

Structural relaxation in tetrahedrally coordinated Co²⁺ along the gahnite-Co-aluminate spinel solid solution

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ABSTRACT

The structural relaxation around the Co²⁺ ion along the gahnite (ZnAl₂O₄)-Co-aluminate (CoAl₂O₄) join was investigated by a combined X-ray diffraction (XRD) and electronic absorption spectroscopy (EAS) approach. Monophasic spinel samples (Zn_{1-y}Co_yAl₂O₄ with $y = 0, 0.25, 0.5, 0.75,$ and 1 apfu) were obtained through solid-state reaction (1300 °C with slow cooling). The cobalt incorporation induces a linear increase of the unit-cell parameter (a) accompanied by an increasing inversion parameter (up to 0.07) so that the Co²⁺ for Al³⁺ substitution in the octahedral site is, at a first approximation, the cause of the lattice expansion. However, a careful consideration of T-O distances highlights the role played by an enhanced covalence degree of Zn-O bonds. The optical spectra are characterized by the occurrence of electronic transitions of Co²⁺ in tetrahedral coordination affected by a strong spin-orbit coupling, causing a threefold splitting of spin-allowed bands. Further complications stem from mixing of quadruplet and doublet states (leading to a consistent intensity gain of spin-forbidden bands) and vibronic effects (producing intense sidebands). Crystal field strength goes from 4187 to 4131 cm⁻¹ with increasing cobalt amount, while the Racah B parameter is in the 744–751 cm⁻¹ range ($C \sim 3375$ cm⁻¹). To achieve a reliable estimation of the local Co-O distance, the tetrahedral distance evolution was recast to eliminate the effects of the inversion degree. By this way, a relaxation coefficient as low as $\epsilon = 0.47$ was obtained, i.e., significantly smaller than literature data for other spinel systems. The gahnite-Co-aluminate join seems to be constrained by the strong preference of Zn²⁺ for the tetrahedral site in which its enhanced covalency can be exerted, limiting the cation exchange between tetrahedral and octahedral sites as well as the lattice flexibility.

Keywords: Gahnite, Co-aluminate, spinel structure, X-ray powder diffraction, Rietveld refinement, electronic absorption spectroscopy, structural relaxation