Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Magnesium aluminium chromite

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Received 12 November 2004
Accepted 4 January 2005
Online 12 February 2005

The cation distribution in a natural magnesium aluminium chromite spinel (cubic, space group $Fd\bar{3}m$), $Al_{0.41}Cr_{1.42}Fe_{0.65}Mg_{0.4}O_4$, was determined by electron-microprobe analysis, Mössbauer spectroscopy and single-crystal X-ray analysis. Several structural models of the octahedral and tetrahedral cation distributions were tested; the most probable is $(Mg^{2+}_{0.40\,(11)},Al^{3+}_{0.28\,(5)},Fe^{2+}_{0.39\,(4)})[Al^{3+}_{0.13\,(5)},Cr^{3+}_{1.42\,(6)},Fe^{3+}_{0.26\,(4)},\Phi_{0.19}]O_4^{2-}$, where (...) and [...] represent the tetrahedral and octahedral sites, respectively, and Φ represents a vacancy.

Comment

Chromite, $(Fe)[Cr]_2O_4$, which belongs to the spinel group of minerals, is an important material widely used in the metallurgical and chemical industries (Rollinson, 1973). The first structural studies concerning spinels were performed by Bragg (1915) and Nishikawa (1915). Spinels are mixed-valence compounds, AB_2X_4, and for most compounds, X is oxygen, A is a divalent cation and B is a trivalent cation. The spinels may be classified as normal spinel, $(A)[B_2]O_4$, and inverse spinel, $(B)[A,B]O_4$, where (...) and [...] represent the tetrahedral and octahedral sites, respectively. In general, $(A_{1-i}, B_i)[A_i, B_{2-i}]O_4^{2-}$ represents a partially inverse spinel, where i is the degree of inversion. Chromite is a normal spinel with cubic $Fd\bar{3}m$ symmetry. Several overviews of spinels and their properties are available in the literature (O'Neill & Navrotsky, 1983; Valenzuela, 1994, and references therein).

In natural chromites, chromium and iron may be replaced by other metallic cations with similar charges and/or ionic radii. Therefore, because a wide variety of solid solutions may form in natural spinels, it can be helpful to use complementary experimental techniques in order to establish their structures. This strategy can be seen in several studies concerning chromites, *e.g.* powder and single-crystal X-ray diffraction (Salviulo *et al.*, 2000), and Mössbauer spectroscopy and single-crystal X-ray diffraction (Lenaz *et al.*, 2004; Figueiras & Waerenborgh, 1997).

This work forms part of a project involving the structural studies of natural spinels from Brazil. In particular, attention is focused on the cation distribution in this class of compounds.

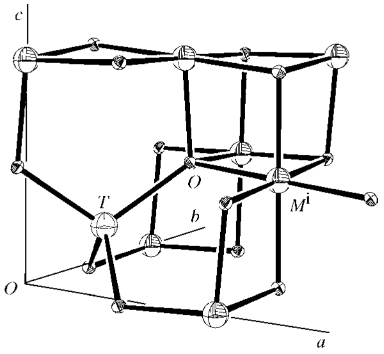

Figure 1
An *ORTEP-3* (Farrugia, 1997) plot of the chromite structure from Piumhi. T (large ellipsoid with boundary) represents the tetrahedral site containing the Fe^{2+}, Mg^{2+} and Al^{3+} ions. M (large ellipsoid with shading) represents the octahedral site containing the Cr^{3+}, Fe^{3+} and Al^{3+} ions. The ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $x, y - \frac{1}{4}, z - \frac{1}{4}$.]

The structures of a magnesium- and aluminium-rich natural chromite have been analysed by single-crystal X-ray diffraction combined with Mössbauer spectroscopy and electron microprobe analysis. Single crystals were collected at a geological site near Piumhi town (20° 22′ 00″ S and 45° 56′ 00″ W), Minas Gerais, Brazil. A typically well shaped chromite single crystal was mounted on a diffractometer to perform the X-ray data collection. This same crystal was later characterized by electron microprobe analysis as $(Mg_{0.45\,(8)},Al_{0.41\,(5)},Cr_{1.49\,(4)},Fe_{0.65\,(6)})O_4$ (s.u. values are calculated from measurements on four different points using MgO, Al_2O_3, Cr_2O_3 and Fe_2O_3 as standards. Mössbauer spectra of a powder sample showed that around 70% of the total Fe content is tetrahedral Fe^{2+} and 30% is octahedral Fe^{3+}. The refined chemical formula and cation distribution is $(Mg^{2+}_{0.40\,(11)},Al^{3+}_{0.28\,(5)},Fe^{2+}_{0.39\,(4)})[Al^{3+}_{0.13\,(5)},Cr^{3+}_{1.42\,(6)},Fe^{3+}_{0.26\,(4)},\Phi_{0.19}]O_4^{2-}$, where Φ represents the vacancy. This composition is in agreement with the microprobe analysis and the Mössbauer data. Moreover, the tetrahedral site occupancy is 1.1 (1) and the crystal electroneutrality is maintained with a total cation charge of +7.9 (3). Fig. 1 shows the structure of the Mg/Al-rich chromite. As can be seen, it has a trigonal distortion in the [111] direction. Table 1 gives selected geometric parameters.

Experimental

Single crystals were extracted from rocks by mechanical separation, followed by a bath in deionized water. The aluminosilicate minerals were dissolved by repeated treatment with hot HCl and HF solutions. The residue was rinsed with distilled water and the purity of the crystals was checked by powder X-ray diffraction.

Crystal data

$Al_{0.41}Cr_{1.42}Fe_{0.65}Mg_{0.40}O_4$
$M_r = 194.94$
Cubic, $Fd\bar{3}m$
$a = 8.31058\ (5)$ Å
$V = 573.98\ (1)$ Å^3
$Z = 8$
$D_x = 4.512$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 98 reflections
$\theta = 20.0$–$32.8°$
$\mu = 8.67$ mm^{-1}
$T = 298\ (1)$ K
Octahedron, black
0.07 × 0.07 × 0.07 mm

DOI: 10.1107/S0108270105000338

Data collection

Siemens *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: analytical (Lundgren, 1982)
$T_{\min} = 0.385$, $T_{\max} = 0.445$
5083 measured reflections
220 independent reflections
219 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.049$
$\theta_{\max} = 56.4°$
$h = -1 \rightarrow 19$
$k = -19 \rightarrow 19$
$l = -19 \rightarrow 19$
3 standard reflections every 297 reflections intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.015$
$wR(F^2) = 0.041$
$S = 1.40$
220 reflections
14 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0138P)^2 + 0.6778P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.96$ e Å^{-3}
$\Delta\rho_{\min} = -0.69$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0152 (10)

Table 1
Selected geometric parameters (Å, °).

T represents the tetrahedral site containing the Fe^{2+}, Mg^{2+} and Al^{3+} ions, and *M* represents the octahedral site containing the Cr^{3+}, Fe^{3+} and Al^{3+} ions.

O—*M*	1.9790 (4)	O—*T*	1.9797 (8)
O—*M*—O	83.81 (3)	O—*T*—O$^{\text{ii}}$	109.5

Symmetry code: (ii) $x, -y + \frac{1}{4}, -z + \frac{1}{4}$.

The microprobe analysis result $(Mg_{0.45\,(8)}Al_{0.41\,(5)}Cr_{1.49\,(4)}Fe_{0.65\,(6)})O_4$ was used as a first approximation for cation substitution. In all refinements, different atoms on the same site were constrained to share the same anisotropic displacement parameter. Models with an inverse distribution or a partial degree of inversion were rejected for chemical reasons and on the basis of the refinement results. Four normal spinel models have been tested:

(i) Model 1: $(Mg^{2+}_{0.52\,(1)},Fe^{2+}_{0.48\,(1)})[Cr^{3+}_{1.57\,(3)},Al^{3+}_{0.43\,(3)}]O_4^{2-}$, with $R(F_o) = 0.0163$, $wR(F_o^2) = 0.0456$, $S(F_o^2) = 1.477$ and NP = 12 (where NP is the number of parameters varied).

(ii) Model 2: on the basis of the Mössbauer data, Fe^{3+} was added to the octahedral site, keeping the total amount of iron given by the electron microprobe analysis. The refined formula is $(Mg^{2+}_{0.51\,(1)},Fe^{2+}_{0.49\,(1)})[Al^{3+}_{0.47\,(3)},Cr^{3+}_{1.37\,(3)},Fe^{3+}_{0.16\,(1)}]O_4^{2-}$, $R(F_o) = 0.0167$, $wR(F_o^2) = 0.0470$, $S(F_o^2) = 1.478$ and NP = 13. From a statistical point of view, this model is not better than model 1.

(iii) Model 3: according to O'Neill & Navrotsky (1983, 1984), Al^{3+} in spinels can be found on both octahedral and tetrahedral sites. A refinement with an additional constraint on the total Al content yielded the formula $(Mg^{2+}_{0.26\,(5)},Al^{3+}_{0.30\,(5)},Fe^{2+}_{0.44\,(1)})[Al^{3+}_{0.11\,(5)},Cr^{3+}_{1.49\,(3)},Fe^{3+}_{0.21\,(1)},\Phi_{0.19}]O_4^{2-}$. with $R(F_o) = 0.0155$, $wR(F_o^2) = 0.0409$, $S(F_o^2) = 1.406$ and NP = 14. This refinement clearly indicates that Al^{3+} is present at both sites, but the Mg^{2+} content disagrees with the chemical analysis.

(iv) Model 4: the total tetrahedral site occupancy is relaxed, which yields the formula $(Mg^{2+}_{0.40\,(11)},Al^{3+}_{0.28\,(5)},Fe^{2+}_{0.39\,(4)})[Al^{3+}_{0.13\,(5)},Cr^{3+}_{1.42\,(6)},Fe^{3+}_{0.26\,(4)},\Phi_{0.19}]O_4^{2-}$, with $R(F_o) = 0.0155$, $wR(F_o^2) = 0.0408$, $S(F_o^2) = 1.402$ and NP = 14. Although it does not seem to be statistically different from model 3, this is the preferred model since electroneutrality is reached with a total positive charge of 7.9 (3), against 7.7 (2) for model 3.

Data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2003).

This work was supported by the Minas Gerais Foundation for Research Development, FAPEMIG (grant No. CEX 1123/90). JSS is grateful to the Brazilian Science Research Council, CNPq, for providing a graduate fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1063). Services for accessing these data are described at the back of the journal.

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