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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 $Gro_{36.4}$ $And_{63.6}$ are given. The structure obtained has orthorrombic 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 Fe^{3+} and Al in octahedral sites.

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

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

RESUM

En aquest treball es donen els resultats de l'afinament de l'estructura d'un fragment de granat anisotropic de composició $Gro_{36.4}$ $And_{63.6}$. L'estructura obtinguda es ròmbica (grup espacial Fddd) i es compara amb resultats semblants obtinguts per altres autors. En tots els casos, la reducció de simetria observada en aquests granats es deguda a l'ordenació del Fe^{3+} i el Al en les posicions octaèdriques.

L'aparició d'estructures no cúbiques en les grandites es comenta en relació amb els aspectes òptics, morfològics i de mecanisme de creixement d'aquests minerals.

INTRODUCTION

Anisotropy showed by many grandite garnet specimens has been attributed to several factors as mechanical strain induced by compositional zoning of Fe^{3+}/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 Fe^{3+} 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 $I\bar{1}$, 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 speciments concluded that anisotropy was due to ordering of Fe^{3+} and Al induced in the growth process and proposed the space group Fddd for birrefringent grandites.

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 $I\bar{1}$ 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 Gro_{44} $And_{50.9}$ $(Pyr, Sp)_{5.2}$, 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 = $[1\bar{1}0]$.

EXPERIMENTAL

The results of microprobe analysis of the central growth piramid showed in figure 1 are given in Table I. However the refinement of

Figure 1. — Microphotography of specimen H1. The fragment used for x-ray diffraction data was extracted from the central part of the crystal.

Figura 1. — Microfotografia de l'especimen H1. El fragment utilitzat per a l'obtenció de l'espectre de difracció va esser extret de la part central del cristall.

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 homogeneus and anisotropic.

TABLE I. — Chemical analysis.

Composition in oxides (%)

SiO_2	Al_2O_3	$FeO+Fe_2O_3$	TiO_2	MnO	MgO	CaO
37.00	10.30	14.98	0.03	0.27	1.15	34.15

Number of ions on the basifs of 24 oxygens.

Si	Al	Fe^{3+}	Ti	Mn	Mg	Ca
6.157	2.020	1.875	0.004	0.038	0.285	5.510

REFFINEMENT 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:

a=11.977(4) A	b=11.975(2) A	c=11.977(4) A
α=90.10(1)°	β=90.10(1)°	γ=90.05(1)°

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

$$a' = a + b$$
$$b' = -a + b$$
$$c' = c$$

with values

a'=16.929(4)	b'=16.952(4)	c'=11.977(4)
α'=90.00(1)	β'=90.14(1)°	γ'=90.01(1)°

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^{++}. The value is $Gro_{36.4}$ $And_{63.6}$.

REFINEMENT OF THE STRUCTURE

Data collection was carried out in the same diffractometer, assuming tricilinc 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.

Crystal size (mm)	:	0.15
μ (cm^{-1})	:	45.15
λ (MoKα)	:	0.71069 A (graphite monochromatized)
Scan speed (ω/s)	:	0.015
Scan wide (°)	:	1.00
Scan time (s)	:	45
2 θ max	:	60
Reflexions measured	:	1319
Reflextions accepted	:	1263
Diffractometer	:	Philips PW 1100
Corrections	:	Lp

Only intensities greater than 2,5 σ (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 Ia3d to an R = 6.0 (%) and Rw = 5.8 (%). Atomic coordinates and other parameters are given in table III. Occupancy factors for trivalent cations (*a* Wychoff position) where fixed.

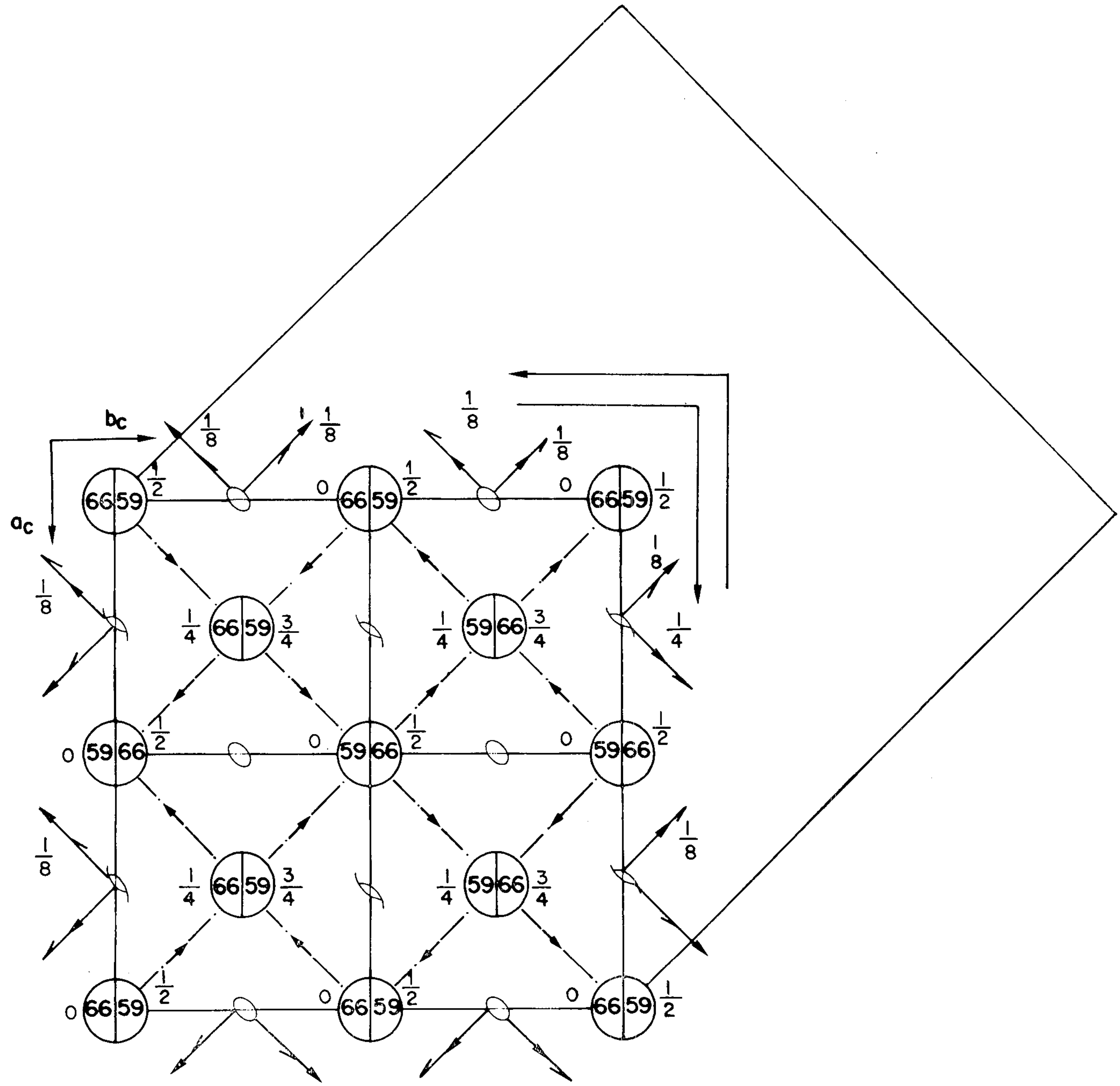

Figure 2. — Projection on (001) plane of occupancy factors for Fe(1) and Fe(2).

Figura 2. — Projecció dels factors d'ocupació de Fe(1)i Fe(2) sobre el plà (001).

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 Rw = 5.3 (%). Occupancy factors for Fe^{3+} and Al in the two octahedral

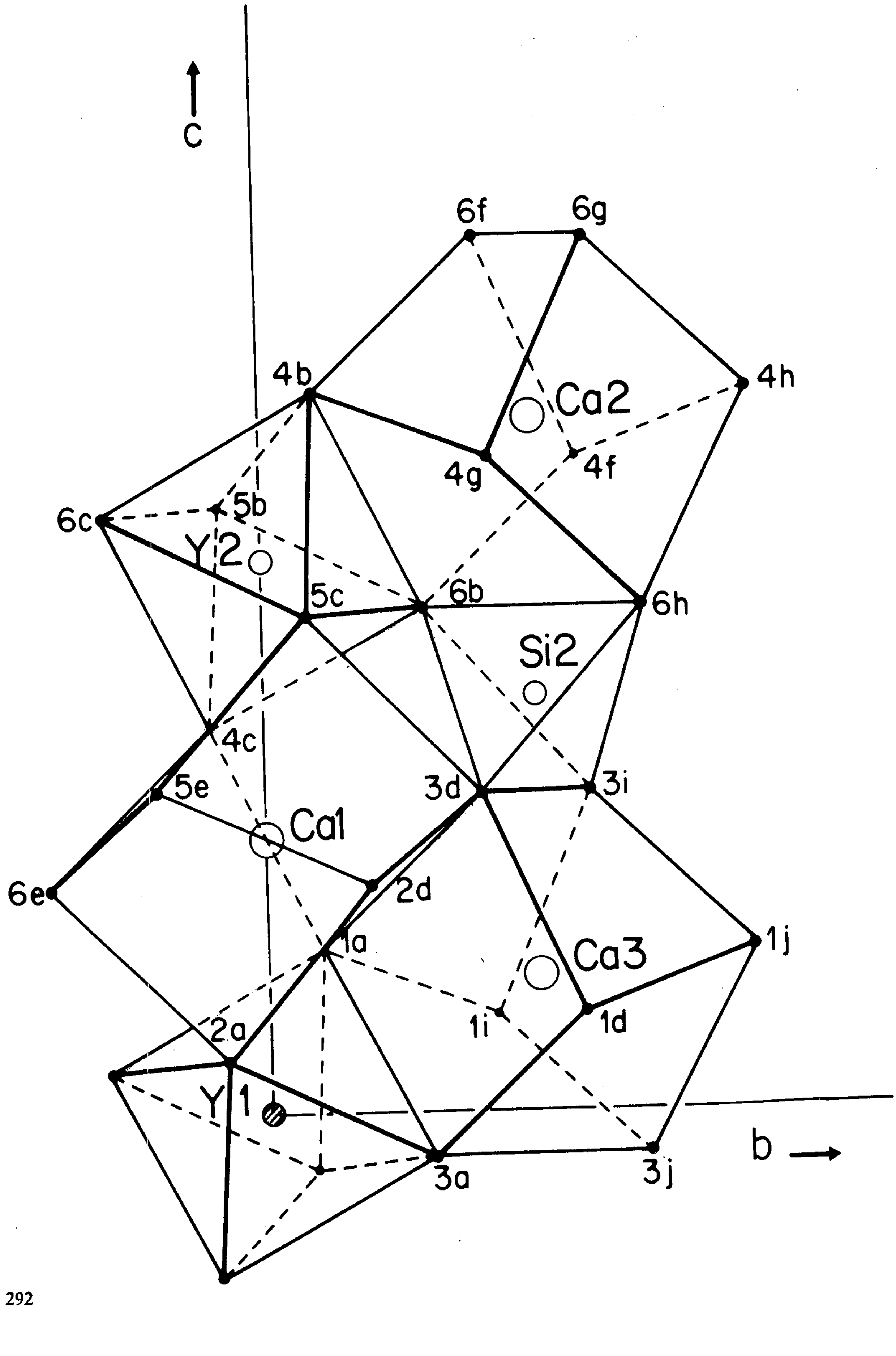
c
6f
6g
4b
Ca2
4h
4g
4f
6c
5b
Y2
5c
6b
6h
Si2
4c
5e
3d
3i
Ca1
6e
2d
1a
Ca3
1j
1i
1d
2a
Y1
b
3a
3j

TABLE VI. — Distortions in dodecahedra.

Dodecahedron	α	δ	δ («Kamaishi»)
Y(1)..Ca(3)..Y(1)	22.8	40.5	37
Y(1)..Ca(1)..Y(2)	22.9	40.6	38
Y(2)..Ca(2)..Y(2)	22.7	41.0	38

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 whetner 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 i octahedral sites.

Another important feature in anisotropic grandites is correlation between the orientation of optical indicatrix with respect the piramid 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 (Fddd 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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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 plà (100).

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