

Structural Studies of Gadolinium Gallium Garnet

JUDIT SASVÁRI^a and PER-ERIK WERNER^b

^a Magyar Tudományos Akadémia Központi Fizikai Intézete, Budapest XII, Konkoly Thege út 29–33, XXVI épület, Hungary and ^b Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

Structural parameters for $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ garnets have been refined with single crystal diffractometer data. The occupancy parameters were strongly influenced by extinction errors. A simple semiempirical extinction correction procedure was shown to improve the result substantially. Topographic studies revealed that dislocations were present in non-calcium induced crystals whereas preparation of crystals in the presence of very small amounts of CaO gave crystals of high quality. From the diffraction data, however, no significant differences between calcium and non-calcium induced crystals were detectable.



Fig. 1. Topographic study of a calcium-induced $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ single crystal. The exposed surface of the crystal is a circular area, about 50 mm in diameter. Evidence for dislocations can be seen within the rectangular area on the figure.

The $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ garnets crystallize in space group $Ia3d$ with eight formula units per cell and are isomorphous with the naturally occurring garnets; that structure was first determined by Menzer.¹ The $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ garnets, below termed GGG, have found application as substrates for magnetic bubble memories. At the Central Research Institute for Physics of the Hungarian Academy of Sciences, one of us (J.S.) attempted to differentiate between GGG single crystals prepared in the absence and the presence of very small amounts of CaO. Dislocations were then observed by X-ray topographic methods in the non-calcium induced crystals. The effect is illustrated in Fig. 1.

The GGG crystals were grown from a melt by weighing the following components into an iridium crucible: Gd_2O_3 53.7 wt % Ga_2O_3 46.3 wt %. The crucible was heated to 1800 °C and single crystals were prepared by a computer-controlled Czochralski method.² The crystals were rotated (10–30 r min^{-1}) around the $[111]$ direction and pulled out at a speed of 6 mm h^{-1} from the melt.

According to the X-ray topographic studies, high quality single crystals, HQ, were obtained from melts containing 80 ppm of CaO, whereas crystals of lower quality, LQ, were obtained from melts without CaO (Fig. 1).

A large number of garnet structures have been investigated, and reviews of the field have been given by Euler and Bruce³ and by Geller.⁴ The cations are all in special positions in space group $Ia3d$, with no positional degrees of freedom, while the oxygen atoms all are in the general position (96h). (Nomenclature according to International Tables of Crystallography, 1974.⁵) The general character of the cation positions and their environments is shown in Fig. 2. In order to provide information about the oxygen and cation

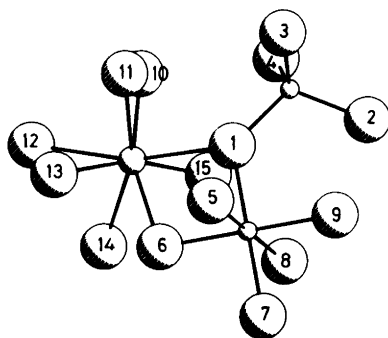


Fig. 2. The arrangement of gadolinium–oxygen dodecahedra gallium–oxygen octahedra and gallium–oxygen tetrahedra in $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ garnet.

positions in GGG and, if possible, the differences between the HQ and LQ forms, an X-ray crystallographic study was performed.

EXPERIMENTAL

The data were collected on a Philips PW1100 diffractometer using pure $\text{MoK}\alpha$ radiation ($\lambda=0.71069 \text{ \AA}$) obtained with a graphite monochromator. Colourless crystals of approximate dimensions $0.03 \times 0.2 \times 0.2 \text{ mm}$ and $0.015 \times 0.1 \times 0.1 \text{ mm}$ were cut from larger HQ and LQ crystals, respectively. The crystal data are listed in Table 1. The diffraction data were collected in the $\theta/2\theta$ scan mode with a scan rate of $1.2^\circ \text{ min}^{-1}$ and a scan width of $\Delta 2\theta=1.8^\circ$. Background counts at the extremes of scan were taken with the total background time equalling the scan time. The intensities of three standard reflections, measured at intervals of 39 reflections throughout the data collection, showed no variation greater than 3 %. Reflections from one

Table 1. Crystal data.

$\text{Gd}_3\text{Ga}_2\text{Ge}_3\text{O}_{12}$
Space group $Ia\bar{3}d$
HQ $a=12.3829(2) \text{ \AA}$ *
LQ $a=12.3820(2) \text{ \AA}$ *
Cell content $Z=8$
$M=1021.0$
$D_x=7.14 \text{ g cm}^{-3}$
$\mu=364.3 \text{ cm}^{-1}$

* Cell parameter determined by the Bond method.⁶

octant were collected to a 2θ limit of 60° ($\sin \theta/\lambda=0.704 \text{ \AA}^{-1}$). Lp and absorption corrections were made, and the data were averaged to give 233 and 229 unique reflections for HQ and LQ, respectively. The minimum and maximum absorption correction factors were 3.2 and 26.3 for HQ. The corresponding factors for the smaller LQ crystal were 1.9 and 4.3.

REFINEMENT

It was stated by Bonnet, Delapalme, Fuess and Thomas⁷ that the crucial point in the refinement of garnet structures from single crystal X-ray diffraction data is an appropriate extinction correction. This conclusion is verified in the present study by the fact that the R-values were reduced by as much as 0.042 and 0.051 for the HQ and LQ refinements, respectively, when empirical extinction corrections were applied (Table 2). Furthermore, for HQ the cation occupancy parameters obtained without extinction corrections were all systematically too small. The latter effect is not found for the smaller LQ crystal, but the calculated standard deviations were very high. In the study by Bonnet *et al.*⁷ several different models for extinction correc-

Table 2. Occupancy parameters and R-values.

Crystal	Extinction correction	Occupancy parameters (in assumed positions)			R	R_w
		k_{Gd} (24c)	k_{Ga} (16a)	k_{Ga} (24d)		
LQ	No	1.09(15)	0.98(20)	1.02(19)	0.128	0.212
HQ	No	0.86(5)	0.68(7)	0.65(6)	0.097	0.135
LQ	Yes	0.91(4)	0.85(6)	0.82(6)	0.077	0.098
HQ	Yes	0.94(5)	0.84(5)	0.82(5)	0.055	0.070

Table 3. Final positional and thermal parameters.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (Å ³)
a. Crystal HQ				
Gd (24c)	1/8	0	1/4	0.0047(7)
Ga(1) (16a)	0	0	0	0.0019(17)
Ga(2) (24d)	3/8	0	1/4	0.0036(17)
O (96h)	0.9720(6)	0.0539(7)	0.1502(6)	0.0044(23)
b. Crystal LQ				
Gd (24c)	1/8	0	1/4	0.0047(10)
Ga(1) (16a)	0	0	0	0.0029(24)
Ga(2) (24d)	3/8	0	1/4	0.0033(23)
O (96h)	0.9727(8)	0.0543(9)	0.1495(8)	0.0010(10)

tions were examined, but it was found that the positional and thermal parameters for the Y₃Fe₅O₁₂ garnet investigated were only slightly influenced by the choice of a particular extinction correction model. Therefore, we decided to use the simple empirical isotropic extinction correction procedure available in the SHELX program.⁸ In the full-matrix least-squares refinement an extinction coefficient, *g*, was refined in the expression

$$F_{\text{corr}} = F_{\text{calc}} (1 - g \cdot F_{\text{calc}}^2 / \sin \theta)$$

The final values of *g* were $(2.6 \pm 0.3) \times 10^{-8}$ and $(3.4 \pm 0.4) \times 10^{-8}$ for HQ and LQ, respectively. The function minimized was

$$R_w = [\sum w (|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2}$$

where the weight *w* was defined by

$$w = 1 / [\sigma^2(F) + bF^2]$$

In the final refinements, with extinction corrections included, the weight parameter *b* was 6.1×10^{-5} for HQ. The corresponding figure for LQ was 3.0×10^{-4} . Tables 2, 3 and 4 list structural parameters and cation–oxygen distances.

DISCUSSION

It was assumed that Gd³⁺ should fill the c site, although it was not considered impossible that some Gd³⁺ could also enter the a position.⁴ From

the present study, there are no indications for gadolinium at the a site. As can be seen from Table 2, the occupancy parameters for the cations are somewhat smaller than unity. This may be an effect of imperfect extinction corrections, although the empirical correction procedure used significantly reduces the *R*-values and improves the determination of the occupancy parameters.

No significant differences between the HQ and LQ crystals can be seen from Tables 2 and 3. This means only that the X-ray diffraction technique, as others, has a limit in its resolving power. The deviations in unit cell dimensions (*cf.* Table 1) and the differences found by X-ray topography (*cf.* Fig. 1) between the HQ and LQ crystals are too small to cause any significant changes in the single crystal diffraction data.

Table 4. Cation–oxygen distances (Å) in Gd₃Ga₅O₁₂ (HQ crystal). The average e.s.d. of cation–oxygen distances is 0.008 Å. The numbering of the atoms is shown in Fig. 2.

Ga tetrahedron	
Ga–O _{<i>i</i>} ; <i>i</i> = 1, 2, 3, 4	1.849
Ga octahedron	
Ga–O _{<i>i</i>} ; <i>i</i> = 1, 5, 6, 7, 8, 9	2.007
Gd dodecahedron	
Gd–O _{<i>i</i>} ; <i>i</i> = 1, 12, 13, 15	2.473
Gd–O _{<i>j</i>} ; <i>j</i> = 6, 10, 11, 14	2.359

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