properties of CoFe_2O_4 and $\text{Zn}_{0.34}\text{Fe}_{2.53}\square_{0.13}\text{O}_4$ ferrites at high-pressure

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Ferrite oxide compounds of MFe_2O_4 ($\text{M} = \text{Co}, \text{Cu}, \text{Mn}, \text{Ni}, \text{Zn}$) with spinel-type crystal structures are being actively researched due to their attraction from both basic and practical viewpoints. These materials, both in bulk and nanosize, have drawn significant interest due to their unique magnetic properties, such as various magnetic phase transitions, topological destruction effects, multiferroic behavior, spin reorientation transitions, spin liquid formation, and spin glass states. The outstanding properties of ferrites make them appropriate for a wide range of technological applications, including transformer cores, radio frequency circuits, magnetic refrigerators, antenna rods, data storage devices, and fluid technology.

Ferrites with a spinel structure exhibit varied cation distributions in tetrahedral (A) and octahedral (B) oxygen coordination depending on the chemical composition and size of nanoparticles, resulting in significant changes in their physical properties. In particular, pressure causes a controlled modification of interatomic distances and bond angles, resulting in changes in the physical properties of ferrite oxides. Therefore, we studied the crystal structure and vibrational spectra of bulk CoFe_2O_4 ferrite and $\text{Zn}_{0.34}\text{Fe}_{2.53}\square_{0.13}\text{O}_4$ cation-deficient nanostructured zinc ferrite (where \square denotes the cation vacancies) using X-ray diffraction and Raman spectroscopy under high pressure.

In there, ferrite CoFe_2O_4 represents an inverse spinel structural type under high pressure up to 35 GPa. We have found a crystal structural transition from the initial cubic phase of $\text{Fm}\bar{3}\text{m}$ symmetry to the orthorhombic CaTi_2O_4 -type phase with space group Bbmm at the pressure of about 22 GPa. It is characterized by a decreasing suppression of the initial cubic phase and an increase in the volume fraction of the orthorhombic phase. The two-phase state is observed in the pressure range of 22 GPa to 30 GPa. Besides, we also discovered the influence of cation vacancies on the pressure dependences of the structural parameters of nanostructured zinc ferrite $\text{Zn}_{0.34}\text{Fe}_{2.53}\square_{0.13}\text{O}_4$ (where \square denotes the cation vacancies) in the pressure range of 0-34 GPa. Our results indicate a phase transition from the initial cubic phase with space group $\text{Fd}\bar{3}\text{m}$ to a high-pressure phase with orthorhombic symmetry of Bbmm at pressures above 18 GPa.

Phase transition of the above two ferrites is accompanied by changes in lattice parameters, unit cell volume, interatomic bond lengths, and vibration mode frequencies.

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