



Structural relaxation and colour in the spinel-magnesiochromite (MgAl₂O₄-MgCr₂O₄) and gahnite-zincochromite (ZnAl₂O₄-ZnCr₂O₄) solid solution series

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Recent studies on binary mineral solid solution series utilising synchrotron based x-ray absorption spectroscopies have indicated strong structural relaxation. For instance, it has been suggested that the real Cr-O bond distances remain nearly constant (relaxation parameter (ε) of 0.85, where $\varepsilon=1$ equals full relaxation) over the entire compositional range of the MgAl₂O₄-MgCr₂O₄ series (Juhin et al. 2007).

In the present study we have measured room temperature optical absorption spectra of synthetic single crystals of the ZnAl_{2-2x}Cr_{2x}O₄ (0.03 ≤ x ≤ 1) and MgAl_{2-2x}Cr_{2x}O₄ (0.02 ≤ x ≤ 1) series with the aim to explore the real architecture of the structure and in particular the Cr-O distance as function of composition.

Our crystals were synthesized by means of flux-growth methods under atmospheric pressure and temperature profiles resulting in an estimated cation ordering temperature of ca 850°C. Crystals close to the spinel (*sensu stricto*) and gahnite end-member compositions were faintly red in colour. With increasing Cr-content the crystals become more intensely red-coloured and at the higher Cr-contents there is a distinct shift towards a dark greenish colouration. These colour changes are reflected in the measured optical spectra by the position and intensity of the two spin-allowed electronic d-d transitions in octahedrally coordinated Cr³⁺ at ca 18000 (⁴A_{2g}-⁴T_{2g} (⁴F) transition) and 25000 cm⁻¹ (⁴A_{2g}-⁴T_{1g} (⁴F) transition). The energy of the first transition (ν_1 -band) is ca 1200 cm⁻¹ lower in magnesiochromite than in weakly Cr-doped spinel (x=0.02) and ca 1400 cm⁻¹ lower in zincochromite than in gahnite with the lowest Cr-content (x=0.03). Concomitantly the energy of the second transition (ν_2 -band) decreases with increasing Cr-content in both series by ca. 1800 cm⁻¹.

From the position of the ν_1 -band, a decrease in crystal field splitting, 10Dq, for six-coordinated Cr³⁺ with increasing Cr-content in the MgAl_{2-2x}Cr_{2x}O₄ and ZnAl_{2-2x}Cr_{2x}O₄ series of 6.5 and 7.5 %, respectively, is determined. Based on a Cr-O bond distance for the CrO₆ polyhedron in magnesiochromite and zincochromite of 1.995 and 1.991 Å respectively (O'Neill and Dollase, 1994) and applying the ligand field relationship 10Dq ≈ C · R⁻⁵ (R equals the M-O distance of the MO₆-polyhedron), Cr-O bond distances in gahnite and spinel with Cr-contents at trace levels are determined to 1.959 and 1.969 Å, respectively. These M-O bond distances are considerably longer than the M-O distances determined for end member gahnite and spinel by XRD-methods (1.9137 and 1.9280 Å, respectively; O'Neill and Dollase, 1994) and shows that there is considerable structural relaxation of M-O bonds in the two present spinel series. The relaxation parameter, ε , determined from the optical absorption spectra is 0.59 and 0.63 for the ZnAl_{2-2x}Cr_{2x}O₄ and MgAl_{2-2x}Cr_{2x}O₄ and series, respectively. These values are lower than those suggested from X-ray absorption spectroscopy (Juhin et al. 2007), which may be explained by second nearest neighbour interactions. In contrast to what may be expected, the interelectronic repulsion parameter, B, for ^{VI}Cr³⁺ decreases with increasing Cr-content and apparent Cr-O bond length in both of the present spinel series. This indicates that interactions between Cr-atoms in neighbouring octahedra become important at increasing Cr-content and result in more covalent Cr-O bonds. This in turn suppresses the energy of ⁴A_{2g}-⁴T_{2g} (⁴F) transition (and calculated 10Dq-values) in octahedrally coordinated Cr³⁺. Consequently, the values of structural relaxation parameters determined from the optical absorption spectra must be regarded as minimum numbers.

Literature

Juhin, A., Calas, G., Cabaret, D. and Galoisy, L. (2007): Structural relaxation around Cr³⁺ in MgAl₂O₄. Physical

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O'Neill, H.St.C. and Dollase, W.A. (1994): Crystal structures and cation distributions in simple spinels from powder XRD structure refinements: MgCr_2O_4 , ZnCr_2O_4 , Fe_3O_4 and the temperature dependence of cation distribution in ZnAl_2O_4 . *Physics and Chemistry of Minerals*, 20, 541-555.