

Tetrahedrally-coordinated Co²⁺ in oxides and silicates: effect of local environment on optical properties

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The Co²⁺ ion in fourfold coordination provides d-d electronic transitions with the strongest optical density among oxides and silicates. For this reason, it is largely used in pigments and dyes to get blue shades detectable down to very low cobalt concentration. Such a low detection limit turns the Co²⁺ ion into a suitable probe to disclose by means of optical spectroscopy the local ligand environment in a wide range of materials. Even if extensively studied in organometallic complexes, an in-depth investigation of optical properties of Co²⁺ in tetrahedral coordination into oxidic structures is limited to some case-studies in minerals and synthetic analogues (gahnite, willemite, calcium cobalt selenite) [1-3]. The present study represents a first attempt to outline crystal structural (by XRD) and optical parameters (10Dq, Racah B and C, band splitting by EAS) in 15 samples of oxides and silicates providing a set of different local fourfold coordination around Co²⁺ added as a dopant (from 0.2 to 0.3 mol). Subtle variation of crystal field strength and interelectronic repulsion can be appreciated in gahnite, hardystonite, Ca-Sr-Ba-åkermanite, willemite (where Co²⁺ substitutes Mg²⁺ or Zn²⁺ by 0.3 apfu) as well as in gehlenite, hibonite and fresnoite (where Co²⁺ substitutes Al³⁺ or Ti⁴⁺ by 0.2 apfu due to charge mismatch). Spectral interpretation is not straightforward owing to the occurrence of different Co²⁺ bands: spin-allowed electronic transitions (totally or partially Laporte-forbidden); spin-forbidden electronic transitions (with or without some energy 'stealing' from the spin-allowed ones); two- or three-fold split bands due to both lowering of point symmetry at the tetrahedron and spin-orbit coupling; further bands of uncertain attribution, presumably caused by vibronic transitions. Optical spectra vary significantly even for apparently small changes in the long-range CoO₄ arrangement as measured by XRD. The predictable relationship between 10Dq and the mean Co-O distance is satisfied, but the accommodation into small AlO₄ sites in gehlenite and hibonite (or otherwise in the tetragonal pyramid TiO₄+1 of fresnoite) implies a significant structural relaxation around the Co²⁺ ion. A negative correlation of crystal field strength and interelectronic repulsion data suggests that a certain enhancement of the covalence degree (i.e. lower Racah B) accompanies shorter Co-O distances (i.e. higher 10Dq). The 3-fold splitting of the spin-allowed 4T₁(F) and 4T₁(P) bands can be related to the angular distortion of the CoO₄ tetrahedra. Overall, changes of spectral features of tetrahedrally-coordinated Co²⁺ can be attributed to different local arrangement of ligands with some effect traceable to second next neighbours.

References

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