18PYB101J-Electromagnetic Theory, Quantum Mechanics, Waves and Optics

Module 2 Lecture-14

Garnets - Introductory ideas and Explanation and Magnetoplumbites

Garnets

Garnet is a group of minerals that have been used since the Bronze Age as gemstones and abrasives. Garnets species are found in many colors including red, orange, yellow, green, blue, purple, brown, black, pink and colorless

Garnets general formula $X_3Y_2(SiO_4)_3$

X site is usually occupied by divalent cations (Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}) and Y site by trivalent cations (Al^{3+}, Fe^{3+}, $Cr^{3+,}$ Mn^{3+}, V^{3+}) in an octahedral/tetrahedral framework with $[SiO_4]_4$ providing the tetrahedra.

➢They crystallize in the isometric system, having three axes that are all of equal length and perpendicular to each other.

➢Garnets do not show cleavage, so when they fracture under stress, sharp irregular pieces are formed.

Examples:

Pyralspite garnets - Aluminium in *Y* site

Almandine : $Fe_3Al_2(SiO_4)_3$

Pyrope : $Mg_3Al_2(SiO_4)^3$

Spessartine : $Mn_3Al_2(SiO_4)^3$

Ugrandite group - calcium in X site

Andradite : $Ca_3Fe_2(SiO_4)^3$

Grossular : $Ca_3Al_2(SiO_4)_3$

Uvarovite : $Ca_3Cr_2(SiO_4)_3$

Less common species

Calcium in X site

Goldmanite : $Ca_3V_2(SiO_4)_3$

Kimzeyit : $Ca_3(Zr,Ti)_2[(Si,Al,Fe^{3+})O4]_3$

Morimotoite : $Ca_3Ti^{4+}Fe^{2+}(SiO_4)_3$

Schorlomit : $Ca_3(Ti_{4+},Fe^{3+})2[(Si,Ti)O_4]_3$

Hydroxide bearing - calcium in X site

Hydrogrossular : $Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$

Hibschite : $Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$ (where x is between 0.2 and 1.5)

Katoite : Ca_3Al_2(SiMagnesium or manganese in X site

Knorringite : Mg3Cr2(SiO4)3

Majorite : Mg3(Fe,Al,Si)2(SiO4)3$O_4)_{3-x}(OH)_{4x}$ (where x is greater than 1.5)

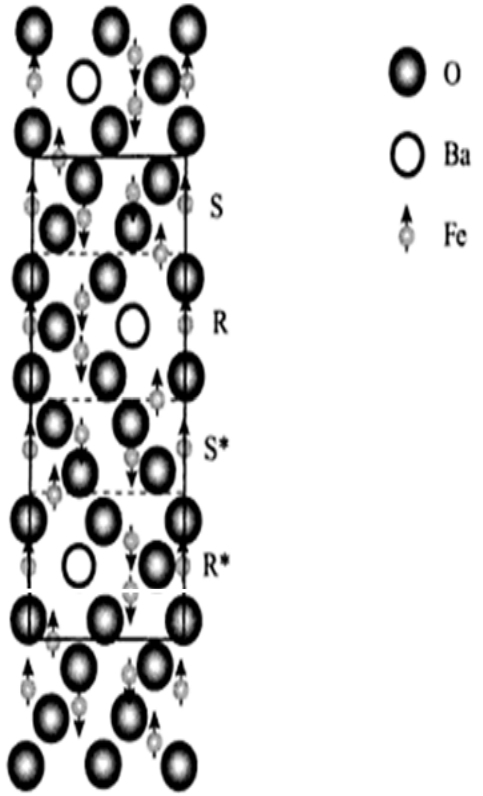
Applications of Garnets:

- Gadolinium gallium garnet, $Gd_3Ga_2(GaO_4)_3$, which is synthesized for use in magnetic bubble memory.
- Yttrium aluminium garnet (YAG), $Y_3Al_2(AlO_4)_3$, is used for synthetic gemstone. When doped with neodymium (Nd^{3+}), these YAl-garnets are useful as the lasing medium in lasers.
- Mixed with very high pressure water, garnet is used to cut steel and other materials in water jets.
- Garnet sand is also used for water filtration media.

Magnetoplumbites

Magnetoplumbites belong to a family of ferrites (barium, strontium or calcium hexaferrites) that is important in at least four areas of modern technologies like permanent magnets, high density magnetic recording, microwave and magnetic-optic applications.

Magnetoplumbites are hexagonal ferrites having the general formula $MFe_{12}O_{19}$, where M is usually Barium (Ba), Strontium (Sr),Calcium (Ca) or Lead (Pb). The structure can be described as a hexagonal structure with stack of oxygen and lead ions, with the iron sites coordinated only by oxygen. There are three octahedral sites, a tetrahedral site and a five-coordinated trigonal bipyramidal site.



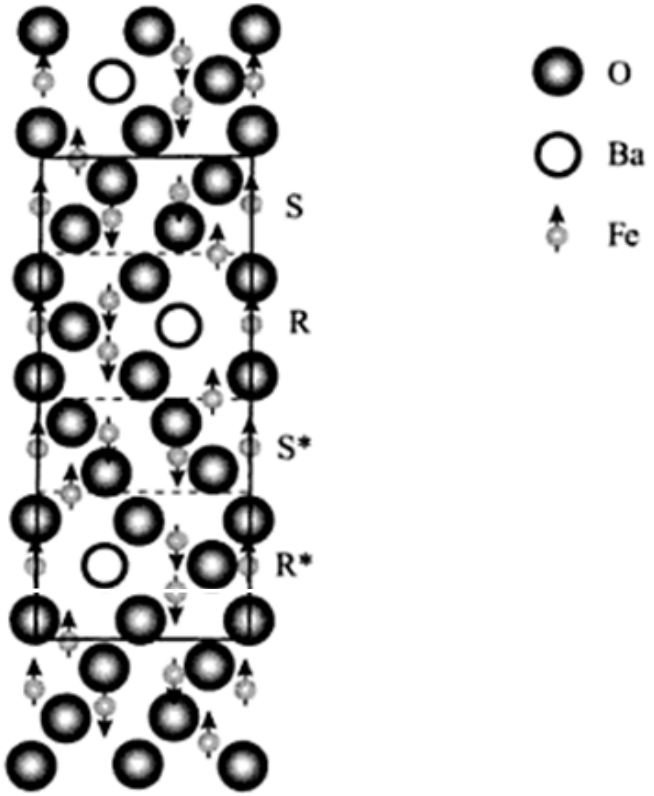
Magnetoplumbites

The most important hexagonal ferrites are barium ferrite ($BaFe_{12}O_{19}$) and Strontium ferrite ($SrFe_{12}O_{19}$). The barium ferrite structure containing ten oxygen layers in its elementary unit cell, and it is constructed from four building blocks, labeled as S,S*, R and R* in the Fig.

The S and S* blocks are spinels with two oxygen layers and six Fe^{3+} ions. Four of the Fe^{3+} ions are in octahedral sites and having their spins aligned parallel to each other and the other two are in tetrahedral sites with the opposite spin direction to the octahedral ions. The S and S* blocks are equivalent but rotated 180° with respect to each other. The R and R* block consists of three oxygen layers, with one of the oxygen anions in the middle layer replaced by a barium ion.

Magnetoplumbites

Each R block contains six Fe^{3+} ions, five of which are in octahedral sites with three up - spin and two down - spin, and one of which is coordinated by five O^{2+} anions and has up-spin. The net magnetic moment per unit cell is $20\mu_{B.}$



Magnetoplumbites

Magnetoplumbites are magnetically hard unlike the cubic ferrites with typical coercivities of around 200KA/m. Also, they are easy to produce by ceramic processing methods, and can be powered and formed easily into any required shape.

They are subclassified into six subclasses namely; M, W, Y, Z, X and U type according to their crystal structure and arrangement of respective S, R and T blocks. Table shows the subclasses of magnetoplumbites with their chemical formulae. Where, A represents Ba, Pb or Sr and M is a divalent transition metal ion.

Magnetoplumbites

Table: Subclasses of Magnetoplumbites

Sl. No.	Magnetoplumbites	Chemical formula
1	M-type	$AFe_{12}O_{19}$
2	Y-type	$A_2M_2Fe_{12}O_{22}$
3	W-type	$AM_2Fe_{16}O_{27}$
4	X-type	$A_2M_2Fe_{28}O_{46}$
5	U-type	$A_4M_2Fe_{36}O_{60}$
6	Z-type	$A_3M_2Fe_{24}O_{41}$

Magnetoplumbites

Applications of Magnetoplumbites

- Barium hexaferrite is used in hybrid microwave devices, monolithic microwave integrated circuits and future replacement for yttrium iron garnet due to its high uniaxial anisotropy and large resistivity.
- Magnetoplumbites are used in magnetic recording media due to their high quality magnetic behavior.
- M-type compound of these system are used in developing glass ceramic.
- Magnetoplumbites can be used as a substrate material for catalyst support.
- After doping with proper ions like Eu^{2+}, it can be used as luminescent materials in lighting tubes.
- Magnetoplumbites can also be used as interface coating on high temperature ceramic matrix composites.

Thank you