

CHAPTER - I

CHAPTER I

PYROCHLORES

1.1 INTRODUCTION: -

Among the ternary metallic oxides, compounds of the general formula $A_2B_2O_7$ represent a family of phases isostructural to the mineral pyrochlore, $(NaCl)(BaTa)O_6F/(HO)$. Here A and B are metals. Generally the A element can be a rare earth (Ln) or an element with inert lone-pair of electrons and the B element can be a transition metal with variable oxidation state or a post transition metal. Such $A_2B_2O_7$ pyrochlore (compounds) exhibit a wide variety of interesting physical properties. They show the electrical nature, which varies from highly insulating through, semiconducting to metallic behavior, with a few compounds exhibiting a semiconductor to metal transition (1). Many phases where A and B elements are present in the maximum possible oxidation states exhibit interesting ferroelectric, piezoelectric and dielectric behavior. The pyrochlores, where a 3d transition element is present at B-site and /or rare earth at A site, shows simple paramagnetism to ferro or antiferromagnetism transition at and below 77 K. Many pyrochlores shows interesting fluorescent, phosphorescent behavior and possibly can act as laser host materials.

Many workers have studied oxide pyrochlores and related phases over the past 4-5 decades. Shannon and Sleight (2) discussed the general features of (3^+ , 4^+) pyrochlores in their work. Knop et al (3, 4) discussed the general features of (2^+ , 5^+) pyrochlores. It should be noted that Shannon and Sleight and Knop et al restricted their work only to identify the structure and stability-field regions of

these compounds. Barker et al. (5) and Mc Cauley (6) discussed the geometrical aspects and oxygen parameter of the various pyrochlores. Sncherbakova et al (7) and Rao and Subba Rao (8) devoted their work to a discussion of the physical properties of $A_2 B_2 O_7$ pyrochlores.

1.2 STRUCTURE OF THE PYROCHLORES: -

The general formula of oxide pyrochlores can be written as $A_2 B_2 O_6 O'$ with four crystallographic nonequivalent kinds of atom. The space group of ideal pyrochlore structure is $Fd\bar{3}m (O_h^7)$. In case of ideal pyrochlore structure there are 8 molecules per unit cell ($Z = 8$). The pyrochlore structure is composed of two types of cation coordination polyhedron as shown in fig 1.1. The A cation (usually 1 \AA ionic radius) are eight coordinated and are located within scalenohedra (distorted cube) that contain six equally spaced anions (O' atoms) at a slightly shorter distance from the central cations. The smaller cations (0.6 \AA ionic radius) are six coordinated and are located within trigonal antiprism with all the six anions at equal distances from the central cations. Many authors do refer to the six fold coordination polyhedra in the pyrochlore structure as octahedral and eight fold coordination polyhedra in pyrochlore structure as cubic coordination polyhedra. This is not exactly correct because the space group requires that these two polyhedra have D_{3d} symmetry and therefore are not octahedra or cubes (but trigonal antiprism and scalenohedra). The condition for the existence of perfect octahedra and cubic coordination polyhedra can not be simultaneously satisfied. Since there are four non-equivalent atoms, there are four possible choices of origin. Two can be referred to the centric origin viz., $3m$ while the other two refer to $43m$ as the origin. Various workers have employed

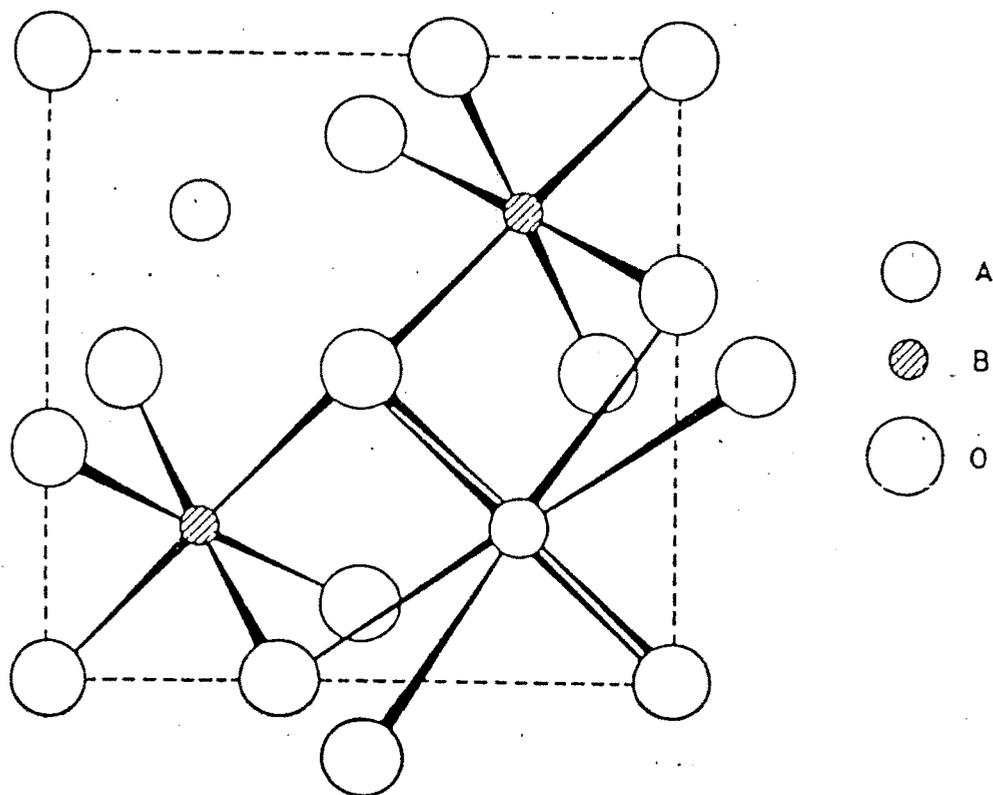


Fig. 1.1 Pyrochlore structure of general formula $A_2B_2O_7$ showing the 6 fold coordination of B and 8 fold coordination of A atoms.

Table 1.1 Pyrochlore ($A_2B_2O_6O'$) Structure data (Origin at B site)^a

Ion	Location	Site	Coordinates
16A	16d	3m(D3d)	(0,0,0; 0,1/2,1/2; 1/2,0,1/2; 1/2,1/2,0) 1/2,1/2,1/2; 1/2,1/4,1/4; 1/4,1/2,1/4; 1/4,1/4,1/2
16B	16c	3(D3d)	0,0,0; 0,1/4,1/4; 1/4,0,1/4; 1/4,1/4,0
48O	48f	Mm(C2V)	x,1/8,1/8; x,7/8,7/8; 1/4-x,1/8,1/8; 3/4+x,7/8,7/8; 1/8,x,1/8; 7/8,x,7/8; 1/8,1/4-x,1/8; 7/8,3/4+x,7/8; 1/8,1/8,x; 7/8,7/8,x; 1/8,1/8 1/4-x; 7/8,7/8,3/4+x
8O'	8b	43m(Td)	3/8, 3/8, 5/8, 5/8, 5/8

x for regular octahedra 0.3125 or $(5/16)^b$

x for regular cube 0.375 or $3/8$

a Space group $Fd_3m (O_h^7)$; 8 molecules per unit cell

b x values for other origins can be obtained by following relationships.

In any case x may be replaced with $(1/4 - x)$

all four but more commonly, the B cation is chosen as the origin and here in we shall use this convention. The pyrochlore structure has only one positional parameter, the oxygen x parameter and there are simple rules to convert the value of this parameter depending upon the choice of origin. The location of atoms, site symmetry and atomic coordinates of the pyrochlore structure are given in table 1.1.

The value of unknown oxygen ' x ' parameter can be determined by the method of x-ray or neutron structure analysis. Though many pyrochlores compositions crystallize in the cubic structure, in a few cases deviation from cubic symmetry by way of tetragonal, rhombohedral and triclinic distortion are noted.

The lattice parameters generally are in 10 \AA (10.51 \AA to 10.76 \AA) where as the ' x ' parameter is found to range from 0.309 to 0.355 (with B site as origin). The shortest A-O and B-O distances in pyrochlores are usually close to the average bond distances encountered in the A and B binary or ternary oxides with eight and six fold coordination respectively.

As mentioned earlier the coordination polyhedra changes shape with the oxygen ' x ' parameter. Even though never realized experimentally, the limiting values of ' x ' are 0.3125 and 0.375 for pyrochlores. For $x = 0.3125$, the B ions has a perfect octahedral coordination (and no D_{3d} symmetry) while A ions occupies the site of coordination eight ($6O + 2O'$) in a form of distorted hexagon of six oxygen (48f) and whose plane is perpendicular to $O'-A-O'$ axis. The $A-O'$ distance is of course shorter than the A-O distance (Fig 1.2). When $x = 0.375$, the A cations will be situated in a regular cubic 8 fold coordination (no

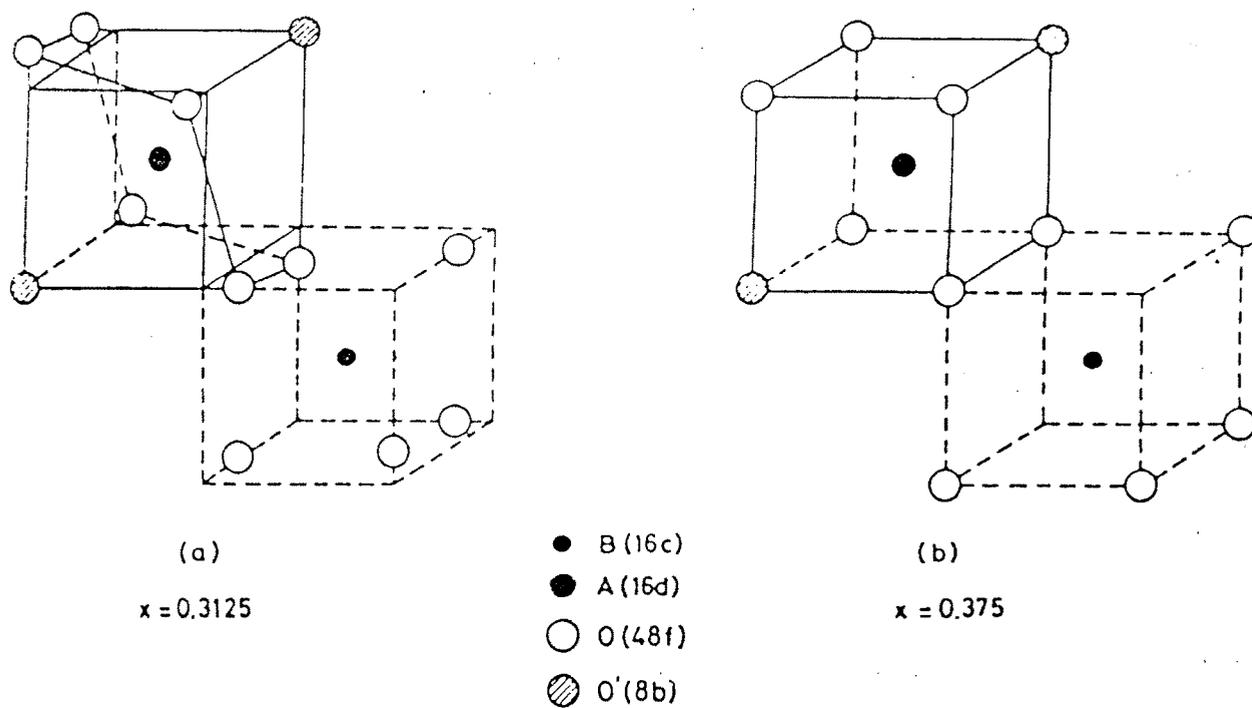


Fig1-2. Change in shape of coordination polyhedra of A and B ions with 48f oxygen parameter x in $A_2B_2O_6O'$ structure. Coordination around B becomes a regular octahedron for $x=0.3125$ ($5/16$) and for $x=0.375$ ($3/8$) the coordination around A becomes a regular cube. After Faucher and Caro (18).

D_{3d} symmetry) where as B ions is at the center of the highly distorted octahedron (trigonal antiprism). In other words the B cation is also of the center of a cube of oxygen with two-body diagonal oxygen missing. Fig 1.3 shows the variation of principal angles and interatomic distances as function of 48f oxygen 'x' parameter (9). In particular one can note that the B-O-B angle which is $109^{\circ} 28'$ for the fluorite structure, increases to $120^{\circ} - 140^{\circ}$ for pyrochlore structure. The A-O' distance independent of oxygen 'x' parameter, is always greater than the A-O distance but become equal to it, when $x = 0.375$. The AO'A angle however, is always $109^{\circ} 28'$ (the tetrahedral angle).

The rules regarding the allowed fundamental reflections in the pyrochlore $Fd3m$ space group are in the international table for x-ray crystallography. When the pyrochlore structure as a fluorite structure, then ^{super} lattice or ordering reflections are (111), (331) and (531) and arise from both cations and anions. The presence of the reflections with h, k, l all odd is indicative of A, B cations and O, O' anions ordering on the 16c, 16d, 48f and 8a sites respectively in space group $Fd3m$. In addition, vacant sites will be ordered on 8b sites will change although the general ordering (16c, 16d, 48f, 8a) is the same when the cations in the pyrochlore structure disorder, there ordering reflections will diminish in intensity.

Although there is a definite correlation between ionic radii of A and B cations and the stabilization of the pyrochlore structure, other factors such as electronegativity of cations, charge neutrality and thermodynamic stability of competitive phases are also important. But in general ionic sizes should be comparable to those of A and B site cations and the combination must yield the

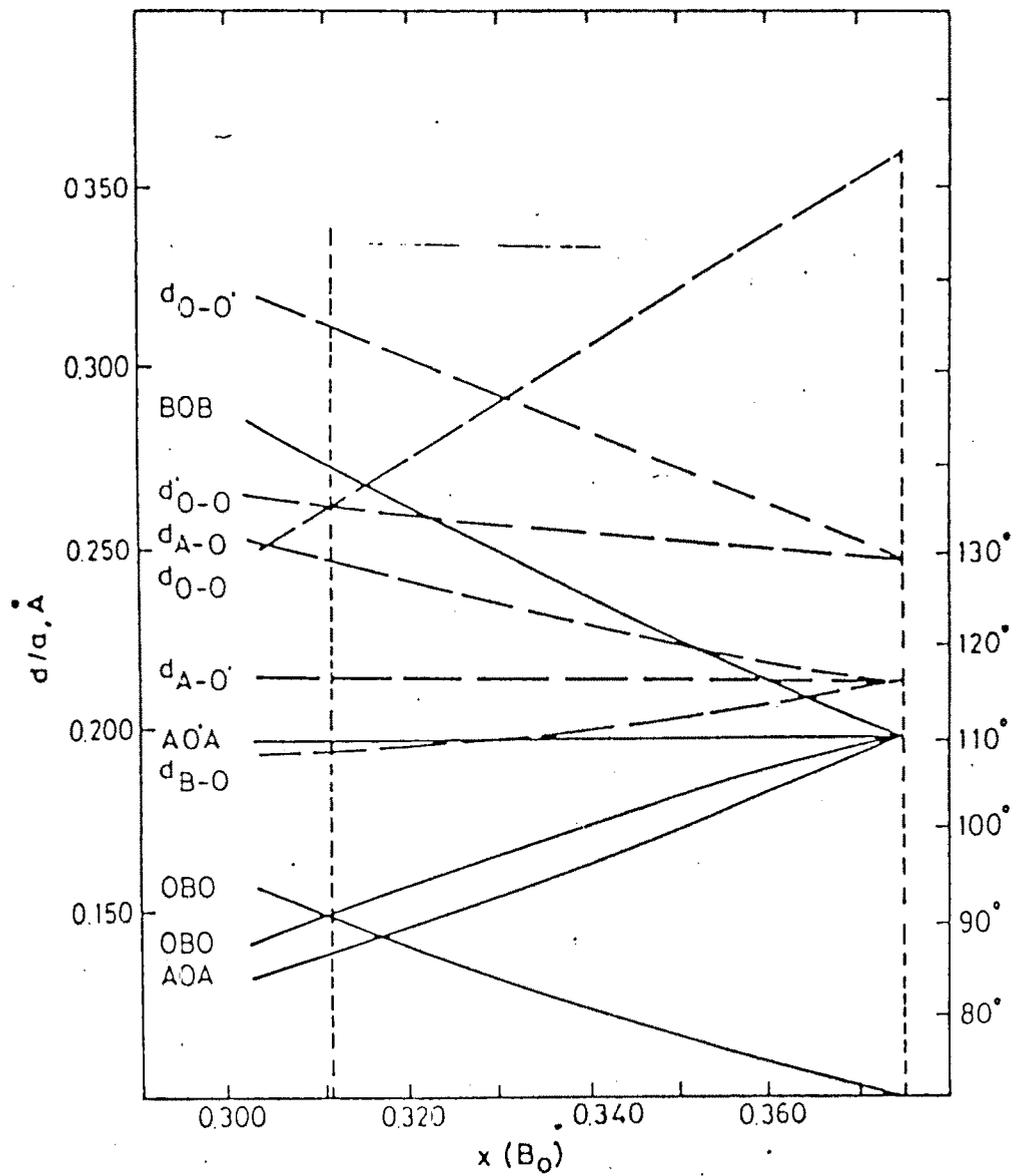


Fig. 1.3 Variation of bond distances (broken lines) and bond angles as a function of 48f oxygen parameters. a is the unit cell parameter. After Pannetier and Lucas (15).

same average charge as the A and B cations to maintain charge neutrality. In case of pyrochlore structure formation the radii ratio of the cations (r_A/r_B) is also important. The substituted cations have ionic radii for the pyrochlore structure according to the upper and lower limits given by Subramanian et al. These values are given as

$$0.87 < r_A < 1.17 \text{ \AA}$$

$$0.58 < r_B < 0.775 \text{ \AA}$$

and

$$0.96 < r_A < 1.29 \text{ \AA}$$

$0.54 < r_B < 0.76 \text{ \AA}$ respectively for ($A^{3+}_2B^{4+}_2O_7$) and ($A^{2+}_2B^{5+}_2O_7$) pyrochlores.

Moreover Subramanian et al. gave the radius ratio

$$1.46 < r_A/r_B < 1.80 \text{ \AA}$$

$1.4 < r_A/r_B < 2.2 \text{ \AA}$ respectively for ($A^{3+}_2B^{4+}_2O_7$) and ($A^{2+}_2B^{5+}_2O_7$) pyrochlores.

1.3 DEFECT PYROCHLORE STRUCTURE:-

The defect pyrochlore structure can be described in different ways similar to the stoichiometric pyrochlores. In terms of the defect fluorite lattice the defect pyrochlore structure is obtained by removing 8b oxygen (O') from the unit cell of the stoichiometric pyrochlore structure. These 8 O' oxygen (8b) per unit cell and removal of all the O' oxygen will lead to the formula for ($A_2B_2O_6$) or (A_2BO_3).

The removal of 8b oxygen, however exposes the A cations to each other across the 8b vacancy and the resulting electrostatic repulsion would tend to

destabilize the structure. In case of (8a) vacancy of a normal nonstoichiometric pyrochlore, the electrostatic repulsion between the exposed B-cations is reduced by partial screening due to the displacement of the 48f oxygen towards the exposed B-cations. In case of 8b vacancy of the defect pyrochlore, there is no such movement of the anions and the stability of the defect structure has been explained mainly due to the bonding between cations through the oxygen vacancy (10). Many $(A_2B_2O_{7-x})$ type oxides formed with the defect pyrochlore structure have weakly basic ions like Tl^+ , Pb^{2+} , Bi^{3+} with a polarizable $6S^2$ lone pair of electrons as the A cations. This leads to an explanation based on the involvement of $6S^2$ electrons in the structure. According to Longo et. al (10) the virtual energy levels of the vacancy are comparable in energy to the 6S & 6P levels of the A ions. The latter are hybridized and are mixed with the virtual levels of the vacancy forming band states involving a cations. This results in bonding between the A cations through the vacancy "trap mediated bond" and implies the polarization of A cations by the oxygen vacancy, resulting in the stabilization of A-A bonds. When this stabilization is greater than the loss in Madelung energy a defect pyrochlore structure can be stabilized in preference to the perovskite structure. According to this model, the 8b-vacancy site must have significant electron density and this has been demonstrated in the case of $Pb_2Ru_2O_6$ by J. M. Longo et. al. The existence of defect pyrochlore structure can also be rationalized from the network model of the stoichiometric pyrochlores. As has already been discussed earlier, a corner shared BO_6 octahedron or B_2O_6 is a basic unit. The A_2O' chains do not interact strongly even though it is an interpenetrating network. The A and O' ions are not very

essential for the stabilization of the basic structure and hence vacancies at both anion and cation sites exist leading to formula $A_2B_2O_6$. Sleight (11) offered another explanation for the existence of $A_2B_2O_6$ (ABO_3) phase with a defect pyrochlore in preference to the adoption of perovskite structure based on the electropositive character of A and B cations. The perovskite and pyrochlore structure both possess corner shared B_2O_6 octahedra network. But in case of perovskite the corner-shared octahedra are arranged in a simple fashion and occur in linear strings running parallel to the cube axis. In case of pyrochlore structure, the chain of octahedra are zigzag lying along the (110) direction with BOB angle 130° . When both A and B cations are not very electropositive, the pyrochlore structure occurs because metal oxygen bonds would then be more covalent and oxygen can form four covalent bonds with a atom. However when both A & B cations are reasonably electropositive, the perovskite structure is found where oxygen will be in 6fold coordination ($4A + 2B$).

In case of ABO_3 composition, the defect pyrochlore structure will have lesser density than the perovskite structure. Hence due to application of high-pressure defect pyrochlore structure transforms in to a perovskite structure. For both $(3^+, 3^+)$ and $(2^+, 4^+)$ combinations the pyrochlore structure has more negative electrostatic energy than the perovskite for 48f oxygen 'x' parameter greater than or equal to 0.33. For a given A cation, the radius of B cation and its electropositive nature will govern pyrochlore formation, because x increase with r_B^{n+} as observed in $PbTiO_3$ (perovskite) and $PbSnO_3$ (pyrochlore). In the case of $A^{1+}_2B^{5+}_2O_6$ compositions, the perovskite structure is more stable than pyrochlore

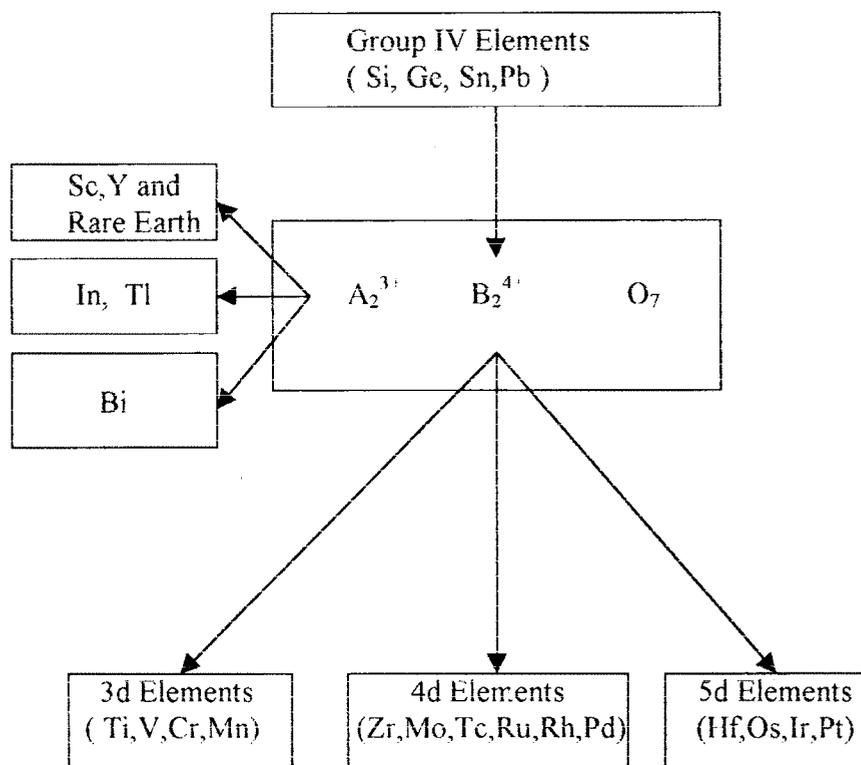


Fig 1.4 Possible substitutions at the A and B sites of $A_2B_2O_7$ oxide Pyrochlore.

for values of x (48f oxygen) $>$ or $=$ 0.32. For $x = 0.30, 0.32$ the A and B cations with large and small radii may stabilize pyrochlore structure.

1.4 TITANATE PYROCHLORES: -

Many pyrochlore oxides in literature are of the $(3 + 4+)$ type $A^{3+}_2B^{4+}_2O_7$, due fact that a large number of A^{3+} and B^{4+} cations have suitable ionic radius for the formation of pyrochlore structure. The A^{3+} ion can be a rare earth and B^{4+} can be a transition metal or any of the group IVA elements (Fig 1.4). A study of $Ln_2B_2O_7$ compounds may be expected to throw light on the stability range of pyrochlores because of the systematic change in the ionic radius of $3+ Ln^{3+}$ ion due to the Lanthanide contraction. Fig 1.5 is shows the stability field diagram for $A^{3+}_2B^{4+}_2O_7$ pyrochlores obtained by plotting Ln^{3+} (8fold coordination) Vs B^{4+} (6fold coordination) from the Shannon ionic radii data (12). From the figure 1.5, it is clear that the relative ionic radii or the ionic radius ratio $RR = r^{3+}_A / r^{4+}_B$ and the oxygen 'x' parameter govern the formation and stability of oxide pyrochlores. Pyrochlore can be form for $r^{3+}_A / r^{4+}_B = 1.46$ to 1.48 at 1 atmosphere. In some cases high pressure and high temperature may be necessary for synthesis of $(3+, 4+)$ pyrochlores, even though r^{3+}_A / r^{4+}_B fall with in expected range 1.4 to 1.8. In some other cases the oxidation-reduction thermodynamic parameters govern the formation of $(3+, 4+)$ pyrochlores (13, 14). Ionic size, radius ratio r^{3+}_A / r^{4+}_B and charge neutrality criteria are, however satisfied for the formation of the above, at 1 atmosphere pressure.

Roth in 1956 first reported the synthesis of $Ln_2Ti_2O_7$ ($Ln = Sm, Yb$ and Y) pyrochlores (14). The compound were later studied in detail by Brixner (16) AND knop et. al (4). Subramanian et al. (17) reported that compounds with Ln

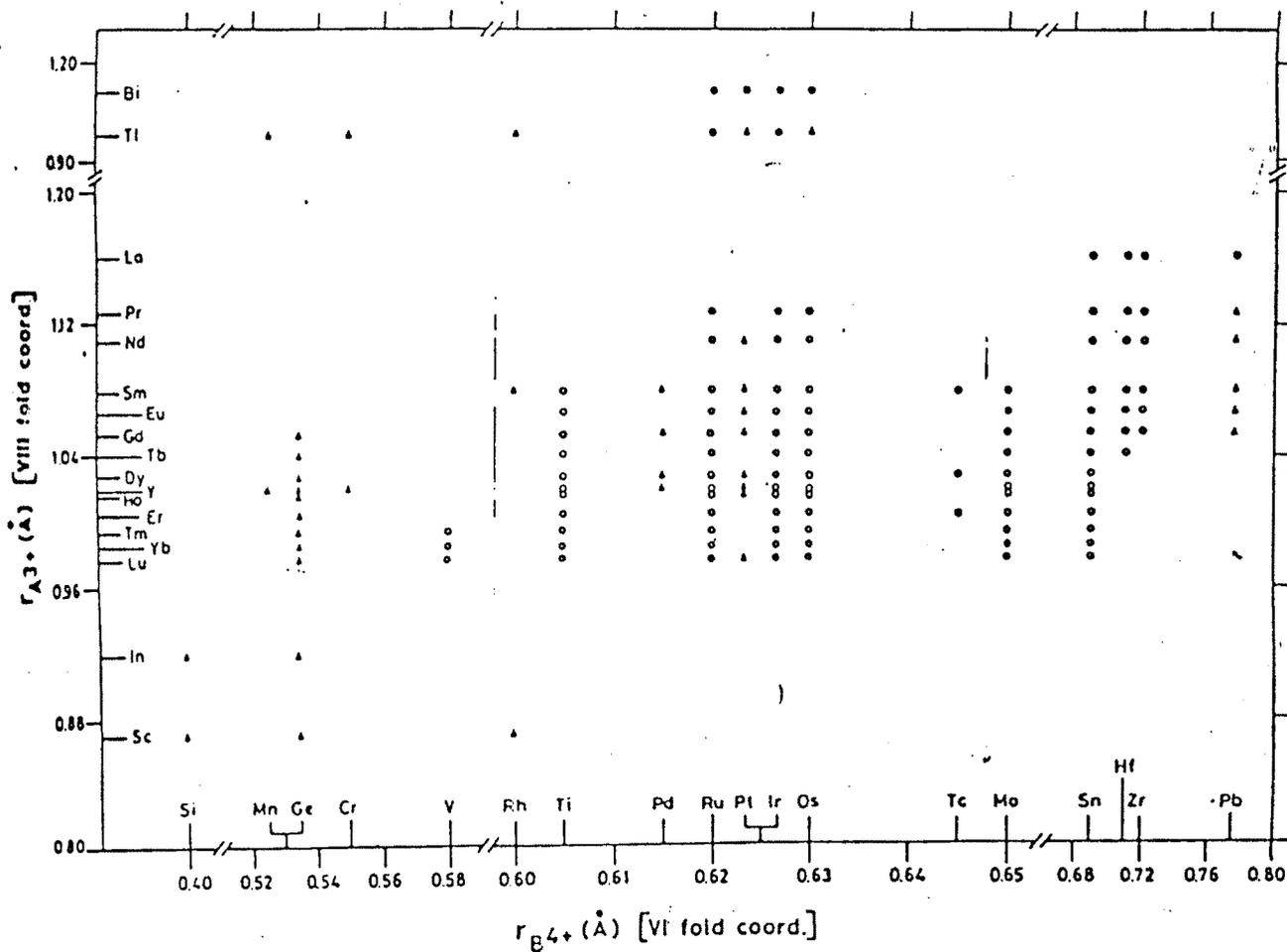


Fig. 1.5 Stability field diagram for $A_2B_2O_7$ pyrochlores. Ionic radii data taken from Shannon (37). For Bi^{3+} the value of 1.10_f (8 fold) is used as discussed in detail by Shannon. (O-one atmosphere and Δ high pressure synthesis).

= La, Ce, Pr and Nd do not crystallize in pyrochlore structure because the RR values preclude their formation. A neutron diffraction study of $\text{Sc}_2\text{Ti}_2\text{O}_7$ has shown that the compound possesses defect fluorite structure (18), while $\text{Bi}_2\text{Ti}_2\text{O}_7$ appear to be a deformed pyrochlore similar to $\text{Bi}_2\text{Sn}_2\text{O}_7$ (19).

The $\text{Ln}_2\text{Ti}_2\text{O}_7$ phases can be synthesized by completing solid state reaction at high temperature (14-21) and single crystals have been grown using flux techniques (22,23). The Lattice parameter of $\text{Ln}_2\text{Ti}_2\text{O}_7$ shows systematic decrease with decrease in radius of the Ln^{3+} ions. As expected Titanate based pyrochlores are refractory substances with melting points 1560 – 2000 °c. Since in $\text{Ln}_2\text{Ti}_2\text{O}_7$, there are no d electrons (Ti^{4+} d^0 system) and f electrons the Ln ions are localized in the inner 4f levels, no electronic conductivity is expected at ordinary temperature. Indeed $\text{Ln}_2\text{Ti}_2\text{O}_7$ are found to be insulating with ρ (300 k) nearly equal to 10×10^{12} ohm cm. However P-type semiconduction is possible at elevated temperature in some titanates (24). Capacitance measurement shown that the $\text{Ln}_2\text{Ti}_2\text{O}_7$ possess relatively high dielectric constant. ϵ (300 k) 30-70.

1.5 APPLICATIONS OF OXIDE PYROCHLORES: -

Oxide Pyrochlores are used in various devices and other application due to their large number of properties such as electrical, dielectric, magnetic, optical and catalytic behavior. All these properties are normally controlled by the parameters such as ionic size, polarizability of the ions, electronic configuration and occasionally on the preparative conditions. Pyrochlores have refractory nature. Some of these pyrochlores are good oxide ionic conductor (25). Many of the applications involve high temperatures and an understanding at the physical properties of these compounds such as thermal expansion will be

useful. Some of the pyrochlore oxides have nuclear potential applications as neutron absorber and radioactive waste forms for final disposal (26).

The electronic behavior of pyrochlore oxides varies widely from insulating through semiconducting to metallic, with a few compounds exhibiting semiconductor to metallic transition. Hence these group of materials can be used in solid state devices. They are used in high permittivity ceramics, Thermistors, thick film resistors and switching elements. Stable, low resistivity oxide pyrochlores have also been used for screen printing on the dielectric for capacitor application (13).

Stable oxide pyrochlores too have good chance of finding use as electrical heating elements provided suitable compositions are chosen and fabrication and evaluation procedures are standardized. Realization of good and stable solid electrolyte through the defect pyrochlores will go a long way in solving the problem of high energy density rechargeable batteries. In addition some non-ferroelectric pyrochlores may serve as technologically useful dielectric in application such as temperature stable and temperature compensating dielectrics or microwave dielectrics (14).

1.6 ORIENTATION OF THE PROBLEM: -

The pyrochlore is one that has received a considerable amount of attention because of its ferroelectric nature (27). Pyrochlore compounds have variety of applications such as thermistors, switching elements, thick film resistors, high permittivity ceramics, can be used as temperature stable and temperature compensating dielectric.

The general formula of the oxide pyrochlores can be written as $A_2B_2O_7$ Or $A_2B_2O_6O'$ with four crystallographic nonequivalent kinds of atoms. By interchanging A, B and Oxygen atoms and substituting A and B elements obtain a number of interesting properties can be obtained. The electrical conductivity of various pyrochlore phases and their solid solutions has been measured (28). The electrical conductivity behavior is also explained generally on the disordered structure of pyrochlore, oxygen vacancies and interstitial positions. The electrical nature of pyrochlores varies from highly insulating through semiconducting to metallic transition. Little work is done on electrical behavior of these pyrochlores and conduction phenomenon.

In order to understand the conduction mechanism in pyrochlores, we have undertaken the following work.

- 1) Preparation of pyrochlores by ceramic method using chemical formula $A_2B_2O_7$ where A = Ce, Nd and B = Ti
- 2) X-ray diffraction study for confirmation of single-phase formation and determination of pyrochlore structure.
- 3) Study of electrical properties such as d.c. Conductivity, TEP measurements, dielectric measurements (variation of dielectric constant and loss tangent) with frequency and also with temperature.

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