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Tetrahedrally coordinated Co^{2+} in oxides and silicates: Effect of local environment on optical properties

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ABSTRACT

The Co^{2+} ion in fourfold coordination provides *d-d* electronic transitions with the strongest optical density among oxides and silicates. For this reason, it is widely used in pigments and dyes to get blue shades detectable down to a very low cobalt concentration. Such a low-detection limit turns the Co^{2+} ion into a suitable probe to disclose the local ligand environment in a wide range of materials by means of optical spectroscopy. Even if extensively studied in organometallic complexes, an in-depth investigation of optical properties of Co^{2+} in tetrahedral coordination into oxidic structures is limited to some case-study in minerals and synthetic analogs (spinel, zincite, gahnite, willemite, calcium cobalt selenite). The present study represents an attempt to outline crystal structural (long-range metal–oxygen distances, O–T–O bond angles, and distortion parameters by XRD) and optical parameters ($10Dq$, Racah B and C, band splitting by EAS) in 13 samples of oxides and silicates providing a wide set of different local fourfold coordination around Co^{2+} added as a dopant. Subtle variations of crystal field strength and interelectronic repulsion can be appreciated in gahnite, Ca-Sr-hardystonite, Ca-Sr-Ba-åkermanite, willemite, $Ba_2MgSi_2O_7$ melilite-related (where Co^{2+} substitutes Mg^{2+} or Zn^{2+} by 0.25–0.3 apfu) as well as in gehlenite and fresnoite (where Co^{2+} substitutes Al^{3+} and Ti^{4+}, respectively, by 0.2 apfu due to charge mismatch). Results are compared with literature data about hibonite, spinel *s.s.*, staurolite, yttrium garnets, and zincite. Spectral interpretation is not straightforward owing to the occurrence of different Co^{2+} bands: spin-allowed and spin-forbidden electronic transitions, two- or threefold split due to both lowering of point symmetry at the tetrahedron and spin-orbit coupling plus presumably vibronic transitions. Optical spectra vary significantly even for apparently small changes in the long-range CoO_4 arrangement as measured by XRD. The expected relationship between $10Dq$ and the mean Co–O distance is fulfilled, but the accommodation into small AlO_4 sites in gehlenite (YAG and hibonite) implies a significant structural relaxation around the Co^{2+} ion. The threefold splitting of the spin-allowed $^4T_1(F)$ and $^4T_1(P)$ bands can be related to the angular distortion of the CoO_4 tetrahedra. Overall, changes of spectral features of tetrahedrally coordinated Co^{2+} can be attributed to different local arrangement of ligands with an effect correlated to the second nearest neighbors by the bond valence theory. This was disclosed contrasting $10Dq$ with the ratio of the observed and ideal bond valence sum for the polyhedra sharing oxygen with the Co-centered tetrahedron.

Keywords: Co^{2+} ion, crystal structure, site distortion, optical properties, tetrahedral coordination