

Solubility Enhancement of Nd^{7+} in Scandium-Substituted Rare Earth-Aluminum Garnets

M. KOKTA

Bell Laboratories, Murray Hill, New Jersey 07974

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An increased solubility of Nd^{3+} in YAG has been achieved by means of expansion of its crystal lattice with Sc^{3+} ions substituting for Al^{3+} ions in the octahedral sites. A number of other scandium substituted rare earth aluminum garnets of general formula $\{\text{R}_3\}[\text{Sc}_2](\text{Al}_3)\text{O}_{12}$ have been prepared and results are compared with similar compounds in $\{\text{R}_3\}[\text{Sc}_2](\text{Fe}_3)\text{O}_{12}$ systems. It is shown that the expansion of the YAG lattice by octahedral substitution significantly increases the solubility of Nd^{3+} on dodecahedral sites. The results of substitution of Sc in other rare earth-aluminum systems appear to be consistent with results obtained in the yttrium-aluminum system and so ions bigger than Gd^{3+} , such as Eu^{3+} and Sm^{3+} , can form garnets $\{\text{Eu}_3\}[\text{Sc}_2](\text{Al}_3)\text{O}_{12}$ and $\{\text{Sm}_3\}[\text{Sc}_2](\text{Al}_3)\text{O}_{12}$.

Introduction

Crystals of YAG doped with Nd^{3+} are currently widely used and receive attention as laser materials. The amount of Nd^{3+} which enters YAG does not exceed 1.5% atomic. Such rather limited solubility constitutes a problem in obtaining maximum laser efficiency. Cockayne et al. (1) have reported that the solubility of Nd^{3+} can be increased by addition of Gd^{3+} in YAG. Kestgian and Holloway (2) found that solubility of Nd^{3+} may be increased by simultaneous incorporation of Lu^{3+} and attributed this to a size compensation effect on dodecahedral sites. Suchow and Kokta (3) offered different explanations for increasing solubility of Nd^{3+} in the latter case. They suggested, that an improvement of the solubility of relatively large Nd^{3+} would be a result of cooperative phenomenon influencing polyhedra sizes rather than a simple matter of reaching a maximum average ionic size on a given crystallographic site. In such cases the expansion of the crystal lattice by octahedral substitution enlarges the dodecahedral holes in the crystal network and doing so allows larger ions to enter them. All conclusions of Suchow and Kokta (3) were drawn on the basis of work with gallium-containing systems (4) and were not supported with substantial experimental evidence obtained on aluminum systems. Schneider, Roth and

Waring (5) showed the possibility of octahedral substitutions in some rare-earth aluminum garnet systems and in a paper by Zeyfang (6) the presence of a small amount of Y^{3+} on octahedral sites in YAG is also indicated. The expansion of the crystal lattice of aluminum garnet can be achieved by substitution of an ion larger than Al^{3+} on the octahedral sites. A suitable ion for such substitution is Sc^{3+} , with an ionic radius 0.73 Å, for sixfold coordination (7) compared with an ionic radius of Al^{3+} for sixfold coordination of 0.53 Å. Recently the increased solubility of Nd^{3+} has also been observed by Brandle and Vanderleeden (11) in $\text{Gd}_3\text{Sc}_2\text{Al}_3\text{O}_{12}$ single crystals.

Preparation

The coprecipitation method (8) was chosen for sample preparation. Rare earth oxides (Research Chem. Corp. and American Potash Co.) 99.99% pure and Sc_2O_3 (99.9% United Mineral and Chem. Corp.) were dissolved in nitric acid and the nitrate solutions were mixed with aluminum nitrate in desired ratios. Hydroxides were precipitated using ammonium hydroxide. After filtration the hydroxides were air dried and heated at 300°C for 2 hr, then pressed into pellets and fired at 1630°C for 12 hr. No changes in X-ray patterns have been found when samples were refired for an additional 24 hr. Resulting

materials were checked for the presence of second phases using the Guinier–Nonius diffraction camera. Lattice constants were determined by measuring d -spacing for the (12, 10, 0) and (12, 10, 2) reflections on a G.E. X-ray diffractometer.

Results and Discussion

The results of preparations according to the general formula $\{R_3\}[Sc_2](Al_3)O_{12}$, where R stands for rare earth ion, are compiled in Table I and lattice parameters of these compounds are compared with calculated values. Lattice constants were calculated employing the method reported in Refs. (4 and 9) as follows. Using an example for Gd^{3+} systems substituted on octahedral and dodecahedral sites

$$a_{calc} = (\text{average } r_{Dod} - R_{Gd^{3+}})(2.15) \\ + (\text{average } r_{oct} - r_{Al^{3+}})(1.56) \\ + a_{GdAl_3O_{12}}$$

The factors 2.15 and 1.56 were derived using Shannon and Prewitt (7) radii and therefore all r values are taken from that reference and separate values given for coordination numbers 6 and 8 were used. From Table I it is also apparent that the lattice constants of the rare earth–aluminum systems are increased to the range of gadolinium gallium garnet lattice parameter and it offers the possibility of their use as substrate materials for thin garnet films. The lattice parameter of $Gd_3Sc_2Al_3O_{12}$ of $a = 12.430 \text{ \AA}$ compared to the

value reported by Brandle and Vanderleeden (11) of $a = 12.395 \text{ \AA}$ is greater by 0.035 \AA , but it is closer to the calculated value. The appearance of second-phase lines in the X-ray pattern is consistent with results obtained by Kokta (10) in studies dealing with octahedral substitution of Sc^{3+} into rare earth–iron garnets. It has been found by Suchow and Kokta (4, 9, 10) that octahedral substitution in rare earth systems is more complicated than simply following the mechanism according to the formula $\{R_3\}[r_xMe_{2-x}](Me_3)O_{12}$, where R is a rare earth, r is a substituent and Me can be a trivalent ion such as Ga^{3+} , Fe^{3+} or Al^{3+} . It has been proposed and experimentally established that a more correct mechanism generally follows the formula $\{R_{3-y}r_y\}[r_xMe_{2-x}](Me_3)O_{12}$ (4, 9, 10). The value y which is the amount of substituent which enters dodecahedral sites in order to form a single phase garnet depends on the difference between the ionic radii of ions on dodecahedral and octahedral sites and the y -value increases when the difference between the ionic radii R and r decreases. It has been found for substitutions of Sc into rare earth iron garnets (10) that the y -value increases from 0.3 to 1.8 in the rare earth series going from Gd^{3+} to Tm^{3+} substituting according to the formula $\{R_{3-y}Sc_y\}[Sc_2](Fe_3)O_{12}$. This is similar to the trend appearing in $\{R_3\}[Sc_2](Al_3)O_{12}$ systems reported here, where the $Gd_3Sc_2Al_3O_{12}$ X-ray pattern shows very weak second phase lines between the {400} and {420} reflection lines. The nature of the second phase is difficult to establish at this stage. Its X-ray lines appear only between 2θ angles from 30 – 32° for $CuK\alpha$ X-ray radiation. The two lines which appear are weak and rather broad. These second phase lines are similar to those observed by Suchow and Kokta (4) in the systems $\{R_3\}[r_xGa_{2-x}](Ga_3)O_{12}$, where R stands for a large rare earth ion such as Nd^{3+} and r stands for small rare earth ions (Lu^{3+} , Yb^{3+} , Tm^{3+}). Two types of second phases were found in these systems. One was the perovskite phase for low x -values. When x exceeded 1.5 reflections of a different type, similar to reflections observed in $\{R_3\}[Sc_2](Al_3)O_{12}$ systems, appeared.

Weak second phase lines indicate a small y -value needed to obtain a single phase, and going along the rare earth series from Gd^{3+} to Yb^{3+} , the intensity of second phase lines increases indicating an increase of y -values similar to the increase observed in the corresponding iron systems. The increase of the dodecahedral ionic radius affects the formation

TABLE I

OBSERVED AND CALCULATED LATTICE CONSTANTS IN THE SYSTEMS $\{R_3\}[Sc_2](Al_3)O_{12}$, WHERE R STANDS FOR RARE EARTH IONS

Composition	Amount of second phase	a (Å), observed	a (Å), calculated
$Y_3Sc_2Al_3O_{12}$	slight	12.324	12.32
$Yb_3Sc_2Al_3O_{12}$	↑	12.162	12.24
$Tm_3Sc_2Al_3O_{10}$	increasing	12.220	12.27
$Er_3Sc_2Al_3O_{10}$		12.300	12.29
$Ho_3Sc_2Al_3O_{12}$		12.324	12.32
$Dy_3Sc_2Al_3O_{12}$		12.360	12.36
$Gd_3Sc_2Al_3O_{12}$		12.430	12.42
$Eu_3Sc_2Al_3O_{12}$	single phase	12.460	12.46
$Sm_3Sc_2Al_3O_{12}$	single phase	12.495	12.49

TABLE II
OBSERVED AND CALCULATED LATTICE CONSTANTS IN THE GARNET SYSTEM
{Y_{3-y}Nd_y}[Sc₂](Al₃)O₁₂

Composition	Amount of second phase	a (Å), observed	a (Å), calculated
{Y ₃ }[Sc ₂](Al ₃)O ₁₂	slight	12.324	12.32
{Y _{2.8} Nd _{0.2} }[Sc ₂](Al ₃)O ₁₂	slight	12.346	12.34
{Y _{2.6} Nd _{0.4} }[Sc ₂](Al ₃)O ₁₂	slight	12.360	12.35
{Y _{2.2} Nd _{0.8} }[Sc ₂](Al ₃)O ₁₂	single phase	12.389	12.38
{Y _{1.8} Nd _{1.2} }[Sc ₂](Al ₃)O ₁₂	single phase	12.418	12.41

TABLE III
OBSERVED AND CALCULATED LATTICE CONSTANTS IN THE GARNET SYSTEM
{Gd_{3-y}Nd_y}[Sc₂](Al₃)O₁₂

Composition	Amount of second phase	a (Å), observed	a (Å), calculated
{Gd ₃ }[Sc ₂](Al ₃)O ₁₂	very weak extra lines	12.430	12.42
{Gd _{2.8} Nd _{0.2} }[Sc ₂](Al ₃)O ₁₂	single phase	12.441	12.44
{Gd _{2.6} Nd _{0.4} }[Sc ₂](Al ₃)O ₁₂	single phase	12.449	12.46
{Gd _{2.4} Nd _{0.6} }[Sc ₂](Al ₃)O ₁₂	single phase	12.462	12.47
{Gd _{2.2} Nd _{0.8} }[Sc ₂](Al ₃)O ₁₂	single phase	12.469	12.49

of single phase garnet, as is demonstrated in Table II and in Table III. From Table II, it can be seen that compounds like {Y₃}[Sc₂](Al₃)O₁₂ and {Y_{2.6}Nd_{0.4}}[Sc₂](Al₃)O₁₂ are not single-phase garnets. However, an increase of the average dodecahedral ionic radius by substitution of 10% (atomic) Nd³⁺ in the compound {Y_{2.2}Nd_{0.8}}[Sc₂](Al₃)O₁₂ is enough to yield a single phase garnet. The situation is similar in Table III where an addition of 2.5% of Nd³⁺ provides an average ionic radius large enough to yield a single phase garnet of composition {Gd_{2.8}Nd_{0.2}}[Sc₂](Al₃)O₁₂. Tables II and III also support the idea of increasing the solubility of Nd³⁺ in the aluminum system by expansion of the crystal lattice. The amount of Nd³⁺ substituted in these compounds exceeds the limited solubility of Nd³⁺ in YAG even though these are not the limits which the scandium substituted compounds can accept. In Fig. 1 are plotted lattice parameters of the system {Y_{3-y}Nd_y}[Sc₂](Al₃)O₁₂ along with values calculated for pertinent compositions. When the data given in Tables II and III are critically evaluated, taking in account the accuracy of lattice constant

determination being 0.005 Å and limits of powder diffraction method with respect to detection of

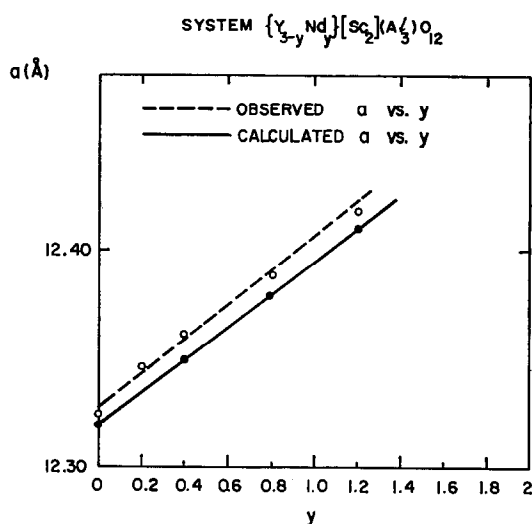


FIG. 1. Lattice parameter variations in the system {Y_{3-y}Nd_y}[Sc₂](Al₃)O₁₂.

second phases, it can be said that the presence of small amounts of Sc in dodecahedral sites especially in the case of $\{\text{Gd}_{3-y}\text{Nd}_y\}[\text{Sc}_2](\text{Al}_3)\text{O}_{12}$ system cannot be ruled out. The results presented here suggest that further study is needed in order to determine the compositions which would yield single-phase garnets in the rare earth-scandium-aluminum systems.

Conclusions

It has been shown that the expansion of the crystal lattice increases the solubility of Nd^{3+} on the dodecahedral sites of aluminum garnet systems. It was also shown that enlargement of dodecahedral holes in the garnet structure by substitution of Sc^{3+} allows ions such as Eu^{3+} and Sm^{3+} to enter the aluminum garnet lattice on dodecahedral sites and completely fills them. In an unsubstituted garnet Gd^{3+} is the largest ion which can completely fill dodecahedral sites. Sc substitution in rare earth-aluminum garnets containing smaller rare earth ions is more complicated and the possibility of Sc distribution between dodecahedral and octahedral sites in these systems should be studied.

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