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BRIEF COMMUNICATION

Electron Density Study of Garnets: $Ca_3(Cr, Al)_2Si_3O_{12}$

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The electron density distribution in a natural garnet, uvarovite $Ca_3(Cr, Al)_2Si_3O_{12}$ with 55% of the octahedral site occupied by Cr, has been studied with single-crystal X-ray diffraction methods through scattering factor refinement procedures. Electron density residuals up to 0.22 $e/Å^3$ in height indicating bonding electrons were detected between Si and oxygen. Characteristic aspherical electron density distribution around the (Cr, Al) site was also seen; six residuals, -0.27 $e/Å^3$ in height, are directed toward the coordinated oxygens, eight with 0.15 $e/Å^3$ height are directed away from the oxygens. [Cubic $Ia\bar{3}d$, $a = 11.956(1)$ Å; $Z = 8$; $D_x = 3.734$ g/cm^3; $F_{000} = 1897$; final R after anharmonic refinement: 0.0039 for 371 equivalent-averaged data.]

In view that garnets represent a structure type which has yet to be explored with present-day techniques for examining the electron density distribution in crystals, the crystal structure refinement of a natural silicate garnet, uvarovite $Ca_3(Cr, Al)_2Si_3O_{12}$, has been determined. A generalized formula for garnets $Z_3X_2T_3O_{12}$ with $Z = Ca$, $X = Cr$, etc., and $T = Si$ will be used hereafter.

A natural specimen of the mineral uvarovite from the Ural mountains was rounded into a sphere of 0.16 mm diameter. The mean values of EPMA analyses for six points in the vicinity of the sample used showed the actual formula to be approximately $Ca_3(Cr_{1.10}Al_{0.80}, Ti_{0.06}, Fe_{0.03})Si_3O_{12}$ with scatter of 5% for Cr, 6% for Al, 19% for Ti, and 50% for Fe with one point below detection threshold. Cell dimensions were determined from the twenty-four equivalents of the 24 16 0 reflection ($2\theta = 117.65°$) using Mo$K\alpha_1$ radiation (0.70926 Å) with a RIGAKU AFC5 automated four-circle diffractometer (40 kV, 30 mA). Intensity data were collected with Mo$K\alpha$ radiation (0.7017 Å); scan conditions, 2θ-ω mode, width $1.8 + 0.35 \tan\theta(°)$ in ω, speed 5°/min, up to 3 repeats until $|F_0| > 200\sigma(F_0)$. For a range $|h|$, $|k|$, $|l| \leq 32, 2\theta \leq 145°$, $\sin\theta/\lambda \leq 1.342$, 20,845 equivalent reflections were measured in full reciprocal space, which were generated from 537 independent data observed with $|F_0| > 6\sigma(F_0)$ from the 1530 measured in a preliminary run with the same scan conditions. Some high-angle reflections in geometrically blind regions could not be measured. Finally, 371 independent data with all measured equivalents observed with $|F_0| > 6\sigma(F_0)$ were averaged from 13,868 of these equivalents ($R_{int} = 0.0049$).

The crystal structure was refined with a modified version of the program RADY (1) applying Lp, absorption [μ(Mo$K\alpha$) = 38.75/cm], and isotropic extinction corrections, using fully ionized scattering factors (2, 3), and dispersion correction values (4). The scattering factor values for the X site were calculated from the EPMA results. Weights proportional to the theoretical number of equivalents for each reflection were allotted. Conventional least-squares refinement with harmonic temperature factors gave $R = 0.0096$, $R_W = 0.0111$. Scattering factor refinement was executed under conditions identical to that described in (5, 6). Minimum R was attained for harmonic scattering factor refinement after 11 repeated runs ($R = 0.0054$, $R_W = 0.0061$). Anharmonic refinement with Gram–Charlier series-expanded parameters up to sixth-rank tensors was run using the harmonically obtained scattering factors (symmetry restrictions taken from (7); $R = 0.0040$, $R_W = 0.0044$). Four additional iterations of scattering factor refinement with anharmonic parameters resulted in $R = 0.0039$, $R_W = 0.0042$.[1]

[1]See NAPS document No. 5410 for 34 pages of supplementary material. This is not a multi-article document. Order from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163-3513. Remit in advance in U.S. funds only $7.75 for photocopies or $5.00 for microfiche. There is a $15.00 invoicing charge on all orders filled before payment. Outside U.S. and Canada add postage of $4.50 for the first 20 pages and $1.00 for each 10 pages of material thereafter, or $1.75 for the first microfiche and $0.50 for each microfiche thereafter.

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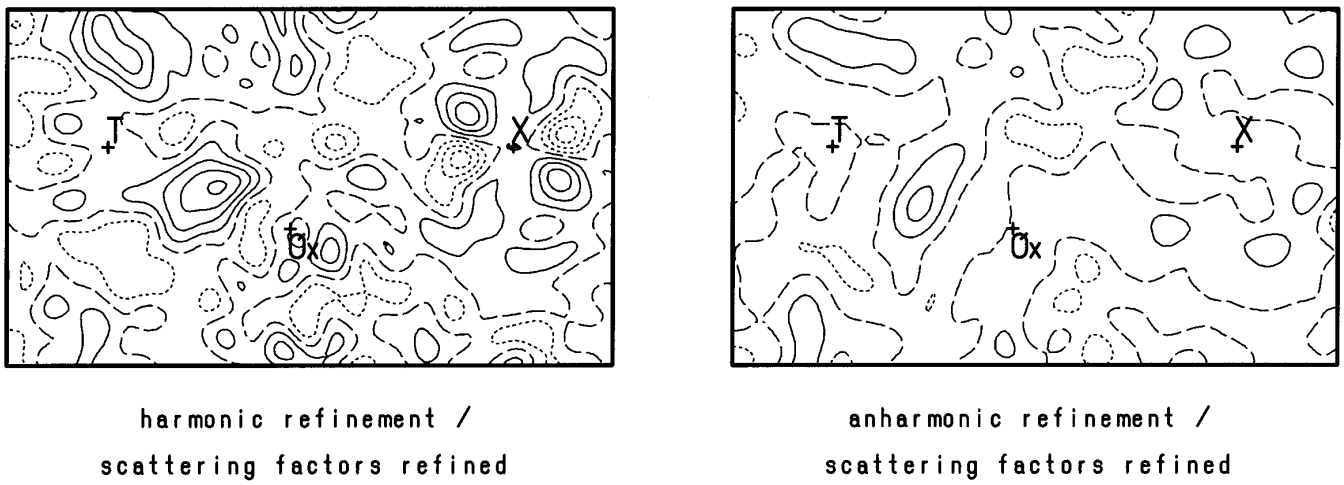

FIG. 1. Difference Fourier sections (see Footnote 1) of a plane passing through the T, X, and O sites. Positive contours are shown in full, zero contours in broken, and negative contours in dotted lines with increments of 0.05 $e/Å^3$. The map dimension is 3×5 Å. Residuals indicating bonding electrons are situated ~ 0.9 Å from the T site, toward 12 o'clock and 4 o'clock directions.

RESULTS AND DISCUSSION

Anharmonic refinement resulted in significantly shortened T–O distance, from 1.6463(3) Å for the harmonic to 1.6439(8) Å for the anharmonic scattering factor refinement (see Footnote 1).

Positive residuals situated between the T and O sites indicating bonding electrons are observed (Fig. 1; see also Footnote 1) with 0.22 $e/Å^3$ height for the harmonic and 0.11 $e/Å^3$ height for the anharmonic scattering factor refinement. For the harmonic refinement, six residuals -0.27 $e/Å^3$ in height are arranged octahedrally around the X site approximately toward the oxygen atoms, while eight 0.15 $e/Å^3$ height are arranged avoiding the oxygen atoms in the octahedral face directions. Similar arrangements of electron density residuals were seen around the Cr site in Cr_2O_3 (8) and $MgCr_2O_4$ (9), which are believed to indicate the aspherically deformed distribution of the d electrons.[2] There are no significant signs of the residual peak observed in the gallium garnets (6) at Wyckoff position 48g (variable coordinate $y = \frac{1}{4}$), which was attributed to constructive interference of X-rays diffracted from domains with different structural motifs.

[2]Conceivably, the peak heights of the residuals around the X site seen in the present work represent those of Cr occupying 55% of the X site. A pure substance would show higher peak heights accordingly.

ACKNOWLEDGMENTS

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