American Mineralogist, Volume 95, pages 456–462, 2010

Structural relaxation around Cr^{3+} and the red-green color change in the spinel (sensu stricto)-magnesiochromite ($MgAl_2O_4$-$MgCr_2O_4$) and gahnite-zincochromite ($ZnAl_2O_4$-$ZnCr_2O_4$) solid-solution series

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Abstract

Optical absorption spectra of flux-grown single crystals in the spinel s.s.-magnesiochromite and gahnite-zincochromite solid solutions were recorded with the aim of exploring variations in local Cr-O bond distance as a function of composition. With increasing Cr contents, the crystals vary in color from pale red to intensely red to dark greenish. These variations are reflected in the optical spectra by the position and intensity of the two spin-allowed electronic *d-d* transitions in six-coordinated Cr^{3+} at ~18 000 (ν_1) and 25 000 cm^{-1} (ν_2). From the shift of the ν_1 band position, a decrease in crystal field splitting, 10*Dq*, for six-coordinated Cr^{3+} with increasing Cr contents is evident in both solid-solution series. Based on published Cr-O bond distances for the CrO_6 polyhedra in magnesiochromite and zincochromite of 1.995 and 1.991 Å, respectively, and applying the ligand field relationships, local Cr-O bond distances in gahnite and spinel with Cr contents at trace levels are determined to be 1.974(2) and 1.960(3) Å, respectively. These local Cr-O distances result in relaxation parameters (ε) equal to 0.69(2) and 0.60(3) for Cr-O bonds in the $Mg(Al_{1-x}Cr_x)_2O_4$ and $Zn(Al_{1-x}Cr_x)_2O_4$ series, respectively. However, the presently obtained Racah *B* values indicate increasing Cr-O bond covalency with increasing Cr^{3+} contents. This suggests that color changes and accompanying 10*Dq* variations may be due to variations in Cr-O bond covalency along the two solid-solution series, without or with very minor local Cr-O bond distance variation. Consequently, the ε values obtained from the present optical absorption spectra should be regarded as minimum values.

Keywords: Crystal synthesis, optical spectroscopy, structural relaxation, spinel, gahnite, Cr^{3+}