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A Crystal Chemical Study of Titanium(IV) and Chromium(III) Substituted Yttrium Iron and Gallium Garnets

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Crystallographic and preparative data are given for the garnet systems: $\{Y_3\}[Cr_xM_{2-x}](M_3)O_{12}$, $\{Y_{3-x}Ca_x\}Ti_xM_{5-x}O_{12}$, $\{Y_{3-x-y}Ca_{x+y}\}Zr_yTi_xM_{5-x-y}O_{12}$ where M = Fe^{3+} or Ga^{3+}. The results indicate that relative to the ionic size in octahedral coordination, the size of the tetrahedral Ga^{3+} ion is reduced more than that of the Fe^{3+} ion. The Ti^{4+} ion enters the tetrahedral as well as the octahedral sites in the garnets. The maximum amounts of Cr^{3+} and Ti^{4+} ions which can be substituted for Fe^{3+} ions in yttrium iron garnet have been deduced.

Introduction

Although it has been shown[1] that Ti^{4+} and Cr^{3+} ions enter the garnet structure, the systems $\{Y_{3-x}Ca_x\}Ti_xM_{5-x}O_{12}$ and $\{Y_3\}[Cr_xM_{2-x}](M_3)O_{12}$ where M = Fe^{3+} or Ga^{3+} have not been characterized in detail from a crystal chemical viewpoint. Of the group IVB elements Zr^{4+} and Hf^{4+} substitutions in yttrium iron garnet have been studied extensively[2,3]; it was shown that these ions prefer exclusively the octahedral sites. There is now evidence that the Ti^{4+} ion will enter the tetrahedral as well as the octahedral sites in the garnets as was predicted by Geller.[1]

Experimental

The starting materials used were oxides and $CaCO_3$ of high purity which were carefully checked for volatile matter (adsorbed H_2O and CO_2) to determine their metal oxide content. Samples of Y_2O_3, Cr_2O_3, ZrO_2, and Ga_2O_3 were fired overnight at 1400° in air, thereby determining the correction to be made on the bulk materials. Appropriate corrections were made on the $CaCO_3$ and TiO_2 after being heated overnight at 250° in air. Utilizing the total Fe assay for the α-Fe_2O_3 a single-phase specimen of YIG (yttrium iron garnet) was prepared. The weight loss above that expected from the Y_2O_3 was attributed to the α-Fe_2O_3.

Appropriate amounts to make 0.001 mole of garnet were thoroughly mixed in an agate mortar, made into a pellet of 0.5-in. diameter, calcined at 500 to 900° if necessary, and fired at approximately 1200° in air for 1–2 hr. Firings at higher temperatures, 1400°, and of longer duration (usually overnight) were then carried out in air, oxygen, or nitrogen. The Cr^{3+} substituted YGaG (yttrium gallium garnet) specimens were fired at approximately 1525°. All reactions were carried out in platinum dishes.[4] X-Ray powder photographs were taken after each firing until a sharply defined, single-phase garnet was obtained. A more detailed account of the refined experimental technique employed is given elsewhere.[4]

X-Ray powder photographs were taken with Straumanis-type Norelco cameras of 114.6-mm. diameter; either Cr K or Cu K radiation was used.

Crystallographic Data

The garnet systems studied may be represented by the general formulas: $\{Y_{3-x}Ca_x\}Ti_xM_{5-x}O_{12}$, $\{Y_3\}[Cr_xM_{2-x}](M_3)O_{12}$, and $\{Y_{3-x-y}Ca_{x+y}\}Zr_yTi_xM_{5-x-y}O_{12}$, where M = Fe^{3+} or Ga^{3+}. The lattice constants of the compounds investigated are listed in Table I and for the first two systems are plotted *vs.* composition in Fig. 1 and 2.

In the system $\{Y_{3-x}Ca_x\}Ti_xFe_{5-x}O_{12}$ single-phase specimens were obtained with x as large as 0.65 (Table I). Specimens with x = 0.75, 0.80, and 1.00 contained extra phase(s), but each contained a sharply defined garnet phase having a lattice constant of 12.401 Å., indicating a maximum of $x = 0.74$ in this system.

Single phase garnet specimens in the system $\{Y_{3-x}Ca_x\}Ti_xGa_{5-x}O_{12}$ were obtained with x as large as 2.00 (Table I). A specimen with x = 2.25 was not single phase. Because of the possibility[5] of excess Y_2O_3 dissolving in higher gallium content specimens when single phase materials are not obtained, it is not feasible to determine the maximum Ti^{4+} ion substitution by extrapolation of the lattice constant *vs.* composition curve to the maximum attainable a. It may be said, however, that the maximum is in the range $2.00 \leq x < 2.25$.

In the system $\{Y_3\}[Cr_xFe_{2-x}](Fe_3)O_{12}$ single-phase specimens were obtained with x as large as 0.50 (Table I). Although not single phase, a specimen with x = 0.75 contained a sharply-defined garnet phase having a lattice constant of 12.359 Å., indicating a maximum x of 0.61. In earlier work, Villers, Pauthenet, and Loriers[6] deduced a maximum x of approximately 0.4.

Single-phase garnet specimens in the system $\{Y_3\}[Cr_xGa_{2-x}](Ga_3)O_{12}$ were obtained with x = 0.75 and 1.00 (Table I). A specimen with x = 2.00 was not single phase.

Discussion

There appear to be structural limitations, crystallographic and electronic, on the extent to which Ti^{4+}

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[1] S. Geller, *J. Appl. Phys.*, **31**, 30S (1960), and pertinent references therein.

[2] S. Geller, R. M. Bozorth, C. E. Miller, and D. D. Davis, *J. Phys. Chem. Solids*, **13**, 28 (1960).

[3] S. Geller, H. J. Williams, G. P. Espinosa, and R. C. Sherwood, *Bell System Tech. J.*, **43**, 565 (1964).

[4] S. Geller, H. J. Williams, R. C. Sherwood, and G. P. Espinosa, *J. Phys. Chem. Solids*, **23**, 1525 (1962).

[5] This possibility is indicated by the report of M. L. Keith and R. Roy, *Am. Mineralogist*, **39**, 1 (1954).

[6] G. Villers, R. Pauthenet, and J. Loriers, *J. Phys. Radium*, **20**, 382 (1959).

TABLE I

LATTICE CONSTANTS OF THE GARNETS INVESTIGATED

$\{Y_{3-x}Ca_x\}Ti_xFe_{5-x}O_{12}$

x	a, Å.
0	12.376[a]
0.20	12.382
0.40	12.390
0.65	12.398
0.75[b]	[12.401]
0.80[b]	[12.401]
1.00[b]	[12.401]

$\{Y_{3-x}Ca_x\}Ti_xGa_{5-x}O_{12}$

x	a, Å.
0	12.274
0.50	12.295
1.00	12.314
1.50	12.334
1.95	12.354
2.00	12.356
2.25	. . .

$\{Y_3\}[Cr_xFe_{2-x}](Fe_3)O_{12}$

x	a, Å.
0.25	12.369
0.35	12.366
0.50	12.362
0.75[b]	[12.359]

$\{Y_3\}[Cr_xGa_{2-x}](Ga_3)O_{12}$

x	a, Å.
0.75	12.272
1.00	12.272
2.00[b]	. . .

$\{Y_{3-x-y}Ca_{x+y}\}Zr_yTi_xFe_{5-x-y}O_{12}$

x	y	a, Å.
0	1.50	12.614[c]
0.60	1.50	12.634

$\{Y_{3-x-y}Ca_{x+y}\}Zr_yTi_xGa_{5-x-y}O_{12}$

x	y	a, Å.
0.30	2.00	12.640
1.20	1.00	12.500
1.50	1.00	12.513

[a] See ref. 3; also F. Bertaut and F. Forrat, *Compt. rend.*, **244,** 96 (1957). [b] These are not single-phase materials. [c] See ref. 3.

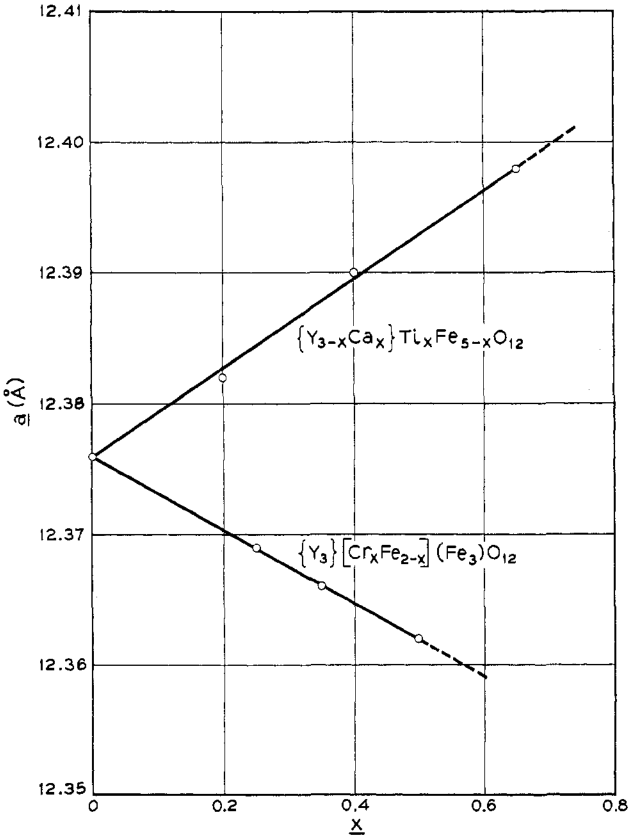

Fig. 1.—Lattice constant *vs.* composition for the systems $\{Y_{3-x}Ca_x\}Ti_xFe_{5-x}O_{12}$ and $Y_3[Cr_xFe_{2-x}](Fe_3)O_{12}$.

and Cr^{3+} ions can be substituted for Fe^{3+} and Ga^{3+} ions in YIG and YGaG. Trivalent chromium assumes a pseudo-spherical electronic configuration (preferred in octahedral and tetrahedral sites in the garnets[7]) only in an octahedral field; therefore, the Cr^{3+} ion, though smaller than the Fe^{3+} ion, is limited to the octahedral site in both YIG and YGaG. However, the Ti^{4+} ion should have a spherical electronic configuration in either an octahedral or tetrahedral field and should therefore have no site preference other than that governed by its size.

The maximum x for $\{Y_3\}[Cr_xFe_{2-x}](Fe_3)O_{12}$ is 0.61 while for $\{Y_3\}[Cr_xGa_{2-x}](Ga_3)O_{12}$ it is >1.00.

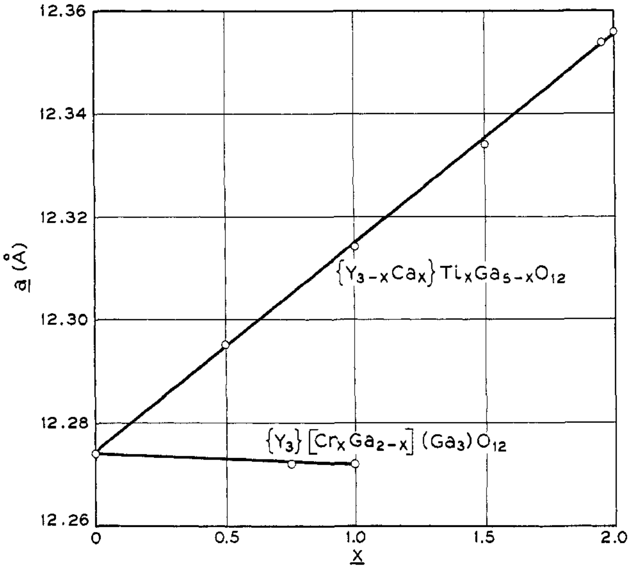

Fig. 2.—Lattice constant *vs.* composition for the systems $\{Y_{3-x}Ca_x\}Ti_xGa_{5-x}O_{12}$ and $Y_3[Cr_xGa_{2-x}](Ga_3)O_{12}$.

The garnet uvarovite, $\{Ca_3\}[Cr_2](Si_3)O_{12}$, has been synthesized.[8] This suggests, as was stated previously,[2] that in this garnet the ratio of the Cr–O to Si–O distances is favorable for the complete octahedral substitution of the Cr^{3+} ion. The octahedral to tetrahedral metal-oxygen distance ratio in YIG is 1.06 Å. (2.00/1.88).[9] From β-Ga_2O_3 the average octahedral to tetrahedral metal-oxygen distance ratio is 1.09 Å. (2.00/1.83),[10] which is probably not much different from that for YGaG. The ratio for $\{Ca_3\}[Fe_2](Si_3)O_{12}$ is probably the largest of the three. These data indicate that the larger the octahedral to tetrahedral metal-oxygen distance ratio the more Cr^{3+} ion that can be substituted octahedrally in the garnet systems discussed. Furthermore, this suggests that the tetrahedral Ga^{3+} ion is reduced more in size than the tetrahedral Fe^{3+} ion relative to the ionic size in octahedral coordination.

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[7] M. A. Gilleo and S. Geller, *Phys. Rev.*, **110,** 73 (1958).

[8] S. Geller and C. E. Miller, *Am. Mineralogist*, **44,** 445 (1959), and pertinent references therein.

[9] S. Geller and M. A. Gilleo, *J. Phys. Chem. Solids*, **3,** 30 (1957); **9,** 235 (1959).

[10] S. Geller, *J. Chem. Phys.*, **33,** 676 (1960).

It was found that the Ti^{4+} ion enters the tetrahedral as well as the octahedral site in the garnets. In the system $\{Y_{3-x-y}Ca_{x+y}\}Zr_yTi_xGa_{5-x-y}O_{12}$ single-phase specimens were prepared with $x = 1.20$ and 1.50 and $y = 1.00$ (Table I). Because the Zr^{4+} ions prefer exclusively the octahedral sites[2] *at least* 0.20 and 0.50 Ti^{4+} ion, respectively, were substituted tetrahedrally. When $x = 0.30$ and $y = 2.00$ the amount of tetrahedral Ti^{4+} is 0.30. By the same reasoning the garnet in the system $\{Y_{3-x-y}Ca_{x+y}\}Zr_yTi_xFe_{5-x-y}O_{12}$ with $x = 0.60$ and $y = 1.50$ (Table I) contains *at least* 0.10 Ti^{4+} ion in tetrahedral coordination.

The lattice constants of the systems $\{Y_{3-x}Ca_x\}$-$Ti_xM_{5-x}O_{12}$ ($M = Ga^{3+}$ or Fe^{3+}) increase with increasing x. When $M = Fe^{3+}$ this increase may be attributed to the Ca^{2+} ion, which is larger than the Y^{3+} ion,[11] while the octahedral Ti^{4+} ion is probably a little smaller than the octahedral Fe^{3+} ion. When $M = Ga^{3+}$ most of the increase is caused by the Ca^{2+} ion but some may be attributed to the tetrahedral Ti^{4+} ion, which is probably larger than the tetrahedral Ga^{3+} ion. In this system x_{max} is larger when $M = Ga^{3+}$ than when $M = Fe^{3+}$, probably because the tetrahedral Ga^{3+} ion is smaller than the tetrahedral Fe^{3+} ion relative to the ionic size in octahedral coordination. This presumably leads to a more favorable octahedral to tetrahedral metal–oxygen distance ratio relative to the requirements of the structure.

In the systems $\{Y_{3-x}Ca_x\}Ti_xM_{5-x}O_{12}$ and $\{Y_3\}$-$[Cr_xM_{2-x}](M_3)O_{12}$ where $M = Ga^{3+}$ or Fe^{3+}, the maximum amount of Ti^{4+} ion which can be substituted for M^{3+} is always greater than the maximum amount of Cr^{3+} ion which can be substituted within a given system. This results from the distribution of the Ti^{4+} ions over two sites which may lead to a more favorable structural situation in these garnets; it also suggests that the Ti^{4+} ion is larger than the Cr^{3+} ion.

Acknowledgment.—The author wishes to thank S. Geller for suggesting this project and for helpful discussion.

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[11] S. C. Abrahams and S. Geller, *Acta Cryst.*, **11**, 437 (1958).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The Preparation and Properties of Trifluoromethoxy Sulfur Pentafluoride [CF_3OSF_5] and *cis*-Bis(trifluoromethoxy)tetrafluorosulfur(VI) [$(CF_3O)_2SF_4$][1]

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Trifluoromethoxy sulfur pentafluoride and *cis*-bis(trifluoromethoxy)tetrafluorosulfur(VI) were prepared by the ultraviolet irradiation of gaseous mixtures of SF_4 with either CF_3OF or CF_3OOCF_3. The products have been characterized and the structures confirmed by mass, infrared, and nuclear magnetic resonance spectra.

Trifluoromethyl hypofluorite can be added across double bonds with cleavage at the O–F bond to yield, in the case of ethylene, $CF_3OCH_2CH_2F$,[2,3] and in the case of carbonyl fluoride, CF_3OOCF_3.[4] It has now been found that trifluoromethyl hypofluorite also can be added to sulfur tetrafluoride to give trifluoromethoxy sulfur pentafluoride.[5] *cis*-Bis(trifluoromethoxy)tetrafluorosulfur(VI) is also produced.

Experimental

Materials.—Trifluoromethyl hypofluorite[6] was obtained as the product of a flow reaction of carbon monoxide and fluorine at 350°. Bistrifluoromethyl peroxide[4] was prepared by passing streams of fluorine and carbon monoxide through a "catalytic" flow reactor[6] with the flow rates: F_2, 4 l./hr., and CO, 2.7 l./hr. The products of this reaction were collected in a trap held at −183°. The peroxide was refined by pumping the product mixture under vacuum through a train consisting of: (1) a 0.75-m. length of 30-mm. tubing packed with granulated soda lime, (2) a trap held at −78°, and (3) a trap held at −183°. The F_2, CF_3OF, CO_2, and COF_2 present in the crude material were absorbed by the soda lime. The water and oxygen formed in the soda lime column, along with CF_3OOCF_3 and CF_4, then passed through the trap at −78° where water was condensed, then to the trap at −183° where the peroxide was deposited while the CF_4 and O_2 present passed on to the vacuum pump. The CF_3OOCF_3 obtained in this manner was used without further purification. Sulfur tetrafluoride was supplied by E. I. du Pont de Nemours and Co., Inc., and was used directly from the cylinder.

Reactions.—Equimolar amounts of gaseous CF_3OF and SF_4 were introduced into a 3-l. Pyrex bulb to a total pressure of 252 mm. A quartz glass finger containing a water-cooled Hanau 4.5-watt mercury arc lamp projected ultraviolet light into the bulb. After irradiation for 3 days the volatile products were condensed and separated by fractional codistillation.[7] They were, in order of decreasing volatility, CF_3OF, SiF_4, COF_2, SO_2F_2, SOF_2, CF_3OOCF_3, CF_3OSF_5, $(CF_3O)_2SF_4$, and a small amount of a still less volatile material which was not identified.

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[1] Presented at the Northwest Regional Meeting of the American Chemical Society, June 20, 1962.

[2] G. H. Cady, Abstracts, XVII International Congress of Pure and Applied Chemistry.

[3] J. A. C. Allison and G. H. Cady, *J. Am. Chem. Soc.*, **81**, 1089 (1959).

[4] R. S. Porter and G. H. Cady, *ibid.*, **79**, 5628 (1957).

[5] (a) This compound has been reported by G. Pass and H. L. Roberts, *Inorg. Chem.*, **2**, 1016 (1963); (b) the n.m.r. spectrum of a sample prepared by the authors was published previously (C. I. Merrill, S. M. Williamson, G. H. Cady, and D. Eggers, Jr., *ibid.*, **1**, 215 (1962).

[6] K. B. Kellogg and G. H. Cady, *J. Am. Chem. Soc.*, **70**, 3986 (1948).

[7] G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).