

Electron Density Study of Garnets: $Y_3X_2Al_3O_{12}$; $X = Al$ and $X = (Al, Cr)$ ¹

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The electron density distribution in two garnets $Y_3Al_2Al_3O_{12}$ [YAG] and $Y_3X_2Al_3O_{12}$; $X = (Al_{0.71}Cr_{0.29})$ [YCG] have been studied with single-crystal X-ray diffraction methods through scattering factor refinement procedures. YAG has broad electron density residuals of $0.3 e/\text{\AA}^3$ height extending between the octahedral Al site and the coordinated oxygen atoms. YCG shows residuals around the Y and oxygen sites indicating significant anharmonicity, along with electron density deformation of the X-site characteristic of octahedral Cr^{3+} sites. Partial substitution of Al by Cr in the X site does not increase the unshared O–O distance or the far Y–O distance in the adjacent Y site. [Cubic $Ia\bar{3}d$, $Z = 8$. For YAG, $a = 12.0095(4)$ Å; $D_x = 4.553$ g/cm³; $F000 = 2224$; final R after anharmonic refinement: 0.0085 for 281 equivalent-averaged data. For YCG, $a = 12.0405(5)$ Å; $D_x = 4.630$ g/cm³; $F000 = 2276$; final R after anharmonic refinement: 0.0107 for 274 equivalent-averaged data.] © 1997 Academic Press

INTRODUCTION

The crystal structure of garnets (solved by Menzer (1, 2)) has gained much attention ever since some of the synthetic varieties were found to possess interesting magnetic or optical properties (see, for instance, (3, 4)). One of the subject materials $Y_3Al_5O_{12}$ (YAG) is now used widely in various applications, from laser materials, substrates, to substitutes for diamonds as gems.

Although structural studies of synthetic and natural garnets with reports of the variable oxygen positional parameters and the harmonic temperature factors of the constituents (and the bond lengths) can be found ((5, 6) are collective, detailed studies which are still very informative), compounds assuming this structure had not been closely

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examined through the latest techniques of electron density distribution determination until the current series of studies.

The scattering factor refinement procedure which will be employed in this study has been successfully applied to Ga and Si garnets (7, 8), as well as structures of the corundum and spinel types (as in (9, 10)).

In the present study, the atomic sites will be denoted Y (yttrium; = Z in the previous studies of the nonyttrium garnets (7, 8)) for the distorted cubical (dodecahedral) site; X, the octahedral site with Al or (Al, Cr); T, the tetrahedral site with Al. The $Y_3Al_2Al_3O_{12}$ garnet will be referred to as YAG, the $Y_3X_2Al_3O_{12}$; $X = (Al_{0.71}Cr_{0.29})$ garnet, as YCG.

EXPERIMENTAL AND STRUCTURE REFINEMENT

For YAG, a specimen cut from a wafer synthesized by SHIN-ETSU was used. The pure composition was assumed.

The YCG crystal was grown from a $PbO-B_2O_3$ flux. The most Cr-rich portion with up to approximately 33% (EPMA analysis) substitution of Cr into the X site was chosen as the sample.

Cell dimensions were determined from the setting angles observed for the 24 equivalents of the 16 16 8 reflection with a RIGAKU AFC5 automated four-circle diffractometer (40 kV, 30 mA) using $MoK\alpha_1$ radiation (0.70926 Å). Intensity data were collected with $MoK\alpha$ radiation (0.7017 Å). Independent reflections were measured ($|h|, |k|, |l| \leq 31$, $2\theta \leq 140^\circ$, $\sin \theta/\lambda \leq 1.322$), from which equivalent reflections were generated from independents observed with $|F_o| > 6\sigma(F_o)$ (7 in addition for $h h h$ reflections, 5 additional for others), and measured (Table 1). Some high diffraction-angle reflections in geometrically blind regions of the diffractometer ended up with fewer measured equivalents. Those with all additionally measured equivalents observed with $|F_o| > 6\sigma(F_o)$ were averaged into the finally used number of independent data.

The crystal structure was refined with a modified version of the program RADY (11) applying L_p , absorption and isotropic extinction corrections, using fully ionized scattering factors (12, 13), and dispersion correction values (14). Weights proportional to the theoretical number of equivalents for each reflection were allotted.

The X-site occupation of Cr for YCG was refined and the linear absorption coefficient was recalculated, this repeated twice until the least-squares shift become insignificant. The resulting Cr occupation was 29(2)%. The average theoretical scattering angle-dependent scattering factor values for this site to be used as initial values in the subsequent scattering factor refinement procedure were calculated based on this result.

Scattering factor refinement with the harmonic parameters was run with the same procedures as mentioned in the previous work (7). There were strong correlations between the scattering factors of the Y site and the remaining sites; therefore, these were refined in separate sets of runs.

Anharmonic refinement was performed with Gram-Charlier series-expanded parameters up to the sixth-rank tensors (symmetry restrictions taken from (15)), first with the scattering factors derived with the harmonic parameters. For YCG, additional iterations of scattering factor refinement with the anharmonic parameters did not improve the R values further, so their results were not adopted. On the other hand, the scattering factors for all sites could be simultaneously refined for YAG with the anharmonic parameters, probably due to a marked improvement of the structural model in the harmonic run.

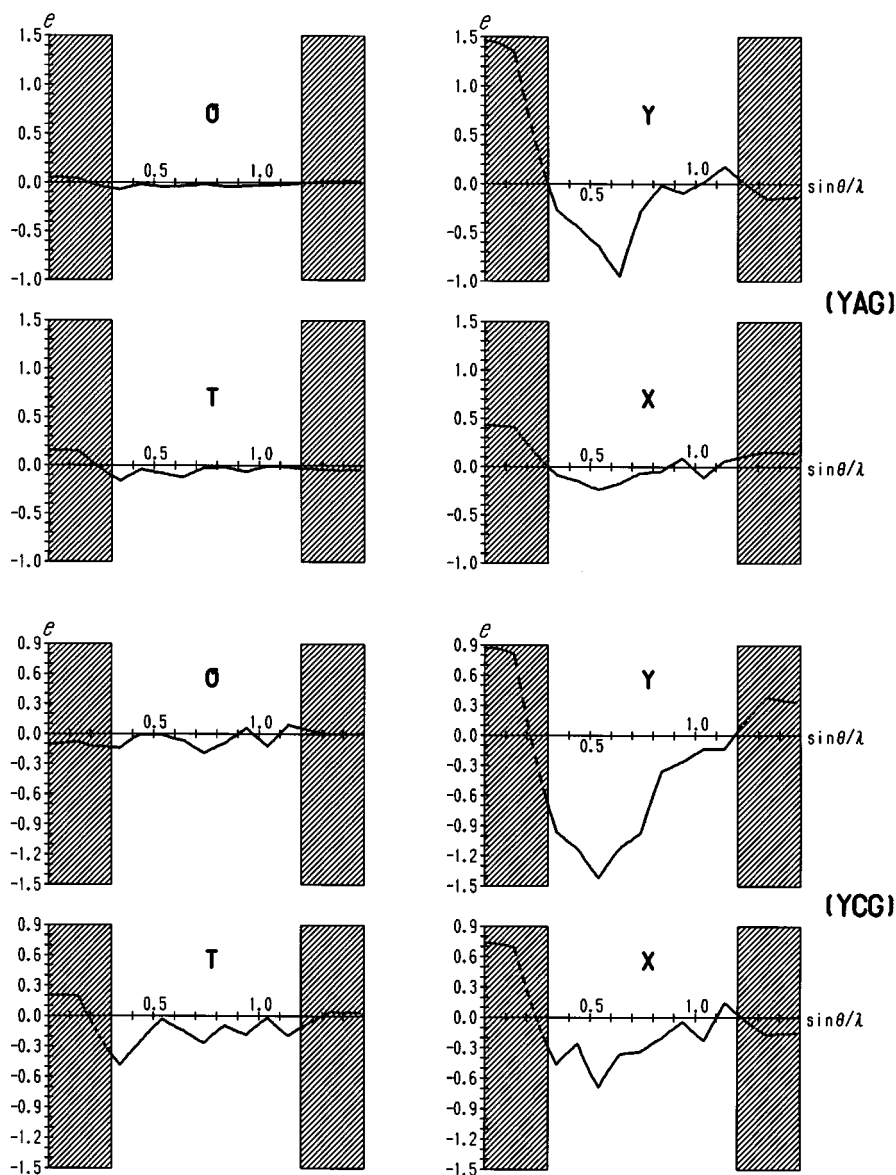


FIG. 1. The difference between the scattering factors derived from scattering factor refinement with the harmonic parameters and the theoretical values, the latter being subtracted from the former. The $\sin \theta / \lambda$ range outside the fully interpolated region is shown hatched.

RESULTS AND DISCUSSION

The cell dimension of YAG shows good agreement with the previously reported values (16–20).

The obtained scattering factor values for the Y site for both YAG and YCG show a marked decrease of $1.0 \sim 1.4e$ from theoretical values at around $\sin \theta/\lambda = 0.55 \sim 0.65$ (Fig. 1). Although minor readjustments also occur proceeding into the anharmonic scattering factor refinement, most are in the more or less unreliable zones where the scattering factor values are calculated through extrapolation preserv-

ing the theoretical scattering angle-dependent curvature. The maximum difference between the harmonically and anharmonically obtained scattering factors does not exceed $0.3e$ for the entire $\sin \theta/\lambda$ range.

The interatomic distances in the coordination polyhedra for these two garnets are shown in Fig. 2. Comparison of the YCG anharmonic results against those of YAG show that all of the shared edges of the Y site are longer, while the unshared edge and the larger Y–O' distance (Od–Of, and Y–Of in Fig. 2) are significantly shorter. The latter two lengths do not differ significantly in the harmonic

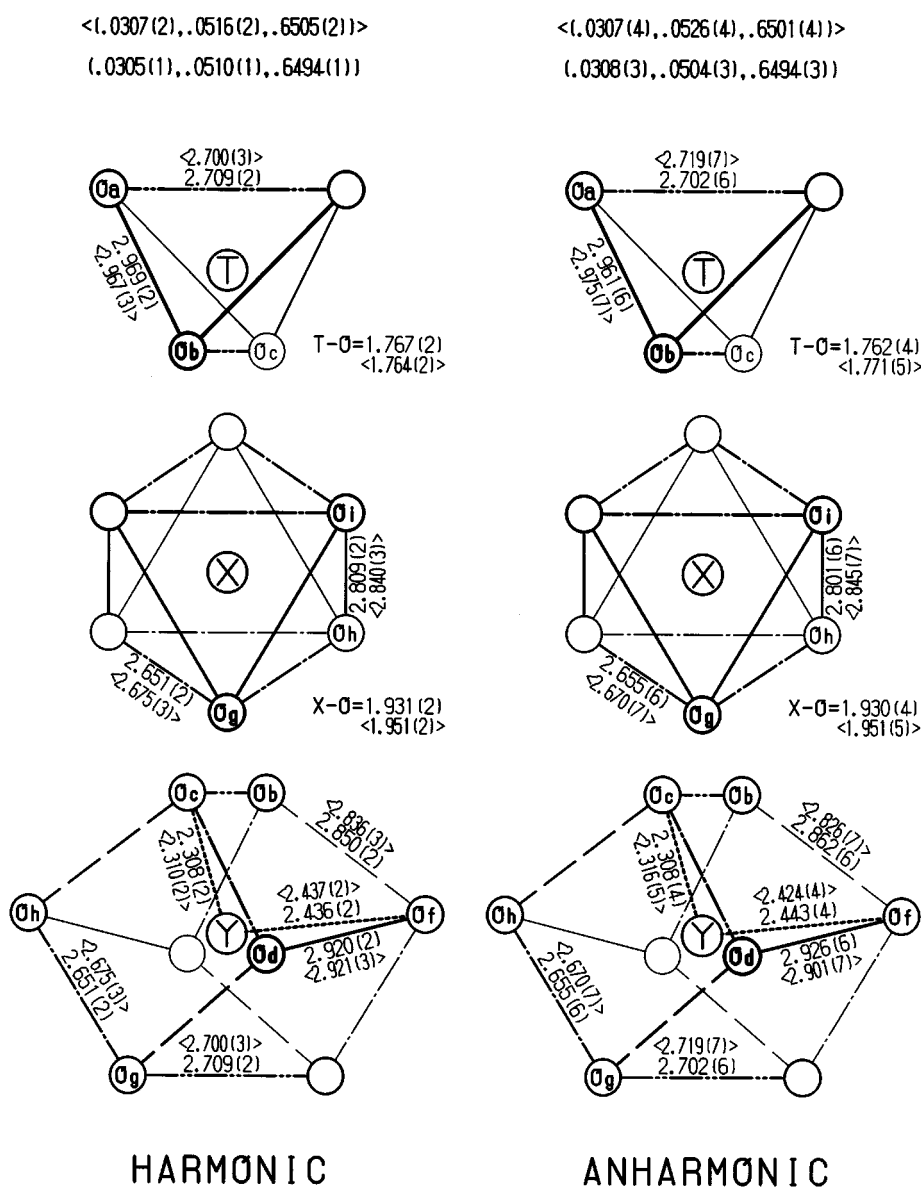


FIG. 2. Schematic illustration of the coordination polyhedra with the interatomic distances in Å inserted. Values for YCG with brackets and those for YAG without brackets. The oxygen atoms are all symmetry-related equivalents of the only one general position; the refined coordinates are shown at the top of the figure. Dashed-double lines indicate edges shared by YO_8 and TO_4 polyhedra, dashed-single-dotted lines indicate edges shared by YO_8 and XO_6 polyhedra, and dashed lines indicate those between a pair of YO_8 polyhedra.

TABLE 1
Experimental and Refinement Conditions for the Two Samples

| | YAG | YCG |
|---|------------------|-----------------|
| Crystal diameter (mm) | 0.14 | 0.18 |
| 2θ value of 16 16 8 (deg) | 90.26 | 89.96 |
| a (Å) | 12.0095(4) | 12.0405(5) |
| D_x (g/cm ³) | 4.553 | 4.630 |
| F 000 | 2224 | 2276 |
| μ (/cm) | 206.47 | 211.79 |
| Scan width: $a + b \tan \theta$ in ω (deg) | | |
| a | 1.45 | 1.6 |
| b | 0.35 | 0.3 |
| Speed/min in ω (deg) | 4 | 6 |
| Maximum number of repeats | 10 | 10 |
| Repeated until: $ F_o >$ | $200\sigma(F_o)$ | $20\sigma(F_o)$ |
| Initially measured independents | | |
| Measured | 1646 | 1503 |
| Observed | 323 | 344 |
| Initially observed (+) | | |
| Generated equivalents | 1902 | 2026 |
| Used to average | 1662 | 1612 |
| Used independent data | 281 | 274 |
| R_{int} | 0.0121 | 0.0171 |
| Harmonic refinement | | |
| Conventional refinement | | |
| R | 0.0202 | 0.0257 |
| R_w | 0.0246 | 0.0310 |
| Number of scattering factor refinement iterations | 4 | 50 |
| R | 0.0127 | 0.0156 |
| R_w | 0.0157 | 0.0182 |
| Anharmonic refinement | | |
| Number of scattering factor refinement iterations | 4 | none |
| R | 0.0085 | 0.0107 |
| R_w | 0.0099 | 0.0117 |

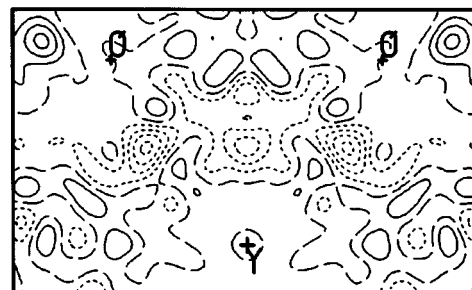
refinement results. The difference Fourier section of the plane passing through these three atoms for the harmonic refinement of YCG (Fig. 3) shows strong peaks of $0.5 \sim 0.6 e/\text{\AA}^3$ height which are completely removed with anharmonic refinement; this is believed to be related to the difference seen between the $Y-O'$ distances in these two refinements, considering the direction of the residuals' appearance.

The seemingly characteristic residual at Wyckoff position 48g seen in $Z_3Ga_5O_{12}$ garnets with $Z = Nd, Sm, Gd, Tb$ (7) does not appear clearly in the present study; irregularly shaped positive residuals present in the neighborhood of this site in the conventional refinement with harmonic parameters become almost completely removed with the application of the scattering factor refinement procedure.

Although spurious peaks with comparable heights coexist, the X site of these crystals show the following features which are consistent with the results from previous studies. In YAG, broad positive residual electron density regions stretching from Al in the X site toward the coordinated oxygens are seen accumulating up to $0.3 e/\text{\AA}^3$ height in the



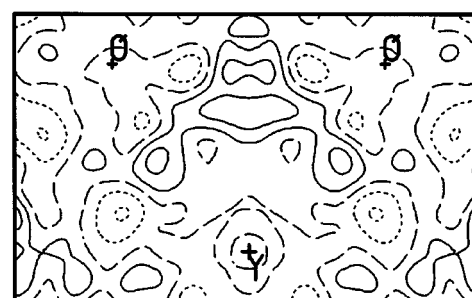
YCG /
harmonic



YCG /
anharmonic



YAG /
harmonic



YAG /
anharmonic

FIG. 3. Difference Fourier sections passing through the Y site and two far O sites. Positive contours are shown in solid lines, zero contours are shown in broken lines, and negative contours are shown in dotted lines with increment $0.1 e/\text{\AA}^3$. Map dimension is $3 \times 5 \text{\AA}$.

harmonic scattering factor refinement barely surviving the inclusion of the anharmonic parameters (Fig. 4). Similar residuals around octahedrally coordinated Al were detected with similar intensities in $\alpha\text{-Al}_2\text{O}_3$ (21) and

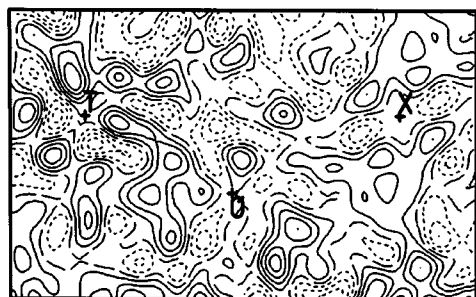
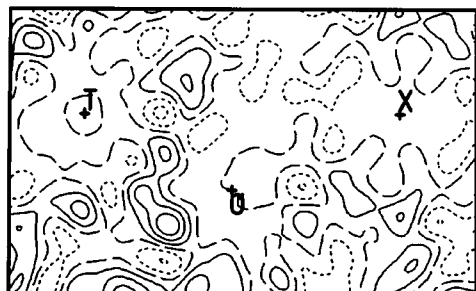
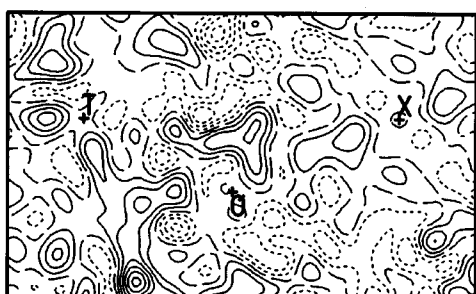
YCG /
harmonicYCG /
anharmonicYAG /
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anharmonic

FIG. 4. Difference Fourier sections passing through the T, X, and O sites. Plot details are as described in the legend for Fig. 3.

$\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (22). Though Al may be considered to be more ionic than Si, on which there are numerous reports of bonding electrons being detected between coordinated oxygens (such as in (8, 22)), nevertheless the remanent covalency is believed to bring about these residuals. No corresponding residual can be seen in YCG. The harmonic difference Fourier section for YCG (Fig. 4) shows the characteristic electron density deformation around the X site seen in several previously studied crystals with an octahedrally coordinated Cr^{3+} (8, 23–25), having negative residuals directed toward oxygen and positive residuals directed away from oxygen. The amplitude of this deformation is lower in YCG, due to the only partial occupation of this site by Cr.

The residuals are distributed around the T site in a rather irregular fashion (Fig. 4) and cannot readily be interpreted.

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