possibly an indication that small amounts of Ti^{4+} ion, from his titanium vessels, are in his garnet. (This is also indicated by the large value for the $Cd_3V_2Si_3O_{12}$; it should be smaller than for the Ca compound in line with the relative values for the analogous Al compounds.) The value of 12.070 Å obtained by STRENS[30] seems better in relation to 12.067 for the $Ca_3Fe_2Si_3O_{12}$. The value, 12.068 Å, for the $Ca_3V_2Si_3O_{12}$ garnet that we synthesized is in very good agreement with STRENS' value.

I would also have expected the lattice constant of $Ca_3Ga_2Si_3O_{12}$ to be larger than that of $Ca_3Cr_2Si_3O_{12}$.

Germanate garnets

There are many new garnets among the simple end-member germanates (Table 4). Fifteen are listed in Table 4 which involve trivalent yttrium or a rare-earth ion in the a sites and the Ca^{2+} or Sr^{2+} ion in the c sites. Those with the Sr^{2+} ion all have lattice constants greater than 13.00 Å, the largest garnet unit cells known to date. All were made by solid-state reaction[49]. MILL' has synthesized some germanates hydrothermally[29,47,49] but all the germanate garnets can be made by solid-state reaction including $Mn_3V_2Ge_3O_{12}$.

The lattice constant, 12.35 Å, given by MILL for $Ca_3V_2Ge_3O_{12}$ is again high with respect to either of the values for the Fe compound. For a specimen of $Ca_3V_2Ge_3O_{12}$ which we prepared, we obtained a value of 12.320 Å. This was synthesized by firing an appropriate compacted mixture of $CaGeO_3$ and V_2O_3 in an evacuated sealed fused silica ampul at 960 °C for 1 hour. The specimen was reground, recompacted and fired in the same manner for an additional hour at 960 °C. The powder photograph showed a faint extra line indicating the presence of an extra phase, possibly $Ca_2Ge_3O_8$. It is not impossible that some V^{5+} ion is incorporated in our specimen, tending to give too large a value for the lattice constant.

We have similarly synthesized a specimen of $Mn_3V_2Ge_3O_{12}$. An appropriate mixture of Mn_2GeO_4, V_2O_3 and GeO_2 was compacted into a pellet, sealed in an evacuated fused silica tube and brought from 400° to 950 °C in 1 hour, then allowed to remain at 950 °C for 2 hours. A garnet with sharp back-reflection lines in the powder photograph (CrK radiation) was obtained having $a = 12.099$ Å as opposed to the value 12.125 Å found by MILL' for his specimen. On the basis of the reasoning given earlier, we suspected that MILL' lattice constant for this garnet, which he prepared hydrothermally,

was too high (as is the case for all his other vanadium garnets so prepared). Our value is 0.026 Å less than his, but is, nevertheless, still somewhat higher than that for the analogous iron compound.

There are actually at least three possible reasons for this: 1) In view of the closeness of lattice-constant values for the analogous V^{3+} and Fe^{3+} garnets, the sizes of the V^{3+} and Fe^{3+} ions may be equal or the V^{3+} ion may even be slightly larger than the Fe^{3+} ion. 2) Some pentavalent V^{5+} ions may be in the tetrahedral sites. 3) Some of the germanate garnets are difficult to obtain as decidedly single phases. There is some evidence[43,44] that it is possible that they have vacancies of some sort, which probably would affect the lattice-constant values.

I do not believe that any of these possibilities can be ruled out at this time. The weight of the evidence from the lattice constants alone favors the conclusion that the size of the V^{3+} ion is equal to or slightly greater than that of the Fe^{3+} ion. Actually this does not affect results of theory[50,51]; the list of radii given above cannot be considered to be perfect. Further, the surroundings of the ions in the perovskite-like[52] and garnet structures may be just sufficiently different to give slight size differences. Another example is that of Mn^{3+} ion which also appears to be slightly smaller than the Fe^{3+} ion in perovskites[12] but the same size as the Fe^{3+} ion in the bixbyite structure, in which case no significant change in lattice constant is observed[53] for $(Mn_{1-x}Fe_x)_2O_3$ for $0.01 \leq x \leq 0.50$. (We have found[54] that αMn_2O_3 itself does not have the bixbyite structure.)

With regard to the Mn^{3+} ion, we had managed[55], apparently, to substitute this ion for 2% of the Fe^{3+} ion in yttrium iron garnet, but

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