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Garnets with Dodecahedral Rare Earths and Scandium, Octahedral Scandium, and Tetrahedral Iron. I. Compositional and Structural Studies*

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It has been found possible to prepare garnets with magnetic trivalent rare-earth ions filling all or most dodecahedral sites while nonmagnetic Sc^{3+} ions fill all octahedral sites and magnetic Fe^{3+} ions fill all or most tetrahedral sites. Phase-pure garnets found include $\{RE_{3-y}Sc_y\}[Sc_2](Fe_3)O_{12}$, where *RE* is Sm, Eu, Gd, Tb, or Dy, and y can be zero with Sm and Eu; $\{Nd_3\}[Sc_2](Fe_zGa_{3-z})O_{12}$; and other Nd–Sc–Fe garnets with small amounts of Y, Gd, or Lu added in order to bring z up to 3. Results are interpreted in terms of "size factor" and "comfort factor."

Introduction

Garnets with rare earths or yttrium on the dodecahedral sites and Fe^{3+} on the octahedral and tetrahedral sites have been almost exhaustively studied (*1*). The discussion of magnetic interactions given in the introduction to an earlier publication from this laboratory (*2*) is very pertinent here but need not be repeated.

Gilleo and Geller (*3*, *4*) reported that octahedral site substitution of Sc^{3+} for Fe^{3+} in garnets such as $\{Y_3\}[Fe_2](Fe_3)O_{12}$[1] increased the observed magnetic moment by widening the difference between the magnetic moments of the ferrimagnetically opposed octahedral and tetrahedral sublattices. Villers *et al.* (*5*) made similar findings and reported that, in the formula $\{Y_3\}[Sc_xFe_{2-x}](Fe_3)O_{12}$, the maximum obtainable value of x was 1.5 and the magnetic moment reached a maximum at $x = 0.8$ before dropping off rather sharply. The same paper described similar studies of the substitution of Sc for some of the octahedral Fe in Gd iron garnet. In this case the maximum x found was 0.8 and, because of the parallel alignment of the Gd spins with those of the octahedral Fe, the ferrimagnetic moment at 4°K was found to decrease with an increase in Sc content. In both cases, Sc addition brought about a regular increase in lattice constant, thereby indicating that the Sc was entering octahedral rather than dodecahedral sites. (Sc cannot enter tetrahedral sites.) In addition, the substitution of Sc lowered the Curie temperatures. Geller *et al.* (*6*) also made preparations in the systems $\{RE_3\}[Sc_xFe_{2-x}](Fe_3)O_{12}$ and reported a maximum x value of 1.62 with $RE = Y$ and 1.68 with $RE = Gd$. The observed magnetic properties have been interpreted in terms of magnetic dilution itself (*7*) or, better, the random canting of the moments of magnetic ions which occurs upon dilution with nonmagnetic ions (*6*, *8*, *9*).

Because Sc^{3+} is larger than Fe^{3+}, its substitution on the octahedral sites permits introduction of more Nd^{3+} on the dodecahedral sites than is possible where all octahedral and tetrahedral sites are filled with Fe^{3+}. This led Loriers *et al.* (*10*) to study the system

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[1] Braces, brackets, and parentheses denote dodecahedral, octahedral, and tetrahedral sites, respectively.

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$\{Nd_3\}[Sc_xFe_{2-x}](Fe_3)O_{12}$, but it was found that single phases occurred only between x values of 0.9 and 1.5. Mill *(11)* studied the similar but more general systems $\{RE_3\}$-$[Sc_xFe_{2-x}](Fe_3)O_{12}$, where *RE* was Nd, Sm, Gd, Tb, Er, Yb, and Y, but found no case in which $x = 2$ could be reached.

Earlier work in our laboratory *(2, 12–14)* has shown that it is possible to fill octahedral sites with the smaller rare earths when larger rare-earth ions occupy the dodecahedral sites, but that it is usually necessary for some of the small rare earths to share the dodecahedral sites if single-phase garnets are to be obtained. Applying this concept to the rare earth–scandium–iron garnet systems has led, as will be described below, to garnets with magnetic rare-earth ions filling all or most dodecahedral sites while nonmagnetic Sc^{3+} ions fill all octahedral sites and magnetic Fe^{3+} ions fill all tetrahedral sites. This affords an opportunity to study any possible dodecahedral–tetrahedral magnetic interactions which might occur in the absence of the strong superexchange interactions found when Fe^{3+} ions occupy both octahedral and tetrahedral sites. Perhaps the only other preparation with a magnetic ion distribution at all related to our new materials is $\{GdCa_2\}[Zr_2](Fe_3)O_{12}$, which has been reported *(6)* as appearing to be a weak ferromagnet at very low temperatures, but as will be seen below, our single-phase preparations have a much higher concentration of magnetic rare-earth ions.

Compositional studies are reported in this paper while the magnetic studies will follow in a later publication.

Preparation and X-Ray Diffraction Study

The preparation procedure employed was essentially that described in *(14)*. Because our Nd_2O_3 was found to have gone over to the hydroxide by absorbing water from the air on standing, it was fired at 1000°C in air for 4 hr shortly before weighing it out.

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

Results and Discussion

Attempts were made to prepare phase-pure garnets of the type $\{RE_{3-y}Sc_y\}[Sc_2](Fe_3)O_{12}$ with all the available rare earths from Pr through Lu, but it was found possible to obtain such compositions only where *RE* was Sm, Eu, Gd, Tb, or Dy. Compositional limits in each case were determined both by seeking lines of secondary phases in X-ray diffraction patterns and by careful measurement of lattice constants. The latter was deemed necessary because of the possibility that a small amount of a secondary phase would not be observable directly but that a leveling off of the lattice constant with composition would indicate its presence. The results of these studies are given in graphical form in Fig. 1 and, for additional convenience and clarity, the lattice constant limits are listed in Table I. The conformance with Vegard's law indicates that only the dodecahedral site composition varies over the single-phase range and that there is no devia-

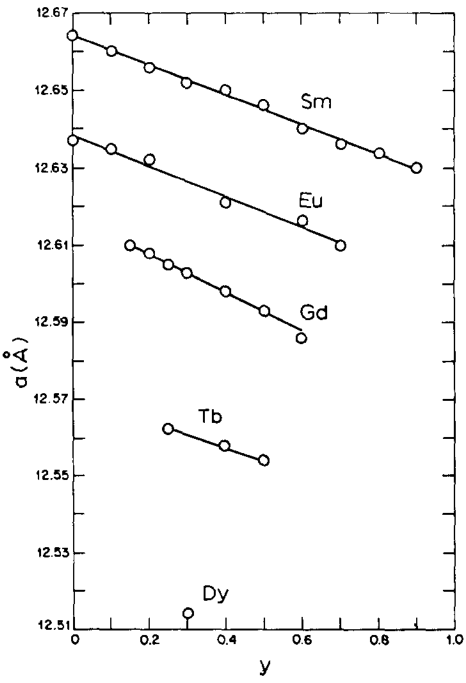

FIG. 1. Lattice constants vs composition (in terms of y) in $\{RE_{3-y}Sc_y\}[Sc_2](Fe_3)O_{12}$, where *RE* is identified in each case.

TABLE I

LIMITING VALUES OF LATTICE CONSTANTS OF PHASE-PURE GARNETS

Garnet compositions	Range of y or z	Range of lattice constants [a (Å)]
$\{Nd_3\}[Sc_2](Fe_zGa_{3-z})O_{12}$	0–2.6	12.657–12.740
$\{Sm_{3-y}Sc_y\}[Sc_2](Fe_3)O_{12}$	0.9–0	12.630–12.664
$\{Eu_{3-y}Sc_y\}[Sc_2](Fe_3)O_{12}$	0.7–0	12.610–12.637
$\{Gd_{3-y}Sc_y\}[Sc_2](Fe_3)O_{12}$	0.6–0.15	12.586–12.610
$\{Tb_{3-y}Sc_y\}[Sc_2](Fe_3)O_{12}$	0.5–0.25	12.554–12.562
$\{Dy_{3-y}Sc_y\}[Sc_2](Fe_3)O_{12}$	0.3	12.514

tion from regularity in the site-filling. One should note that in the cases of Sm and Eu it is possible to prepare the compounds $\{RE_3\}[Sc_2](Fe_3)O_{12}$. It appears that Mill (*11*) should have uncovered $\{Sm_3\}[Sc_2](Fe_3)O_{12}$, but he reported instead a maximum of 1.67 Sc^{3+} ions along with 0.33 Fe^{3+} ion on the octahedral sites. In our Gd and Tb preparations, the compositional limits are found to grow narrower, and finally, with Dy, only one composition occurs phase-pure. Figure 2 illustrates the relationship between the maximum and minimum compositions and the Shannon (*15*) revised radii of the trivalent rare earths (for which see Table II). In Fig. 3, the differences between the maximum and minimum y values (Δy) are plotted vs the rare-earth radii to illustrate that this relationship is also regular.

The average dodecahedral ion radius (calculated from the Shannon revised radii for eightfold coordination given in Table II) in single-phase $\{Dy_{2.7}Sc_{0.3}\}[Sc_2](Fe_3)O_{12}$ is 1.011 Å, which is therefore less than the 1.015 Å value of Ho^{3+}. This leads one to question why $\{Ho_3\}[Sc_2](Fe_3)O_{12}$ does not form. The answer appears to be that there are two factors at work here. One is, of course, ionic size directly (the "size factor," which sets maximum and minimum values of site radii), but the other is the relative ionic sizes of the rare earth and scandium which share the dodecahedral sites. The smaller the rare earth, the more tendency there is for Sc to join it in the

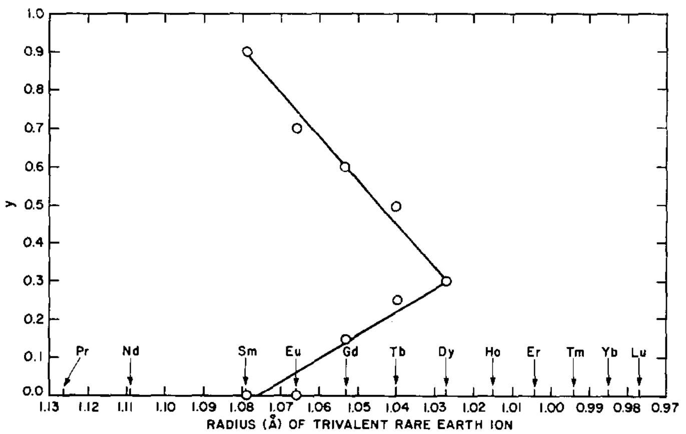

FIG. 2. Relationship between rare-earth radius and maximum and minimum y-values in $\{RE_{3-y}Sc_y\}[Sc_2](Fe_3)O_{12}$.

TABLE II

RELEVANT SHANNON (*15*) REVISED RADII (Å)

Ion	For sixfold coordination	For eightfold coordination
Sc^{3+}	0.745	0.870
Y^{3+}	0.900	1.019
Pr^{3+}	0.99	1.126
Nd^{3+}	0.983	1.109
Sm^{3+}	0.958	1.079
Eu^{3+}	0.947	1.066
Gd^{3+}	0.938	1.053
Tb^{3+}	0.923	1.040
Dy^{3+}	0.912	1.027
Ho^{3+}	0.901	1.015
Lu^{3+}	0.861	0.977

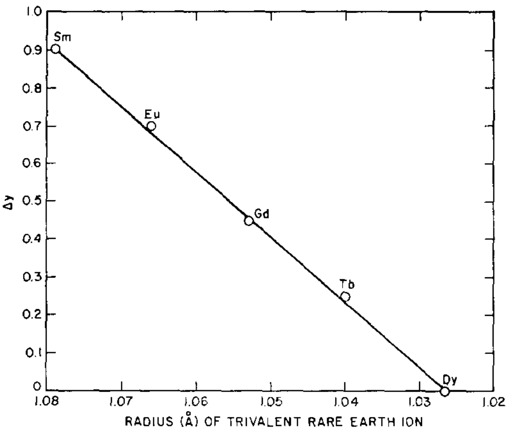

FIG. 3. Relationship between rare-earth radius and Δy (i.e., $y_{max} - y_{min}$) in $\{RE_{3-y}Sc_y\}[Sc_2](Fe_3)O_{12}$.

dodecahedral positions. (We call this the "comfort factor.") This need for Sc^{3+} to "satisfy" the dodecahedral sites if that ion is also to fill all the octahedral sites (that is, for equilibrium to be reached between the sites) results in a theoretical composition in which the average dodecahedral ion radius is too small for the garnet structure to remain stable. This can be proved by analysis of our data: If the lower line of Fig. 2 is extrapolated to Ho^{3+} ($r = 1.015$ Å) a minimum required y value of about 0.37 is indicated. The average dodecahedral ion radius then calculated for hypothetical $\{Ho_{2.63}Sc_{0.37}\}[Sc_2](Fe_3)O_{12}$ is 0.997 Å. Table III gives the values (calculated from Shannon revised radii listed in Table II) for the average dodecahedral site radii of the limiting compositions shown in Fig. 2 and Table I. The decrease in the maximum average dodecahedral site radius with decrease in rare-earth radius is a result of an increase in minimum dodecahedral Sc content, an expression of the comfort factor. The minimum average dodecahedral radii calculated for the materials with maximum Sc content are, on the other hand, found to be essentially constant and therefore give us a minimum limiting value (due to the size factor) which is greater than the 0.997 Å value required by the hypothetical Ho composition.

Phase-pure garnets with Sc and Fe completely filling the octahedral and tetrahedral sites, respectively, could not be prepared with rare earths smaller than Dy, but garnet structures accompanied by one or more additional phases were observed where the rare earths were Ho, Er, and Tm. Garnet phases such as these were not observed at all with Yb and Lu.

Pr and Nd were the only rare earths larger than Sm which were studied. In both cases, only phase-impure garnets were observed with reactant ratios designed to fill the octahedral

TABLE III

CALCULATED AVERAGE DODECAHEDRAL SITE RADII OF THE LIMITING COMPOSITIONS SHOWN IN FIG. 2 AND TABLE I

	Average dodecahedral site radius (Å)	
RE in $\{RE_{3-y}Sc_y\}[Sc_2](Fe_3)O_{12}$	Maximum (i.e., for minimum Sc content)	Minimum (i.e., for maximum Sc content)
Sm	1.079	1.016
Eu	1.066	1.020
Gd	1.044	1.016
Tb	1.026	1.012
Dy	1.011	1.011

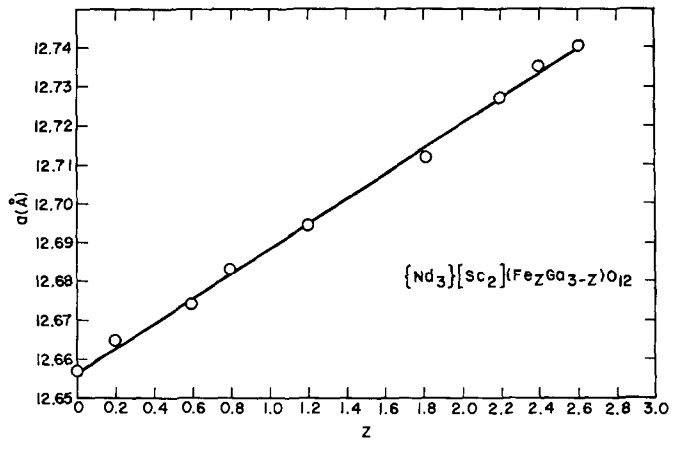

FIG. 4. Lattice constants vs composition (in terms of z) in $\{Nd_3\}[Sc_2](Fe_zGa_{3-z})O_{12}$.

and tetrahedral sites completely with Sc and Fe, respectively. The Nd system was chosen for further study and success was achieved in preparation of single-phase compositions fitting the general formula $\{Nd_3\}[Sc_2](Fe_zGa_{3-z})O_{12}$; the plot in Fig. 4 shows the relationship between Fe^{3+} content and lattice constant (see also Table I). All compositions were found to exist between $\{Nd_3\}[Sc_2](Ga_3)O_{12}$ and $\{Nd_3\}[Sc_2](Fe_{2.6}Ga_{0.4})O_{12}$. The corresponding Pr system was not studied thoroughly, but phase-pure compositions of this type were found not to form with z values of 1.6 or 3.

Probably $\{Nd_{3-y}Sc_y\}[Sc_2](Fe_3)O_{12}$ phases do not form because of an adverse comfort factor. That is, the average dodecahedral ion radius sufficiently small to be below the maximum value allowed (size factor) by the tetrahedral Fe^{3+} ion and the octahedral Sc^{3+} ion cannot be attained with the maximum amount of Sc^{3+} which will share the dodecahedral sites with Nd^{3+} (comfort factor). This is reasonable because of the large difference in the radii for coordination number 8 of Nd^{3+} and Sc^{3+} (see Table II). If one takes our maximum observed dodecahedral radius (1.079 Å, the Sm^{3+} value),[2] the y value with Fe^{3+} ions filling all the tetrahedral sites would have to be 0.38, which we have found to be experimentally unattainable. Such considerations led us to attempt to reduce the average radius of the ions on the dodecahedral site other than Sc^{3+} by substituting for Nd^{3+} small quantities of smaller rare earths (or yttrium) along with, of course, the then minimum required amount of Sc^{3+}. The ions so employed were the nonmagnetic Y^{3+} and Lu^{3+} and the spin-only Gd^{3+}. These were chosen to simplify the interpretation of magnetic measurements as much as possible. Single-phase compositions of this type did indeed form; those with maximum Nd concentrations and their lattice constants are the last four listed in Table IV, but single-phase materials

TABLE IV

OBSERVED AND CALCULATED LATTICE CONSTANTS OF COMPOSITIONS WITH MAXIMUM LATTICE CONSTANTS (MINIMUM DODECAHEDRAL SCANDIUM)

Composition	a_{obs} (Å)	a_{calc} (Å)
$\{Sm_3\}[Sc_2](Fe_3)O_{12}$	12.664	12.69_9
$\{Eu_3\}[Sc_2](Fe_3)O_{12}$	12.637	12.66_6
$\{Gd_{2.85}Sc_{0.15}\}[Sc_2](Fe_3)O_{12}$	12.610	12.61_1
$\{Tb_{2.75}Sc_{0.25}\}[Sc_2](Fe_3)O_{12}$	12.562	12.56_5
$\{Dy_{2.7}Sc_{0.3}\}[Sc_2](Fe_3)O_{12}$	12.514	12.52_7
$\{Nd_{2.4}Y_{0.4}Sc_{0.2}\}[Sc_2](Fe_3)O_{12}$	12.702	12.70_4
$\{Nd_{2.3}Lu_{0.3}Sc_{0.4}\}[Sc_2](Fe_3)O_{12}$	12.698	12.66_1
$\{Nd_{2.3}Lu_{0.4}Sc_{0.3}\}[Sc_2](Fe_3)O_{12}$	12.694	12.67_0
$\{Nd_{2.6}Gd_{0.1}Sc_{0.3}\}[Sc_2](Fe_3)O_{12}$	12.711	12.71_0

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[2] Actually, of course, the true allowed maximum could be somewhat higher but must be less than the 1.109 Å radius of Nd^{3+}.

are also obtained with higher concentrations of small rare earth or yttrium. As seen in the Lu case, this can change the minimum required amount of dodecahedral Sc.

The average dodecahedral radii of the four Nd materials are calculated from the radii given in Table II to be 1.081, 1.064, 1.068, and 1.083 Å for $\{Nd_{2.4}Y_{0.4}Sc_{0.2}\}[Sc_2](Fe_3)O_{12}$, $\{Nd_{2.3}Lu_{0.3}Sc_{0.4}\}[Sc_2](Fe_3)O_{12}$, $\{Nd_{2.3}Lu_{0.4}Sc_{0.3}\}[Sc_2](Fe_3)O_{12}$, and $\{Nd_{2.6}Gd_{0.1}Sc_{0.3}\}[Sc_2](Fe_3)O_{12}$, respectively. These calculations for the Nd–Y and Nd–Gd preparations appear to offer essentially quantitative confirmation of our reasoning. In the case of the Nd–Lu materials, their very existence is significant, but their calculated average dodecahedral radii are somewhat lower than expected, perhaps due to Lu^{3+}–Sc^{3+} site switching, which would make the average dodecahedral radius calculation consideration invalid.

In an earlier publication from this laboratory (*16*), it was proposed that Lu^{3+} increased the solubility of Nd^{3+} in yttrium aluminum garnet single crystals by entering octahedral rather than dodecahedral sites. Because of the relatively small difference in the radii of Lu^{3+} and Sc^{3+} (see Table II), it seems quite likely that some or all of the Lu^{3+} ions in the present cases also enter octahedral sites with a concurrent shift of an equal number of additional Sc^{3+} ions to dodecahedral sites. In an attempt to analyze this situation, we calculated lattice constants for the Nd-containing materials as we did earlier for gallium garnets (*2*, *12*). In this case, the factor $\Delta a/\Delta r_{\text{dod}}$ was obtained from the data for $\{RE_3\}[Fe_2](Fe_3)O_{12}$ compounds compiled in (*17*), and the factor $\Delta a/\Delta r_{\text{oct}}$ from data for the system $\{Y_3\}[Sc_xFe_{2-x}](Fe_3)O_{12}$ (*9*). Calculations were then made from

$$\begin{aligned} a_{\text{calc}} &= (\text{average } r_{\text{dod}} - r_{Lu^{3+}})\,(2.53) \\ &\quad + (\text{average } r_{\text{oct}} - r_{Fe^{3+}})\,(1.61) \\ &\quad + a_{\{Lu_3\}[Fe_2](Fe_3)O_{12}} \\ &= (\text{average } r_{\text{dod}} - 0.977)\ (2.53) \\ &\quad + (\text{average } r_{\text{oct}} - 0.645)\,(1.61) \\ &\quad + 12.280. \end{aligned}$$

The lattice constants calculated on the assumption that all the Lu^{3+} is on dodecahedral sites (see Table IV) are, however, virtually indistinguishable from those where complete switching is postulated. On the other hand, when these calculations were made with the older Shannon–Prewitt (*18*) radii before Shannon brought the revised values to our attention, lattice constants calculated for complete switching of Lu^{3+} to octahedral sites were 0.007–0.009 Å higher than when all the Lu^{3+} was assumed to be dodecahedral. Because lattice constants calculated for dodecahedral-only Lu from the older radii are not very different from those based on the revised ones, the higher values were closer to the experimental lattice constants and appeared to offer some support for Lu^{3+}–Sc^{3+} switching. Since Shannon has revised the eightfold coordination radii for the rare earths but not their sixfold coordination radii (except for Pr^{3+}), it is possible that the latter also require adjustment to make them conform (but Shannon (*19*) does not believe so). We have, of course, not proven that switching occurs, but this will not affect our magnetic studies because both Lu^{3+} and Sc^{3+} are diamagnetic ions. In the Nd–Y–Sc and Nd–Gd–Sc preparations, where switching is not expected to occur, calculated and observed lattice constants agree very well.

If the average dodecahedral ion radius of a neodymium preparation is only slightly different from that of Sm^{3+}, one would expect the lattice constant to be very close to that of $\{Sm_3\}[Sc_2](Fe_3)O_{12}$. The data in Table IV indicate that this is not exactly so—the Nd materials all have lattice constants significantly higher than that of the Sm compound. This led us to calculate lattice constants for all the *RE*–Sc–Fe garnets with maximum rare-earth concentration. The results, also in Table IV, show fair to excellent agreement for most of the materials, but the $\{Sm_3\}[Sc_2](Fe_3)O_{12}$ value is further off than one would wish (and the same is true when Shannon–Prewitt radii are employed). The lattice constants of the neodymium preparations are therefore justifiably high and it is the Sm compound value which is low. The reason for this apparent shrinkage is not entirely clear. However, if one plots the reported lattice constants of $\{RE_3\}[Fe_2](Fe_3)O_{12}$ compounds

(*17*) vs either Shannon revised or Shannon–Prewitt rare-earth radii, the experimental lattice constant of the Sm compound also falls somewhat below the extrapolation of a straight line drawn through the other points. A Shannon revised radius of 1.075 Å (rather than 1.079 Å) would fall on the line; this radius for Sm^{3+} yields a calculated lattice constant for $\{Sm_3\}[Sc_2](Fe_3)O_{12}$ of 12.68_9 Å which compares more favorably with the observed value.

The assignment of some Sc^{3+} to dodecahedral sites is based on the inability of that ion to enter tetrahedral positions. If a single-phase garnet composition has more than two Sc^{3+} ions per formula unit, some of the Sc must therefore be on dodecahedral sites. Sc^{3+} in the dodecahedral positions of the garnet structure is quite unusual; to our knowledge, the only other reported instance of this is in $\{Nd_{3-y}Sc_y\}[Sc_xFe_{2-x}](Fe_3)O_{12}$ with x values less than 0.75 (*10*).

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