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Inversion parameter of the $CoGa_2O_4$ spinel determined from single-crystal X-ray data

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(Co/Ga-O) = 0.002 Å
Disorder in main residue
R factor = 0.017
wR factor = 0.023
Data-to-parameter ratio = 23.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Single crystals of cobalt digallium tetraoxide, $CoGa_2O_4$, have been grown by cooling slowly a 1:1 mixture of CoO and Ga_2O_3 from 1473 K to room temperature under the presence of a PbF_2 flux. The compound crystallizes with the cubic spinel structure (space group $Fd\bar{3}m$). The occupancy refinement based on single-crystal X-ray diffraction data shows $CoGa_2O_4$ to be a largely normal spinel with an inversion parameter of 0.575 (4), resulting in a structural formula of $^{IV}(Co_{0.425}Ga_{0.575})^{VI}[Co_{0.575}Ga_{1.425}]O_4$, where $^{IV}()$ and $^{VI}[]$ represent the tetrahedral and the octahedral sites, respectively.

Comment

Typical cation arrangements of spinels, $^{IV}(A_{1-x}B_x)^{VI}[A_xB_{2-x}]O_4$, are normal-type ($x$ = 0) and inverse-type (x = 1), where $^{IV}()$ and $^{VI}[]$ represent the tetrahedral and the octahedral sites, respectively. The inversion parameter (x) depends on the species of constituent cations and temperature of equilibrium; its value approaches $\frac{2}{3}$, corresponding to a completely random cation distribution between the two sites, with increasing temperature. In many spinels, the x values observed at ambient conditions are in the range $0 < x < \frac{2}{3}$ or $\frac{2}{3} < x < 1$; the former case is termed 'largely normal spinel' and the latter 'largely inverse spinel'.

Physical properties of spinels are known to depend largely on their cation distributions (*e.g.* Gorter, 1950; Schulkes & Blasse, 1963; Blasse, 1966). Moreover, investigations of cation distributions in spinels can provide an insight into the relative stability of cations in tetrahedral and octahedral coordination. From these points of view, the crystal chemistry of spinels has been intensively systematized (Hill *et al.*, 1979; Sickafus & Wills, 1999). However, as to the cation distributions of some spinel compounds, there have been disagreements between different studies. $CoGa_2O_4$ is one such example [x = 0.6 (largely normal spinel) at 40 K (Soubeyroux *et al.*, 1986), $x \simeq 1$ (largely inverse spinel) for the sample synthesized hydrothermally at 703 K (Christensen *et al.*, 1995), x = 0.72 (largely inverse spinel) for the sample quenched from 1473 K (Porta & Anichini, 1980)]. These disagreements may be because displacement parameters, correlated greatly with occupancies, were not determined in these previous studies, which were performed on the basis of powder diffraction data. We report here the inversion parameter of the $CoGa_2O_4$ spinel determined from a full structure refinement based on single-crystal data, including anisotropic displacement parameters.

The refinement resulted in an inversion parameter of x = 0.575 (4), which shows that $CoGa_2O_4$ is a largely normal spinel with a structural formula of $^{IV}(Co_{0.425}Ga_{0.575})^{VI}[Co_{0.575}Ga_{1.425}]O_4$. This result shows that Ga^{3+} in the $CoGa_2O_4$ spinel prefers the octahedral site rather than the tetrahedral

site, in contradiction to every effect of cation size ($r_{Ga} < r_{Co}$; Shannon, 1976), electronegativity ($\chi_{Co} = 1.47 < \chi_{Ga} = 2.10$; Sanderson, 1967) and the ligand field of Co^{2+}. Such a peculiar cation distribution was also reported in $MgAl_2O_4$ (*e.g.* Maekawa *et al.*, 1997; Ito *et al.*, 2000; Nakatsuka *et al.*, 2004), $CoAl_2O_4$ (Greenwald *et al.*, 1954; Toriumi *et al.*, 1978; Porta & Anichini, 1980; O'Neill, 1994; Nakatsuka *et al.*, 2003), $FeAl_2O_4$ (Larsson *et al.*, 1994; Harrison *et al.*, 1998) and $MnGa_2O_4$ spinels (García Casado & Rasines, 1982).

Displacement ellipsoids and selected interatomic distances of the title compound are given in Fig. 1 and Table 1, respectively.

Experimental

Single crystals of the $CoGa_2O_4$ spinel were grown using a PbF_2 flux. Special grade reagents (99.99%) of CoO and Ga_2O_3 were used as starting materials and mixed together with the PbF_2 flux in the molar ratio $CoO:Ga_2O_3:PbF_2$ = 1:1:9. This mixture was placed in a 30 cm^3 platinum crucible and heated slowly to 1473 K. The melt of the mixture was then cooled at rates of 5 K h^{-1} from 1473 to 973 K and of 10 K h^{-1} from 973 to 573 K. Subsequently, the heating was turned off and the samples were removed from the furnace at room temperature.

Crystal data

$CoGa_2O_4$
M_r = 262.37
Cubic, $Fd\bar{3}m$
a = 8.3281 (3) Å
V = 577.61 (4) Å^3
Z = 8
D_x = 6.034 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 38 reflections
θ = 20.0–24.7°
μ = 24.01 mm^{-1}
T = 296 K
Prism, dark blue
0.13 × 0.11 × 0.09 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.060, T_{max} = 0.115
613 measured reflections
248 independent reflections
215 reflections with $F > 3\sigma(F)$
R_{int} = 0.023
θ_{max} = 60.0°
$h = 0 \rightarrow 20$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 20$
3 standard reflections
every 100 reflections
intensity decay: 1.0%

Refinement

Refinement on F
$R[F > 3\sigma(F)]$ = 0.017
$wR(F)$ = 0.023
S = 1.72
215 reflections
9 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} < 0.0001$
$\Delta\rho_{max}$ = 0.84 e Å^{-3}
$\Delta\rho_{min}$ = −0.43 e Å^{-3}
Extinction correction: isotropic Type I (Becker & Coppens, 1974*a*,*b*)
Extinction coefficient: 3.06 (6) × 10^{-4}

Table 1
Selected interatomic distances (Å).

Co1/Ga1—O	1.9245 (16)	O···O^{iii}	2.746 (3)
Co2/Ga2—O^{i}	2.0144 (16)	O···O^{iv}	2.9478 (16)
O···O^{ii}	3.143 (3)		

Symmetry codes: (i) $-x+1, y+\frac{1}{4}, z+\frac{1}{4}$; (ii) $-x+\frac{1}{4}, y, -z+\frac{1}{4}$; (iii) $-x+\frac{3}{4}, -y+\frac{3}{4}, z$; (iv) $x-\frac{1}{4}, y+\frac{1}{4}, -z+\frac{1}{2}$.

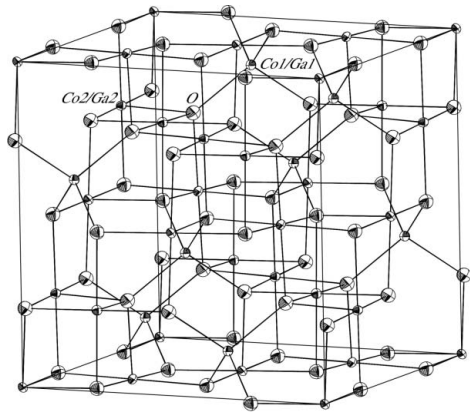

Figure 1
The crystal structure of the $CoGa_2O_4$ spinel with displacement ellipsoids drawn at the 65% probability level.

The occupancies of the cations at the tetrahedral and the octahedral sites were constrained on the basis of the structural formula $^{IV}(Co_{1-x}Ga_x)^{VI}[Co_xGa_{2-x}]O_4$; consequently, the variable occupancy parameter was only the Ga^{3+} occupancy at the tetrahedral site, *i.e.* the inversion parameter (x).

Data collection: *WinAFC* (Rigaku Corporation, 1999); cell refinement: *WinAFC*; data reduction: *RADY* (Sasaki, 1987); program(s) used to solve structure: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to refine structure: *RADY*; molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *TEXSAN*.

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