

that there might be a vacancy or combination vacancy-interstitial situation. It is somewhat difficult to believe that the large ions of the same species are going into both c and a sites simultaneously even though there is little evidence to the contrary. Perhaps the most substantial evidence is given by the germanate garnets, with rare earth ions in a sites, made by MILL⁷, which seem to require large c -site and smaller a -site ions. But there is evidence to support, at least

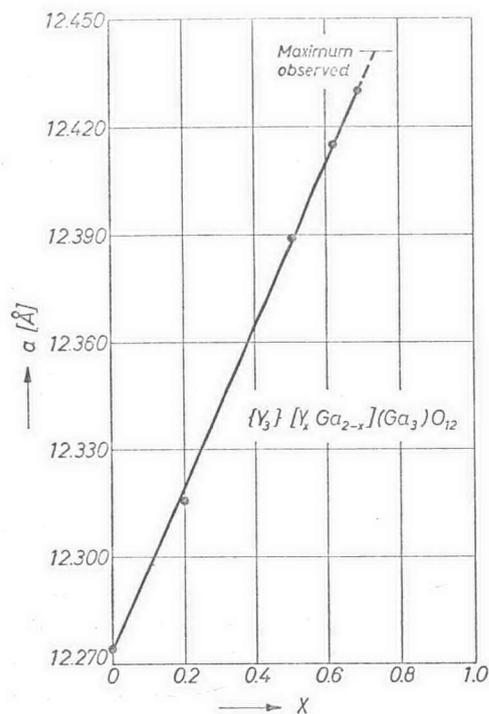


Fig. 5. Lattice constant vs x

tentatively, the substitutional or combined vacancy-interstitial hypothesis, and this evidence is our own⁴⁵. We have made several specimens with increasing $Y_2O_3:Ga_2O_3$ ratios. A plot of the lattice constant vs composition is given in Fig. 5. The lattice constant of the ideal stoichiometric garnet is 12.274 Å while that obtained for the "garnet" in the 3:3.25 specimen, which was not single phase, was 12.438 Å—a very large increase indeed. The maximum lattice constant, 12.441 Å in the system was reported by SCHNEIDER *et al.*⁵⁷ for the 1:1 ratio. The maximum solid solution probably has the ratio 3:3.42 or the formula $Y_{3.74}Ga_{4.26}O_{12}$. The specimen with $Y_2O_3:Ga_2O_3$ of 3:3.5⁵⁸

i.e. $Y_{3.69}Ga_{4.31}O_{12}$, was also not quite single phase. On the powder-diffraction pattern taken with $CuK\alpha$ radiation, there are some extra lines with very low intensity at spacings: 4.17, 3.05, 2.88 Å. Nevertheless, the density of the specimen was measured pycnometrically and found to be 5.73 g/cm³. Now if the formula of the specimen is written $\{Y_3\}[Y_{0.69}Ga_{1.31}](Ga_3)O_{12}$, assuming eight of these per unit cell with lattice constant 12.430 Å, the theoretical x-ray density would be 5.67 g/cm³ in good agreement with the measured value. Any other formula requires oxygen as well as Ga vacancies and would result in lower density. The x-ray density, 5.80 g/cm³, of ideally stoichiometric yttrium gallium garnet is higher than that of $\{Y_3\}[Y_{0.69}Ga_{1.31}](Ga_3)O_{12}$, but this is actually to be expected.

I think that it would still be very interesting to examine the structure of a single crystal of this compound. It must, of course, have uniform composition if such an investigation is to be worthwhile. But obtaining such a crystal does not appear to be a simple task.

In the Tables 3–5 inclusive, I have not put down all values by all investigators. In some cases, I have shown more than one to indicate priority for the particular investigators even though I may believe their value is poorer than a later one. In some few cases, I have seen no point in adding a later one if it appears to be poorer than an earlier one.

Survey of the ions which enter garnets

While I shall try to cite most references, I do not expect this survey to be exhaustive of the references. I hope, however, to succeed in covering all the ions known to enter the garnets. But for a few cases, I shall not be considering slight amounts of ions that by fine spectroscopic measurements are found in a site.

Group IA

1. Li^+ : a and d sites

$\{Ca_3\}[LiM^{2+}](V_3)O_{12}$ ⁷⁰ , $M \equiv Mg$	$a = 12.412 \text{ \AA}$	
	Co	12.404
	Ni	12.340
	Cu	12.398
	Zn	12.420

⁷⁰ G. BAYER, Vanadates $A_3B_2V_3O_{12}$ with garnet structure. J. Amer. Ceramic Soc. 48 (1965) 600.