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New Substituted Gallium Garnets Containing Trivalent Lanthanum on Dodecahedral Crystallographic Sites

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A number of new garnet compounds containing trivalent lanthanum on dodecahedral sites have been prepared. Incorporation of La^{3+} into dodecahedral crystallographic sites was achieved by means of expansion of the crystal lattice of gallium garnet by substitution for Ga^{3+} on the octahedral sites. It is shown that substitution of trivalent scandium in the octahedral sites of gallium garnet expands its lattice and enlarges dodecahedral holes enough to allow relatively large La^{3+} ions to fill the dodecahedral sites almost completely. It has been found that small rare earth ions such as Lu^{3+}, Yb^{3+}, and Tm^{3+} may also be used instead of Sc^{3+} to prepare the lanthanum-containing garnets. It has been observed that such substituted compounds are not strictly stoichiometric according to the formula $\{La_3\}[R_2](Ga_3)O_{12}$, where R may be Sc^{3+}, Lu^{3+}, Yb^{3+} or Tm^{3+}, but they rather follow the formula $\{La_{3-y}R_y\}[R_2](Ga_3)O_{12}$ with the value of y increasing with ionic radius of R. The minimum values of y needed in order to obtain single-phase materials were determined.

Introduction

The importance of a role of ionic radii in isomorphism in the garnet compounds has been established years ago (*1*, *2*). The limitations placed by ionic sizes on formation of rare earth–trivalent ion garnets, $RE_3Me_5O_{12}$, where RE is a rare earth ion and Me is any other trivalent ion, may be found elsewhere (*3*). It is known that the largest rare-earth ions which completely fill dodecahedral sites of iron garnet is Sm^{3+} ($r = 1.09$ Å). The larger Nd^{3+} ion may be only partially substituted in dodecahedral sites of iron garnets (*4*). In the rare earth–aluminum system, the largest rare earth ion completely occupying the dodecahedral sites is Gd^{3+} ($r = 1.06$ Å), while in the gallium systems it is Pr^{3+} ($r = 1.14$ Å). The fact that the octahedron and tetrahedron share edges with the dodecahedron in the garnet structure (*3*) implies restrictions on the size of ions entering available crystallographic sites in a given system. On the other hand, it also implies that matching polyhedra sizes may lead to successful substitutions in the garnet structure. In previous work, it has been stated and experimentally established that large rare earth ions on dodecahedral sites can open the crystal lattice of gallium garnets and allow octahedral sites to be filled with smaller rare earth ions (*5*). Such an idea may also be applied to open the crystal lattice by means of substitutions on the octahedral sites in order to incorporate larger ions on dodecahedral sites. Substitutions in the rare earth–gallium system may result in a garnet with the relatively large ion, La^{3+}, ($r = 1.18$ Å) on the dodecahedral sites. A garnet of this type could be potentially useful as a host material for all other rare earth ions which may be easily substituted in dodecahedral sites. For example, Nd^{3+}-substituted lanthanum garnet may be of some use as a laser host material. Some limited possibilities may also exist for the substitution of rare earth ions in the octahedral sites of such a garnet. All the ionic radii throughout the text were taken from Shannon and Prewitt papers (*6*, *7*).

Preparations

All samples were prepared by solid state reactions among pertinent oxides. Rare earth oxides (Research Chem. Corp. and American Potash Co., 99.99% pure) were heated at 1100°C for 12 hr to free them of H_2O and CO_2. The Sc_2O_3 used was 99.9% pure, a product of United

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Mineral and Chem. Corp. The Ga_2O_3 was 99.99% pure purchased from Eagle Picher.

The oxides were weighed in desired ratios, carefully ground together in an agate mortar, and pressed into pellets. The pellets were wrapped in Pt foil to avoid evaporation losses of Ga_2O_3 at elevated temperatures. Samples were then heated at 1400°C in a tube furnace (in air) for 12 hr. After heating, samples were furnace-cooled and the pellets were crushed and reground. Resulting materials were checked for the presence of any secondary phases using a Guinier Nonius diffraction camera. Lattice constants of garnet phases were determined by measuring d-spacings of (12, 10, 0) and (12, 10, 2) reflections on a G. E. X-ray diffractometer. Repeated heating was required in most cases.

Result and Discussion

The results of substitutions according to the formula $\{La_3\}[R_2](Ga_3)O_{12}$, where R stands for Sc, Lu, Yb, Tm and Er, are compiled in Table I. The increasing amounts of second phase (most probably the 3:1 phase, that is $3Ln_2O_3 \cdot Ga_2O_3$, where Ln is rare earth ion) suggest that the small rare earth ions are distributed among the octahedral and dodecahedral sites. A similar situation was found in the $\{Nd_3\}[R_2](Ga_3)O_{12}$ and $\{Pr_3\}[R_2](Ga_3)O_{12}$ systems (*5*). In order to obtain a single phase garnet, substitutions were made according to the formula $\{La_{3-y}R_y\}[R_2](Ga_3)O_{12}$, increasing the value of y from 0 by increments of 0.1 until only one phase was present. Compositions of single phase garnets are compiled in Table II along with their lattice parameters. These compositions were determined for Sc, Lu, Yb and Tm on octahedral sites because Er, as can be seen from Table I, did not form the garnet phase when substituted according to the formula $\{La_3\}[Er_2](Ga_3)O_{12}$. But when some erbium was substituted in dodecahedral sites, at levels of $y = 0.5$, the garnet phase appeared. This indicates that single phases are expected for compositions $\{La_{3-y}R_y\}[R_2](Ga_3)O_{12}$ or $\{La_{3-y}R_y\}[Ga_{2-x}R_x](Ga_3)O_{12}$ where R stands for Er, Ho, Dy and other larger rare earth ions.

TABLE I

SUBSTITUTIONS IN SYSTEMS $\{La_3\}[R_2](Ga_3)O_{12}$
$R = Sc^{3+}, Lu^{3+}, Yb^{3+}, Tm^{3+}$ AND Er^{3+}

Nominal composition	a(Å)	Amount of second phase
$\{La_3\}[Sc_2](Ga_3)O_{12}$	12.847	very small
$\{La_3\}[Lu_2](Ga_3)O_{12}$	13.034	increasing
$\{La_3\}[Yb_2](Ga_3)O_{12}$	13.049	increasing
$\{La_3\}[Tm_2](Ga_3)O_{12}$	13.043	increasing
$\{La_3\}[Er_2](Ga_3)O_{12}$	—	no garnet
$\{La_3\}[Ho_2](Ga_3)O_{12}$	—	no garnet

TABLE II

COMPOSITION OF SINGLE PHASES IN
$\{La_{3-y}R_y\}[R_2](Ga_3)O_{12}$ SYSTEMS
$R = Sc^{3+}, Lu^{3+}, Yb^{3+}, Tm^{3+}$

R	Minimum y	a(Å)
Sc^{3+}	0.1	12.847
Lu^{3+}	0.3	12.997
Yb^{3+}	0.4	13.007
Tm^{3+}	0.5	13.010

TABLE III

INTENSITIES OF X-RAY REFLECTIONS OF
$\{La_{2.9}Sc_{0.1}\}[Sc_2](Ga_3)O_{12}$
$a_0 = 12.847$ Å

d(Å)	$h\,k\,l$	$h^2+k^2+l^2$	$I/I_0(\%)$
5.2444	2 1 1	6	6
4.5421	2 2 0	8	7
3.4335	3 2 1	14	6
3.2117	4 0 0	16	17
2.8726	4 2 0	20	100
2.6223	4 2 2	24	25
2.5195	4 3 1	26	2
2.3455	5 2 1	30	8
2.2710	4 4 0	32	4
2.0840	6 1 1 and 532	38	8
2.0312	6 2 0	40	8
1.8941	6 3 1	46	1
1.8543	4 4 4	48	14
1.7815	6 4 0	52	26
1.7482	7 2 1, 633 and 552	54	3
1.7167	6 4 2	56	22
1.6315	7 3 2 and 651	62	2
1.6058	8 0 0	64	10
1.4363	8 4 0	80	5
1.4017	8 4 2	84	16
1.3694	6 6 4	88	4
1.1928	10 4 0 and 864	116	12
1.1727	10 4 2	120	4
1.1355	8 8 0	128	5

TABLE IV

INTENSITIES OF X-RAY REFLECTIONS OF
$\{La_{2.7}Lu_{0.3}\}[Lu_2](Ga_3)O_{12}$
$a_0 = 12.997$ Å

d(Å)	$h\,k\,l$	$h^2+k^2+l^2$	I/I_0(%)
5.3060	2 1 1	6	8
4.5950	2 2 0	8	9
3.4736	3 2 1	14	6
3.2492	4 0 0	16	52
2.9062	4 2 0	20	93
2.6530	4 2 2	24	100
2.5489	4 3 1	26	2
2.3729	5 2 1	30	8
2.1089	6 1 1 and 532	38	9
2.0550	6 2 0	40	6
1.9163	6 3 1	46	2
1.8759	4 4 4	48	5
1.8023	6 4 0	52	26
1.7686	7 2 1, 633 and 552	54	3
1.7368	6 4 2	56	61
1.6506	7 3 2 and 651	62	2
1.6246	8 0 0	64	15
1.4534	8 4 0	80	14
1.4180	8 4 2	84	14
1.3855	6 6 4	88	11
1.2067	10 4 0 and 864	116	12
1.1864	10 4 2	120	12
1.1487	8 8 0	128	8

The crystallographic data obtained from powder patterns of $\{La_{2.9}Sc_{0.1}\}[Sc_2](Ga_3)O_{12}$ and $\{La_{2.7}Lu_{0.3}\}[Lu_2](Ga_3)O_{12}$ are given in Tables III and IV. The presence of Sc or rare earth on octahedral sites is deduced from values of lattice constants. This argument is valid because single phase materials were obtained and neither Sc^{3+} nor rare earth ions can enter the tetrahedral sites of garnets. The presence of rare earth ions on the octahedral sites may also be confirmed from intensity shifts of several reflection lines. Although the garnets with rare earth ions on dodecahedral and octahedral sites have X-ray diffraction patterns similar to those of unsubstituted garnets, there are a number of intensity shifts. Suchow and Mondegarian (*8*) using structure factor calculations, found that notable shifts in relative intensity should occur in lines at $h^2+k^2+l^2 = 20$ and 24; 52 and 56; 80, 84, and 88; and 116 and 120. The $h^2+k^2+l^2 = 24$ line became the strongest in the patterns of garnets with rare earth ions on two crystallographic sites. The calculations performed by Suchow and Mondegarian show excellent agreement with intensities found for such garnets as shown in Tables III and IV.

In addition, it has been found that lanthanum-containing gallium garnets melt congruently at temperatures close to 1500°C. Samples were melted at 1600°C and furnace-cooled. X-ray analysis revealed the same phases as those found before melting.

Summary

It has been shown that garnets may be prepared with trivalent lanthanum predominantly filling dodecahedral sites. The distribution of Sc or small rare earth ions among octahedral and dodecahedral sites was observed and the compositions of single phase garnets were determined for several systems. It was also shown that the substitution of rare earth ions in octahedral sites of lanthanum containing garnets is possible. As suggested above, the lanthanum garnets may be potentially useful as a host material for other rare earth ions, particularly large ones, since they may be easily substituted in dodecahedral sites. The relatively low melting point and congruent nature of the melting make these compounds suitable for single crystal growth, because losses of Ga_2O_3 at 1500°C would probably not present any serious problems. Further studies are needed to explore the possibilities of substitutions of rare earth ions larger than Tm in the octahedral sites of lanthanum-containing garnets.

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