

A NEW YTTRIUM MAGNESIUM SILICATE GARNET, $Y_6Mg_5Si_5O_{24}$
AND ITS RARE EARTH AND NICKEL ANALOGUES

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ABSTRACT

A new magnesium yttrium silicate garnet and its rare-earth analogues with 4 and 6 coordinated magnesium and nickel ions have been synthesized hydrothermally. Its solid solubility with yttrium aluminum garnet was investigated.

Yttrium iron (or aluminum) garnets (space group $Ia\bar{3}d$) have been thoroughly studied lately. Various substitutions in three crystallographic sites (1), \underline{c} (8), \underline{a} (6) and \underline{d} (4) have been reported. Geller (2) has given a complete survey of the ions in the synthetic and natural compounds having the garnet structure.

In the course of a study on rare earth silicate apatites, a new yttrium-magnesium silicate having the garnet structure was synthesized hydrothermally at 720°C under 2 kilobars H_2O pressure in a cold-seal steel bomb with a silver liner. The starting material was precipitated $Mg(OH)_2$ in a yttrium silicate hydrate suspension.

Magnesium ions have been known to enter the \underline{c} (8) or \underline{a} (6) sites in previously reported garnet compounds: $Mg_3Al_2Si_3O_{12}$, pyrope \underline{c} (8); $NaCa_2Mg_2As_3O_{12}$, berzeliite, \underline{a} (6); $Gd_3Mg_2GaGe_2O_{12}$, \underline{a} (6); and $Gd_2MgMg_2Ge_3O_{12}$, \underline{c} (8) and \underline{a} (6). In the magnesium garnet here described, magnesium ions occupy

both a (6) and d sites with the following formula:

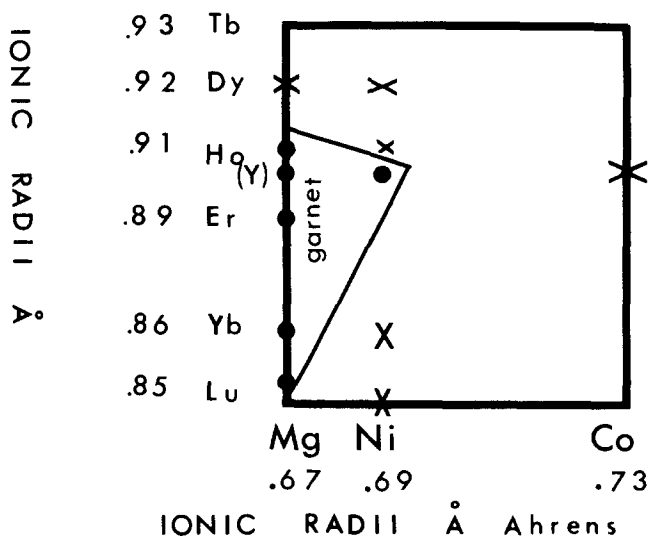
$Y_6Mg_4(6)Mg(4)Si_5O_{24}$. Nickel ions also enter d (4) sites in the same manner. The possibility of the substitution of magnesium in c (8) sites as was demonstrated by Geller (3) in $Y_2Mg(8)Mg_2(6)Ge_3O_{12}$ was suspected but virtually disproved for the garnets described in this study. The composition corresponding to $Y_2Mg_3Si_3O_{12}$ did not give a garnet phase under the conditions for the $Y_6Mg_5Si_5O_{24}$ garnet. Hydrothermal treatment of this composition always gave the low temperature polymorph of α - $Y_2Si_2O_7$ (4) and a silicate apatite-like phase. In the presence of larger ions such as yttrium, it seems more likely that Mg^{2+} and Ni^{2+} occupy tetrahedral and octahedral sites than dodecahedral sites.

The emission spectrographic analysis of the yttrium magnesium silicate garnet gave major impurity, $\sim 0.05\%$ Na, adsorbed in the starting gels. This does not suffice to accommodate the following replacement in the garnet formula, $NaY_5Mg_4Si_6O_{24}$ (theoretical $Na_2O = 5.5\%$). It is also known from the writer's study on apatite silicates, that this composition readily forms the following apatite $(Na,Mg,Y)_{10}Si_6O_{24}(OH)_2$, under the present conditions. Infrared spectroscopic analysis did not detect OH in the same sample. Thus, the possible hydrogarnet type replacement by H_2O with vacant d (4) sites, such as $Y_6Mg_4Si_5H_2O_{24}$ was also discarded.

The limits of composition range for this garnet at $720^\circ C$ and 2 kilobars are illustrated in Fig. 1. Rare-earth ions larger than holmium did not form this garnet but formed magnesium analogues of cerite, $Ln_7Mg_3Si_7O_{27}OH$, zinc, copper, cobalt and ferrous iron analogues were also not obtained. Only the nickel-yttrium analogue was formed. Yttrium-magnesium-silicate garnet is stable in air at $1,180^\circ C$. It decomposed to Y_2SiO_5 (4) and amorphous phase at $1,200^\circ C \pm 10^\circ C$. in air. At $1,330^\circ C$ it finally is converted to a high temperature polymorph of β - $Y_2Si_2O_7$ (5) and an Mg-oxy apatite-like phase. Heating of the starting gels at $1,050^\circ C$ in air gave a single phase silicate apatite which at $1,200^\circ C$ was converted to Y_2SiO_5 (4).

FIG. 1

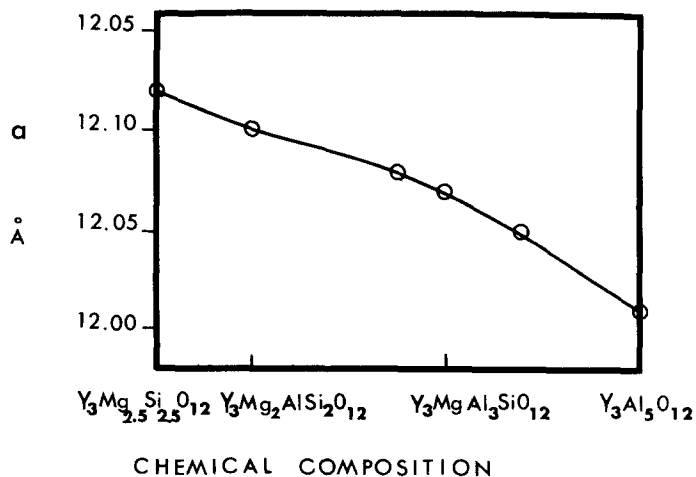
Compositional range for the formation of magnesium-yttrium silicate garnet and its analogues by the substitution of other rare-earths and divalent ions. Ionic radii by Ahrens (6). Closed circle = garnet X = other phases (cerite, silicate-apatite, etc.)



Solid solubility exists between yttrium-aluminum garnet and yttrium-magnesium garnet under hydrothermal conditions (Fig. 2). Although solid solubility may exist between yttrium-iron garnet and yttrium-magnesium silicate garnet at higher temperatures, the resulting products in this study gave

FIG. 2

Unit cell dimensions of YAlG to $Y_6Mg_5Si_5O_{12}$ series.



two garnets, indicating the possibility of the solvus above the present conditions.

Unit cell dimensions of the present synthetic garnets are given in Table 1. Under the microscope, the garnets appeared as tiny round isolated crystals up to 3 - 5 μ in diameter. The refractive index of yttrium-magnesium garnet measures 1.79. The indexed X-ray powder data of the yttrium end member are given in Table 2. The unit cell dimensions vary almost linearly as a function of the rare-earth radii

as demonstrated in Fig. 3.

TABLE 1

Unit Cell Dimensions of Yttrium-Magnesium
Silicate Garnets and its Analogues
Synthesized at 720°C, 2 Kilobars

Formula	a (Å)	Color
$Y_6Mg_4Mg Si_5O_{24}$	12.12	pale yellow
$Y_6Ni_4Ni Si_5O_{24}$	12.08	blue
$Ho_6Mg_4Mg Si_5O_{24}$	12.12	pale brown
$Er_6Mg_4Mg Si_5O_{24}$	12.08	pale pink
$Yb_6Mg_4Mg Si_5O_{24}$	12.02	colorless
$Lu_6Mg_4Mg Si_5O_{24}$	11.99	colorless
$Y_3Mg_2AlSi_2O_{12}$	12.10	colorless
$Y_3MgAl_3SiO_{12}$	12.07	colorless

Only the holmium-magnesium analogue showed noticeable magnetism by test with an ordinary hand magnet.

Yttrium rich garnets do not seem to contain enough magnesium to occupy tetrahedral sites. All the existing chemical analyses of naturally occurring yttrium bearing garnets show very low concentration of MgO (0.17%) (7). However, it seems worth noting that under the conditions of moderate pressures and temperatures, Mg^{2+} ions can occupy all octahedral a sites and part of the tetrahedral d sites but not the dodecahedral c sites. In pyrope, $Mg_3Al_2Si_3O_{12}$, however, Mg does occupy the c sites but this phase is stable under high pressures.

TABLE 2

X-Ray Powder Data of Yttrium-Magnesium
Silicate Garnet, $Y_6Mg_5Si_5O_{24}$ ($a_0 = 12.12 \text{ \AA}$)
Isometric Ia3d. Cu $K\alpha$, Ni Filter

hkl	d (\AA) obs.	I/I ₀	d calc. (\AA)
211	4.95	40	4.95
220	4.28	20	4.29
321	3.241	30	3.239
400	3.031	45	3.030
420	2.710	100	2.710
422	2.475	35	2.473
510	2.377	10	2.377
521	2.213	30	2.213
440	2.143	5	2.143
611	1.966	35	1.966
631	1.789	5	1.786
444	1.749	25	1.749
640	1.679	35	1.681
552	1.648	10	1.650
642	1.619	30	1.619
800	1.515	10	1.515

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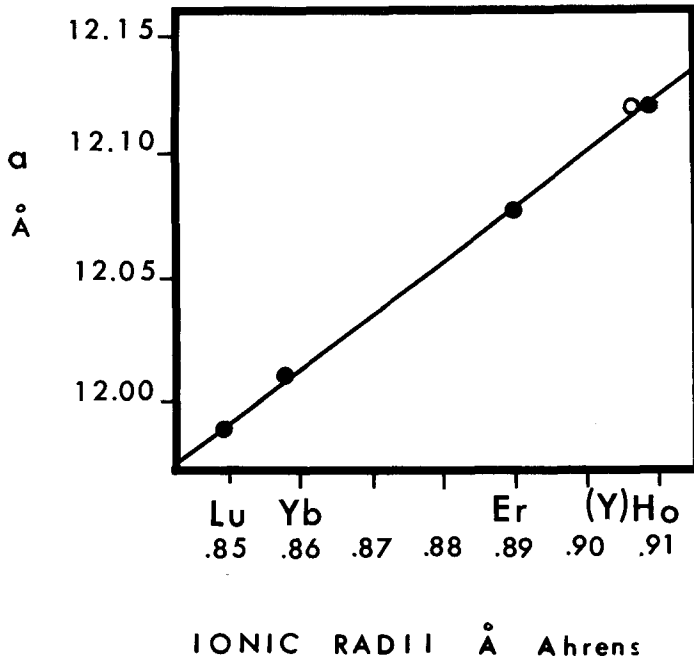


FIG. 3

Unit cell dimensions of rare-earths-yttrium-magnesium silicate garnets. Ionic radii by Ahrens (1952).

References

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