

## New Garnet Compounds with Trivalent Rare-Earth Ions on Both Dodecahedral and Octahedral Sites\*

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This study deals with preparation of garnets of the type  $\{Nd_{3-y}R_y\}[R_xGa_{2-x}](Ga_3)O_{12}$ , in which R is Lu, Yb, Tm, Er, Ho, or Dy. It has been found that the placement of large rare-earth ions such as  $Nd^{3+}$  on the dodecahedral sites opens up the lattice so that small rare-earth ions may enter the octahedral sites. For the case of  $R = Lu$  single-phase  $\{Nd_3\}[Lu_2]Ga_3O_{12}$  (i.e.,  $y = 0$ ,  $x = 2$ ) has been prepared. Calculations indicate that similar compounds of Yb and perhaps Tm have also been prepared, though impure. To prepare single-phase Yb and Tm compounds with  $x = 2$ , it is necessary simultaneously to place determined minimum amounts of R in the dodecahedral positions. This minimum required value of  $y$  increases with increasing radius of R. Many single-phase garnet solid solutions have also been prepared; the region in which pure garnets occur is indicated in a ternary diagram.

### Introduction

The simultaneous occurrence of rare-earth ions on more than one site in a given compound is quite interesting in itself, and could, perhaps, also result in interesting magnetic or optical properties. Some examples are  $PrLuO_3$  and  $LaMO_3$ , where  $M = Y^{3+}$ ,  $Ho^{3+}$ ,  $Er^{3+}$ ,  $Tm^{3+}$ ,  $Yb^{3+}$ , and  $Lu^{3+}$  (1); these compounds all have perovskite structures with distortion to orthorhombic. Their existence is due to the considerable difference in radii of rare-earth ions which enables large ones to enter positions of twelfold coordination while the small ones enter the octahedral positions.

Rare earths have also been observed to distribute themselves, at least to some extent, on two crystallographic sites in some garnets. The garnet structure, space group  $Ia3d$ , is typified by the mineral grossularite,  $\{Ca_3^{2+}\}[Al_2^{3+}](Si_3^{4+})O_{12}$ , where the curly brackets indicate eightfold dodecahedral coordination (a distorted cube), the square brackets sixfold octahedral coordination, and the parentheses fourfold tetrahedral coordination. It has been found possible also to prepare garnets with small trivalent ions, such as  $Al^{3+}$ ,  $Ga^{3+}$ , and  $Fe^{3+}$ , replacing  $Si^{4+}$  on the tetrahedral sites if charge compensation is achieved by substituting for  $Ca^{2+}$  on the dodecahedral sites

any of a number of trivalent ions of the rare earths or yttrium. Some examples are  $\{Gd_3^{3+}\}[Fe_2^{3+}](Fe_3^{3+})O_{12}$  (or  $Gd_3Fe_5O_{12}$ ),  $\{Y_3^{3+}\}[Al_2^{3+}](Al_3^{3+})O_{12}$  (or  $Y_3Al_5O_{12}$ ), and  $\{Nd_3^{3+}\}[Ga_2^{3+}](Ga_3^{3+})O_{12}$  (or  $Nd_3Ga_5O_{12}$ ).

On studying double oxides of trivalent elements, Keith and Roy (2) found that many  $ABO_3$  compositions assumed the perovskite structure if A is a large ion and B a small one. In several systems, however, the garnet structure was also observed, though usually accompanied by perovskite or distorted perovskite phases when the starting composition of oxides was equimolar. These systems were  $Y_2O_3-Al_2O_3$ ,  $Ce_2O_3-Ga_2O_3$ ,  $Nd_2O_3-Ga_2O_3$ ,  $Sm_2O_3-Ga_2O_3$ , and  $Y_2O_3-Ga_2O_3$ . The garnet structure was obtained with 1:1 compositions apparently because solid solutions like  $\{Y_3\}(Y, Al)_2(Al_3)O_{12}$  formed. A solid-solution composition with an equal number of Y and Al ions on the octahedral sites would have exactly the same composition as perovskite phases so that the relative amounts of the two would be determined by preparative conditions. Results rather similar to these, but differing somewhat in detail, were obtained by Roth (3) in the  $Y_2O_3-Al_2O_3$  system. Schneider, Roth, and Waring (4) investigated the extent of garnet solid solution formation in systems containing  $Ga_2O_3$  with  $Nd_2O_3$ ,  $Sm_2O_3$ ,  $Eu_2O_3$ ,  $Gd_2O_3$ ,  $Dy_2O_3$ ,  $Ho_2O_3$ ,  $Er_2O_3$ ,  $Tm_2O_3$ ,  $Yb_2O_3$ ,  $Lu_2O_3$ , or  $Y_2O_3$ , and also in systems containing  $Al_2O_3$  along with either  $Yb_2O_3$

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or  $\text{Lu}_2\text{O}_3$ . In the gallia garnets, maximum solubility of rare earth on the octahedral sites was found at  $\text{Tm}^{3+}$  and fell off in both directions along the rare earth series (though the solubility of  $\text{Yb}^{3+}$  was not significantly lower). The formula of the composition with maximum Tm is  $\{\text{Tm}_3\}[\text{Tm}_{0.8}\text{Ga}_{1.2}](\text{Ga}_3)\text{O}_{12}$ . If the number of octahedral rare-earth ions per formula unit is called  $x$  (0.8 in the  $\text{Tm}_2\text{O}_3$ - $\text{Ga}_2\text{O}_3$  garnet), then  $x$  was found to be approximately 0.16 for alumina garnets containing maximum Yb or Lu.

Schneider, Roth, and Waring (4) found a maximum value of  $x$  approximating 0.74 in the  $\text{Y}_2\text{O}_3$ - $\text{Ga}_2\text{O}_3$  garnet. Geller and Espinosa (5) prepared several compositions in this system and found a linear increase in lattice constant with increasing  $x$ . The maximum  $x$  value they observed was about the same as that reported by Schneider, Roth, and Waring (4), and impurity phases were usually also present.

Mill (6) prepared a large number of germanate garnets with large divalent alkaline earth ions (Ca and Sr) on the dodecahedral sites and small trivalent rare-earth ions (Dy, Ho, Er, Tm, Yb, Lu, and also Sc and Y) on the octahedral sites (e.g.,  $\text{Sr}_3\text{Tm}_2\text{Ge}_3\text{O}_{12}$  and  $\text{Ca}_3\text{Yb}_2\text{Ge}_3\text{O}_{12}$ ) by reaction of the oxides at  $1250^\circ\text{C}$ . Ito (7) later reported that he was able to prepare one of Mill's compounds,  $\text{Sr}_3\text{Yb}_2\text{Ge}_3\text{O}_{12}$ , by precipitation from strong NaOH solution in air at  $100^\circ\text{C}$ .

These results suggested to us that it might be possible to prepare gallia or alumina garnets with trivalent rare earth ions on both dodecahedral and octahedral sites, perhaps to exclusion of all other ions on the octahedral sites (i.e.,  $x=2$ ), if the dodecahedral sites were filled with large rare earths to open up the lattice so that small ones could more easily enter the octahedral sites. In the meantime, Morozova and Feofilov (8) were able to prepare the garnet  $\{\text{Y}_3\}[\text{Sc}_2](\text{Ga}_3)\text{O}_{12}$ . Y and Sc are not rare earths, however; they contain no  $f$  electrons, and their trivalent ions are diamagnetic. Although Y is rather small, Sc is so much smaller that it is able to enter the octahedral sites, and the compound is closely related to the compounds reported in the present paper.

Experiments have proved the hypotheses stated above to be essentially correct, though with some interesting complications, as will be seen.

#### Preparation and X-Ray Diffraction Study

All preparations were made by solid state reaction among rare-earth oxides at least 99.9% pure and  $\text{Ga}_2\text{O}_3$  99.999% pure. 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  $1500^\circ\text{C}$  in open platinum crucibles in a muffle furnace. Following this, the samples were reground and reheated 5 hr under the same conditions. This procedure was found to be sufficient for equilibrium to be reached in all cases. Because of the limitation of the furnace used,  $1500^\circ\text{C}$  was the maximum temperature employed; it was found that increasingly incomplete reaction was obtained as the reaction temperature was lowered.

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

#### Results and Discussion

Exploratory experiments indicated that it was possible to prepare gallia garnets of the type sought where the large rare earth for the dodecahedral position was, for instance,  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ , or  $\text{Eu}^{3+}$ . For the present study  $\text{Nd}^{3+}$  was chosen, but it is anticipated that a future paper will report results obtained with other ions in the dodecahedral position.  $\text{Nd}^{3+}$  is a good choice because its radius is among the largest found in the rare earths. Although it enters the dodecahedral position of gallia garnets with ease, it will not go into the octahedral position at all. (This finding (4) has been confirmed in the present study.) Figure 1 shows that the lattice constant of  $\{\text{Nd}_3\}[\text{Ga}_2](\text{Ga}_3)\text{O}_{12}$  decreases with increasing addition in solid solution of  $\{\text{Yb}_3\}[\text{Ga}_2](\text{Ga}_3)\text{O}_{12}$  (that is, with increase of  $y$  in the formula  $\{\text{Nd}_{3-y}\text{Yb}_y\}[\text{Ga}_2](\text{Ga}_3)\text{O}_{12}$ ). When sufficient Ga is present to

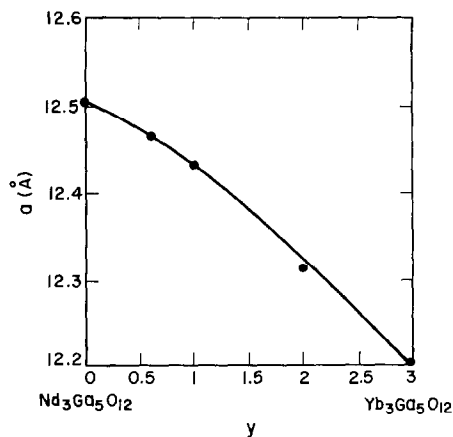


FIG. 1. Lattice constants versus  $y$  for  $\{\text{Nd}_{3-y}\text{Yb}_y\}[\text{Ga}_2](\text{Ga}_3)\text{O}_{12}$ .

fill both the octahedral and tetrahedral sites, all rare earths, whether Nd or R, enter only dodecahedral positions. Increases in  $x$ , the amount of R on octahedral sites, would, of course, increase the lattice constant, as shown in earlier studies referenced above.

Upon attempting to prepare  $\{\text{Nd}_3\}[\text{R}_2](\text{Ga}_3)\text{O}_{12}$  compounds with the small trivalent rare earth ion, R, being  $\text{Dy}^{3+}$ ,  $\text{Ho}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$ ,  $\text{Yb}^{3+}$ , and  $\text{Lu}^{3+}$ , it was found that garnets were formed in all cases but that, except for  $\{\text{Nd}_3\}[\text{Lu}_2](\text{Ga}_3)\text{O}_{12}$ , which contains the smallest of all the rare earths, impurity phases were also present. This suggested the possibility that pure garnet phases would be found in compositions  $\{\text{Nd}_3\}[\text{R}_x\text{Ga}_{2-x}](\text{Ga}_3)\text{O}_{12}$ , up to some maximum value of  $x$ . Therefore, attempts were made to prepare solid solutions of  $\{\text{Nd}_3\}[\text{Ga}_2](\text{Ga}_3)\text{O}_{12}$  with the nominal compositions  $\{\text{Nd}_3\}[\text{R}_2](\text{Ga}_3)\text{O}_{12}$ , and to determine the relationship between composition and lattice constant.

In many of the compositions prepared, garnet phases were accompanied by impurities but appreciable changes in lattice constants were observed. The results, plotted in Fig. 2, indicated that Vegard's law was not obeyed, but rather that each of the curves contained two segments with different slopes. The first segments, with small additions of R (i.e.,  $x$  small), have much lower slopes than the second segments, where  $x$  is large, and some of the first segment slopes are actually zero or negative. A logical explanation for this appeared to be that some of the small rare earth, R, was actually entering dodecahedral positions along with the Nd, while simultaneously entering octahedral positions. Since the first would decrease the lattice constant and the second would increase it, the net change would be small, which is precisely what was observed. In addition, with R entering dodecahedral sites and Nd unable to enter octahedral sites, one would expect that a surplus of Nd would result. This is in fact the case, for one impurity phase found was the perovskite,  $\text{NdGaO}_3$ , when  $x$  was  $< \sim 0.6$  for Lu,  $< \sim 1.2$  for Yb and Tm,  $< 1.8$  for Er, and 0–2 for Ho and Dy. Additional impurity phases found when  $x = 1.1$ –2 for Yb, 1–2 for Tm, 0.9–2 for Er, and 0.8–2 for Ho and Dy have not been identified. The loss of Ga available to the garnet phase, which results from formation of the 1:1 perovskite phase will, of course, affect the amount of garnet which can form and the magnitude of its lattice constant. It is for the reasons outlined here that the abscissa in Fig. 2 is labelled "Nominal  $x$ ," which means the amount introduced into the mixture of reactants based on the expected ideal solid solution formation.

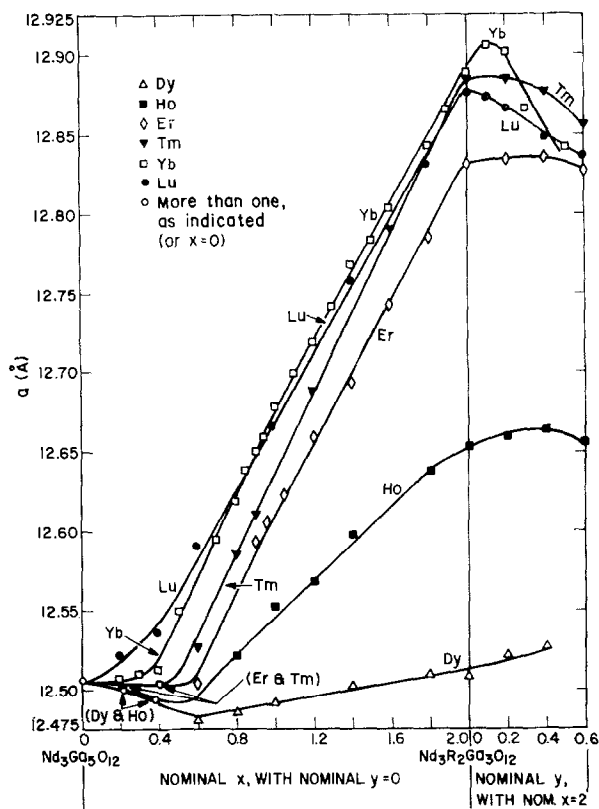


FIG. 2. Lattice constants versus nominal  $x$  for nominal  $\{\text{Nd}_3\}[\text{R}_x\text{Ga}_{2-x}](\text{Ga}_3)\text{O}_{12}$  and versus nominal  $y$  for nominal  $\{\text{Nd}_{3-y}\text{R}_y\}[\text{R}_2](\text{Ga}_3)\text{O}_{12}$ .

The sharp rises of the second segments of the curves in Fig. 2 indicate that, following partial filling of the dodecahedral positions with R, the octahedral positions fill up more exclusively. The lower levels of the Er, Ho, and Dy curves indicate that the true maximum values of  $x$  attained in these nominal systems were lower than with the smaller ions of Tm, Yb, and Lu.

If some of the small rare earth, R, enters dodecahedral sites and thus leaves insufficient R for the octahedral sites, then one might expect further addition of R, with corresponding decrease in Nd, actually to result in further expansion of the lattice, at least up to the point where a maximum value of  $x$  is reached. This should occur because such further addition would provide sufficient R both to satisfy the dodecahedral sites and to continue filling of the octahedral sites. None of the rare earths will enter the tetrahedral sites in substitution for Ga. One might now think in terms of the formula  $\{\text{Nd}_{3-y}\text{R}_y\}[\text{R}_x\text{Ga}_{2-x}](\text{Ga}_3)\text{O}_{12}$ ; it is the nominal value of this  $y$  (with nominal  $x = 2$ ), which is plotted in the right

portion of Fig. 2. In the case of Lu, where the composition  $\{\text{Nd}_3\}[\text{Lu}_2](\text{Ga}_3)\text{O}_{12}$  is single-phase, one would expect to find an immediate decrease, and this is indeed so. In all the other cases, either an increase or a levelling off is observed. The maintenance of a constant value is also significant here because a true increase in  $y$  in a single-phase material could only cause a decrease in lattice constant. However, with the exception of the Lu preparations, none was pure garnet when  $y$  was 0 (or greater than 0 but small) and  $x$  was 2. Note that the value of  $y$  at the peak or at the end of the constant level region tends to increase with increase in the radius of R. It was found during this aspect of the investigation that if  $y$  was large enough, single-phase garnets were obtained. In four cases, then, a nominal composition was chosen where the perovskite impurity lines in the X-ray diffraction powder pattern were strongest, and values of  $y$  were varied while  $x$  was held constant. In the Lu system, this value of  $x$  was 0.5, while for Yb, Tm, and Er, it was 0.8.

It was found that as the value of  $y$  approached the minimum required for the preparation of single-phase materials, plots of lattice constant versus composition became more linear, and at the value of  $y$  which yields purity it was linear; that is, Vegard's

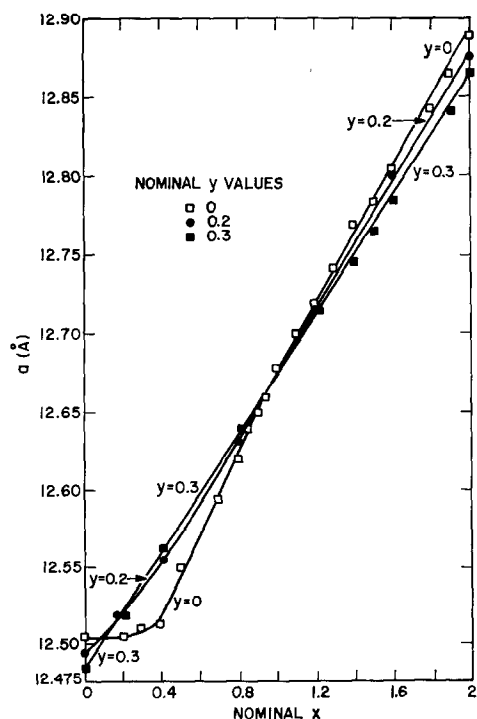


FIG. 3. Lattice constants versus nominal  $x$  with several values of nominal  $y$  for  $\{\text{Nd}_{3-y}\text{Yb}_y\}[\text{Yb}_x\text{Ga}_{2-x}](\text{Ga}_3)\text{O}_{12}$ .

law was now obeyed because both dodecahedral and octahedral sites were satisfied. The progressive increase in linearity for the system  $\{\text{Nd}_{3-y}\text{Yb}_y\}[\text{Yb}_x\text{Ga}_{2-x}](\text{Ga}_3)\text{O}_{12}$  is seen in Fig. 3. The plots for four systems,  $\{\text{Nd}_{3-y}\text{R}_y\}[\text{R}_x\text{Ga}_{2-x}](\text{Ga}_3)\text{O}_{12}$ , with the value of  $y$  required for linearity, are given in Fig. 4. All preparations indicated therein are single-phase except for the one with Er at  $x = 2$ . It appears that in this case the limiting value of  $x$  might be about 1.8. Note that since  $y$  for Er is 1.1, the dodecahedral ions cause less expansion of the lattice. An attempt to obtain a single-phase composition  $\{\text{Nd}_{3-y}\text{Er}_y\}[\text{Er}_2](\text{Ga}_3)\text{O}_{12}$  by increasing values of  $y$  with  $x$  held at 2 was unsuccessful, probably at least partly because this further decreases the average size of the dodecahedral ion and, therefore, causes even less enlargement of the octahedral sites.

Figure 5 illustrates the effect of the ionic radius of the small rare earth on the amount ( $y$ ) which enters the dodecahedral position. In Fig. 5(a) is the relationship between the ionic radius and the break points in terms of nominal composition ( $x$ ) taken from the curves in Fig. 2. As explained above, the nominal  $x$  value at the break point is in reality related to  $y$ .

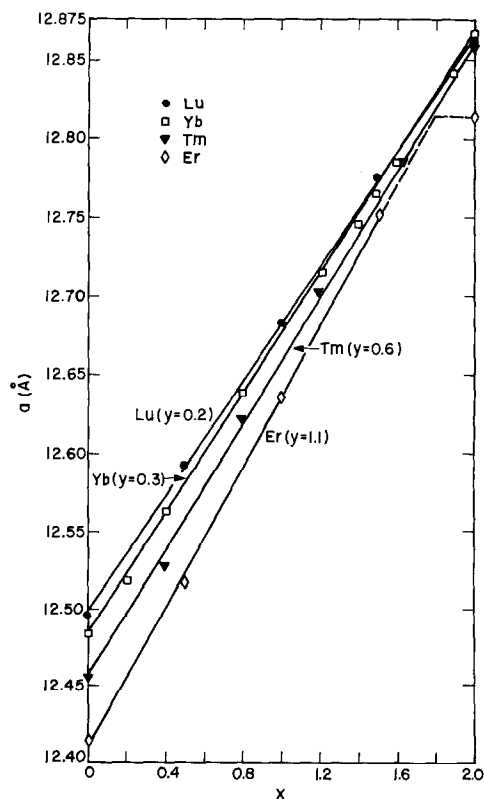


FIG. 4. Lattice constants versus  $x$  for  $\{\text{Nd}_{3-y}\text{R}_y\}[\text{R}_x\text{Ga}_{2-x}](\text{Ga}_3)\text{O}_{12}$ .

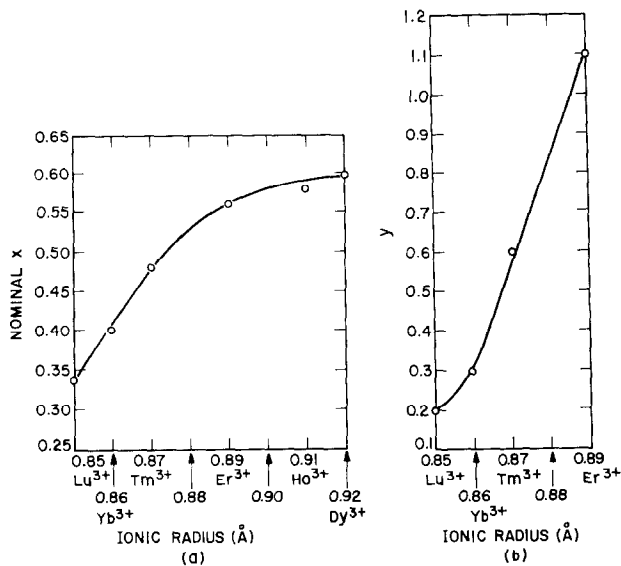


FIG. 5. (a) Nominal  $x$  values at break points in curves of Fig. 2 versus ionic radii of trivalent rare earths,  $R$ ; (b)  $y$  values required to yield single-phase garnets and straight lines in Fig. 4 versus ionic radii of trivalent rare earths,  $R$ .

Figure 5(b) is a plot of the ionic radii versus the  $y$  values required to satisfy (not saturate) the dodecahedral sites and thus obtain the pure garnets and the straight lines of Fig. 4. It should be noted that these  $y$  values are perhaps not the minimum required for purity at all compositions. For instance,  $\{Nd_3\}[Lu_2](Ga_3)O_{12}$  may be obtained as a single-phase material, but a  $y$  value of 0.2 is required to yield single-phase materials throughout the composition range along with a linear relationship between lattice constant and composition. Extrapolation of the curve in Fig. 5(b) to the radii of  $Ho^{3+}$  (0.91 Å) and  $Dy^{3+}$  (0.92 Å) predicts  $y$  values of 1.65 and 1.9, respectively. In these cases, then, the dodecahedral site would contain more small rare earth than Nd, and so would likely permit even less to enter the octahedral site; the result would probably be to yield straight lines in these systems only to values less than  $x = 2$  as in the Er case, and almost surely the limiting  $x$  values would be even lower than that indicated for the Er case in Fig. 4.

Figure 6 is a diagram of the ternary system  $Nd_2O_3$ - $Yb_2O_3$ - $Ga_2O_3$ , but serves to represent in

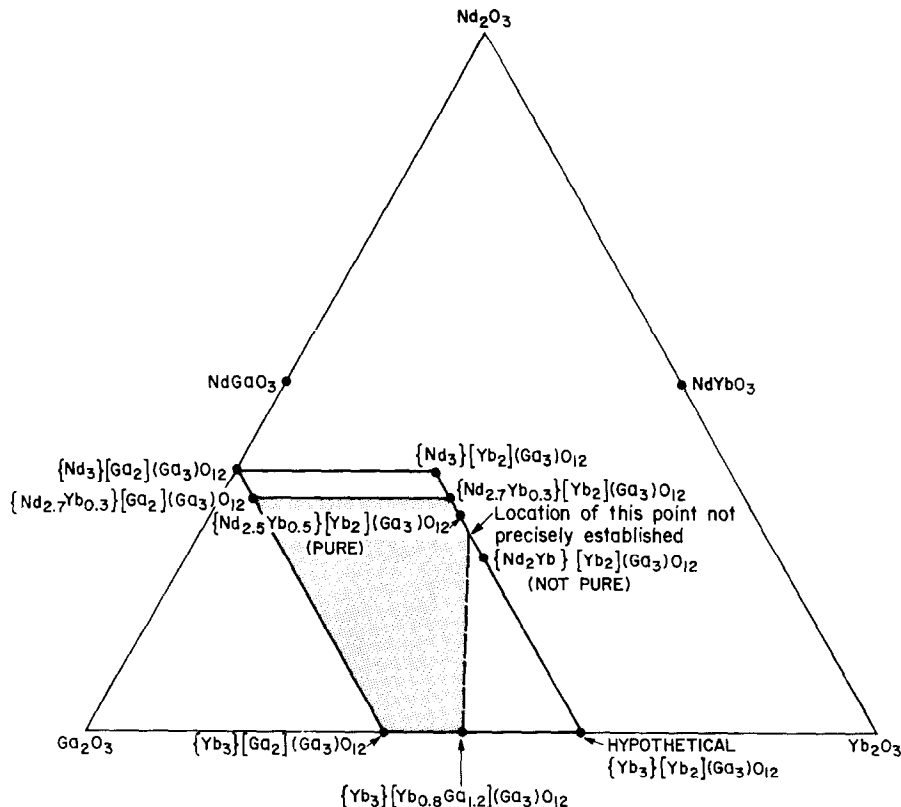


FIG. 6. The ternary system  $Nd_2O_3$ - $Ga_2O_3$ - $Yb_2O_3$ . Single-phase garnets are found only in the shaded area and along the line between  $\{Nd_3\}[Ga_2](Ga_3)O_{12}$  and  $\{Nd_{2.7}Yb_{0.3}\}[Ga_2](Ga_3)O_{12}$ .

form, though not in detail, all ternary systems studied. It will be seen that the line representing the pseudobinary system that yielded single-phase garnets and the straight line in Figs. 3 and 4 (i.e.,  $\{\text{Nd}_{2.7}\text{Yb}_{0.3}\}[\text{Ga}_2](\text{Ga}_3)\text{O}_{12}$ - $\{\text{Nd}_{2.7}\text{Yb}_{0.3}\}[\text{Yb}_2](\text{Ga}_3)\text{O}_{12}$ ) is parallel to the line representing the nominal system,  $\{\text{Nd}_3\}[\text{Ga}_2](\text{Ga}_3)\text{O}_{12}$ - $\{\text{Nd}_3\}[\text{Yb}_2](\text{Ga}_3)\text{O}_{12}$ , results for which are given in Fig. 2. (The distance between these parallel lines would of course be somewhat different for the other systems studied.) Single-phase garnets have been found only in the shaded area and along the line between  $\{\text{Nd}_3\}[\text{Ga}_2](\text{Ga}_3)\text{O}_{12}$  and  $\{\text{Nd}_{2.7}\text{Yb}_{0.3}\}[\text{Ga}_2](\text{Ga}_3)\text{O}_{12}$ . The solubility limit represented by the point at  $\{\text{Yb}_3\}[\text{Yb}_{0.8}\text{Ga}_{1.2}](\text{Ga}_3)\text{O}_{12}$  is from the paper by Schneider, Roth, and Waring (4).

Table I contains a list of lattice constants obtained for key compositions plotted, especially end members. It also contains lattice constants calculated as follows:

As the average radius of ions on the dodecahedral site decreases, the lattice constant should also decrease. Similarly, the lattice constant should increase as the average radius of ions on the octa-

hedral site increases. If both occur simultaneously the net result will be the difference between the magnitudes of the two effects. The extent of the effect of the radius of dodecahedral ions on the lattice constant was taken from the change in lattice constant from  $\{\text{Nd}_3\}[\text{Ga}_2](\text{Ga}_3)\text{O}_{12}$  to  $\{\text{Yb}_3\}[\text{Ga}_2](\text{Ga}_3)\text{O}_{12}$ . Although Fig. 1 indicates that the relationship is not quite linear, the calculations assumed linearity since only a slight error would be introduced by such an assumption. The extent of the effect of the radius of octahedral ions on the lattice constant was taken from the difference between values for  $\{\text{Nd}_3\}[\text{Ga}_2](\text{Ga}_3)\text{O}_{12}$  and  $\{\text{Nd}_3\}[\text{Lu}_2](\text{Ga}_3)\text{O}_{12}$ . Linearity was again assumed.

For the dodecahedral case,

$$\frac{a_{\{\text{Nd}_3\}[\text{Ga}_2](\text{Ga}_3)\text{O}_{12}} - a_{\{\text{Yb}_3\}[\text{Ga}_2](\text{Ga}_3)\text{O}_{12}}}{r_{\text{Nd}^{3+}} - r_{\text{Yb}^{3+}}} = \frac{12.504 - 12.203}{1.04 - 0.86} = 1.72 \text{ \AA } \Delta a / \text{ \AA } \Delta r_{\text{dod}}$$

For the octahedral case,

$$\frac{a_{\{\text{Nd}_3\}[\text{Lu}_2](\text{Ga}_3)\text{O}_{12}} - a_{\{\text{Nd}_3\}[\text{Ga}_2](\text{Ga}_3)\text{O}_{12}}}{r_{\text{Lu}^{3+}} - r_{\text{Ga}^{3+}}} = \frac{12.881 - 12.504}{0.85 - 0.62} = 1.64 \text{ \AA } \Delta a / \text{ \AA } \Delta r_{\text{oct}}$$

Lattice constants were then calculated from

$$a_{\text{calc}} = (\text{average } r_{\text{dod}} - r_{\text{Nd}^{3+}})(1.72) + (\text{average } r_{\text{oct}} - r_{\text{Ga}^{3+}})(1.64) + a_{\text{Nd}_3\text{Ga}_5\text{O}_{12}}$$

where  $r_{\text{dod}}$  and  $r_{\text{oct}}$  represent radii of ions on the dodecahedral and octahedral sites, respectively.

The results shown in Table I indicate good agreement between observed and calculated values when one is dealing with single phases and therefore knows the true values of  $x$  and  $y$ . The results also indicate that the preparation with nominal formula  $\{\text{Nd}_3\}[\text{Yb}_2](\text{Ga}_3)\text{O}_{12}$  has a true formula which is probably actually quite similar despite the small amount of impurities observed to be present. Similarly, the preparation with nominal formula,  $\{\text{Nd}_3\}[\text{TM}_2](\text{Ga}_3)\text{O}_{12}$ , is probably not too far from this in actual formula. As the small rare earth increases in size, the agreement in the nominal cases becomes increasingly poorer, as would be expected from other results described above. Apparently the low values observed for the Er, Ho, and Dy preparations with nominal  $x = 2$  in Fig. 2 are due to increasing tendency

TABLE I

OBSERVED AND CALCULATED LATTICE CONSTANTS

Compound or Solid Solution	Lattice Constant, $a$ (Å)	
	Observed	Calculated
$\{\text{Nd}_3\}[\text{Ga}_2](\text{Ga}_3)\text{O}_{12}$	12.50 <sub>4</sub>	<sup>a</sup>
$\{\text{Yb}_3\}[\text{Ga}_2](\text{Ga}_3)\text{O}_{12}$	12.20 <sub>3</sub>	<sup>a</sup>
$\{\text{Nd}_3\}[\text{Lu}_2](\text{Ga}_3)\text{O}_{12}$	12.88 <sub>1</sub>	<sup>a</sup>
$\{\text{Nd}_3\}[\text{Yb}_2](\text{Ga}_3)\text{O}_{12}$	12.89 <sub>0</sub> <sup>b</sup>	12.89
$\{\text{Nd}_3\}[\text{Tm}_2](\text{Ga}_3)\text{O}_{12}$	12.88 <sub>2</sub> <sup>b</sup>	12.91
$\{\text{Nd}_3\}[\text{Er}_2](\text{Ga}_3)\text{O}_{12}$	12.83 <sub>1</sub> <sup>b</sup>	12.94
$\{\text{Nd}_3\}[\text{Ho}_2](\text{Ga}_3)\text{O}_{12}$	12.65 <sub>2</sub> <sup>b</sup>	12.98
$\{\text{Nd}_3\}[\text{Dy}_2](\text{Ga}_3)\text{O}_{12}$	12.51 <sub>0</sub> <sup>b</sup>	12.99
$\{\text{Nd}_{2.8}\text{Lu}_{0.2}\}[\text{Lu}_2](\text{Ga}_3)\text{O}_{12}$	12.86 <sub>6</sub>	12.86
$\{\text{Nd}_{2.7}\text{Yb}_{0.3}\}[\text{Yb}_2](\text{Ga}_3)\text{O}_{12}$	12.86 <sub>4</sub>	12.86
$\{\text{Nd}_{2.5}\text{Yb}_{0.5}\}[\text{Yb}_2](\text{Ga}_3)\text{O}_{12}$ <sup>c</sup>	12.85 <sub>5</sub>	12.84
$\{\text{Nd}_{2.4}\text{Tm}_{0.6}\}[\text{Tm}_2](\text{Ga}_3)\text{O}_{12}$	12.85 <sub>4</sub>	12.86
$\{\text{Nd}_{1.9}\text{Er}_{1.1}\}[\text{Er}_2](\text{Ga}_3)\text{O}_{12}$	12.81 <sub>3</sub>	12.85
$\{\text{Nd}_{1.35}\text{Ho}_{1.65}\}[\text{Ho}_2](\text{Ga}_3)\text{O}_{12}$ <sup>d</sup>	—	12.85
$\{\text{Nd}_{1.1}\text{Dy}_{1.9}\}[\text{Dy}_2](\text{Ga}_3)\text{O}_{12}$ <sup>d</sup>	—	12.86

<sup>a</sup> Calculations based on these.

<sup>b</sup> From nominal compositions.

<sup>c</sup> Note that this preparation contains more Yb ( $y = 0.5$ ) on the dodecahedral site than the minimum ( $y = 0.3$ ) required to obtain a single-phase garnet.

<sup>d</sup> Hypothetical compositions with  $y$  values obtained upon extrapolation of curve in Fig. 5(b).

for R to join the Nd on the dodecahedral sites as the radius of R increases, thereby simultaneously making less space available for the entry of R into the octahedral sites. The smallest rare earths yield pure materials with lower  $y$  values because they have less tendency to join the  $\text{Nd}^{3+}$  on the larger sites.

It should be noted that the somewhat higher values of the lattice constants observed for impure nominal compositions with nominal  $y = 0$  as compared with single-phase compositions where  $y$  was adjusted at required values  $>0$  indicate the possibility of preparing single-phase compounds of the type  $\{\text{Nd}_3\}[\text{R}_2](\text{Ga}_3)\text{O}_{12}$  for cases other than that with  $\text{R} = \text{Lu}$ . This could perhaps be achieved at higher temperature.

The calculations confirm the tendency observed in Fig. 4 for all single-phase preparations with  $x = 2$  and with the minimum required  $y$  values to have approximately the same lattice constant. Even the unattained hypothetical Er compound with  $x = 2$  (see Fig. 4) appears to have approximately the same lattice constant if one extrapolates the straight line. Calculated  $a$  values for Ho and Dy compositions with  $x = 2$  and with  $y$  values those obtained upon extrapolation of the curve in Fig. 5(b) are coincident with the others. There appears, then, to be a strong size relationship that determines the concentration of R on the dodecahedral site in these materials.

It seems desirable to summarize the reasoning that has permitted assignment of ions to different crystallographic positions. It should be understood that it was possible to make definite assignments only when dealing with single-phase materials of known stoichiometric composition.  $\text{Nd}^{3+}$  can enter only dodecahedral sites.  $\text{Ga}^{3+}$  can enter both tetrahedral and octahedral but not dodecahedral sites. The small

rare earth,  $\text{R}^{3+}$ , can enter both dodecahedral and octahedral but not tetrahedral sites. If sufficient  $\text{Nd}^{3+}$  and  $\text{R}^{3+}$  are present to fill both dodecahedral and octahedral sites,  $\text{Ga}^{3+}$  will enter only tetrahedral sites. If there is less than enough total rare earth present than needed to fill the dodecahedral and octahedral sites, then the  $\text{Ga}^{3+}$  added which is over the amount required to fill the tetrahedral sites will go into octahedral positions. Therefore, in any stoichiometric single-phase garnet of the type reported in this paper, all the  $\text{Nd}^{3+}$  must be in dodecahedral positions, the tetrahedral positions must be filled with three  $\text{Ga}^{3+}$  ions, and  $\text{R}^{3+}$  must be distributed over the dodecahedral and octahedral sites so that there is a total of three ions of  $\text{Nd}^{3+}$  and  $\text{R}^{3+}$  on the former and two ions of  $\text{R}^{3+}$  and  $\text{Ga}^{3+}$  on the latter sites. There are no other possibilities. Compositions with  $x = 0$  or 2, or with  $y = 0$  or 3 are just special cases subject to the same rules.

## References

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