SYNTHESIS OF GARNETS WITH LARGE CATIONS

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SYNTHESIS OF GARNETS WITH LARGE CATIONS

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The presence in the garnet structure of three different positions for cations—with 8-, 6-, and 4-fold coordination by oxygen ions—opens broad possibilities for isomorphism (^{1}). However, not all possible combinations of cations of these three types can be realized: for the formation of garnet a definite ratio of ion sizes is required (in some cases their electronic configuration is also important). For example, the garnets $Mn_3In_2Ge_3O_{12}$ and $Mn_3Sc_2Ge_3O_{12}$ have not been obtained, since Mn^{2+} (r = 0.80 Å∗) is not a sufficiently large ion to occupy the large dodecahedral (coordination number 8) voids when such large ions as In^{3+} (0.81 Å) and Sc^{3+} (0.81 Å) are in the octahedral positions (^{3}). The garnet $Nd_3Fe_5O_{12}$ is unknown, where, conversely, Nd^{3+} (1.04 Å) is too large (^{1}). Even for known compounds there is a definite correlation between the ease of their formation and the ratio of cation sizes in the structure (^{3}, ^{4}).

Until now it has been considered that Sr^{2+} (1.12 Å) is too large a cation to occupy all the dodecahedral positions, and can only partially replace other cations in them (^{1}); true, in this connection the existence of Sr hydrogarnets $3SrO \cdot Ga_2O_3 \cdot 6H_2O$ (^{5}) and $3SrO \cdot Al_2O_3 \cdot 6H_2O$ (^{6}) was forgotten. In attempting to synthesize Sr garnets, we proceeded from the assumption that, for their formation, the cations occupying the tetrahedral and, especially, the octahedral positions must also be sufficiently large. The largest of the known trivalent "octahedral" cations are In^{3+} and Sc^{3+}. Indeed, garnet was obtained only with them ($Sr_3In_2Ge_3O_{12}$ and $Sr_3Sc_2Ge_3O_{12}$), whereas with smaller ones, for example Fe^{3+} (0.64 Å), it did not form. As expected, Si^{4+} (0.42 Å) proved too small for Sr garnets.

The lattice constant of $Sr_3In_2Ge_3O_{12}$ is 12.87 Å; however, the Sr hydrogarnets have considerably larger parameters: 13.15 Å** for the gallium compound and 13.02 Å for the aluminum compound. A recent determination of the structure of the hydrogarnet $3CaO \cdot Al_2O_3 \cdot 6H_2O$ (^{7}) showed the absence of any special distortions of the coordination polyhedra in comparison with the structures of other garnets. Thus, the existence of unknown garnets with lattice constants exceeding 13 Å seemed in principle possible.

Substitutions in $Sr_3In_2Ge_3O_{12}$ of Sr^{2+} by Ba^{2+} (in 8-coordination), or of Ge^{4+} by Sn^{4+} and Ti^{4+} (in 4-coordination), did not yield a garnet; therefore we attempted to introduce rare-earth-element ions (REE) into the octahedral positions. It is believed that, because of their large sizes, they can have only 8-fold coordination in garnets (1)***. But, first, In^{3+} is close in size—closer to the last members of the lanthanide family (Yb^{3+} (0.86 Å) and Lu^{3+} (0.85 Å)); second, scandium is similar to the rare-earth elements in its chemical and crystal-chemical behavior, and it enters 6-coordination in garnets. Finally, for a number of gallates and aluminates of the rare-earth elements and yttrium with the garnet structure, solid solutions are known that can be interpreted as the result of replacing part of Ga^{3+} or Al^{3+} in octahedra by rare-earth ions and Y^{3+} (10). Recently, spinels containing rare-earth ions in octahedral positions have been synthesized (11).

Table 1

Conditions for preparation and characteristics of garnet ceramics

Formula	t, °C	τ, h	$a_0 \pm 0.01$ Å	d_X, g/cm^3	$a_0' \pm 0.01$ Å	Color
$Sr_3Sc_2Ge_3O_{12}$	1200	48	12.79	4.84	12.785	White
$Sr_3In_2Ge_3O_{12}$	1200	48	12.87	5.62	12.88	»
$Sr_3Lu_2Ge_3O_{12}$	1250	24	13.01	6.17		»
$Sr_3Yb_2Ge_3O_{12}$	1250	24	13.03	6.12		»
$Sr_3Tu_2Ge_3O_{12}$	1250	24	13.04	6.06		»
$Sr_3Er_2Ge_2O_{12}$	1250	24	13.065	6.00		Pink
$Sr_3Ho_2Ge_3O_{12}$	1250	24	13.09	5.94		Yellowish
$Sr_3Y_2Ge_3O_{12}$	1250	24	13.085	5.04		White
$Ca_3Lu_2Ge_3O_{12}$	1250	24	12.73	5.66		»
$Ca_3Yb_2Ge_3O_{12}$	1250	24	12.74	5.62		»
$Ca_3Tu_2Ge_3O_{12}$	1250	24	12.765	5.55		»
$Ca_3Er_2Ge_3O_{12}$	1250	24	12.785	5.50		Pink
$Ca_3Ho_2Ge_3O_{12}$	1250	34	12.81	5.43		Yellowish
$Ca_3Dy_2Ge_3O_{12}$	1250	24	12.83	5.38		White
$Ca_3Y_2Ge_3O_{12}$	1250	24	12.805	4.48		»
$Ca_3Ga_2Sn_3O_{12}$	1400	2	12.69	5.24		»
$Ca_3In_2Ge_3O_{12}$	1200	48	12.59	5.06	12.59	»

[*] r —ionic radii according to Ahrens (2); no corrections were made for the change in coordination number.

[**] Calculated by us from the pycnometric density given in (5).

[***] In general, garnets with large cations in 6-coordination are known. In the defect structure $12CaO \cdot 7Al_2O_3$, part of the Ca^{2+} is located in octahedra together with Al^{3+} (8). Ringwood carried out, at 700° and a pressure of 40–70 kbar, the transition of pyroxene $CaGeO_3$ to garnet according to the scheme $4CaGeO_3 \rightarrow \{Ca_3\}^{VIII}[CaGe]^{VI}(Ge_3)O_{12}$. An analogous transformation at 700°

Formula	t, °C	τ, h	$a_0 \pm 0.01$ Å	d_X, g/cm^3	$a'_0 \pm 0.01$ Å	Color
$Cd_3In_2Ge_3O_{12}$	1050	44	12.515	6.62	12.515	»
$Ca_3Sc_2Si_3O_{12}$	1350	17	12.255	3.51	12.265	»

In order that, in the present case, the rare-earth ions enter 6-coordination, larger cations must occupy the dodecahedral positions—these may be Sr^{2+} and Ca^{2+} (0.99 Å). The existence of Ca-rare-earth garnets with large lattice constants made it possible to hope for obtaining them: 12.73 Å for $Ca_3Fe_2Sn_3O_{12}$ (12) and 12.74 Å for $3CaO{\cdot}Fe_2O_3{\cdot}6H_2O$ (6), whereas the parameter of $Ca_3In_2Ge_3O_{12}$ was only 12.59 Å (Table 1).

We began with the smallest of the rare-earth elements—Lu^{3+} (0.85 Å)—and, after achieving success, gradually increased the size of the octahedral cation. Thus 13 garnets were synthesized containing rare-earth and yttrium ions in 6-coordination: Ca garnets for the series Lu^{3+}–Dy^{3+} and Y^{3+}, and Sr garnets for the series Lu^{3+}–Ho^{3+} and Y^{3+} (Table 1). Cd^{2+} (0.97 Å), because of its smaller size compared with Ca^{2+} and also, probably, owing to features of its electronic structure, did not form garnets even with the smallest rare-earth elements.

It should be noted that garnets of the type $M_3^{2+}Ln_2^{3+}Ge_3O_{12}$ are known, where $M = Mn, Co, Mg$ and $Ln = Y, Gd$; however, in them the rare-earth ions are located in dodecahedral positions, i.e., the distribution is as follows: $\{M^{2+}Ln_2\}[M_2^{2+}](Ge_3)O_{12}$ (12). We attempted to prepare garnets of the compositions $CaLa_2Ca_2Ge_3O_{12}$, $CaLa_2Cd_2Ge_3O_{12}$, $CaNd_2Ca_2Ge_3O_{12}$, and $CaNd_2Cd_2Ge_3O_{12}$, containing Ca^{2+} or Cd^{2+} in octahedra (La^{3+} and Nd^{3+} are larger than Ca^{2+}). As was to be expected, the results were negative. Compositions corresponding to the formulas $Sr_3Y_2Sn_3O_{12}$, $Ba_3Y_2Sn_3O_{12}$, and $Ba_3Y_2Ge_3O_{12}$ likewise did not give garnets. Apparently, in $Sr_3Ho_2Ge_3O_{12}$ ($a_0 = 13.09$ Å) the upper limit of isomorphism is reached for individual anhydrous oxygen compounds with a garnet-type structure; with a further increase in cation size—for example, replacing Ho^{3+} (0.91 Å) by the slightly larger Dy^{3+} (0.92 Å)—this limit is exceeded, and the garnet is not formed (at least under the conditions of the present work). Ba^{2+} (1.34 Å) and Sn^{4+} (0.71 Å) are evidently too large for this type of garnet, although solid solutions can probably be prepared with partial replacement of Sr^{2+} by Ba^{2+}, Ho^{2+} by a larger rare-earth ion, or Ge^{4+} by Sn^{4+}.

It was possible to hope to obtain garnets with larger parameters by virtue of isomorphism in 4-coordination. Of the tetravalent cations, apart from Si^{4+} and

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and above 10 kbar was observed also for $CdGeO_3$ (9). In these compounds the large cations occupy octahedral positions paired with small ones, and the average cation radius is not too large.

Ge^{4+}, Sn^{4+} enters the tetrahedral voids in appreciable amounts. The garnet $Ca_3Fe_2Sn_3O_{12}$ synthesized by Geller and co-workers has the cation distribution $\{Ca_3\}[Fe_{0.2}Sn_{1.8}](Fe_{1.8}Sn_{1.2})O_{12}$, i.e., 1.2 of the 3 Sn^{4+} ions are located in tetrahedra (^{11}). We attempted to replace Fe^{3+} in this compound by other trivalent cations and succeeded only in the case of Ga^{3+} (0.62 Å). Owing to the stronger preference of Ga^{3+} for tetrahedral coordination compared with Fe^{3+}, an even smaller fraction of Sn^{4+} will be in 4-coordination in $Ca_3Ga_2Sn_3O_{12}$. Substitution by Sc^{3+} and In^{3+}, paired with Ca^{2+}, Sr^{2+}, and Ba^{2+}, did not yield Sn-garnets. Consequently, for 4-coordination, only substitution of the orthogroups GeO_4^{4-} by $(OH)^{4-}$, with formation of a hydrogarnet, leads to large unit-cell dimensions. Because of the greater "flexibility" of the hydrogarnet structure, in $3SrO \cdot Ga_2O_3 \cdot 6H_2O$ the upper limit of isomorphism may not be reached, and hydrogarnets with larger octahedral cations, for example with Fe^{3+}, may exist.

Unfortunately, the structural and thermodynamic data available for garnets are clearly insufficient for predicting the existence of new compounds, determining the limits of isomorphism, and assessing distortions of coordination polyhedra. The use in the present work of such simple geometric factors as ionic radii made it possible to synthesize a large number of new garnets containing large cations, often (rare-earth elements and yttrium) in an unexpected, "forbidden," coordination. An analogous approach is at present being widely and fruitfully applied by a number of researchers to the synthesis of compounds in the structural types of perovskite, spinel, and others.

All compounds were obtained in ceramic form by firing pressed mixtures of stoichiometric composition in air, followed by quenching. The starting components were $CaCO_3$ (special purity), $SrCO_3$ (reagent grade), In_2O_3 (reagent grade), Sc_2O_3 ($> 99\%$), GeO_2 ($> 99.99\%$), and oxides of the rare-earth elements and yttrium of purity not worse than 99.9%, except for holmium oxide, where the impurity content could reach 1%. The sintering products were studied by X-ray diffraction. Debyegrams were recorded in a camera of diameter 57.3 mm using filtered copper radiation. The synthesized substances gave X-ray diffraction patterns with sharp reflections in the back-reflection region; extraneous lines were absent or weak. The lattice constants were calculated from the last lines ($\theta > 60^\circ$) and extrapolated to $\theta = 90^\circ$.

Table 1 lists the synthesized compounds and gives the conditions of their formation (t —temperature, τ —firing duration), lattice constants a_0, X-ray densities d_X, color, and lattice constants a_0' for some garnets obtained under hydrothermal conditions. Added to the list of new compounds are the garnets previously synthesized hydrothermally (^{13}): $Ca_3In_2Ge_3O_{12}$, $Cd_3In_2Ge_3O_{12}$, and $Ca_3Sc_2Si_3O_{12}$, which in the course of the present investigation were prepared by the ceramic method. However, $Ca_3In_2Si_3O_{12}$ could not be prepared in this way up to 1500°, and, consequently, it forms only under pressure. $Sr_3In_2Ge_3O_{12}$ and $Ca_3Sc_2Ge_3O_{12}$ were also synthesized under hydrothermal-

conditions at 550° and 1300 atm in a 6% aqueous solution of NH_4Cl and 10% $SrCl_2$ (the procedure is described in more detail in (^{13})). Table 2 gives typical experiments for the hydrothermal synthesis of these garnets.

As can be seen from Table 2, in contrast to calcium garnets (^{3}), strontium garnets are formed better from a charge containing strontium oxide rather than carbonate. As before, an excess in the charge or solvent of divalent ions occupying the dodecahedral positions in the structure promotes synthesis.

Table 2

Conditions for the hydrothermal synthesis of Sr garnets

Charge(M = In or Sc)	$Sr_3In_2Ge_3O_{12}$ 6% NH_4Cl	$Sr_3In_2Ge_3O_{12}$ 10% $SrCl_2$	$Sr_3Sc_2Ge_3O_{12}$ 6% NH_4Cl	$Sr_3Sc_2Ge_3O_{12}$ 10% $SrCl_2$
$3SrO + M_2O_3 + 3GeO_2$	–*	not very much	–	little
$6SrO + M_2O_3 + 3GeO_2$	not very much	much	little	much
$3SrCO_3 + M_2O_3 + 3GeO_2$	–	not very much	–	little
$6SrCO_3 + M_2O_3 + 3GeO_2$	–	much	–	much

* Garnet does not form.

$Sr_3In_2Ge_3O_{12}$ crystallizes as colorless transparent crystals up to 0.25 mm in size, bounded by the faces of the rhombododecahedron {110} and tetragontrioctahedron {211}. $Sr_3Sc_2Ge_3O_{12}$ was obtained as colorless transparent crystals several hundredths of a millimeter in size, without a clearly expressed faceting. The lattice constants of these two garnets, obtained by the ceramic route and under hydrothermal conditions, agree well with one another, indicating the absence of appreciable hydration of the garnets when they form in the presence of water.

Recently N. A. Toropov and co-workers (^{15}) reported obtaining crystals of yttrium orthosilicate $Y_4Si_3O_{12}$ with the garnet structure, which above 1550° irreversibly transforms into a hexagonal modification. The unusual composition and the proposed distribution of cations $\{Y_2\}Y_2O_{12}$ prompted us to attempt to synthesize this compound and its Ge analogue by the ceramic route; however, the attempts were unsuccessful. Possibly the reason here is stabilization of the structure by K^+ and F^- impurities contained in the crystals according to the results of chemical analysis (^{15}).

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