

Effect of tetrahedrally coordinated Co²⁺ in spinel and melilite solid solutions.

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A fundamental problem in determining the chemical and physical properties of a crystal structure is the precise distribution of atoms in its lattice. While in the early application of X-ray diffraction, the lattice constant as well as the mean atomic bond distances were assumed to linearly scale with the composition of the investigated structures (i.e. Vegard law), it is now well known that many solid solutions deviate from the linearity predicted by the Vegard law. The study of those deviations are of fundamental importance when the intrinsic properties (physical, chemical, mechanical, electric, magnetic, ...) of minerals, compounds, or alloys are considered. Since no single experimental method can determine the average long-range crystal structure and, at the same time, give indication on the local distances between the central ion and its surrounding atoms, the long- vs. short-range properties of a crystal structure along a join have to be obtained through the combination of diffraction and spectroscopy techniques. In this work, the structural relaxation around four-fold coordinated Co²⁺ ion along the gahnite (ZnAl₂O₄) – Co-aluminate (CoAl₂O₄) as well as the hardystonite (Ca₂ZnSi₂O₇) – Co-åkermanite (Ca₂CoSi₂O₇) solid solutions (ss) was investigated by a combined X-ray powder diffraction (XRPD) and electronic absorption spectroscopy (EAS) approach. Monophasic samples were obtained through solid state reaction synthesis. Distinct behaviors of the two structure-types are observed as a function of the cobalt incorporation. While in the spinel ss the Co²⁺ doping induces a linear increase of the unit-cell parameter, the melilite ss is characterized by a non-linear variation of the lattice constants, revealing a negative excess volume of mixing due to the single isovalent substitution of Co for Zn in the tetrahedral site. A careful inspection of T–O distances for both spinel- and melilite-type structures 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 (plus the lowering of point symmetry in melilites) causing a 3-fold splitting of spin-allowed bands. In agreement with the diffraction data, deconvolution of the optical spectra show a progressive decreasing of the crystal field strength parameter 10Dq moving toward the cobalt end-members, meaning that the local cobalt-oxygen bond distance, <Co–O>_{local}, increases along the join with the amount of cobalt. In order to achieve a reliable estimation of the local Co–O distance for the spinel ss, the tetrahedral distance evolution was recast to eliminate the effects of the inversion degree, although very small (i.e. the maximum inversion degree was 0.07, found for the Co-aluminate end member). By this way, a relaxation coefficient as low as $\varepsilon=0.47$ was obtained, i.e. significantly smaller than literature data for other spinel systems. At variance with this latter value, the calculated structural relaxation for the Ca₂(Zn_{1-x}Co_x)Si₂O₇ join was $\varepsilon=0.69$ (far from the Vegard's prediction, i.e. $\varepsilon=0$). This difference is consistent with the largest constraints existing on the spinel structure, based on cubic closest packing, compared to the more flexible layered melilite structure.