63. Optical Anomaly and Structure of Silicate Garnets

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Garnet crystals which have well established cubic symmetry (Menzer, 1926) often exhibit double refraction. Among silicate garnets, especially those of the grossular (Ca$_3$Al$_2$Si$_3$O$_{12}$)-andradite (Ca$_3$Fe$_2$Si$_3$O$_{12}$) series commonly show considerable birefringence. In spite of extensive structural studies on garnets (Geller, 1967; Novak and Gibbs, 1971), it has not been successful, to date, to characterize structurally such an optical anomaly of garnets; it has been a long standing crystallographic enigma in the field of mineral science. The above mentioned garnets comprise, in general, complicated microscopic or submicroscopic lamellae or patch works which have hindered routine structural investigation.

To disclose this enigma, we made a survey on a number of garnet crystals from various localities. As the result, we were finally successful to separate, under microscope, from a crystal exhibiting strong double refraction, a fragment which was considered to be a 'single crystal'. It has a proper optical property, showing under crossed nicols well defined extinction positions. The crystal came from a skarn deposit locating at Munam, Whanghedo, North Korea. An electron microprobe analysis (analyst: Gen Sato) showed that the crystal was chemically homogeneous, giving a chemical formula, Ca$_{2.91}$Al$_{1.36}$Fe$_{0.68}$Si$_{2.97}$O$_{12}$.

The fragment which has the shape of a thin plate with dimensions, 0.15×0.25×0.05 mm$^3$, gave, from single crystal diffractometry (Mo K$_\alpha$, $\lambda=0.71069$ Å), the following cell dimensions:

- $a_1=11.9197$ (16) Å, $\alpha=90.03$ (1)°,
- $a_2=11.9225$ (16), $\beta=90.12$ (1)°,
- $a_3=11.9199$ (16), $\gamma=89.98$ (1)°.

The result suggests that the cubic cell for garnet is distorted, though very slightly, to monoclinic with $a_2$ as unique axis; reciprocal points were therefore indexed based on a set of monoclinic axes, $a=a_1$, $b=a_2$, $c=a_3$, $\beta=90.12$°, to collect intensity data.

The $\omega-2\theta$ scan technique was used to measure, on a four-circle diffractometer, one-half of monochromatized Mo K$_\alpha$ intensity data up to 60° in 2$\theta$. Among a total of approximately 6000 reflections measured, 2390 had intensities larger than 2$I(I)$. After due cor-
Fig. 1. Relationship between the monoclinic lattice of Munam garnet (thin lines) and orthorhombic cell (heavy lines), broken lines indicating the lattice of cubic garnet. The $\beta$ angle of the monoclinic lattice is exaggerated.

Fig. 2. Difference Fourier sections, $z=0$ and $z=1/4$, of Munam garnet (monoclinic cell), showing two kinds of residual peaks, M(1) and M(2), at the octahedral positions; the atomic positions of Ca and Si for the cubic structure are indicated by squares and triangles respectively. Contours are drawn at an interval of $2e\AA^{-3}$ starting with one-electron contours, negative contours being broken.
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Table I. Atomic parameters (monoclinic cell)

| Atom | x       | y       | z       | B(A²)  |
|------|---------|---------|---------|--------|
| Ca(1)| 0.12503(7) | -0.00031(7) | 0.25013(7) | 0.44(1) |
| Ca(2)| 0.25    | 0.125   | 0       | 0.44(2) |
| Ca(3)| 0.75    | 0.375   | 0       | 0.44(2) |
| M(1) | 0       | 0       | 0       | 0.28(1) |
| M(2) | 0.5     | 0       | 0.5     | 0.44(1) |
| Si(1)| 0.37511(9) | -0.00074(9) | 0.25064(9) | 0.42(2) |
| Si(2)| 0.25    | 0       | 0       | 0.45(1) |
| O(1) | 0.0386(2) | 0.0463(2) | 0.6520(2) | 0.55(3) |
| O(2) | 0.6530(2) | 0.0392(2) | 0.0408(2) | 0.56(3) |
| O(3) | 0.0467(2) | 0.6519(2) | 0.0885(2) | 0.58(3) |
| O(4) | 0.5386(2) | 0.4527(2) | 0.3469(2) | 0.55(3) |
| O(5) | 0.1521(2) | 0.4613(2) | 0.9635(2) | 0.54(3) |
| O(6) | 0.5468(2) | 0.8465(2) | 0.9611(2) | 0.56(3) |

Anisotropic temperature factors (×10⁶)

| Atom | β₁₁ | β₁₂ | β₂₂ | β₁₃ | β₂₃ |
|------|-----|-----|-----|-----|-----|
| Ca(1)| 48(3)| 92(4)| 82(4)| 0(4)| -6(3)| 18(4)|
| Ca(2)| 82(5)| 59(8)| 82(6)| 0   | 21(7)| 0   |
| Ca(3)| 90(5)| 41(8)| 90(5)| 0   | -15(7)| 0   |
| M(1)| 52(6)| 46(5)| 43(6)| 3(5)| 7(4)| 1(5)|
| M(2)| 74(6)| 78(6)| 69(6)| -1(5)| 6(4)| 1(5)|
| Si(1)| 65(5)| 80(5)| 69(5)| -2(5)| 1(4)| -1(5)|
| Si(2)| 75(8)| 73(7)| 82(8)| 0   | 10(6)| 0   |
| O(1)| 93(15)| 102(14)| 85(16)| 6(12)| 7(11)| 10(12)|
| O(2)| 100(14)| 95(14)| 93(15)| -14(12)| 20(16)| -16(13)|
| O(3)| 97(15)| 116(15)| 85(15)| -4(12)| -3(11)| -10(12)|
| O(4)| 87(15)| 104(15)| 87(15)| -8(12)| 15(11)| 15(11)|
| O(5)| 83(15)| 91(14)| 97(15)| 3(12)| -17(11)| -1(12)|
| O(6)| 106(15)| 82(14)| 93(15)| -12(12)| 16(11)| 6(12)|

M(1) = 0.424(3)Fe + 0.576Al, M(2) = 0.224Fe + 0.776Al.

reactions, including those for absorption, they were reduced to structure factors. A statistics on the distribution of |F|^2 then revealed that the diffraction symmetry was well consistent with an orthorhombic symmetry, mmm; the three mirror planes are (010), (101) and (101). The orthorhombic axes a₀, b₀, c₀ are respectively related to the above monoclinic axes in the following way: a₀ = a + c, b₀ = b, c₀ = -a + c. It should be noted that the two-dimensional lattice generated by a and c is a diamond lattice because the length of a can be considered to be identical to that of c. Therefore, the two diagonals, a + c and -a + c, in the monoclinic cell necessarily cross at an angle of 90° (Fig. 1). The most probable space group was found to be Fddd. The space group consistent with the monoclinic lattice is then given by I2₁/c, which was adopted as working space group for structure analysis. Using an average form factor for octahedral cations, Al and Fe, structure factors were calculated based on the atomic
coordinates for andradite (Novak and Gibbs, 1971), giving the value of R=7.8% for all reflections; for hkl’s, if k=2n+1, the value was, however, as large as 16%. The difference Fourier synthesis then calculated revealed that peaks at the sixteen octahedral positions per cell were divided into two groups: those at a set of eight positions have a positive value, while those at the other set of eight positions a negative value (Fig. 2), showing cation ordering. It was found that in Fddd the positions corresponding to each set of the eight positions are equivalent, confirming the possibility of that space group. Least-squares refinement was then carried out based on Fddd; it was converged to give an R=3.8%. Final atomic parameters are given in Table I. Average bond lengths are: Ca(1)−O =2.413(2) Å, Ca(2)−O=2.415(2) Å, Ca(3)−O=2.414(2) Å, Si(1)−O =1.647(2) Å, Si(2)−O=1.648(2) Å, M(1)−O=1.967(2)Å, M(2)−O =1.950(2) Å.

The present study thus revealed that crystals of Munam garnet have a non-cubic structure based on cation ordering in the octahedral positions, thereby explaining their optical anomaly. Patch works, or twinnings, shown by these crystals are made up of such a non-cubic structure. It is then very likely that optical anomaly of garnets at least in the Gr–An series in general can be explained in the way similar to the present case. Miyazaki et al. (1975) have also reported, in terms of diffraction symmetry, another existence of such an orthorhombic garnet. For oxide garnets, a tetragonal structure has been reported for CdGeO₃ (Prewitt and Sleight, 1969).

Finally, a mention should be made of end-member garnets that do exhibit optical anomaly. The anomaly in such a case would probably be due to mere distortion of the cubic structure; the existence of dodecahedra about X cations (X=Ca, Mn, Fe, or Mg) in the structure is presumably favorable with distortion.

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