HYDROTHERMAL SYNTHESIS OF GARNETS CONTAINING V^{3+}, In^{3+}, AND Sc^{3+}

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HYDROTHERMAL SYNTHESIS OF GARNETS CONTAINING V^{3+}, In^{3+}, AND Sc^{3+}

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In recent years interest has greatly increased in compounds with a garnet-type structure. A typical representative of this crystal-chemical group is the mineral grossular, $Ca_3Al_2Si_3O_{12}$. In the structure of grossular, Ca^{2+} ions are in eightfold coordination with respect to oxygen ions, Al^{3+} are at the centers of oxygen octahedra, and Si^{4+} are in tetrahedra. In the general case Ca^{2+} may be replaced by Cd^{2+} and Mn^{2+}; Al^{3+} by Fe^{3+}, Cr^{3+}, Ga^{3+}, and Sc^{3+}; and Si^{4+} by Ge^{4+} ([1,2]) (only isovalent substitutions are meant). We have succeeded in synthesizing under hydrothermal conditions new garnets containing V^{3+}, In^{3+}, and Sc^{3+} ions in octahedral positions.

In natural garnets, vanadium is present in amounts not exceeding 0.1%. However, S. T. Badalov has described the occurrence of a garnet containing 5% V_2O_3 ([3]) (about 30% V_2O_3 should be contained in $Ca_3V_2Si_3O_{12}$). We synthesized the following vanadium-bearing garnets: $Ca_3V_2Si_3O_{12}$, $Ca_3V_2Ge_3O_{12}$, $Cd_3V_2Si_3O_{12}$, $Cd_3V_2Ge_3O_{12}$, and $Mn_3V_2Ge_3O_{12}$. In addition to the Sc-garnets $Ca_3Sc_2Ge_3O_{12}$ and $Cd_3Sc_2Ge_3O_{12}$ obtained by Tauber ([2]), $Ca_3Sc_2Si_3O_{12}$ was synthesized. Indium is considered too large a cation to fully occupy octahedral positions in garnets. In indium-substituted yttrium iron ferrite $Y_3Fe_{2-x}In_{xFe}3O_{12}$, already at $x \geqslant 0.65$, along with garnet, a perovskite phase is formed ([4]). We obtained the garnets $Ca_3In_2Si_3O_{12}$, $Ca_3In_2Ge_3O_{12}$, and $Cd_3In_2Ge_3O_{12}$, in which the octahedral positions are completely occupied by indium.

For the synthesis we used a method developed earlier for yttrium iron garnet ([5]). Aqueous solutions of the chlorides NH_4Cl, $CaCl_2$, $CdCl_2$, and $MnCl_2$ served as solvents. The concentration of ammonium chloride was 6%; the other solvents were used as 10% solutions. The starting substances were $Ca(OH)_2$, $CaCO_3$, CdO, $CdCO_3$, MnO, $MnCO_3$, V_2O_4, V_2O_5, In_2O_3, Sc_2O_3, SiO_2, and GeO_2. The charge was placed in titanium liners, into which the solvent was poured; the same solution was also poured into the autoclave. One autoclave of volume 150 cm^3 held 4-5 liners, each with an internal volume of about 7 cm^3. The experiments were carried out without a temperature gradient at 550° and a pressure of about 1300 atm (the pressure was determined from the P—V—T—X data for NaCl solutions ([6])). The heating time was 2.5-3.5 days; after the experiment was completed, the autoclaves were rapidly cooled.

The synthesis products were washed with dilute nitric acid, dried at 140°, and studied under a microscope and by X-ray diffraction. Debyegrams were taken in a camera of diameter 57.3 mm using filtered copper radiation. For several garnets, infrared spectra were recorded (on a UR-10 instrument), and densities were measured. The densities were determined pycnometrically at 25° in benzene. The refractive indices of the new garnets were also measured.

The crystals of the synthesized substances had a faceting characteristic of garnets: the principal form was the rhombododecahedron {110}, the edges of which are often truncated by strips of the faces of the tetragontrioctahedron {211}.

Good-quality Debyegrams were obtained, on which lines of other phases were either absent or weak. Comparison with Debyegrams of natural garnets revealed the complete set of lines characteristic of the garnet structural type. The lattice constants of the new garnets were determined from the last 5 lines, corresponding to reflection angles $\theta > 60^\circ$. The values obtained for a_0 lay within the range of values known for garnets (11.5–12.5 Å). Since the synthesis proceeded with the participation of water, the formation of hydrogarnets could have been expected. However, judging from the infrared spectra recorded for $Ca_3V_2Ge_3O_{12}$, $Cd_3V_2Ge_3O_{12}$, and $Mn_3V_2Ge_3O_{12}$, they do not contain any appreciable amounts of constitutional water, although its complete absence cannot be asserted (for comparison we note that 1.44 wt.% water contained in the garnet $Ca_3Ga_2Ge_3O_{12}$, synthesized by us under analogous conditions, is detected on the spectrogram).

All the new garnets were synthesized in NH_4Cl solutions, but $Ca_3V_2Si_3O_{12}$, $Cd_3V_2Si_3O_{12}$, and $Mn_3V_2Ge_3O_{12}$ could not be obtained from a charge of stoichiometric composition with this solvent. It was observed that an excess of divalent cations favors the synthesis. Thus, $Ca_3V_2Si_3O_{12}$, $Cd_3V_2Si_3O_{12}$, and $Mn_3V_2Ge_3O_{12}$ were synthesized from charges of the compositions $6CaCO_3 + V_2O_4 + 2SiO_2$, $6CdO_2 + V_2O_4 + 3SiO_2$, and $6MnO + V_2O_4 + 3GeO_2$; for the other garnets, with an excess of divalent cations in the starting mixture, an increase in yield and in crystal size was observed. When metal chlorides whose cations occupy the positions of Ca^{2+} in the grossular structure were used as solvents—i.e., $CaCl_2$ solutions for Ca-garnets, $CdCl_2$ for Cd-garnets, and $MnCl_2$ for $Mn_3V_2Ge_3O_{12}$—the synthesis proceeded equally well from charges of both stoichiometric and nonstoichiometric composition (with an excess of divalent cations), with one exception: for the formation of $Cd_3V_2Si_3O_{12}$ an excess of cadmium oxide was required. The advantage of $CaCl_2$, $CdCl_2$, and $MnCl_2$ over NH_4Cl apparently consists in the fact that, when they are used, the solution already contains an excess of divalent cations, which promotes synthesis.

The synthesis was also affected by the form in which the components of the charge were taken. In the case of Ca-garnets, considerably better results were obtained if Ca^{2+} was introduced as $CaCO_3$, rather than as $Ca(OH)_2$. However, for cadmium and manganese garnets the use of cadmium and manganese carbonates in the starting mixture instead of the corresponding oxides reduced the yield and size of the crystals. In the case of V-garnets it is better to take vanadium pentoxide. Thus, for example, $Ca_3V_2Si_3O_{12}$ did not form from the mixture $6CaCO_3 + V_2O_4 + 3SiO_2$ and was obtained when V_2O_4 in it was replaced by V_2O_5; $Ca_3V_2Ge_3O_{12}$ is not the only product of synthesis when V_2O_4 is used in the starting mixture, whereas with V_2O_5 a single garnet formed. This is apparently connected with the greater solubility of vanadium pentoxide and with the fact that V^{5+} is more metastable with respect to stable V^{3+} than is V^{4+} (V_2O_3 can be synthesized from V_2O_5 under hydrothermal conditions at 550-700° (7)).

Only in the case of $Ca_3V_2Ge_3O_{12}$, $Cd_3V_2Ge_3O_{12}$, and $Mn_3V_2Ge_3O_{12}$ was a single garnet obtained; in the synthesis of the other garnets, other phases also formed, whose identification was not carried out. The crystallization of $Ca_3Sc_2Si_3O_{12}$ proceeded worst of all; its crystals often did not have a clearly expressed faceting and were very small. The largest crystals were obtained for $Mn_3V_2Ge_3O_{12}$. During its synthesis, crystals up to 0.7 mm grew on the bottom, walls, and lid of the liner. In one such liner two further experiments were carried out. It is interesting that growth proceeded almost exclusively on seed crystals remaining in the liner after the first experiment; the sizes of the crystals on the lid increased to 1.1 mm in the 2nd cycle and to 1.4 mm in the 3rd cycle. Special experiments to find conditions for the formation of larger crystals of either $Mn_3V_2Ge_3O_{12}$ or the other garnets were not undertaken.

The sizes of the crystals, lattice constants (a_0), X-ray (d_x) and pycnometric (d_{pycn}) densities, color, and refractive indices (n) of the new garnets are given in Table 1, which also includes the Taube-described

garnet $Ca_3Sc_2Ge_3O_{12}$ [2], which we synthesized hydrothermally.

It should be noted that $Ca_3In_2Si_3O_{12}$ and $Ca_3In_2Ge_3O_{12}$ have the largest lattice constants among the known silicate and germanate garnets. The measured densities for three garnets practically coincided

Table 1

Properties of the synthesized garnets

Composition	a_0, Å	d_X	d_{pycn}	n	Color	Maximum crystal size, mm
$Ca_3V_2Si_3O_{12}$	12.09	3.73		1.85_5	Dark green	0.05
$Ca_3V_2Ge_3O_{12}$	12.35	4.44	4.45 ± 0.01	1.90	Green	0.1
$Cd_3V_2Si_3O_{12}$	12.03	5.44			Black	0.2
$Cd_3V_2Ge_3O_{12}$	12.29	6.06	6.06 ± 0.02	2.04	Green	0.2
$Mn_3V_2Ge_3O_{12}$	12.125	5.04	5.05 ± 0.015	1.99_5	Dark green	1.4

Composition	a_0, Å	d_X	d_{pycn}	n	Color	Maximum crystal size, mm
$Ca_3In_2Si_3O_{12}$	12.35	4.42		1.77	White	0.03
$Ca_3In_2Ge_3O_{12}$	12.62	5.01		1.83	White	0.05
$Cd_3In_2Ge_3O_{12}$	12.515	6.62		1.96	Grayish-greenish	0.1
$Ca_3Sc_2Si_3O_{12}$	12.27	3.48			White	0.02
$Ca_3Sc_2Ge_3O_{12}$*	12.51	4.19			White	0.02

* According to Tauber [2], $Ca_3Sc_2Ge_3O_{12}$ has $a_0 = 12.507$ Å.

with the X-ray values. Table 1 gives the mean values of d_{pycn} from two determinations and indicates the scatter. The refractive indices were measured in yellow light; the accuracy of determination was ±0.01. The green color of the vanadium garnets is evidently due to the V^{3+} ion, for whose compounds this color is characteristic.

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Note: Figure translations are in progress. See original paper for figures.