Reduction of symmetry in grandite solid solution.

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SUMMARY

The results of a crystal structure refinement of an anisotropic grandite garnet specimen with composition Gro₄₄, And₃₄ are given. The structure obtained has orthorhombic symmetry (space group Fddd) and is compared with similar results obtained by other authors. In all cases the reduction of symmetry is due to the ordering of Fe³⁺ and Al in octahedral sites.

Non cubic structures of grandites are discussed in connection with optical, morphological and growth features of these minerals.

Key words: grandite, structure, refinement, symmetry, growth.

INTRODUCTION

Anisotropy showed by many grandite garnet specimens has been attributed to several factors as mechanical strain induced by compositional zoning of Fe³⁺/Al (Verkaeren, 1971) or an hypothetical magneto-optical effect (Blanc et Maisonneuve 1973). However, after the work of Takéuchi et al (1982) it is clear that anisotropy in these minerals is due to ordering of Fe³⁺ and Al cations.

Takéuchi et al found, through x-ray diffraction data refinements, two different ordering schemes for substituted cations, giving rise to space groups Fddd and I1, both, subgroups of the regular space group of garnet Ia3d.

On the other hand Fraga et al (1982) through optical studies of nine birregringent grandite specimens concluded that anisotropy was due to ordering of Fe³⁺ and Al induced in the growth process and proposed the space group Fddd for birrefraredgrandites.

Later (Gali, 1983) showed that ordering produced by the mechanism of growth give rise to space groups Fddd or any of its centrosymmetric subgroups: F2/d I2/a or I1 as long as only fragments of a piramidal sector of growth is considered.

In this paper the author presents the refinement of the structure of a specimen with global composition Gro₄₄, And₃₄, (Pyr, Sp)₅, from a skarn of Hortsavinya (Barcelona) Spain. The specimen with well developed [110] morphology and differentiated growth piramids (fig. 1) was optically studied by Fraga et al who reported the following optical data: maximum birrefringence 0.006; 2Vz 85.5; optical axis in growth piramid (110) X = [110] Y = [001] Z = [110].

EXPERIMENTAL

The results of microprobe analysis of the central growth piramid showed in figure 1 are given in Table I. However the refinement of
cell parameters and occupancy factors of Fe\(^{3+}\) and Al do not coincide with the analysis, due to chemical inhomogeneity of these minerals. The specimen used in x-ray data collection was obtained from the central part of specimen in fig. 1. The specimen was crushed gently between two glass plates, and a fragment with maximum dimension about 0.2 mm was selected, after verifying that was optically homogenous and anisotropic.

**TABLE I.**—Chemical analysis.

<table>
<thead>
<tr>
<th>Composition in oxides (%)</th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>FeO + Fe(_2)O(_3)</th>
<th>TiO(_2)</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>37.00</td>
<td>10.30</td>
<td>14.98</td>
<td>0.03</td>
<td>0.27</td>
<td>1.15</td>
<td>34.15</td>
</tr>
</tbody>
</table>

Number of ions on the basis of 24 oxygens.

<table>
<thead>
<tr>
<th>Si</th>
<th>Al</th>
<th>Fe(^{3+})</th>
<th>Ti</th>
<th>Mn</th>
<th>Mg</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.157</td>
<td>2.020</td>
<td>1.875</td>
<td>0.004</td>
<td>0.038</td>
<td>0.285</td>
<td>5.510</td>
</tr>
</tbody>
</table>

**REFINEMENT OF CELL PARAMETERS**

The specimen was mounted in a four cicle automated diffractometer Philips PW 1100 and 20 reflections where found and centered. Of these, sixteen where used in least square refinement of the cell parameters. This procedure was repeated eight times during the collection of intensity data. The mean values for cell parameters and their standard deviation are:

\[
\begin{align*}
a &= 11.977(4) \text{ Å} & b &= 11.975(2) \text{ Å} & c &= 11.977(4) \text{ Å} \\
\alpha &= 90.10(1) ^\circ & \beta &= 90.10(1) ^\circ & \gamma &= 90.05(1) ^\circ \\
\end{align*}
\]

From these parameters, the «best» monoclinic cell is obtained by the relations.

\[
\begin{align*}
a' &= a + b \\
b' &= -a + b \\
c' &= c \\
\end{align*}
\]

with values

\[
\begin{align*}
a' &= 16.929(4) & b' &= 16.952(4) & c' &= 11.977(4) \\
\alpha' &= 90.00(1) & \beta' &= 90.14(1) ^\circ & \gamma' &= 90.01(1) ^\circ \\
\end{align*}
\]

The composition used in the refinement of atomic parameters was estimated from the cell edges, considering that these varied linearly with composition and neglecting divalent cations other than Ca\(^{2+}\). The value is Gro\(_{36.4}\) And\(_{40.4}\).

**REFINEMENT OF THE STRUCTURE**

Data collection was carried out in the same diffractometer, assuming triclinic symmetry of a body centered cell in pseudocubic axes. Experimental conditions are given in table II.

**TABLE II.**—Experimental conditions of X-ray data collection.

<table>
<thead>
<tr>
<th>Crystal size (mm)</th>
<th>0.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\mu) (cm(^{-1}))</td>
<td>45.15</td>
</tr>
<tr>
<td>(\lambda) (MoKa)</td>
<td>0.71069 Å (graphite monocromatized)</td>
</tr>
<tr>
<td>Scan speed (ω/s)</td>
<td>0.015</td>
</tr>
<tr>
<td>Scan wide ((^\circ))</td>
<td>1.00</td>
</tr>
<tr>
<td>Scan time (s)</td>
<td>45</td>
</tr>
<tr>
<td>2 (\theta) max</td>
<td>60</td>
</tr>
<tr>
<td>Reflections measured</td>
<td>1319</td>
</tr>
<tr>
<td>Reflections accepted</td>
<td>1263</td>
</tr>
<tr>
<td>Diffractometer</td>
<td>Philips PW 1100</td>
</tr>
<tr>
<td>Corrections</td>
<td>(Lp)</td>
</tr>
</tbody>
</table>

Only intensities greater than 2.5 \(\sigma\) (I) where used at initial stages. All refinements where carried out by full matrix least squares using the program SHELX (Sheldrix, 1976). The refinement was initiated with symmetry Ib3d to an \(R = 6.0\%\) and \(R_w = 5.8\%\). Atomic coordinates and other parameters are given in table III. Occupancy factors for trivalent cations (a Wychoff position) where fixed.
The next step was the refinement in Fddd space group. The orientation of cell edges in this group was the same as for the monoclinic cell given above, because it was thought that the symmetry of the fragment could be F2/d, in agreement with the cell parameters. In spite of strong cubic pseudosymmetry, the refinement in the Fddd space group was terminated at a $R = 5.5 \%$ and $R_w = 5.3 \%$. Occupancy factors for Fe$^{3+}$ and Al in the two octahedral
TABLE VI. — Distortions in dodecahedra.

<table>
<thead>
<tr>
<th>Dodecahedron</th>
<th>α</th>
<th>δ</th>
<th>δ («Kamaishi»)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(1) . Ca(3) . Y(1)</td>
<td>22.8</td>
<td>40.5</td>
<td>37</td>
</tr>
<tr>
<td>Y(1) . Ca(1) . Y(2)</td>
<td>22.9</td>
<td>40.6</td>
<td>38</td>
</tr>
<tr>
<td>Y(2) . Ca(2) . Y(2)</td>
<td>22.7</td>
<td>41.0</td>
<td>38</td>
</tr>
</tbody>
</table>

The results of this refinement are to be added to those given by Takéuchi et al for grandite garnets with symmetry I1 («Munam» and «Moravia») and Fddd («Kamaishi»). Apart from structural details the main question to be solved is whether exist or not two (or more) non cubic structures for anisotropic grandite garnets.

The starting point is to consider optical and chemical inhomogeneity of anisotropic grandites. It has been observed by several authors (Fraga et al 1982, Velasco et al 1981) that anisotropy is not directly related to composition in zoned garnets, and lately Takéuchi et al afforded concluding proofs that anisotropy is due to the degree of ordering in octahedral sites.

Another important feature in anisotropic grandites is correlation between the orientation of optical indicatrix with respect the pyramid of growth based on {110} faces, in such a way that the crystal with {110} morphology can be considered as an optical twin (Fraga et al). In fact, each growing face {110} controls optical properties, or what amounts the same, ordering in octahedral sites. Bearing in mind these facts, the only conclusion that can be drawn from the structure refinements of grandite fragments is that the structures obtained (Fdd and I1) are only average structures of small fragments, and by no means can be generalized to whole anisotropic grandite crystals. Gali (1983) proposed a method for derivation centrosymmetric structures of grandite garnets assuming that crystal grows on {110} faces.

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REFERENCES


Figure 3.— Projection on (100) plane of Y(1), Y(2), Ca(2), Ca(3) and Si(2) polyhedra.

Figura 3. — Projecció dels poliedres Y(1), Y(2), Ca(1), Ca(2), Ca(3) i Si(2) sobre el pla (100).