YTTRIUM IRON GARNET

2.1 <u>JEWEL GARNETS</u>.

Garnet often refers to jewel stones belonging to the orthosilicate group (which has the Latin name granatus). These garnets have the chemical formula $R^{2+}R^{3+}(SiO_4)_3$, where R^{2+} can be Mg, Fe^{2+}, Mn^{2+} or Ca and R^{3+} can be Al, Fe^{3+} or Cr^{3+}. Different jewels in this group are;

a. Pyrope have the formula $Mg_3Al_2(SiO_4)_3$. The colors of these stones are dark red.

b. Almandine have the formula $Fe_3Al_2(SiO_4)_3$. The colors of these stones can be red, brown or black.

c. Spessartine have the formula $Mn_3Al_2(SiO_4)_3$. The colors of these stones can be dark red, brown or orange-yellow.

d. Grossula have the formula $Ca_3Al_2(SiO_4)_3$. The colors can be light green, brown, red or a honey color.

e. Andradite have the formula $Ca_3Fe_2(SiO_4)_3$. The colors of these stones can be yellow, brown, black or transparent green.

f. Uvarovite have the formula $Ca_3Cr_2(SiO_4)_3$ and their colors are green or jade green.

g. Schorlomite have the formula $Ca_3(Fe,Ti)_2(SiO_4)_3$ and are black in color.

Man-made garnets are prepared from oxides mixtures containing the stochiometric amounts needed to form the compound. Their production require high pressures and high temperatures.

2.2 Ferrimagnetic Garnets. (3)

Among the man-made garnets, $R_3Fe_5O_{12}$ (R being yttrium or an rare earth element) has found wide applications as a magnetic compound. Their crystal structure is cubic, with 160 atoms per unit cell containing 8 formula units. The crystal structure is shown in Figure 2.1. There are three types of lattice sites, c, a and d which the cations can occupy.
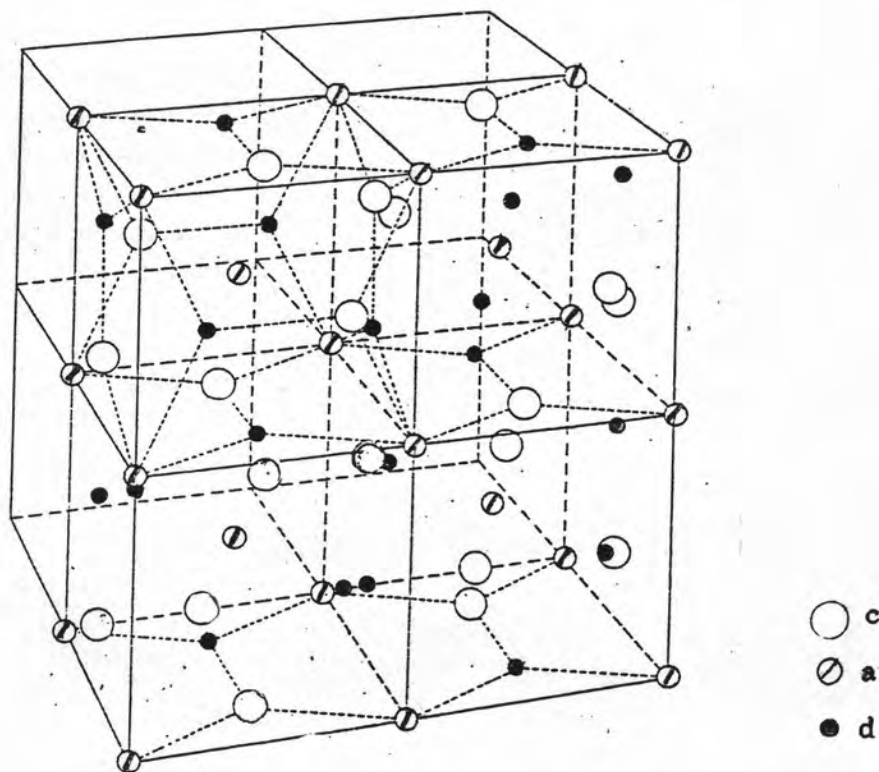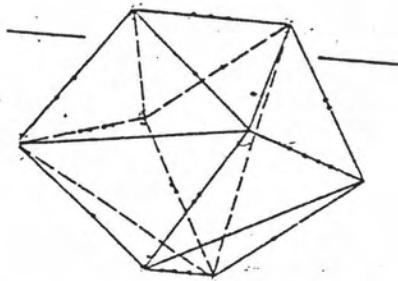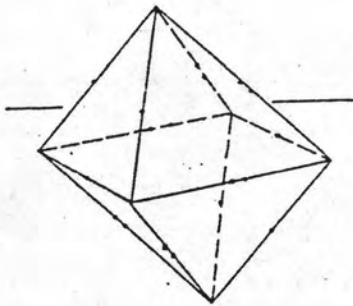

○ c
⌀ a
● d

Figure 2.1 Arrangement of the cations in {c}, [a] and (d) sites in four octants of the garnet unit cell.
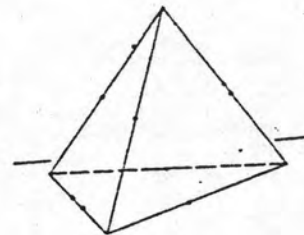
The 'a' site ions form a bcc lattice with the 'c' and 'd' site ions lying on the faces of the cube. The metallic R^{3+} occupy the c-sites, while the Fe^{3+} ions occupy the 'a' and 'd' sites. The unit cell has 24{c} sites, 16[a] sites and 24(d) sites.

(a) The {c} sites.

(b) The (a) sites

(c) The [d] sites

Figure 2.2   Coordination of the {c}, [a] and (d) sites.
a. Coordination polyhedron of oxygen ions about the yttrium ion (.2.68,.. 2.81,... 2.87,.... 2.96 Å)
b. Coordination octahedron of oxygen ions about Fe^{3+} (a) ion (. 2.68, .. 2.99 Å).
c. Coordination tetrahedron of oxygen ions about Fe^{3+} (d) ion (. 3.16, .. 2.87 Å).

Each 'a' site is surrounded by six oxygen ions (becoming an octahedral coordinated); each 'c' site, by eight oxygen sites (becoming a dodecahedral coordinated); and each 'd' site, by four oxygen sites (becoming tetrahedral coordinated) (see Figure 2.2). The 96 oxygen ions occupy the "h" sites.

The above crystal structure belongs to the space group O_h^{10} (Ia3d) (Geller and Gilleo (1957 a,b)). The unit cell edge of a typical yttrium iron garnet specimen is $(12.376 + 0.004) * 10^{-10}$ m. The density is $5.17 * 10^3$ kgm^{-3}. The edge lengths in any of the polyhedron are not equal, even though the oxygen parameters would permit this to occur simultaneously in the octahedra and the tetrahedra. The Fe^{3+}-O^{2-} distances are constant in these two polyhedron ($2.00 * 10^{-10}$ m in the octahedra and $1.88 * 10^{-10}$ m in the tetrahedra). There are two O^{2-}- Fe^{3+}- O^{2-} angles in the octahedra $87.2°$ and $96.6°$, and two in the tetrahedra, $99.9°$ and $114.3°$. The distances and angles between the ions is given in Table 2.1. The positions of the ions in yttrium iron garnet having the Ia3d symmetry are

Y:(24c)   ± (1/8,0,1/4;5/8,0,1/4)   ;tr;B.C

Fe(1):(16a)   0,0,0;1/4,1/4,1/4   ;B.C,F.C

Fe(2):(24d) ± (3/8,0,1/4;7/8,0,1/4)   ;tr;B.C

O:(96h)   ± (x,y,z;x+1/2,1/2-y,z;x,y+1/2,1/2-z;1/2-x,y,

z+1/2;y+1/4,x+1/4,z+1/2;y+3/4,1/4-x,3/4-z;

3/4-y,x+3/4,1/4-z;1/4-y,3/4-x,z+3/4) ;tr;B.C

where x = -0.0275, y = 0.0572 and z = 0.1495.

2.3 Fabrication of $Y_3Fe_5O_{12}$. (2)

2.3.1 Polycrystalline Specimens. Polycrystalline yttrium iron garnets (YIG) are usually formed by some type of solid state chemical reaction. In order to produce such a reaction in a reasonable time span, an intimate mixture of Y_2O_3 and Fe_2O_3 must be raised to a high temperature, often of order 1000° C. The substance produced by the reaction must then be reground into a fine powder so that it can be pressed into some desired shape. The pressed powder is then heated to a very high temperature for extended period. During this sintering process, the powder fuses together to form a solid polycrystalline phase.

It is of the utmost importance to be able to make materials of known composition and properties in a reproducible manner. This requires that both the initial (calcinating stage) and final (sintering stage) firing conditions can be controlled. Since some of the cations (Fe and other transition metal elements) in the garnets can exist in different valence states, firing in different atmospheres can result in the ions being either divalent 2+ or trivalent 3+ and thus lead to a different crystal structure being formed. Changing the firing temperature can lead to different microstructures, i.e., grain sizes, grain size distributions, porosity or density. Variations of these properties can lead to marked changes in the electrical properties, resistivity, saturation magnetization, coercive force, etc.

TABLE 2.1

(Geller and Gilleo, 1957)

(a) Nearest-neighbour interionic distances in yttrium

iron garnet

Ion	Interionic distances (Å)
Y^{3+}	$4Fe^{3+}(a)$ at 3·46
	$6Fe^{3+}(d)$ at 3·09(2), 3·79(4)
	$8O^{2-}$ at 2·37(4), 2·43(4)
$Fe^{3+}(a)$	$2Y^{3+}$ at 3·46
	$6Fe^{3+}(d)$ at 3·46
	$6O^{2-}$ at 2·00
$Fe^{3+}(d)$	$6Y^{3+}$ at 3·09(2), 3·79(4)
	$4Fe^{3+}(a)$ at 3·46
	$4Fe^{3+}(d)$ at 3·79
	$4O^{2-}$ at 1·88
O^{2-}	$2Y^{3+}$ at 2·37, 2·43
	$1Fe^{3+}(a)$ at 2·00
	$1Fe^{3+}(d)$ at 1·88
	$9O^{2-}$ at 2·68(2), 2·81, 2·87
	2·96, 2·99(2), 3·16(2)

(b) Interionic angles in yttrium iron garnet

Ions	Angles (°)
$Fe^{3+}(a)-O^{2-}-Fe^{3+}(d)$	126·6
$Fe^{3+}(a)-O^{2-}-Y^{3+}$	102·8[a]
$Fe^{3+}(a)-O^{2-}-Y^{3+}$	104·7[b]
$Fe^{3+}(d)-O^{2-}-Y^{3+}$	122·2[a]
$Fe^{3+}(d)-O^{2-}-Y^{3+}$	92·2[b]
$Y^{3+}-O^{2-}-Y^{3+}$	104·7
$Fe^{3+}(a)-O^{2-}-Fe^{3+}(a)(4·41)$	147·2[c]
$Fe^{3+}(d)-O^{2-}-Fe^{3+}(d)(3·41)$	86·6
$Fe^{3+}(d)-O^{2-}-Fe^{3+}(d)(3·68)$	78·8
$Fe^{3+}(d)-O^{2-}-Fe^{3+}(d)(3·83)$	74·7
$Fe^{3+}(d)-O^{2-}-Fe^{3+}(d)(3·83)$	74·6

[a]$Y^{3+} - O^{2-}$ distance = 2.43 Å

[b]$Y^{3+} - O^{2-}$ distance = 2.37 Å

[c]Numbers in parentheses are the longer $Fe^{3+}(a$ or $d)-O^{3-}$

distances. The shorter distances are $Fe^{3+}(a)-O^{2-}$ = 2.00 Å,

$Fe^{3+}(d)-O^{2-}$ = 1.88 Å.

In summary, the fabrication of yttrium iron garnets is accomplished in four steps:

1. Mixing (intimate) of the oxides (the carbonates can also be used) with the metal ions in the ratio they are to be in the final product.

2. Prefiring (calcinating) to achieve the solid state reaction.

3. Regrinding the calcinated lumps into fine powder, which are then pressed into desired shapes.

4. Sintering to form the final product.

Swallow and Jordan (1964) noted that the purposes of step 1 were:

a. to decompose the oxides or carbonates so that gases were not evolved during the final sintering process.

b. to assist in homogenizing the material.

c. to reduce the effects of variations in the composition of the raw materials.

d. to reduce or control the shrinkage of the material which occurs during the final firing.

During the pre-sintering (pre-firing), the raw materials partly react to form the final product. The amount of reaction depends on the reactivity of the components and on the presintering temperature. The solid state reaction is a relatively slow one, a form of diffusion process where the diffusion rate depends on the temperature. It follows that high temperatures (up to 1000° C for the pre-sintering and 1400° C to 1500° C for sintering)

must be maintained for several hours. In order to obtain the right proportion of the metal ions in their correct valency, careful control of the furnace is essential.

2.3.2 <u>Single Crystal Specimens</u>.(4) These are obtained by a flux method in which the oxides are melted in PbO in a platinum crucible at about 1325°C. The melt is cooled at about one degree per hour until it becomes solid (around 980°C). Very little crystal growth occurs below this temperature. The method can be improved by using approximately equal amount of PbF_2 and PbO as the flux. The formation of large crystals is enhanced by keeping the top of the crucible a few degrees hotter than the bottom so that the nucleation on the surface of the melt is reduced. Since we are not concerned with single crystal specimens in this work, we will not go into the details of this topic.

2.4 <u>Ferrimagnetism of the Yttrium Iron Garnets</u>.

The first magnetic measurements of the rare earth iron garnets was by Pauthenet (1958). These early magnetic measurements on the YIG have only historical value since they were obtained for polycrystalline specimens having high degree of impurities. More refined measurements were taken by Geller et al. (1965a) and Harrison et al. (1965) on single crystal specimens. The magnetic properties of the garnets can be interpreted on the basis of the collinear Néel model. Written as

$$Y_3 \quad Fe_2 \uparrow\uparrow Fe_3\downarrow\downarrow O_{12}$$
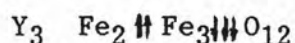
the magnetic moments on the 'a' and 'd' sites of the yttrium iron garnet are aligned antiparallel and the moments on the 'c' sites are antiparallel to those on the 'd' sites. The net moment m (in terms of Bohr magnetons per formula unit) is

$$m = 3m_c - (3m_d - 2m_a)$$

Since Y^{3+} has no net magnetic moment, the system is very simple (one with only one type of magnetic ions (Fe^{3+}) distributed among the 'a' and 'd' sites) one. The magnitude of the magnetic moment of YIG at T = 0 K would be m_d and be directed towards the tetrahedral (3d) sites (Figure 2.3).
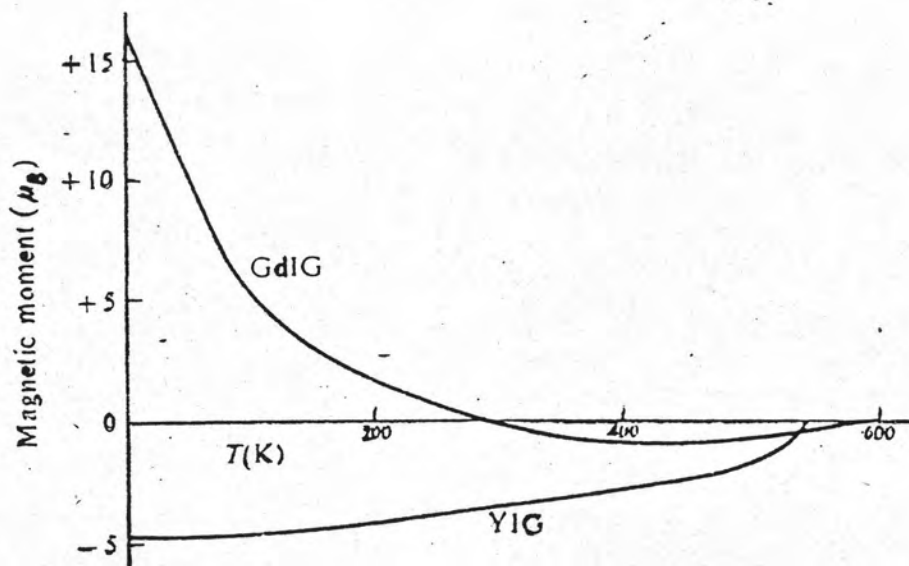

Figure 2.3 Variation of the spontaneous magnetic moment with temperature for $Gd_3Fe_5O_{12}$ (GdIG) and $Y_3Fe_5O_{12}$ (YIG) in Bohr magnetons per formula unit.

At temperatures above T = 0 K but below the Néel temperature, the spontaneous anti-alignment of the spins on the 'a' and 'd' sites would still cause a net magnetization of YIG. Above the Néel temperature (545 K), the thermal motion would destroy the spontaneous anti-alignment of the spins, leading to a non magnetic state. The application of an external field would give rise to a paramagnetic behavior. The net result is that the inverse susceptibility (Figure 2.4) is given by

$$1/\chi = T/C + 1/\chi_o - \sigma/(T-\theta) \qquad (2.1)$$

where C is the usual Curie constant. The other parameters are functions of the molecular field constants and the number of ions on each sublattice.
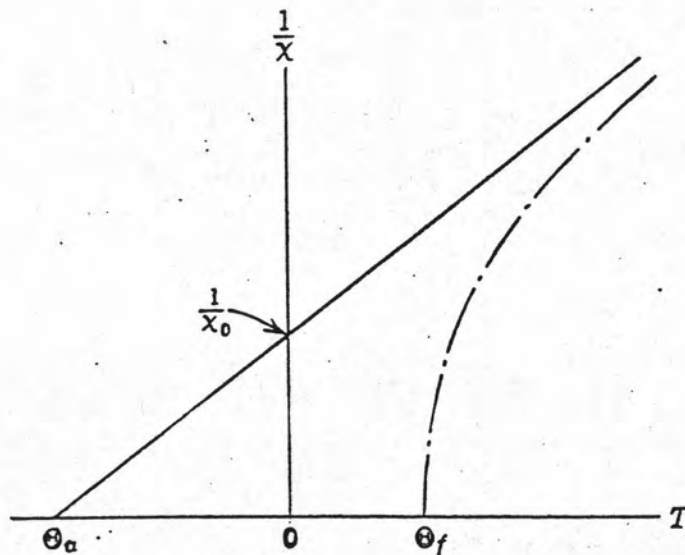

Figure 2.4 The $1/\chi$ vs T curve of ferrimagnetism.

2.5 Anisotropy.

The anisotropy of the iron garnets is small for diamagnetic rare earth ions. Many of the physical properties of the garnets are affected by the anisotropy. The anisotropy of the garnets have been measured by static magnetization measurements, by torque measurements, by microwave resonance measurements and by magnetostriction methods. The spherically symmetric s-state of the rare earth ion give a component to the magnetization which is independent of the temperature.

2.6 Substituted Yttrium Iron Garnets.

As we have already pointed out, the arrangement of the moments in $Y_3Fe_5O_{12}$ is

$$\uparrow\uparrow 2\ Fe_a^{3+} \quad 3\ Fe_d^{3+} \downarrow\downarrow\downarrow$$
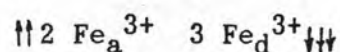
so that substitution of non magnetic ions in place of the Fe^{3+} ions in the octahedral 'a' sites would bring about an increase in the net magnetization; while substitution into the tetrahedral 'd' sites would bring about a decrease in the net magnetization. The ions In^{3+} and Sc^{3+}, being larger than the Fe^{3+} ions, usually substitute into the larger octahedral sites; while the smaller Al^{3+} and Ga^{3+} ions substitute in to the smaller tetrahedral sites. Since the replacement of the Fe^{3+} ions by non magnetic ions leads to a reduction of the Fe^{3+}-O-Fe^{3+} interaction, the Curie temperatures of the substituted garnets, $Y_3Al_xFe_{5-x}O_{12}$, $Y_3Ga_xFe_{5-x}O_{12}$ and $Y_3In_xFe_{5-x}O_{12}$, are lower than that of $Y_3Fe_5O_{12}$.