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Praseodymium–Small Rare Earth Gallium Garnets With Rare Earths On Two Crystallographic Sites*

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Garnets of the type $\{Pr_{3-y}R_y\}[R_xGa_{2-x}](Ga_3)O_{12}$, in which R is Lu, Yb, Tm, or Er, have been synthesized and studied. They are analogous to materials reported earlier with Nd in place of Pr, but the minimum y values which result in compliance with Vegard's law are higher. This is the case because the larger Pr^{3+} ion requires a greater amount than does Nd^{3+} of a given small rare earth ion, R^{3+}, to reduce the average dodecahedral site radius to a value which satisfies the R^{3+} on the octahedral site. Magnetic susceptibility measurements over the temperature range 78–300°K show the materials to be paramagnetic with Curie–Weiss behavior but with Curie constants somewhat lower than expected.

I. Introduction

Suchow, Kokta, and Flynn (*1*) have reported neodymium–small rare earth gallium garnets with the rare earths on both the dodecahedral and the octahedral sites, and they have also studied the magnetic properties of these materials (*2*). These neodymium preparations were of the type $\{Nd_{3-y}R_y\}[R_xGa_{2-x}](Ga_3)O_{12}$, where the braces indicate eightfold dodecahedral coordination (a distorted cube), the brackets sixfold octahedral coordination, and the parentheses fourfold tetrahedral coordination. For the case of $R = Lu^{3+}$, it was possible to prepare single-phase $\{Nd_3\}[Lu_2](Ga_3)O_{12}$ (i.e., $y=0$, $x=2$). For $R = Yb^{3+}$ or Tm^{3+} with $x=2$, it was necessary that y be simultaneously greater than zero and that its minimum value be determined experimentally. This minimum required value was found to increase with increasing radius of R. For $R = Er^{3+}$, Ho^{3+}, and Dy^{3+} the maximum x value attainable was less than 2 even with suitable y values.

In the garnet structure there is sharing of edges by dodecahedra with tetrahedra, octahedra, and other dodecahedra so that the limits of existence of compounds and solid solutions of the type under discussion must depend upon ratios of radii of the cations on the three crystallographic sites. In the present study, the tetrahedral positions were once more filled with Ga^{3+} ions, but the large rare earth employed was Pr^{3+} instead of Nd^{3+} [Shannon–Prewitt (*3*) 'IR' radii for coordination no. 8: $r_{Pr^{3+}} = 1.14$ Å, $r_{Nd^{3+}} = 1.12$ Å]. The use of a larger ion on the dodecahedral site was expected to yield further information regarding the relationship between relative sizes of cations in dodecahedral and octahedral positions and the resulting effect on the minimum y value.

This paper reports the results of these studies as well as measurements of the magnetic properties of the new materials.

II. Preparation and X-Ray Diffraction Study

All preparations were made by solid state reaction among rare earth oxides at least 99.9% pure and Ga_2O_3 99.999% pure. Most of the rare earth oxides employed were sesquioxides, but the praseodymium compound was Pr_6O_{11}. It was found that the oxidation state of the Pr in the products of reaction was independent of its initial oxidation state in the reactant. Desired quantities of oxides were carefully weighed and intimately mixed by grinding with an agate mortar and pestle. The mixtures were then heated 3 hr at 1350°C in open platinum crucibles

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in a muffle furnace. Following this, the samples were reground and reheated 5 hr under the same conditions. This procedure was found sufficient for equilibrium to be reached in all cases.

All preparations were studied by the X-ray diffraction powder method using Norelco equipment with 57.3 mm radius powder cameras.

IIA. Results and Discussion

As in the case where the large dodecahedral ion was Nd^{3+} (*1*), it was found that attempts to prepare $\{Pr_3\}[R_2](Ga_3)O_{12}$, where R is a small trivalent rare earth ion, usually led to garnet phases with one or more impurity phases also present. When an attempt was made to prepare solid solutions in the several series,

$$\{Pr_3\}[R_2](Ga_3)O_{12}–\{Pr_3\}[Ga_2](Ga_3)O_{12},$$

the results, given in Fig. 1, were rather similar to those obtained with Nd though somewhat different in the fact that an actual decrease in lattice constant was observed as the first amount of small rare earth was added, even for $R = Yb^{3+}$. In the corresponding Nd system, the first Yb addition had little effect on the lattice constant. In both cases, further addition of Yb caused the lattice constant to rise. The fact that the first Yb has a greater negative effect on the lattice constant in the Pr preparations indicates greater entry of the Yb into the dodecahedral positions, and this is seen to be true as well in the other systems which are plotted in Fig. 1.

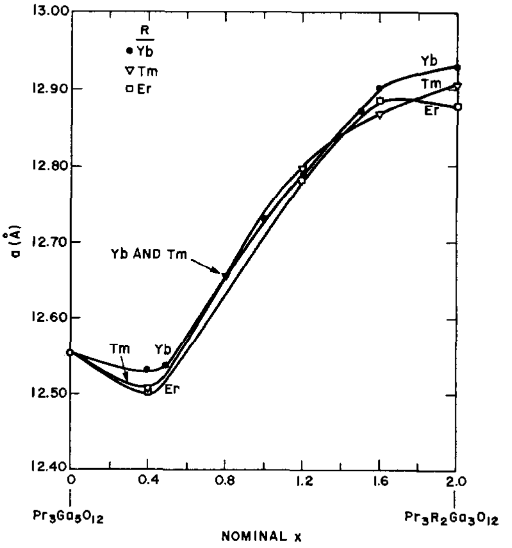

FIG. 1. Lattice constant versus nominal x for nominal $\{Pr_3\}[R_xGa_{2-x}](Ga_3)O_{12}$.

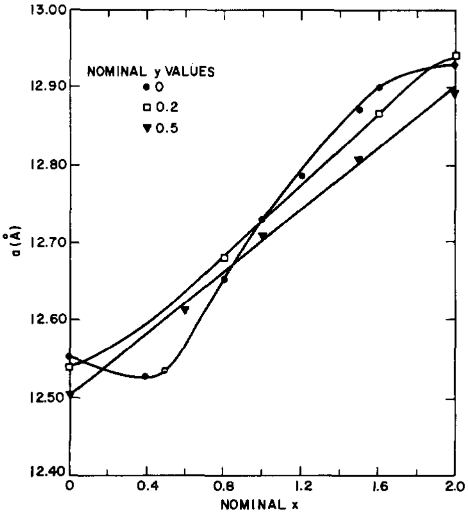

FIG. 2. Lattice constant versus nominal x with several values of nominal y for $\{Pr_{3-y}Yb_y\}[Yb_xGa_{2-x}](Ga_3)O_{12}$.

By the same experimental method described earlier (*1*), we have found the minimum y values (i.e., the amount of small rare earth on dodecahedral sites) which yield straight lines when lattice constants are plotted vs x for the systems $\{Pr_{3-y}R_y\}[R_xGa_{2-x}](Ga_3)O_{12}$. One example of the effect of y on the form of this curve is given in Fig. 2. At the minimum y value which yields a straight line, all compositions are single phase. The plots for three systems with the value of y required for linearity are given in Fig. 3. As with the Nd preparations, the maximum possible x

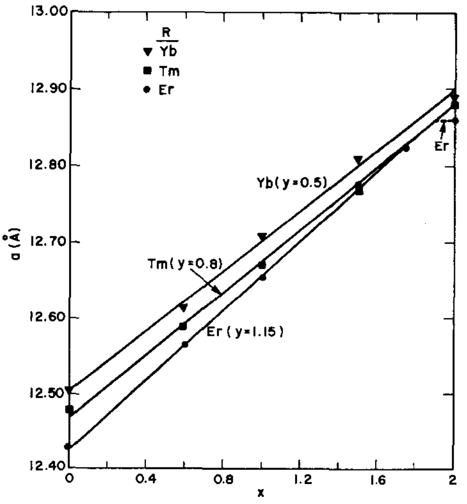

FIG. 3. Lattice constant versus x for $\{Pr_{3-y}R_y\}[R_xGa_{2-x}](Ga_3)O_{12}$.

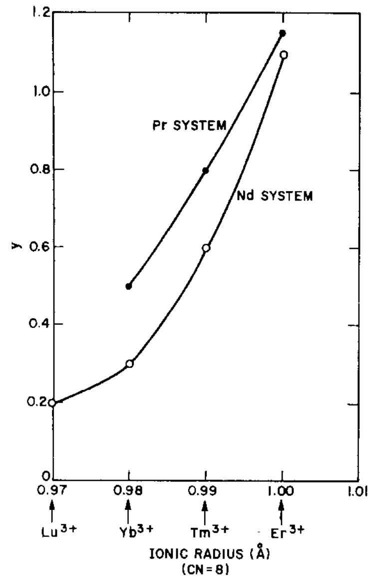

FIG. 4. *y* values required to yield single-phase garnets and straight lines in Fig. 3 [and in Fig. 4 of Ref. (*1*)] versus ionic radii of trivalent rare earths, R.

value with R = Er^{3+} was less than 2. Although we did not determine the *y* value with Lu^{3+} as the small rare earth, it was found possible to prepare single-phase $\{Pr_3\}[Lu_2](Ga_3)O_{12}$. Figure 4 contains a plot of the *y* values required to yield the single-phase Pr garnets and straight lines in Fig. 3 versus Shannon–Prewitt 'IR' radii (*3*) for the small rare earths in eightfold coordination. It also contains a similar plot for the Nd materials. The latter was given earlier (*1*), but Ahrens (*4*) radii for coordination no. 6 were then employed.

In the Nd preparations, it was found that the minimum *y* value increased with increasing size of the small rare earth. The same is true here, but it is now seen, in addition, that the minimum *y* value for any given small rare earth is higher in the Pr materials than in the Nd materials. These results are consistent and may be rationalized on the basis that both the Nd^{3+} and Pr^{3+} radii are somewhat higher than optimum for these systems so that certain amounts of small rare earth are attracted to the dodecahedral sites to lower the average radii of ions on those sites. The smaller the small rare earth, the less is required to attain a given average radius; this is seen to be true in both the Nd and the Pr systems. Regarding the large rare earth, since Pr^{3+} is larger than Nd^{3+}, more of the small rare earth ion is required to reduce the average to a given value.

TABLE I

CALCULATED AVERAGE SHANNON–PREWITT 'IR' RADII FOR THE DODECAHEDRAL SITE CONTAINING Nd^{3+} OR Pr^{3+} AND MINIMUM *y* VALUE AMOUNTS OF SMALL RARE EARTHS (R)

		Av dodecahedral site radius (Å)	
R^{3+}	Radius of R^{3+} for coordination no. 6	Nd^{3+} Compounds	Pr^{3+} Compounds
Yb^{3+}	0.868	1.10_6	1.11_4
Tm^{3+}	0.880	1.09_4	1.10_0
Er^{3+}	0.890	1.07_6	1.08_6

Table I lists the calculated average Shannon–Prewitt 'IR' radii for the dodecahedral site containing Nd^{3+} or Pr^{3+} along with minimum *y* value amounts of the various small rare earths. As shown, the averages involving any given small rare earth, R, are very close for Nd^{3+} and Pr^{3+}, but the average decreases slightly as the radius of R (which also goes into octahedral positions) increases.

Table II contains a list of lattice constants obtained for key compositions plotted. It also contains lattice constants calculated as described

TABLE II

OBSERVED AND CALCULATED LATTICE CONSTANTS

Composition[a]	a_{exp} (Å)	a_{calc} (Å)
$\{Pr_3\}[Ga_2](Ga_3)O_{12}$	12.55_2	12.55
$\{Pr_3\}[Lu_2](Ga_3)O_{12}$	12.94_2	12.92
$\{Pr_3\}[Yb_2](Ga_3)O_{12}$[b]	12.92_8	12.93
$\{Pr_{2.5}Yb_{0.5}\}[Ga_2](Ga_3)O_{12}$	12.50_5	12.49
$\{Pr_{2.5}Yb_{0.5}\}[YbGa](Ga_3)O_{12}$	12.70_6	12.68
$\{Pr_{2.5}Yb_{0.5}\}[Yb_2](Ga_3)O_{12}$	12.89_0	12.88
$\{Pr_3\}[Tm_2](Ga_3)O_{12}$[c]	12.90_4	12.95
$\{Pr_{2.2}Tm_{0.8}\}[Ga_2](Ga_3)O_{12}$	12.48_0	12.46
$\{Pr_{2.2}Tm_{0.8}\}[TmGa](Ga_3)O_{12}$	12.67_0	12.66
$\{Pr_{2.2}Tm_{0.8}\}[Tm_2](Ga_3)O_{12}$	12.88_2	12.87
$\{Pr_3\}[Er_2](Ga_3)O_{12}$[c]	12.88_2	12.97
$\{Pr_{1.85}Er_{1.15}\}[Ga_2](Ga_3)O_{12}$	12.43_3	12.43
$\{Pr_{1.85}Er_{1.15}\}[Er_{1.75}Ga_{0.25}](Ga_3)O_{12}$	12.82_3	12.80
$\{Pr_{1.85}Er_{1.15}\}[Er_2](Ga_3)O_{12}$[b]	12.86_0	12.85

[a] Single phase unless otherwise noted.
[b] Almost single phase.
[c] Nominal composition, not single phase.

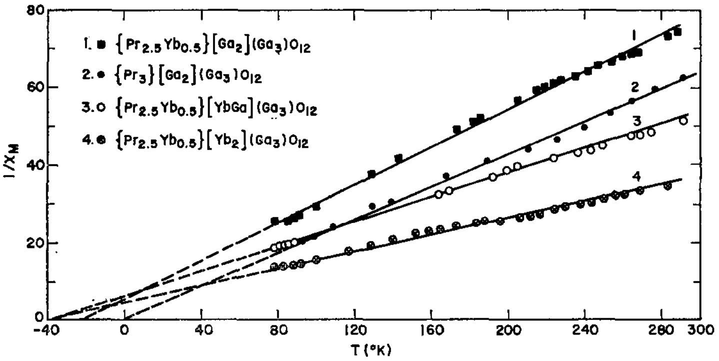

FIG. 5. Reciprocal molar susceptibility versus absolute temperature for materials with R = Yb.

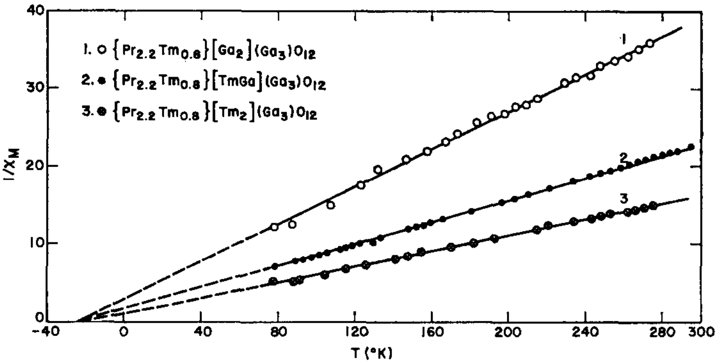

FIG. 6. Reciprocal molar susceptibility versus absolute temperature for materials with R = Tm.

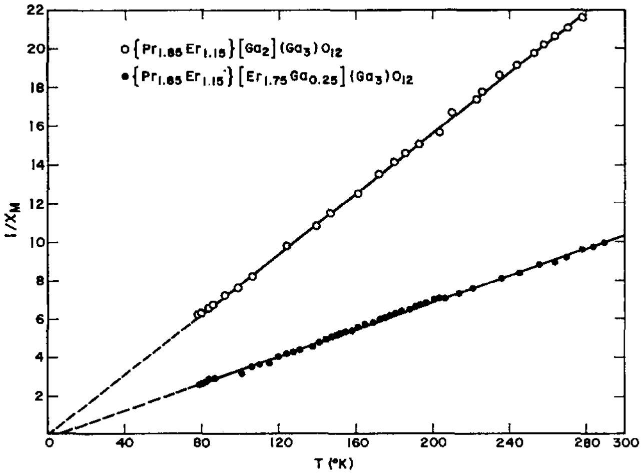

FIG. 7. Reciprocal molar susceptibility versus absolute temperature for materials with R = Er.

earlier (*1*, *2*) from Shannon–Prewitt 'IR' radii employed in the formula

$$a_{\text{calc}} = (\text{av } r_{\text{dod}} - 1.12)(2.15) + (\text{av } r_{\text{oct}} - 0.620)(1.56) + 12.504,$$

where r_{dod} and r_{oct} represent radii of ions on the dodecahedral and octahedral sites, respectively. In most cases where the preparations are single phase, the correspondence is good, but a bit less so than with the Nd compounds.

TABLE III

EXPERIMENTAL AND CALCULATED MOLAR CURIE CONSTANTS (C_M) OF GARNET SOLID SOLUTIONS

	C_M		
Composition	Experimental	Theoretical	Calculated from experimental values for ions on dodecahedral and octahedral sites
$\{Pr_{2.5}Yb_{0.5}\}[Ga_2](Ga_3)O_{12}$	4.10	5.26	4.93
$\{Pr_{2.5}Yb_{0.5}\}[YbGa](Ga_3)O_{12}$	6.23	7.82	7.39
$\{Pr_{2.5}Yb_{0.5}\}[Yb_2](Ga_3)O_{12}$	9.27	10.4	9.85
$\{Pr_{2.2}Tm_{0.8}\}[Ga_2](Ga_3)O_{12}$	8.28	9.17	8.72
$\{Pr_{2.2}Tm_{0.8}\}[TmGa](Ga_3)O_{12}$	14.2	16.3	15.0
$\{Pr_{2.2}Tm_{0.8}\}[Tm_2](Ga_3)O_{12}$	19.4	23.4	21.4
$\{Pr_{1.85}Er_{1.15}\}[Ga_2](Ga_3)O_{12}$	12.8	16.0	14.2
$\{Pr_{1.85}Er_{1.15}\}[Er_{1.75}Ga_{0.25}](Ga_3)O_{12}$	28.6	35.9	31.0

III. Magnetic Measurements

The single-phase preparations described herein were subjected to measurement at temperatures from 78 to 300°K with the Faraday apparatus previously described (*5*) (at a field strength of about 6 kG). The data were put into the form of $1/\chi_M$ vs T plots, and Curie constants determined from the slopes of the resulting straight-line portions in the temperature range 78–300°K, as discussed in Ref. (*5*).

IIIA. Results and Discussion

The magnetic data were treated as in our earlier work (*2*). That is, the molar Curie constants (C_M) found over the range 78–300°K were compared with values calculated from theoretical values and from experimental values (for ions on octahedral and dodecahedral sites) of the individual gram-atom Curie constants ($C_{M(\mathrm{ind})}$). Most of the $C_{M(\mathrm{ind})}$ values employed are given in Ref. (*2*). The experimental C_M value for $Pr_3Ga_5O_{12}$ was 4.72, which leads to a $C_{M(\mathrm{ind})}$ value of 1.57 for Pr^{3+} in the dodecahedral position; the theoretical value is 1.59 (*6*). Results of the measurements are plotted in Figs. 5–7. The materials are all paramagnetic and obey the Curie–Weiss law, at least over the range 78–300°K. The broken-line portions are extrapolations to $1/\chi_M = 0$ in order to indicate the magnitudes of the Weiss constants. Experimental C_M values obtained from the 78–300°K portions of the plots in Figs. 5–7 are given in Table III along with calculated values.

In no case is there any evidence from our data of ferromagnetic, ferrimagnetic, or antiferromagnetic ordering. The paramagnetic C_M values obtained experimentally are in all cases closer to those calculated from experimental values for ions on dodecahedral and octahedral sites than to theoretical values. In fact, they are lower than those calculated from experimental values, unlike the values for most of the corresponding Nd materials (*2*). This could possibly be due to greater quenching in the Pr garnet solid solutions or to the presence of small amounts of Pr^{4+} and accompanying R^{2+} ions. These ions could result from an oxidation–reduction process, but this seems likely only with $R = Yb$. There is some optical evidence that small amounts of these ionic species are present when R is Yb, and it is anticipated that this will be discussed in a future publication.

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