Confirmation by Structure Factor Calculations of the Filling by Rare Earths of Two Crystallographic Sites of the Garnet Structure*

LAWRENCE SUCHOW AND ROSTAM MONDEGARIAN

Chemistry Division, Newark College of Engineering, Newark, New Jersey 07102

Calculations of structure factors for garnets with previously deduced distributions of ions have confirmed the structural formulae $\{Nd_{2.7}Yb_{0.3}\}[Yb_2](Ga_3)O_{12}$ and $\{Pr_3\}[Lu_2](Ga_3)O_{12}$; that is, rare earths fill all dodecahedral and octahedral sites.

Introduction

The partial filling of the octahedral sites of the garnet structure by rare earth when the same rare earth also completely fills the dodecahedral sites was first reported by Keith and Roy (*1*) and later studied further by Roth (*2*), by Schneider, Roth, and Waring (*3*), and by Geller and Espinosa (*4*). Suchow, Kokta, and Flynn (*5, 6*) were able to prepare gallium garnets of this type with the octahedral sites fully occupied by the smaller trivalent rare earth ions by "opening up" the lattice by means of placing large rare earth ions (Nd^{3+} and Pr^{3+}) on the dodecahedral sites. In some cases it was possible to prepare single-phase materials with only the large rare earth on the dodecahedral sites, but in most cases it was necessary to place at least a minimum amount of the smaller rare earth on these sites along with the larger rare earth.

The general formula for the known compounds of this type may be taken as $\{M_{3-y}R_y\}[R_xA_{2-x}]$-$(A_3)O_{12}$, where M is the large rare earth, R the small one, and A either Ga or Al. The braces signify eight-fold dodecahedral coordination (a distorted cube), the brackets six-fold octahedral coordination, and the parentheses four-fold tetrahedral coordination.

In all the papers cited above, the presence of rare earth ions on octahedral sites was deduced from an observed increase in lattice constant and the fact that these ions had no other possible

sites to enter in the garnet structure after the dodecahedral sites were filled. This argument is especially valid when the products are single-phase materials. Until now, however, there has been no direct confirmation of this picture by means of structure factor calculations; such confirmation is the purpose of the current work. Two materials were chosen for the calculations—$\{Nd_{2.7}Yb_{0.3}\}[Yb_2](Ga_3)O_{12}$ and $\{Pr_3\}[Lu_2]$-$(Ga_3)O_{12}$ [structural formulae indicated are those previously deduced (*5, 6*)].

Preparation

The specific materials with which this paper deals were prepared somewhat differently from those described earlier (*5, 6*). In the case of the neodymium compound, this made it possible to lower the preparation temperature from 1500°C. to 1350°C. and thereby not make unreasonable demands on the silicon carbide element muffle furnace.

The procedure employed commences by dissolving weighed stoichiometric quantities of the desired oxides in nitric acid and then gently boiling down to dryness. The residue is collected and heated for 3 hr at 500°C. in an open porcelain crucible in order to decompose the nitrates. This product is ground in an agate mortar and again heated, but now for 6 hr at 1350°C. in an open platinum crucible. The resulting material is then ground once more in an agate mortar and heated 16 hr longer at 1350°C. The heating is in all cases carried out in air in a muffle furnace.

TABLE I

Observed and Calculated Intensities of Allowable Lines in Nd–Yb Gallium Garnet $(a = 12.856$ Å$)^a$

		I_{calcd} for postulated structural formulae		
$h^2 + k^2 + l^2$	I_{obsd}	$\{Nd_{2.7}Yb_{0.3}\}[Yb_2](Ga_3)O_{12}$	$\{Nd_{0.7}Yb_{2.3}\}[Nd_2](Ga_3)O_{12}$	$\{Nd_{2.7}Yb_{0.3}\}[Ga_2](Yb_2Ga)O_{12}$
6	9.8	13.3	18.0	0.1
8	7.2	17.2	4.3	7.7
14	6.1	7.2	10.4	0.0
16	52.9	60.6	48.7	22.1
20	97.7	94.0	100	100
22	—	0.1	0.5	0.7
24	100	100	78.5	32.8
26	1.3	1.1	1.0	0.7
30	7.5	7.5	9.2	0.8
32	—	0.9	0.0	2.8
38	7.8	7.5	9.1	0.8
40	5.2	5.1	1.6	1.1
42	—	0.0	0.0	0.0
46	2.4	1.1	1.6	0.0
48	5.9	5.1	7.9	15.0
50	—	0.0	0.0	0.0
52	27.0	25.2	26.4	25.7
54	3.0	3.0	4.0	0.1
56	68.6	64.6	51.7	23.0
62	1.3	1.6	2.3	0.1
64	18.6	18.4	16.7	11.2
66	—	0.1	0.0	0.1
68	—	0.1	0.1	0.1
70	—	0.4	0.7	0.0
72	1.6	1.8	0.4	1.0
74	—	0.0	0.0	0.0
78	—	0.4	0.6	0.0
80	15.9	15.5	12.3	5.4
84	16.6	15.0	16.1	16.4
86	1.2	1.2	1.6	0.0
88	12.2	12.3	10.1	4.4
90	—	0.2	0.1	0.0
94	1.2	0.9	1.2	0.0
96	0.9	0.8	0.2	0.3
98	—	0.2	0.2	0.2
100	—	0.0	0.0	0.0
102	—	0.3	0.4	0.0
104	—	1.1	0.1	1.5
106	—	0.0	0.0	0.0
110	1.2	1.2	1.6	0.0
114	—	0.0	0.0	0.0
116	13.3	12.3	13.2	13.4
118	—	0.6	0.7	0.0
120	13.6	13.3	10.5	4.6
122	—	0.0	0.0	0.0
126	0.9	1.0	1.3	0.0
128	8.1	8.8	8.0	5.4
134	—	0.7	0.9	0.0
136	—	0.4	0.0	0.7
138	—	0.0	0.0	0.0

TABLE I—*continued*

$h^2 + k^2 + l^2$	I_{obsd}	I_{calcd} for postulated structural formulae		
		$\{Nd_{2.7}Yb_{0.3}\}[Yb_2](Ga_3)O_{12}$	$\{Nd_{0.7}Yb_{2.3}\}[Nd_2](Ga_3)O_{12}$	$\{Nd_{2.7}Yb_{0.3}\}[Ga_2](Yb_2Ga)O_{12}$
140	—	0.0	0.0	0.0
142	—	0.1	0.2	0.0
144	5.9	5.8	4.6	2.0
146	—	0.0	0.0	0.0
148	2.8	2.5	2.7	2.8
150	—	0.5	0.7	0.0
152	13.9	13.4	10.6	4.6
154	—	0.0	0.0	0.0
158	—	0.3	0.4	0.0
160	—	0.0	0.1	0.2
162	—	0.0	0.0	0.0
164	—	0.0	0.0	0.0
166	—	0.8	0.7	0.1
168	—	0.5	0.1	0.3
170	—	0.0	0.0	0.0
174	—	0.4	0.6	0.0
176	0.8	0.8	1.5	7.0
178	—	0.0	0.0	0.0
180	7.4	6.6	7.1	7.2
182	—	0.5	0.7	0.0
184	7.5	6.8	5.3	2.3
186	—	0.0	0.0	0.0
190	—	0.1	0.2	0.0
192	3.8	3.5	3.2	2.1
194	—	0.0	0.0	0.0
196	—	0.0	0.0	0.0
198	—	0.3	0.4	0.0
200	—	0.7	0.1	0.2
202	—	0.0	0.0	0.0
206	—	0.7	1.0	0.0
208	2.9	3.3	2.6	1.1
210	—	0.0	0.0	0.0
212	6.7	5.9	6.4	6.5
214	—	0.1	0.2	0.0
216	14.7	14.7	11.6	5.1
218	—	0.0	0.0	0.0
222	—	0.4	0.5	0.0
224	—	0.4	0.1	0.4
226	—	0.0	0.0	0.0
230	—	0.9	1.2	0.0
232	—	0.2	0.0	0.2
234	—	0.0	0.0	0.0
236	—	0.0	0.0	0.0
238	—	0.0	0.5	0.0
242	—	0.0	0.0	0.0
244	5.6	6.7	7.3	7.5
246	—	0.4	0.6	0.0
248	17.5	16.7	13.1	5.6
250	—	0.0	0.0	0.0
R factor[a] (%):		9.6	19.6	50.2

$$^aR = [\sum (|I_{obsd} - I_{calcd}|)/\sum I_{obsd}] \times 100$$

[a] Precision lattice constant from film pattern by Straumanis method.

TABLE II

Observed and Calculated Intensities of Allowable Lines in Pr–Lu Gallium Garnet
$(a = 12.925 \text{ Å})^a$

$h^2 + k^2 + l^2$	I_{obsd}	I_{calcd} for postulated structural formulae		
		$\{Pr_3\}[Lu_2](Ga_3)O_{12}$	$\{PrLu_2\}[Pr_2](Ga_3)O_{12}$	$\{Pr_3\}[Ga_2](Lu_2Ga)O_{12}$
6	8.3	11.7	18.0	0.0
8	9.7	19.7	4.0	7.4
14	6.2	6.1	10.1	0.0
16	57.5	60.2	48.1	22.2
20	88.1	89.5	100	100
22	—	0.1	0.5	0.9
24	100	100	77.8	33.0
26	1.2	1.1	1.0	0.7
30	8.0	7.0	9.1	0.6
32	1.1	1.1	0.0	2.7
38	7.8	6.9	9.1	0.6
40	4.7	5.9	0.0	0.0
42	—	0.0	0.0	0.0
46	1.7	0.9	1.6	0.0
48	4.1	4.5	8.1	15.0
50	—	0.0	0.0	0.0
52	30.6	24.0	26.5	25.7
54	2.1	2.6	3.5	0.1
56	76.9	64.4	50.8	23.1
62	1.5	1.4	2.2	0.1
64	20.3	18.0	16.6	11.3
66	—	0.1	0.1	0.1
68	—	0.1	0.1	0.0
70	—	0.3	0.6	0.0
72	2.3	2.2	0.4	1.0
74	—	0.0	0.0	0.0
78	—	0.4	0.6	0.0
80	17.0	15.5	12.1	5.4
84	17.4	14.1	16.0	16.3
86	0.9	1.0	1.6	0.1
88	12.5	12.6	9.9	4.4
90	—	0.2	0.1	0.1
94	0.9	0.8	1.2	0.0
96	0.9	0.9	0.2	0.3
98	—	0.2	0.2	0.2
100	—	0.0	0.0	0.0
102	—	0.2	0.4	0.0
104	1.4	1.3	0.1	0.7
106	—	0.0	0.0	0.0
110	1.6	1.1	1.6	0.0
114	—	0.0	0.0	0.0
116	11.8	11.7	13.2	13.4
118	—	0.5	0.7	0.0
120	16.4	13.2	10.4	4.6
122	—	0.0	0.0	0.0
126	—	0.9	1.3	0.0
128	9.7	8.6	8.0	5.4
134	0.6	0.6	0.7	0.0
136	—	0.5	0.0	0.6

TABLE II—*continued*

$h^2 + k^2 + l^2$	I_{obsd}	I_{calcd} for postulated structural formulae		
		{Pr$_3$}[Lu$_2$](Ga$_3$)O$_{12}$	{PrLu$_2$}[Pr$_2$](Ga$_3$)O$_{12}$	{Pr$_3$}[Ga$_2$](Lu$_2$Ga)O$_{12}$
138	—	0.0	0.0	0.0
140	—	0.0	0.0	0.0
142	—	0.2	0.4	0.0
144	6.5	5.8	4.6	2.0
146	—	0.0	0.0	0.0
148	2.3	2.4	2.7	2.8
150	—	0.5	0.7	0.0
152	13.5	13.4	10.4	4.6
154	—	0.0	0.0	0.0
158	—	0.3	0.4	0.0
160	—	0.3	0.0	0.2
162	—	0.0	0.0	0.0
164	—	0.0	0.0	0.0
166	0.8	0.7	0.9	0.0
168	—	0.5	0.0	0.3
170	—	0.0	0.0	0.0
174	—	0.4	0.6	0.0
176	1.3	0.7	1.6	3.5
178	—	0.0	0.0	0.0
180	6.6	6.3	7.2	7.2
182	—	0.5	0.7	0.0
184	7.4	6.8	5.3	2.3
186	—	0.0	0.0	0.0
190	—	0.1	0.2	0.0
192	4.3	3.4	3.2	2.2
194	—	0.0	0.0	0.0
196	—	0.0	0.0	0.0
198	—	0.2	0.4	0.0
200	0.9	1.0	0.1	0.5
202	—	0.0	0.0	0.0
206	0.7	0.6	1.0	0.0
208	4.2	3.3	2.5	1.1
210	—	0.0	0.0	0.0
212	6.0	5.6	8.6	6.5
214	—	0.1	0.2	0.0
216	15.5	14.8	11.5	5.1
218	—	0.0	0.0	0.0
222	—	0.3	0.5	0.0
224	—	0.4	0.0	0.4
226	—	0.0	0.0	0.0
230	0.8	0.8	1.1	0.0
232	—	0.2	0.0	0.2
234	—	0.0	0.0	0.0
236	—	0.0	0.0	0.0
238	—	0.3	0.5	0.0
242	—	0.0	0.0	0.0
244	6.5	6.4	9.7	7.6
246	—	0.4	0.6	0.0
248	17.6	17.2	13.2	5.8
250	—	0.0	0.0	0.0
R factor (%)		9.9	27.7	54.5

^{a} Precision lattice constant from film pattern by Straumanis method.

TABLE III

OBSERVED AND CALCULATED INTENSITIES OF NINE KEY LINES IN
Nd–Yb GALLIUM GARNET ($a = 12.856$ Å)

$h^2 + k^2 + l^2$	I_{obsd}	I_{calcd} for postulated structural formulae with indicated values of w in ${Nd_{2.7-w}Yb_{0.3+w}}[Nd_wYb_{2-w}](Ga_3)O_{12}$				
		$w = 0$	0.5	1.0	1.5	2.0
20	97.7	94.0	100	100	100	100
24	100	100	94.9	91.2	78.4	78.4
52	27.0	25.2	26.7	26.6	24.7	26.4
56	68.6	64.6	63.9	59.5	51.4	51.7
80	15.9	15.5	14.8	14.2	12.2	12.3
84	16.6	15.0	16.0	16.0	14.9	16.1
88	12.2	12.3	12.5	11.6	10.0	10.1
116	13.3	12.3	13.1	13.1	12.2	13.2
120	13.6	13.3	12.6	12.1	10.5	10.5
R' factor (%)[a]		3.5	4.3	6.9	15.1	14.0

[a] For definition of R', see text of paper.

X-Ray Diffraction Powder Patterns

All materials prepared in this way have been found to have X-ray diffraction film powder patterns (obtained with Norelco equipment) essentially identical with those of corresponding materials prepared by the earlier procedure. Although the garnets with rare earth ions filling two crystallographic sites have X-ray patterns quite similar to those of the rare earth garnets containing gallium on both octahedral and tetrahedral sites, there are a number of marked intensity shifts which should be accounted for by structure factor calculations if the assumed structures are correct. Most notable among such shifts in relative intensity are those in lines at $h^2 + k^2 + l^2 = 20$ and 24; 52 and 56; 80, 84, and 88; and 116 and 120. The 24-line does, in fact, become the strongest in the patterns of the materials with rare earths on two sites.

Quantitative intensity data for comparison with calculated intensities were obtained with a General Electric Company XRD–6 unit with an

TABLE IV

OBSERVED AND CALCULATED INTENSITIES OF NINE KEY LINES IN
Pr–Lu GALLIUM GARNET ($a = 12.925$ Å)

$h^2 + k^2 + l^2$	I_{obsd}	I_{calcd} for postulated structural formulae with indicated values of w in ${Pr_{3-w}Lu_w}[Pr_wLu_{2-w}](Ga_3)O_{12}$					
		$w = 0$	0.3	0.5	1.0	1.5	2.0
20	88.1	89.5	94.5	98.0	100	100	100
24	100	100	100	100	93.2	85.1	77.8
52	30.6	24.0	25.3	26.2	26.7	26.6	26.5
56	76.9	64.4	64.6	64.6	60.4	55.4	50.8
80	17.0	15.5	15.5	15.5	14.4	13.2	12.1
84	17.4	14.1	14.9	15.5	15.9	16.0	16.0
88	12.5	12.6	12.7	12.7	11.8	10.8	9.9
116	11.8	11.7	12.5	13.8	13.1	13.7	13.2
120	16.4	13.2	13.3	13.3	12.4	11.3	10.4
R' (%)[a]		7.7	8.6	9.5	13.4	17.9	21.7

[a] For definition of R', see text of paper.

SPG2 spectrogoniometer (diffractometer). Values given in the tables are integrated intensities, taken by measuring areas under peaks.

Calculation of Structure Factors

The garnet space group is $Ia3d-O_h^{10}$, for which the structure factor formula may be found in Ref. 7. The dodecahedral sites are $24(c)$, the octahedral sites $16(a)$, and the tetrahedral sites $24(d)$. These are all special positions, but the oxide ions are in $96(h)$ general positions. To obtain calculated intensities (with an RCA System 3 computer), the various ions were first assigned to these sites with various postulated distributions, and scattering factors were taken from Ref. 8 for the trivalent cations and from Ref. 7 for the oxide ion. Appropriate corrections were made for multiplicity factors, Lorentz and polarization factors, and temperature factors (assuming for the Debye parameter, B, an overall isotropic value of 1.5, which is a rather average value for inorganic compounds). Absorption factors were not included because they do not vary with θ when the data is obtained with an "infinitely thick" sample in a powder diffractometer. The x, y and z values for the oxide ions in general positions $96(h)$ were taken as -0.025, $+0.049$, and $+0.149$, respectively; these are average values for garnets and were found, when used in a test, to give good calculated intensities for $Yb_3Ga_5O_{12}$, a compound whose X-ray pattern and observed intensities are known (9) and whose x, y, and z values have been determined precisely as -0.0259, $+0.0563$, and $+0.1519$, respectively (10). Variations of ±0.01, ±0.015, and ±0.03 in the average values of x, y, and z, respectively, were found not to cause any changes in calculated intensities of $Yb_3Ga_5O_{12}$ which were significant enough to have a serious effect on the comparison with powder data.

Results of full calculations are given in Tables I and II. Included therein are calculations for the cation distributions indicated by the formulae in the Introduction section above as well as other distributions which do not really seem very logical from the viewpoint of crystal chemistry. These calculations confirm the earlier deduced structural formulae $\{Nd_{2.7}Yb_{0.3}\}[Yb_2](Ga_3)O_{12}$ and $\{Pr_3\}[Lu_2](Ga_3)O_{12}$. Because of a remaining possibility that there was partial, even if small, switching of large and small rare earths on the dodecahedral and octahedral sites, additional calculations were carried out for a number of such formulae but using only the nine key planes discussed in the X-Ray Diffraction Powder Patterns section above. The results given in Tables III and IV indicate that there is no such switching. The R' factors given in these tables are R factors calculated only from these nine lines. In cases where structural formulae are the same in Tables I and III or Tables II and IV, R and R' are therefore slightly different. It is obvious, however, that agreement becomes poorer and progressively so as switching is postulated. The relative intensities of lines at $h^2 + k^2 + l^2 = 20$ and 24 are especially sensitive to rare earth distribution and one can see very nicely, and perhaps even better than from the R' factors, exactly the same trend simply by comparing the observed intensities of these two lines with the several calculated values. It might be noted that the calculations account very well for the observed intensity shifts in the X-ray patterns of the compounds with the previously deduced structures with rare earths on two crystallographic sites as compared with $\{RE_3\}[Ga_2](Ga_3)O_{12}$. Further improvement in both the R factors and the calculated intensities of the 8-lines can almost surely be brought about by refinement of the x, y, and z values and also by determining good B values for the various ions on appropriate sites and then applying the resulting better temperature factors to the terms for the ions to which they pertain, rather than using overall values. Of course, best results would be obtained by comparison of calculated intensities with single crystal data.

References

1. M. L. KEITH AND R. ROY, Amer. Mineral. 39, 1 (1954).

2. R. S. ROTH, *J. Res. Nat. Bur. Stand.* **58**, 75 (1957).

3. S. J. SCHNEIDER, R. S. ROTH, AND J. L. WARING, *J. Res. Nat. Bur. Stand.* **65A**, 345 (1961).

4. S. GELLER AND G. P. ESPINOSA, work reported for the first time in a review paper by S. Geller, *Z. Kristallogr. Kristallgeometie. Kristallphys. Kristallchem.* **125**, 1 (1967).

5. L. SUCHOW, M. KOKTA, AND V. J. FLYNN, *J. Solid State Chem.* **2**, 137 (1970).

6. L. SUCHOW AND M. KOKTA, *J. Solid State Chem.*, in press.

7. "International Tables for X-Ray Crystallography," International Union of Crystallography, Kynoch Press, Birmingham, England (1952).

8. L. H. THOMAS AND K. UMEDA, *J. Chem. Phys.* **26**, 293 (1957).

9. Card No. 12–768 of the Powder Diffraction File of the Joint Committee on Powder Diffraction Standards, taken from U.S. National Bureau of Standards Monograph 25, Section 1, 1961.

10. F. EULER AND J. A. BRUCE, *Acta Crystallogr.* **19**, 971 (1965).