

X-ray powder refinement of a natural garnet from Diamantina, Minas Gerais, Brazil

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Key indicators

Powder X-ray study
 $T = 293$ K
Mean $\sigma(\text{Si}-\text{O}) = 0.002$ Å
Disorder in main residue
 R factor = 0.079
 wR factor = 0.113
Data-to-parameter ratio = 3.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The chemical composition, $[\text{Mg}_{0.015(2)}, \text{Al}_{1.20(2)}, \text{Si}_{2.99(1)}, \text{Ca}_{3.00(2)}, \text{Ti}_{0.027(3)}, \text{Mn}_{0.017(3)}, \text{Fe}_{0.75(3)}] \text{O}_{12}$ (magnesium aluminium silicon calcium titanium manganese iron dodecaoxide), of a natural garnet collected at Diamantina, Minas Gerais, Brazil was determined by electron microprobe analysis. The structure refinement from X-ray powder data is insensitive to the small amounts of Ti, Mn and Mg. The determined cation distribution using the Rietveld method is $\{\text{Ca}_3^{2+}\}[\text{Al}_{1.338(8)}^{3+}, \text{Fe}_{0.662(8)}^{3+}](\text{Si}_3^{4+})\text{O}_{12}^{2-}$, which is in agreement with a solid solution of the grossular-andradite series. The arrangement of the cations around the O atom is best described as a highly distorted tetrahedral.

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Comment

Natural garnets may be gems, and some of them occur even as beautiful precious stones. Artificial garnets doped with different rare-earth ions are used as laser materials (Pawlak *et al.*, 1999) and magnetic ceramics (Valenzuela, 1994). Most garnets crystallize in the body-centered space group $Ia\bar{3}d$. The crystal structure of garnet was first investigated by Menzer (1926), who showed that the unit cell contains eight formula units. Garnets have general formula $\{X\}_3[Y]_2(Z)_3\text{O}_{12}$ where $\{ \}$ refers to dodecahedral sites, $24c$, $[\]$ represents the octahedral sites, $16a$, and $()$ refers to tetrahedral sites, $24d$. The O atoms are located at general positions, $96h$ (Novak and Gibbs, 1971). A great variety of cations are known to occupy the first three sites. For natural garnets, the X site is frequently occupied by Mg^{2+} , Ca^{2+} , Mn^{2+} and/or Fe^{2+} . The Y site is generally occupied by Al^{3+} , Cr^{3+} , and/or Fe^{3+} . Commonly, the Z site is Si^{4+} .

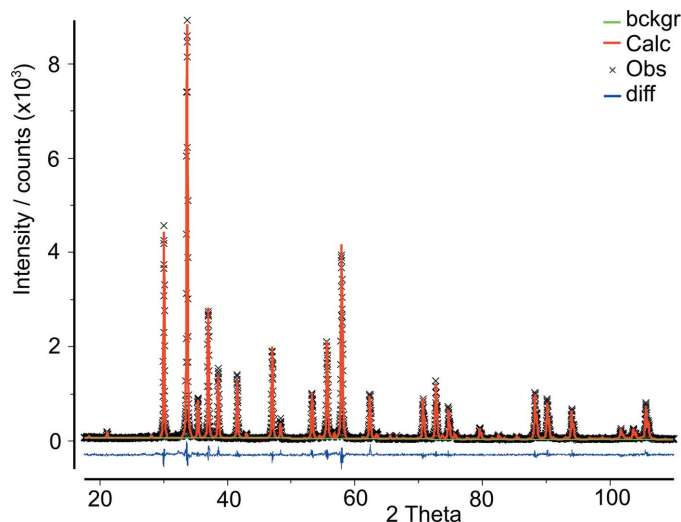
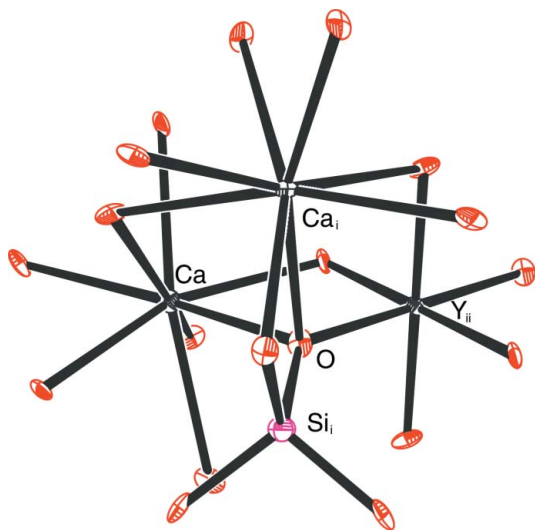


Figure 1

The observed, fitted and difference X-ray diffraction profile for Diamantina garnet.


Figure 2

A view of the structure of Diamantina garnet, with displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (i) y, z, x ; (ii) $\frac{1}{4} + y, \frac{1}{4} + x, \frac{1}{4} + z$].

According to Eeckhout *et al.* (2002), most of the solid solutions are found with intermediary compositions forming various series. One of them is known as the 'pyralspite: pyrope-almandine-spessartine' series, $\{\text{Mg}_3^{2+}\}[\text{Al}_2^{3+}](\text{Si}_3^{4+})\text{O}_{12}^{2-}$, $\{\text{Fe}_3^{2+}\}[\text{Al}_2^{3+}](\text{Si}_3^{4+})\text{O}_{12}^{2-}$ and $\{\text{Mn}_3^{2+}\}[\text{Al}_2^{3+}](\text{Si}_3^{4+})\text{O}_{12}^{2-}$, respectively. Another very common series is the 'ugrandite: uvarovite-grossular-andradite' series, $\{\text{Ca}_3^{2+}\}[\text{Cr}_2^{3+}](\text{Si}_3^{4+})\text{O}_{12}^{2-}$, $\{\text{Ca}_3^{2+}\}[\text{Al}_2^{3+}](\text{Si}_3^{4+})\text{O}_{12}^{2-}$, and $\{\text{Ca}_3^{2+}\}[\text{Fe}_2^{3+}](\text{Si}_3^{4+})\text{O}_{12}^{2-}$, respectively.

In this work we describe the structure of a garnet sample from Diamantina, Minas Gerais, Brazil. It was fragmented for electron microprobe analysis and X-ray powder diffraction measurements.

The powder diffraction pattern of the garnet was analysed using the Rietveld method. The refined cation distributions are $\{\text{Ca}_3^{2+}\}[\text{Al}_{1.338(8)}^{3+}, \text{Fe}_{0.662(8)}^{3+}](\text{Si}_3^{4+})\text{O}_{12}^{2-}$. The observed and fitted diffraction profile is shown in Fig. 1. As can be seen from Table 1, the bond lengths have intermediate values between those reported for the formal end members grossular (Geiger & Armbruster, 1997) and andradite (Novak and Gibbs, 1971). Moreover, they agree with data for other solid solutions of the uvarovite-grossular-andradite series (Takéuchi *et al.*, 1982; Basso *et al.*, 1984). Fig. 2 shows the structure of the garnet from Diamantina. The O atom links one Si, one Y site and two Ca atoms. Fig. 2 also illustrates a highly distorted tetrahedral coordination around the O atom. The O atom is displaced by 0.267 (7) Å from the plane defined by Ca^{2+} , Si^{4+} (y, z, x) and $Y = \text{Al}^{3+}/\text{Fe}^{3+}$ ($\frac{1}{4} + y, \frac{1}{4} + x, \frac{1}{4} + z$).

Experimental

The garnet sample was collected at Diamantina, Minas Gerais, Brazil. The crystals were chosen for optical clarity, homogeneity, size and shape. The five selected crystals were analyzed by electron microprobe analysis, using a Jeol JXA-8900RL device. The average sample composition was determined from 25 different sample points. The

standards used were MgO, Al_2O_3 , SiO_2 , CaO, TiO_2 , MnO and FeO. The average chemical formula may be expressed as $[\text{Mg}_{0.015(2)}, \text{Al}_{1.20(2)}, \text{Si}_{2.99(1)}, \text{Ca}_{3.00(2)}, \text{Ti}_{0.027(3)}, \text{Mn}_{0.017(3)}, \text{Fe}_{0.75(3)}]\text{O}_{12}$.

Crystal data

$\text{Ca}_3\text{Al}_{1.338}\text{Fe}_{0.662}\text{Si}_3\text{O}_{12}$
 $M_r = 469.56$
 Cubic, $Ia\bar{3}d$
 $a = 11.922(1)$ Å
 $V = 1694.5(2)$ Å³
 $Z = 8$
 $D_x = 3.681$ Mg m⁻³

Cu $K\alpha_1$ radiation
 $\lambda = 1.5405$ Å
 Cu $K\alpha_2$ radiation
 $\lambda = 1.5443$ Å
 $T = 293(1)$ K
 Yellow

Data collection

Siemens D5000 diffractometer
 Specimen mounting: packed powder pellet
 Specimen mounted in reflection mode

Scan method: step
 $2\theta_{\min} = 4$, $2\theta_{\max} = 110^\circ$
 Increment in $2\theta = 0.02^\circ$

Refinement

Refinement on I_{net}

$R_p = 0.079$

$R_{\text{wp}} = 0.113$

$R_{\text{exp}} = 0.077$

$S = 1.47$

Excluded region(s): 4 to $17.5^\circ/2\theta$

Profile function: CW Profile

function number 3 with 19 terms
 Pseudo-Voigt profile coefficients as parameterized in Thompson *et al.* (1987). Asymmetry correction (Finger *et al.*, 1994). [1(GU) = 0.000; 2(GV) = -12.617; 3(GW) = 21.783; 4(GP) = 0.000; 5(LX) = 4.905; 6(LY) = 7.311; 7(S/L) = 0.0005; 8(H/L) = 0.0005; 9(trns) = 2.09; 10(shft) = -6.3415; 11(stec) = -7.31; 12(pte) = 0.89; 13(sfec) = 0.00; 14(L11) = 0.011; 15(L22) = -0.041; 16(L33) = -0.048; 17(L12) = 0.027;

18(L13) = -0.016; 19(L23) = 0.088. Peak tails are ignored where the intensity is below $0.0100 \times$ peak Aniso. broadening axis 0.0 0.0 1.0

185 reflections

49 parameters

Weighting scheme based on measured s.u.'s $1/\sigma^2$

$(\Delta/\sigma)_{\max} = 0.10$

Preferred orientation correction:

Spherical Harmonic ODF
 spherical harmonic order = 10.
 The sample symmetry is: cylindrical (fiber texture) Index = 4 0 1
 Coeff = -0.0996 Index = 6 0 1
 Coeff = 0.2026 Index = 8 0 1
 Coeff = -0.8999 Index = 10 0 1
 Coeff = 0.0695. Preferred orientation correction range: min = 0.97227, max = 1.07803

Table 1

Table 1: Unit cell dimension (Å) and selected bond lengths (Å) of the analysed garnets. Y represent atoms on the octahedral sites.

	Grossular ^a	Diamantina ^b	Andradite ^c
Lattice parameter a	11.847 (1)	11.922 (1)	12.058 (1)
Tetrahedral			
Si—O	1.646 (1)	1.6425 (17)	1.643 (2)
Octahedral			
Y—O	1.926 (1)	1.9705 (17)	2.024 (2)
Dodecahedral			
Ca—O	2.487 (1)	2.4804 (17)	2.500 (2)
Ca ⁱ —O	2.322 (1)	2.3409 (18)	2.366 (2)

Notes: (a) $[\text{Ca}_3^{2+}][\text{Al}_2^{3+}](\text{Si}_3^{4+})\text{O}_{12}$ (Geiger and Armbruster, 1997). (b) this work. (c) $[\text{Ca}_3^{2+}][\text{Fe}_2^{3+}](\text{Si}_3^{4+})\text{O}_{12}$ (Novak and Gibbs, 1971). Symmetry code: (i) y, z, x .

The chemical composition determined from microprobe analysis was used in several Rietveld refinement cycles. The final composition obtained from X-ray powder data was $\{\text{Ca}_3^{2+}\}[\text{Al}_{1.338(8)}^{3+}, \text{Fe}_{0.662(8)}^{3+}](\text{Si}_3^{4+})\text{O}_{12}^{2-}$. Al^{3+} and Fe^{3+} were constrained to share the same site and the same anisotropic displacement parameters. The addition of Ti, Mn and Mg atoms to the model did not result in better reliability factors. Therefore, the refined composition is slightly different in comparison with the composition determined from electron microprobe analysis, $[\text{Mg}_{0.015(2)}, \text{Al}_{1.20(2)}, \text{Si}_{2.99(1)}, \text{Ca}_{3.00(2)},$

Ti_{0.027(3)}Mn_{0.017(3)}Fe_{0.75(3)}O₁₂. To compensate the absence of Ti⁴⁺ or even Mn³⁺, the refined amount of Al³⁺ was increased and the amount of Fe³⁺ was decreased during the refinement cycles. Refinements using scattering factors for the ions O²⁻ (Rez *et al.*, 1994), Al³⁺, Si⁴⁺ and Ca²⁺ gave better agreement factors than refinements using scattering factors for neutral atoms. For all cations the scattering factors were taken from Wilson (1995). (Ionic model: $S = 1.47$, $R_p = 7.72$, $R_{\text{Bragg}} = 4.64$; neutral atom model: $S = 1.50$, $R_p = 8.16$, $R_{\text{Bragg}} = 4.81$). A total of 49 independent parameters were refined, including the zero point, scale factor, five background polynomial coefficients, unit-cell parameters, half-width and asymmetry parameters for the peak shape, spherical harmonic preferential orientation, atomic coordinates, occupancy for Fe³⁺/Al³⁺ and anisotropic atomic displacement parameters for all atoms.

Data collection: *DIFFRAC/AT* (Siemens, 1993); cell refinement: *CELREF* (Laugier & Bochu, 2002); data reduction: *JANA2000* (Petricek & Dusek, 2000); program(s) used to solve structure: *JANA2000*; program(s) used to refine structure: *GSAS* (Larson & Von Dreele, 2000) and *EXPGUI* (Toby, 2001); molecular graphics: *ORTEP3* (Farrugia, 1997); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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