A Structural Study of Facet and Off-Facet Parts of Rare-Earth Garnets, $Gd_3Sc_2Al_3O_{12}$, $Gd_3Sc_2Ga_3O_{12}$, and $La_3Lu_2Ga_3O_{12}$

Satoru Yamazaki,* Fumiyuki Marumo,† Kiyoaki Tanaka,* Hideki Morikawa,* Nobuhiro Kodama,‡ Kenji Kitamura,§ and Yasuto Miyazawa§

*Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta 4259, Midori, Yokohama 227, Japan; †Department of Earth Sciences, Nihon University, Sakurajosui 3-25-40, Setagaya-ku, Tokyo 156, Japan; ‡Toyo Soda Co. Ltd., Hayakawa 2743-1, Ayase, Kanagawa 252, Japan; and §National Institute for Research in Inorganic Materials, Namiki 1-1, Tsukuba, Ibaraki 305, Japan

The crystal structures of facet and off-facet parts of rare-earth garnets $Gd_3Sc_2Al_3O_{12}$ (GSAG), $Gd_3Sc_2Ga_3O_{12}$ (GSGG), and $La_3Lu_2Ga_3O_{12}$ (LLGG) have been refined with the single-crystal X-ray diffraction method. The crystals are cubic with the space group $Ia3d$, containing eight formula units in a unit cell. The final weighted reliability factors are 0.014, 0.017, and 0.020 for 1786, 2318, and 2331 reflections of the facet parts of GSAG, GSGG, and LLGG, respectively, and 0.014, 0.017, and 0.019 for 2143, 2190, and 2420 reflections of the off-facet parts of the respective crystals. The bond lengths between the tetrahedral cations (T) and the oxygen atoms in GSAG and GSGG as well as those between the dodecahedral cations (M^{viii}) and oxygen atoms in all the examined crystals are in accordance with the sums of ionic radii both in facet and off-facet parts, whereas the octahedral cations (M^{vi}) in all the crystals and the tetrahedral cation in LLGG have bond lengths longer than the sums of the ionic radii. A cation replacement at the T sites was not observed, whereas the M^{vi} and M^{viii} sites were revealed to be partly replaced by cations with smaller ionic radii. © 1994 Academic Press, Inc.

INTRODUCTION

Considerable effort has been made to grow optically homogeneous single-crystals of various rare-earth garnets in view of their application as host materials for lasers tunable over wide wavelength ranges or for high-power lasers. These crystals are usually grown with the Czochralski method along [111]. However, the resulting crystals often show facets, which induce strain in the crystals. Kitamura et al. (1) revealed that the strain was caused by the difference in cell dimensions between the facet and off-facet regions at room temperature, and attributed the origin of the cell-dimension difference to a slight difference in chemical composition between the two regions caused by nonstoichiometry of the crystals.

The present authors carried out structure refinements of the facet and off-facet parts of the title crystals with the intentions of revealing the cation distributions among the three independent cation sites in the cubic garnet structure and of gathering evidence of the difference in chemical composition between the two parts.

EXPERIMENTAL

The crystals used in the present study were grown with the Czochralski method at the National Institute for Research in Inorganic Materials by Kodama et al. (2). The chemicals Al_2O_3, Ga_2O_3, Gd_2O_3, and Sc_2O_3 with purities of 99.999% and Cr_2O_3, La_2O_3, and Lu_2O_3 with purities of 99.99% were used as the starting material. Crystals of $Gd_3Sc_2Al_3O_{12}$ (GSAG) and $Gd_3Sc_2Ga_3O_{12}$ (GSGG) were grown at the congruent compositions, whereas those of $La_3Lu_2Ga_3O_{12}$ (LLGG) were grown at an incongruent composition of $La_{2.70}Lu_{2.28}Ga_{3.00}Cr_{0.02}O_{12}$ where the compositions of the liquid and crystal are close, since the LLGG solid solution has no congruent composition. Though small amounts of Cr were doped to GSGG and LLGG for the purpose of checking the laser emission, the amounts were so small that the Cr could be neglected in the course of structure refinements of the crystals.

Pieces of the crystals were cut from the facet and off-facet regions and were used for the ICP emission analyses and X-ray diffraction experiments. The ICP emission analyses gave the chemical formulas given in Table 1 for the respective specimens. The errors of the values in the formulas were roughly estimated to be 0.02 for the major components, and the analyses could not reveal the compositional differences between the facet and off-facet regions. Crystals shaped into spheres with diameters ranging from 0.088 to 0.120 mm were used for diffraction experiments. The symmetries of the crystals were confirmed to be cubic with the space group $Ia3d$ with the Weissenberg photographs. Cell dimensions were determined with the least-squares method, utilizing 2θ values of 48 reflections (24, 8, 0; 16, 16, 8; and their symmetry equivalents) collected on a four-circle diffractometer (Ri-

TABLE 1
Crystal Data for the Facet and Off-Facet Parts of GSAG, GSGG, and LLGG

		Chemical composition[a]	Space group	a(Å) at 296 K	Z	μ for Mo $K\alpha$ (cm^{-1})	d_x(g cm^{-3})
GSAG	facet	$Gd_{2.95}Sc_{1.87}Al_{3.18}O_{12}$	$Ia3d$	12.3888(1)	8	226.2	5.769
	off-facet	$Gd_{2.96}Sc_{1.87}Al_{3.17}O_{12}$	$Ia3d$	12.3926(2)	8	226.2	5.773
GSGG	facet	$Gd_{3.04}Sc_{1.84}Cr_{0.04}Ga_{3.08}O_{12}$	$Ia3d$	12.5588(1)	8	297.7	6.502
	off-facet	$Gd_{3.06}Sc_{1.84}Cr_{0.04}Ga_{3.07}O_{12}$	$Ia3d$	12.5600(1)	8	296.8	6.517
LLGG	facet	$La_{2.49}Lu_{2.58}Cr_{0.01}Ga_{2.92}O_{12}$	$Ia3d$	12.9807(2)	8	414.1	7.248
	off-facet	$La_{2.49}Lu_{2.58}Cr_{0.01}Ga_{2.92}O_{12}$	$Ia3d$	12.9837(1)	8	413.8	7.243

[a] The values were determined by the ICP emission analysis.

TABLE 2
Experimental Condition in Intensity Measurements

Radiation: Mo $K\alpha$
Monochromator: pyrolitic graphite
Maximum of 2θ: 100°
Scan mode: $\omega - 2\theta$
Scan speed: 4°/min

		GSAG facet	GSAG off-facet	GSGG facet	GSGG off-facet	LLGG facet	LLGG off-facet
Scan width parameter[a]							
$2\theta < 30°$	A	1.5	1.6	1.5	1.8	1.5	1.5
	B	0.5	0.5	0.5	0.5	0.5	0.5
$30° < 2\theta < 60°$	A	1.2	1.6	1.2	1.5	1.5	1.5
	B	0.5	0.5	0.5	0.5	0.5	0.5
$2\theta > 60°$	A	1.2	1.4	1.2	1.2	1.5	1.5
	B	0.5	0.5	0.5	0.5	0.5	0.5
Number of measured reflections		2338	2143	2318	2190	2331	2420
Number of used reflections		1786	1717	1760	1615	1135	1235
Number of independent		598	566	594	585	390	425
Diameter of specimen (mm)		0.118	0.116	0.114	0.120	0.088	0.108

[a] The scan width parameters are those in the expression: scan width (degree) $= A + B \tan \theta$.

TABLE 3
The Maximum and Minimum of the Absorption Correction Factor A^*

		Maximum	Minimum
GSAG	facet	6.35	3.82
	off-facet	6.19	3.76
GSGG	facet	9.82	4.72
	off-facet	11.02	4.96
LLGG	facet	11.48	5.05
	off-facet	18.04	6.11

TABLE 4
The Reliability Factor R and the Weighted Reliability Factor R_w after the Refinements with Isotropic Extinction Corrections for the Type I and Type II Cases

		Type I R	Type I R_w	Type II R	Type II R_w
GSAG	facet	0.0117	0.0146	0.0173	0.0270
	off-facet	0.0119	0.0170	0.0185	0.0318
GSGG	facet	0.0186	0.0186	0.0244	0.0324
	off-facet	0.0210	0.0202	0.0256	0.0325
LLGG	facet	0.0192	0.0204	0.0221	0.0248
	off-facet	0.0191	0.0201	0.0260	0.0310

TABLE 5

The Final Reliability Factor R and the Weighted Reliability Factor R_w after the Refinements with and without Vacancies in the Structure Model

		Without vacancy		With vacancy	
		R	R_w	R	R_w
GSAG	facet	0.0116	0.0145	0.0115	0.0141
	off-facet	0.0110	0.0142	0.0108	0.0141
GSGG	facet	0.0181	0.0179	0.0171	0.0170
	off-facet	0.0200	0.0190	0.0173	0.0172
LLGG	facet	0.0188	0.0199	0.0184	0.0198
	off-facet	0.0187	0.0196	0.0177	0.0191

gaku AFC-5) with Mo $K\alpha_1$ radiation in the range $2\theta > 83°$ at 296 ± 1 K. The obtained values are given in Table I together with other crystallographic data.

Intensities were measured on the same four-circle diffractometer as the above with Mo $K\alpha$ radiation monochromated by pyrolitic graphite in a $\frac{1}{16}$ range of the reciprocal space up to $2\theta = 100°$. Indices of the measured reflections were selected to satisfy the conditions $0 \le h \le 27$, $0 \le k \le h$, $0 \le l \le 27$. When a reflection had only one or two symmetry equivalents in this region, additional equivalents lying outside the region were measured to make a set of three equivalent reflection data. Further, all the equivalent reflections were measured for four strong reflections 400, 800, 420, and 422. There are 60 reflections belonging to this group altogether for the respective specimens. The experimental conditions in intensity measurements are summarized in Table 2.

The observed intensities were corrected for the Lorentz and polarization factors. Corrections for absorption were carried out using the correction factors (A^*'s) for spherical crystals given in the "International Tables for X-Ray Crystallography" (3). The minimum and maximum values of the correction factors are given in Table 3 for the respective crystals. The corrections for extinction effects were performed at the final stage of the refinements, adopting the formulas given by Becker and Coppens (4, 5). The reflections which did not satisfy the condition $|Fo| > 3\sigma$ ($|Fo|$) were omitted from the data sets used in the structure refinements, where σ ($|Fo|$) was the estimated standard deviation based on the counting statistics. When one of the three equivalent reflections did not satisfy the condition, the remaining reflections were discarded. The effects of simultaneous reflection were estimated with the program MDCTIT (written by one of the authors, K. Tanaka), and reflections, for which the effects amounted to more than 5% of the observed intensities, were also rejected from the data sets. The numbers of measured and used reflections are given in Table 2.

TABLE 6

Final Atomic Parameters Obtained by Allowing Vacancies at the Tetrahedral Cation and Oxide Anion Sites

Wyckoff notation			Facet	Off-facet
			(a) GSAG	
Gd	24d	P	0.970(3)	0.968(3)
		U11	378(3)	375(3)
		U22 = U33	559(2)	550(2)
		U23	117(3)	109(3)
Sc	24d	P	0.030	0.032
Sc	16a	P	0.856(4)	0.850(5)
		U11 = U22 = U33	451(12)	435(8)
		U12 = U13 = U23	−19(7)	−24(7)
Al	16a	P	0.144	0.150
Al	24c	P	0.954(7)	0.960(5)
		U11	360(22)	378(23)
		U22 = U33	523(16)	516(17)
O	96h	P	0.983(13)	0.985(12)
		x	−0.03216(8)	−0.03220(7)
		y	0.05493(6)	0.05503(7)
		z	0.15566(6)	0.15578(7)
		U11	569(25)	584(26)
		U22	665(25)	683(26)
		U33	602(25)	608(26)
		U12	−14(21)	−46(22)
		U13	55(19)	51(20)
		U23	−84(20)	112(21)
			(b) GSGG	
Gd	24d	P	1	1
		U11	326(4)	335(4)
		U22 = U33	416(3)	469(3)
		U23	78(4)	76(4)
Sc	16a	P	0.918(2)	0.947(4)
		U11 = U22 = U33	426(6)	368(7)
		U12 = U13 = U23	−32(9)	−34(11)
Ga	16a	P	0.037(2)	0.020(4)
Ga	24c	P	0.951(3)	0.947(3)
		U11	243(8)	261(11)
		U22 = U33	392(6)	399(8)
O	96h	P	0.970(7)	0.974(8)
		x	−0.02897(9)	−0.02918(9)
		y	−0.05698(9)	0.05717(10)
		z	0.15347(9)	0.15371(7)
		U11	505(33)	347(36)
		U22	549(34)	592(37)
		U33	397(32)	335(34)
		U12	−51(28)	−61(31)
		U13	64(26)	60(30)
		U23	−58(27)	10(30)
			(c) LLGG	
La	24d	P	0.851(8)	0.850(7)
		U11	503(14)	494(12)
		U22 = U33	674(9)	666(8)
		U23	108(20)	100(15)

TABLE 6—Continued

Wyckoff notation			Facet	Off-facet
Lu	24d	P	0.149	0.150
Lu	16a	P	1	1
		U11 = U22 = U33	578(4)	550(4)
		U12 = U13 = U23	−54(9)	−62(7)
Ga	24c	P	0.985(4)	0.965(4)
		U11	602(30)	508(21)
		U22 = U33	583(21)	507(14)
O	96h	P	0.994(15)	0.985(14)
		x	−0.03102(22)	−0.03097(19)
		y	0.05636(20)	0.05624(18)
		z	0.15698(21)	0.15686(17)
		U11	889(101)	744(85)
		U22	896(92)	954(83)
		U33	703(94)	622(78)
		U12	−226(81)	−285(68)
		U13	237(76)	114(63)
		U23	−58(75)	2(64)

Note. In GSGG vacancies are also allowed for the octahedral cation sites. P stands for the population of the relevant atom. Thermal parameters are given in the form

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^*$$
$$+ 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)],$$

and the values are multiplied by 10^5 Å^{-2}. Equivalent values are assume for the atoms located at the same positions.

STRUCTURE REFINEMENTS

In the cubic garnet structures, all the cations occupy the special positions having no positional variables. Starting from the atomic parameters given by Shinohara (6), all the structures were refined by the least-squares method with the program LINEX (7). Based on the results of ICP emission analyses, the following constraints were set in the refinements besides the crystal neutrality. In all the crystals no vacancies were assumed at the initial stages of refinements. The tetrahedral sites were assumed to be occupied by Al in GSAG and by Ga in GSGG and LLGG, the octahedral sites by Sc and Al in GSAG, Sc and Ga

in GSGG, and by Lu in LLGG, and the dodecahedral site with eightfold coordination by Gd and Sc in GSAG, Gd in GSGG, and by La and Lu in LLGG. The corrections for extinction were carried out at the later stages as already stated. Since the type I model (4) gave better agreement between the observed and calculated structure factors for all the crystals at the isotropic correction stage, as seen in Table 4, the final refinements were performed on the type-I model in anisotropic mode. The weighted reliability factor, $R_w = [\Sigma(|Fo| - |Fc|)^2/\Sigma|Fo|^2]^{1/2}$, converged to values less than 0.02 for all the crystals after the extinction corrections, supporting the allocations of cations. At this stage, the difference Fourier maps were synthesized and it was found that all the crystals gave negative peaks at the tetrahedral cation sites. Therefore, further refinements were continued by assuming vacancies at the tetrahedral cation and O^{2-} anion sites under the restriction of crystal neutrality. At the final stage vacancy was also introduced for the octahedral site in GSGG, since a hollow was observed on the difference Fourier map synthesized at this stage. Then, the R and R_w values reduced slightly. The final R and R_w values are given in Table 5. The atomic scattering factors for Al^{3+}, Ga^{3+}, Gd^{3+}, La^{3+}, Lu^{3+}, and Sc^{3+} ions and the dispersion correction factors for all the ions were taken from the "International Tables for X-Ray Crystallography" (8). The atomic scattering factors given by Tokonami (9) were used for O^{2-} ions. The final atomic parameters and extinction correction parameters (7) are given in Tables 6 and 7, respectively.

RESULTS AND DISCUSSION

Bond distances are given in Table 8. The positional coordinates did not shift beyond the estimated standard deviations on allowing vacancies in the structure model from the values obtained for the model without vacancies. The distances between the terahedral cation (T) and oxygen atoms are in accordance with the sums of ionic radii (10) except those in LLGG, where the observed distances are longer by 0.016 Å than the sum of the ionic radii both in the facet and off-facet crystals. All the octahedral cation (M^{vi})–oxygen distances are longer than the sums of the

TABLE 7
Anisotropic Extinction Parameters ($\times 10^4$ sec)

		G_{11}	G_{22}	G_{33}	G_{12}	G_{13}	G_{23}
GSAG	facet	617(14)	634(15)	654(29)	79(10)	68(17)	−71(17)
	off-facet	545(21)	662(23)	763(19)	193(16)	165(14)	253(13)
GSGG	facet	463(10)	461(16)	603(24)	21(9)	−41(10)	−57(10)
	off-facet	780(31)	463(13)	463(12)	−108(12)	−59(12)	40(9)
LLGG	facet	141(6)	140(8)	223(16)	−00(5)	−25(8)	−22(10)
	off-facet	214(8)	327(18)	242(16)	−12(8)	11(7)	−45(10)

TABLE 8
Bond Distances in GSAG, GSGG, and LLGG (Å)

		MVIII–O	MVIII–O′	MVI–O	T–O
GSAG	facet	2.479(1)	2.371(1)	2.083(1)	1.776(1)
	off-facet	2.478(1)	2.371(1)	2.086(1)	1.775(1)
GSGG	facet	2.477(1)	2.392(1)	2.088(1)	1.854(1)
	off-facet	2.476(1)	2.393(1)	2.092(1)	1.851(1)
LLGG	facet	2.579(3)	2.469(3)	2.202(3)	1.866(3)
	off-facet	2.581(2)	2.469(2)	2.201(2)	1.867(2)

ionic radii calculated by taking into account the cation populations and disregarding the vacancies. The difference is largest in LLGG (0.04 Å) and smallest in GSAG (0.01 Å). There are two crystallographically independent bonds between the cation with an eightfold coordination (M^{viii}) and O^{2-} ions, and the difference of lengths between the two bonds amounts to 0.1 Å. However, the mean values of M^{viii}–O distances are in good agreement with the sums of the ionic radii estimated by taking into account the site occupancies. These observations hold for both facet and off-facet crystals. The structure refinement of GSGG was performed by Kondratyuk et al. (11). The T–O distance is significantly shorter (about 0.01 Å) in their result than in the present study, whereas the M^{vi}–O and M^{viii}–O distances are approximately equal in the two studies.

The present refinements suggest that the tetrahedral cation sites are occupied only by Al or Ga. On the other hand, the octahedral sites of GSAG and GSGG are partly occupied by Al and Ga, respectively. Specifically, replacement of Sc with Al in GSAG amounts to about 15%. Since the crystal of LLGG is rich in Lu compared with the stoichiometric composition, the octahedral sites are completely occupied by Lu, and the excess Lu are at the dodecahedral sites, replacing La. The refinement also indicated partial replacement of Gd by Sc at the dodecahedral sites in GSAG.

The lengths of T–O in GSGG and M^{vi}–O in GSAG and GSGG showed larger differences between the facet and off-facet parts than the sums of the estimated standard deviations for the relevant bonds. Namely, the T–O distance in the off-facet part of GSGG is shorter by 0.003 Å than that in the facet part, and the M^{vi}–O distances in the off-facet parts of GSAG and GSGG are longer by 0.003 and 0.004 Å than those in the facet parts, respectively. The differences are quite small, but large enough to explain the observed differences of the cell dimensions between the facet and off-facet parts. However, there is no systematic relation between the obtained bond distances and the cation populations. Although a comparison of the results of Kondratyuk et al. with those in the present study implies that the cell dimension differences between the facet and off-facet parts are due to the differences of cation and/or vacancy populations in the two parts, a more precise determination of the populations is required to elucidate the origin of the cell dimension difference. The chemical compositions derived from the structure refinements are compared with those obtained by the ICP emission analysis in Table 9.

TABLE 9
Comparison of Chemical Compositions Obtained by ICP Emission Analyses and Structure Refinements Based on X-Ray Diffraction Data

		ICP emission analysis	X-ray diffraction
GSAG	facet	$Gd_{2.95}Sc_{1.87}Al_{3.18}O_{12}$	$Gd_{2.96}Sc_{1.83}Al_{3.20}O_{12}$
	off-facet	$Gd_{2.96}Sc_{1.87}Al_{3.17}O_{12}$	$Gd_{2.95}Sc_{1.82}Al_{3.23}O_{12}$
GSGG	facet	$Gd_{3.04}Sc_{1.84}Ga_{3.08}O_{12}:Cr_{0.04}$	$Gd_{3.09}Sc_{1.89}Ga_{3.02}O_{12}$
	off-facet	$Gd_{3.06}Sc_{1.84}Ga_{3.07}O_{12}:Cr_{0.04}$	$Gd_{3.08}Sc_{1.94}Ga_{2.96}O_{12}$
LLGG	facet	$La_{2.49}Lu_{2.58}Ga_{2.92}O_{12}:Cr_{0.01}$	$La_{2.57}Lu_{2.46}Ga_{2.97}O_{12}$
	off-facet	$La_{2.49}Lu_{2.58}Ga_{2.92}O_{12}:Cr_{0.01}$	$La_{2.59}Lu_{2.49}Ga_{2.94}O_{12}$

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