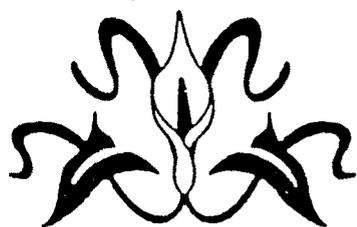


CHAPTER I



INTRODUCTION TO PYROCHLORES

1.1 INTRODUCTION

Materials with the pyrochlore structure are numerous and exhibit a rich crystal chemistry variety (1). Among the ternary metallic oxides, compounds of the general formula, $A_2 B_2 O_7$ (A and B are metals) represent a family of phases isostructural to the mineral pyrochlore, $(NaCa) (NbTa) O_6 F / (OH)$. These compounds about 150 in number are predominantly cubic and ionic in nature, lend themselves to a wide variety of chemical substitution at the A, B and O sites provided the ionic radius and charge neutrality criteria are satisfied (2). Crystal structure also tolerates A and O sites to a certain extent with the result that, cation migration within the solid is made easy. $A_2 B_2 O_7$ Compounds exhibit a wide variety of interesting physical properties. This is because the B element can be a transition metal with variable oxidation state or a post transition metal, and the A element can be a rare earth (Ln) or an element with inert lone pair of electrons. Thus the electrical nature of the pyrochlores varies from highly insulating through semiconducting to metallic behavior with a few compounds exhibiting a semiconductor-to-metal transition. Many phases where A and B elements are present in the maximum possible oxidation state exhibit interesting dielectric piezo- and ferro-electric behavior many of the oxide pyrochlores are excellent refractors while some Ln-containing ones exhibit interesting fluorescent and phosphorescent behavior and possibility can act as laser host materials.

Oxide pyrochlore and related phases have been studied by many workers over the past several years and there is available a considerable body of experimental data to allow correlation's of body of experimental data to allow correlation's to be made with various crystal chemical properties Shanon and Sleight (3) and Knop et al (4) while presenting their own work, discussed the general features of (3+, 4+) and (2+, 5+) pyrochlores respectively, but their treatment pertained mainly to the structure and stability-field regions of these compounds. similarly Barker et al, (5) and Mc Cauley (6) discussed the geometrical aspects and oxygen parameter of the various pyrochlores. While Sncherbukova et al (7) Rao and Subba Rao (8) devoted a sizeable portion of their article to a discussion of the physical properties of $A_2B_2O_7$ Compounds.

Only one parameter the 48 f oxygen X value, needs to be defined in the structure containing four different kinds of atoms A, B, O and O'. However the 8 - and 6- fold Co-ordination polyhedra of oxygen around the A and B cations respectively in $A_2B_2O_7$ Change shape with X and the entire structure can be viewed in seven different ways. A Comprehensive account of the $A_2^{3+} B_2^{4+}O_7$ (3+, 4+), $A_2^{2+} B_2^{5+}O_7$ (2+, 5+) and various substituted pyrochlores is presented below. The (3+ , 4+) Phases are large in number compared to the (2+ , 5+) compounds and the existence of Ln^{3+} ions with a systematic variation in ionic radius enables one to exactly define the stability field of (3+, 4+) Pyrochlores in terms of radius ratio. Interesting physical properties are exhibited by both the (3+, 4+) and (2+ , 5+) pyrochlores.

1.2 STRUCTURE OF THE PYROCHLORE

The space group of the ideal pyrochlore is $Fd\bar{3}m$ (O_h^7). There are 8 molecules per unit cell ($z = 8$). The structure of pyrochlore is composed of two kinds of cation coordination polyhedron shown in Fig 1.1

The A cation (usually $\sim 1 \text{ \AA}$ ionic radius) are eight coordinated and are located within scalenohedra (distorted cube) that contains six equally spaced anions (O^{2-} atoms) at a slightly shorter distance from the central cation. The smaller B cations ($\sim 0.6 \text{ \AA}$ ionic radius) are six coordinated and are located within trigonal antiprisms with all the six anions at the equal distances from the central cations. Many authors do refer to the six fold and eight fold co-ordination polyhedra in the pyrochlore structure as octahedral and cubic coordination polyhedra respectively. 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 antiprisms and scalenohedra) The conditions for the existence of perfect octahedra and cubic coordination polyhedra can not be simultaneously satisfied. Since there are four nonequivalent atoms, there are four possible choices of origin. Two can be referred to the centric origin viz. $3m$, while the other two refer to $\bar{4}3m$ as the origin. All four have been employed by the various workers but more commonly, the B cation is chosen as the origin and herein 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 on the choice of the origin.

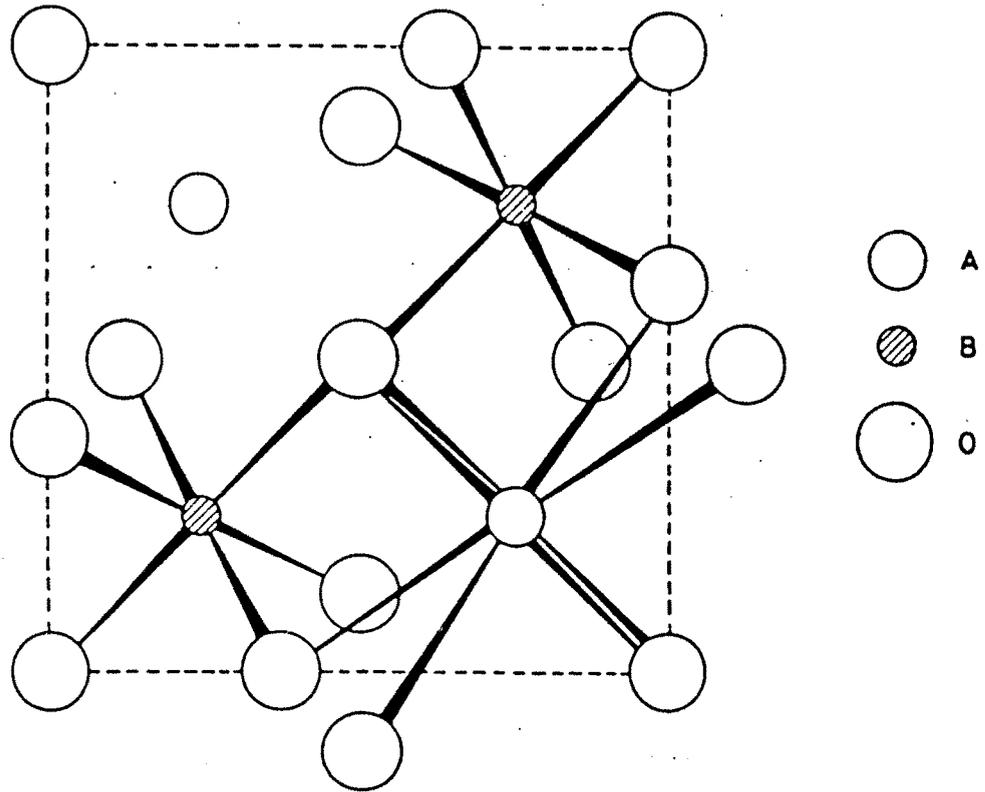


Fig. 1.1 Pyrochlore structure of general formula $A_2B_2O_7$ showing the 6 fold coordination of B and 8 fold coordination of A atoms.

The value of unknown oxygen X parameter can be determined by the methods of x-ray or neutron structure analysis. In many cases X-ray powder data have been refined using the observed intensities while in other cases X values have been inferred from lattice parameters and assumed bond distances taking the geometry of the crystal structure into consideration. Although many pyrochlore compositions crystallize in the cubic structure, in a few cases deviations from cubic symmetry by way of tetragonal, rhombohedral and triclinic distortion are noted. The lattice parameters generally are $\sim 10 \text{ \AA}$ whereas the X parameter is found to range from 0.309 to 0.355 (with B_o - ion chosen as origin). The shortest A-O and B-O distances in pyrochlores are usually close to the average bond distance encountered in the A and B binary or ternary oxides with eight and six - fold coordination respectively. The pyrochlore structure has been described in seven different ways. Various descriptions arise because the coordination polyhedra around the A and B cations change shape with the value of the oxygen X parameter. Bestron (9) and others (10, 11, 12) described the pyrochlore as a network structure of corner linked BO_6 octahedra with the A atoms filling the interstices. Aleshin and Roy (13) and Longo et al; (14) described it on the basis of an anion deficient fluorite unit cell. More generalised descriptions involving (i) interpenetrating networks of BO_6 octahedra and A_2O chains of A_4 and B_4 tetrahedra (15) with oxygens suitably placed inside or outside (ii) framework structure in terms of distorted layers of B_2O_6 units of the hexagonal tungston- bronze type parallel to [111] and joined by intervening layers of widely- spaced BO_6 octahedra (16). However in fact remains that no single

7
description can explain all the structural and other characteristics of the pyrochlores.

As mentioned earlier the coordination polyhedra change shape with the oxygen x parameter. Eventhough never relized experimentally, the limiting values of X are 0.3125 and 0.375. For $X = 0.3125$, the B ion has a perfect octahedral coordination (and no D_{3d} symmetry) while the A ion occupies the site of coordination eight in the form of distorted hexagon of six oxygens (48f) and whose plane is perpendicular to O'-A-O' axis. The A-O distance is of course, shorter than the A-O distance shown in Fig 1.2, when $X = 0.375$, the A cations will be situated in a regular cubic 8- fold coordination (no D_{3d} symmetry), whereas the B ion is at the centre of a highly distorted octahedron (trigonal antiprism). In otherwords the B cation is also at the centre of a cube of oxygens with two body diagonal oxygen missing. Fig 1.3 shows variation of principle angles and interatomic distances as function of 48f oxygen x parameter (15). In particular, one can note that the B-O-B angle which is $109^{\circ} 28'$ for the fluorite structure increases to 120° - 140° for pyrochlore structure.

Compounds with stoichiometry $A_2 B_2 O_7$ often forms with the pyrochlore structure. Very elegant description of the pyrochlore structure with a continuous three - dimensional B_2O_6 framework of cornersharing octahedra, the remaining A_2O atoms being in the tunnel as shown in Fig 1.4. The vacancies occur in pairs across the body diagonals of MO_8 cubes in such a way as to form chains of six coordinated cations parallel to each of the $[110]$ directions shown in fig 1.5.

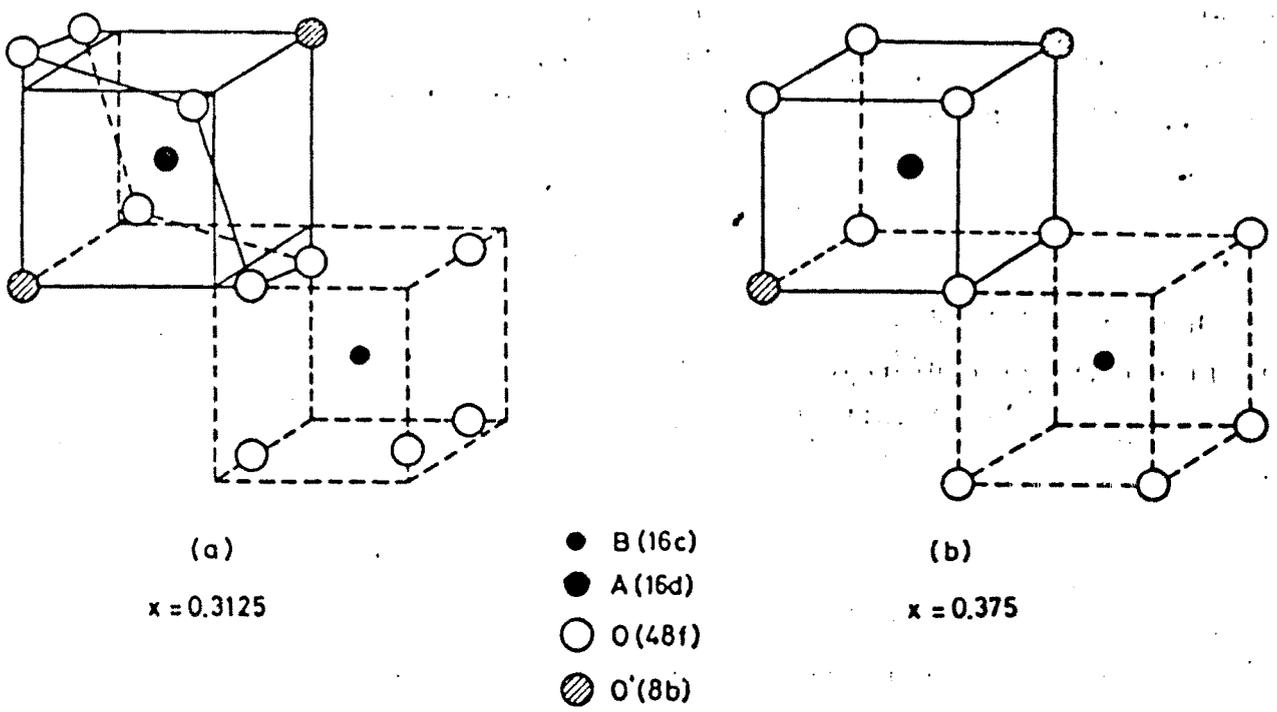


Fig1-2. Change in shape of coordination polyhedra of A and B ions with 48f oxygen parameter x in $A_2B_2O_6O'$ structure. Coordination around B becomes a regular octahedron for $x=0.3125$ ($5/16$) and for $x=0.375$ ($3/8$) the coordination around A becomes a regular cube. After Faucher and Caro (18).

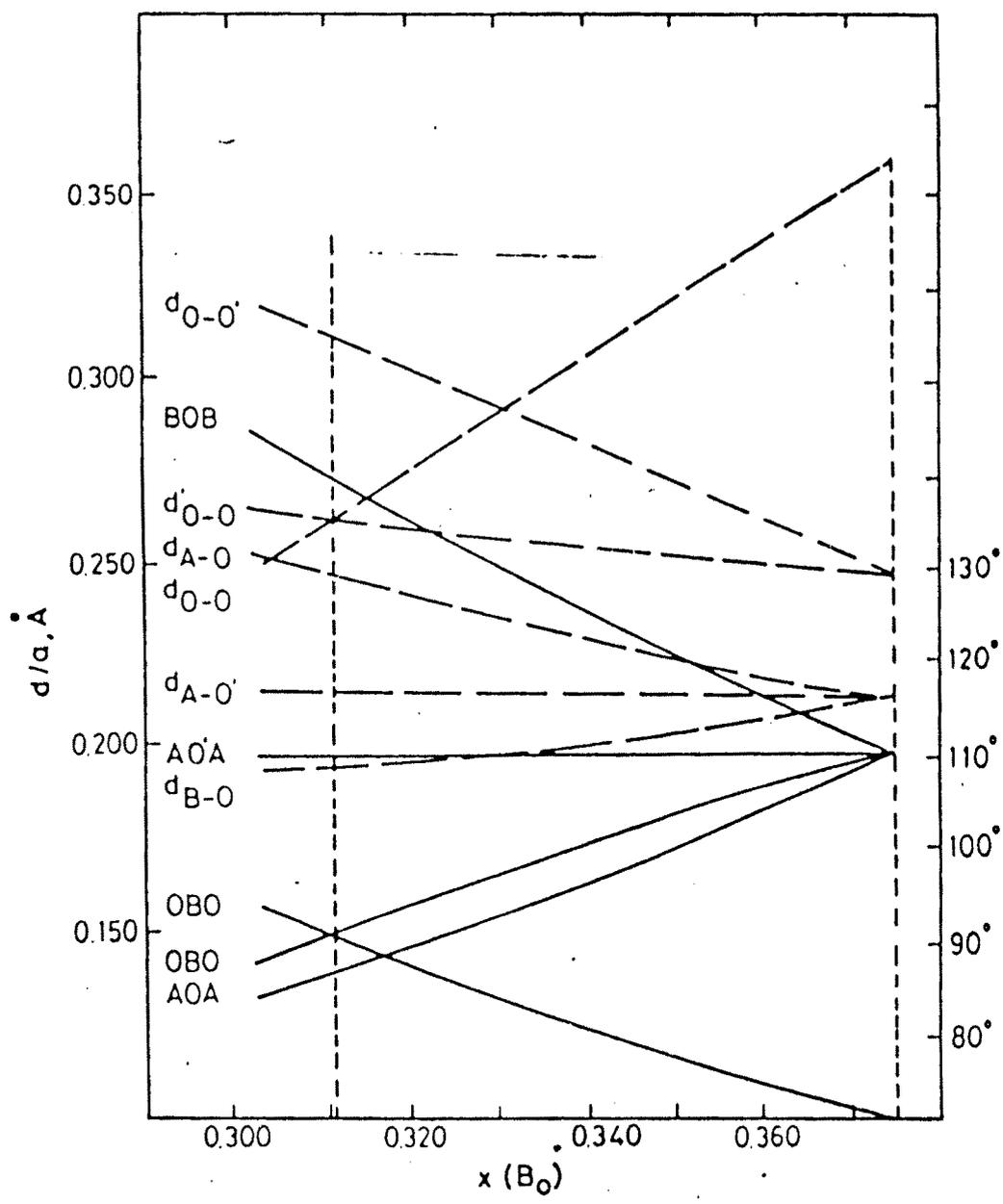


Fig. 1.3 Variation of bond distances (broken lines) and bond angles as a function of 48f oxygen parameters. a is the unit cell parameter. After Pannetier and Lucas (15).

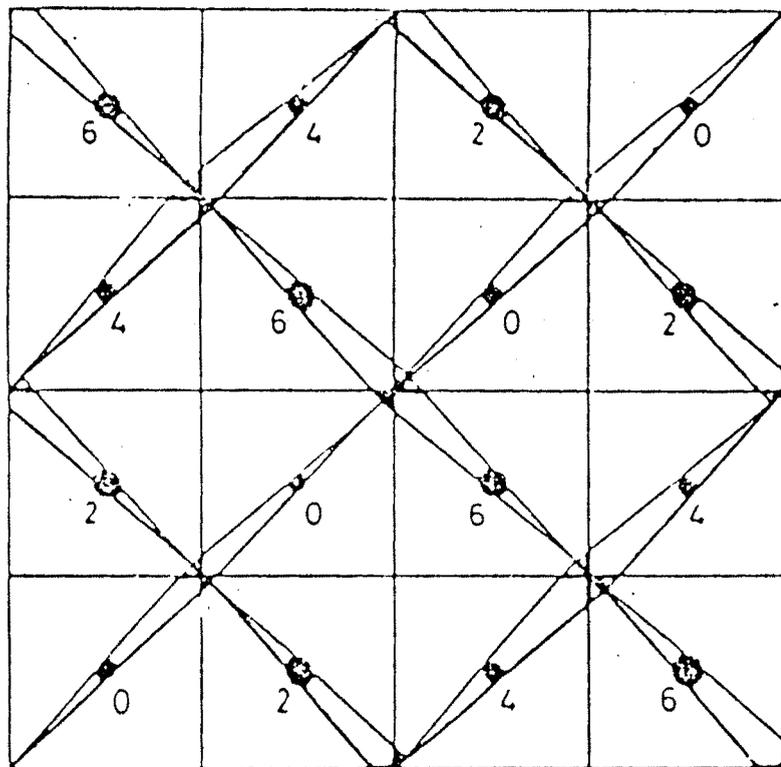


Fig. 1-5 Diagrammatic representation of a projection of the ideal pyrochlore structure along [100]. Anions occur at the corners of the cube-projections. Cations occur at different levels as indicated by the different sized circles. The heights of six-coordinated cations are indicated by their height in eighths of a unit-cell edge and the "anion vacancies" responsible for this reduction in coordination number are indicated by the sloping bars. Thus a zig-zag chain of ideal anion vacancies at levels of $1/8$ and $7/8$ results in the [110] string of six coordinated cations at level 0.

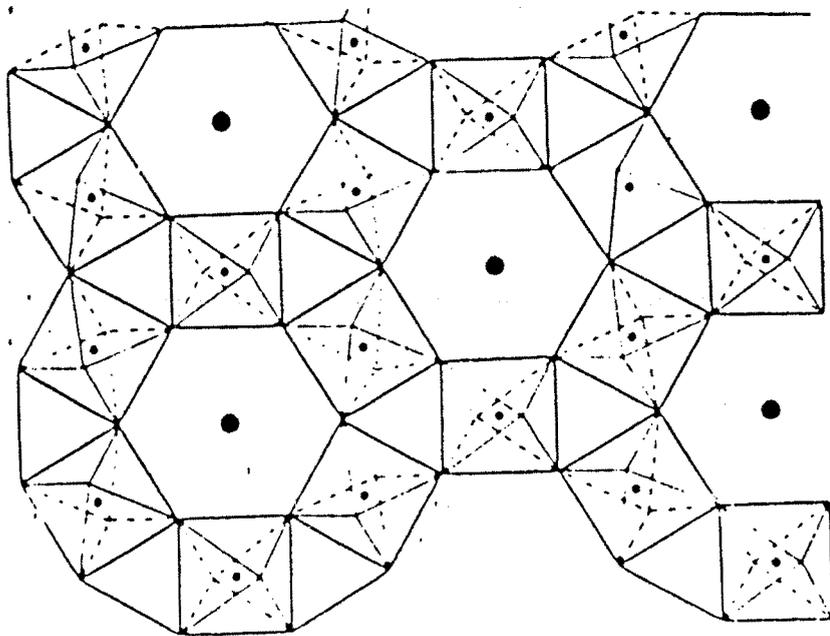


Fig. 1-4 The tunnel representation of the pyrochlore structure projected along [111] (after Knop et al., 1965). The relationship between this projection and that along [001] of a hexagonal tungsten bronze is obvious but in the pyrochlore these "tunnels" run along all $\langle 111 \rangle$ directions (Hyde, B.G., personal communication). The BO_4 octahedra are shown along with the projection of the A atoms in the "tunnels".

The name pyrochlore originally referred to the mineral $(\text{Ca}, \text{Na}; \text{U})_2 (\text{Nb}, \text{Ta})_2 \text{O}_6(\text{OH}, \text{F})$ (JCPDS Card No 13-254) which can be generalised as $\text{A}_2 \text{B}_2 \text{O}_7$ or $\text{A}_2 \text{B}_2 \text{OO}'$ (30). The simple pyrochlore structure is face centered cubic with space group $\text{Fd}\bar{3}\text{m}$ (No 227). There are 88 atoms in a unit cell: 16 A cations in position (C); 16 B cations in position (d), 8 O' anions in position (a) and the remaining 48 O anions in position (f). The coordination of ions in a normal pyrochlore structure are AO_6 , O'_2 , BO_6 , $\text{OA}_2 \text{B}_2$, and $\text{O}' \text{A}_4$ and B_4 (is a vacancy). The larger A cations are eight coordinated and located within scalenohedra (distorted cubes) that contain six equally spaced anions (the O anions) and two additional axial anions (the O' anions) at a slightly shorter distance from the central cations. The smaller B cations are six coordinated and located within trigonal antiprisms (distorted octahedra) with six anions equidistant from the central cations. The atomic arrangement in the pyrochlore structure is completely satisfied except for the coordinate of the 48 O positions which is found to range from 0.375 to 0.4375 (with A ion chosen as origin) depending on the ionic radii.

The rules regarding the allowed fundamental reflexions in the pyrochlore $\text{Fd}\bar{3}\text{m}$ space group are in the International Tables for x-ray crystallography. However superlattice or ordering reflexions (when supposing the pyrochlore as a fluorite derivative) are $[111]$, $[331]$ and $[531]$ and arise from both cations and anions. The presence of these reflexions, 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 $\text{Fd}\bar{3}\text{m}$.

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 reflexions 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 the thermodynamic stability of competitive phases are also important. However in general ionic sizes should be comparable to those of A and B site cations and the combination must yield the same average charge as the A and B cations to maintain charge neutrality. In addition as an indication of formation of the pyrochlore crystal structure the radius 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

$$0.87 < r_A < 1.17 ,$$

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

and $0.96 < r_A < 1.29 ,$

$$0.54 < r_B < 0.76 \text{ \AA}$$

respectively for $A_2^{3+} B_2^{4+} O_7$ and $A_2^{2+} B_2^{5+} O_7$ pyrochlores.

Moreover subramanian et.al gave the radius ratio

$$1.46 < r_A/r_B < 1.80$$

and $1.4 < r_A/r_B < 2.2$

respectively for $A_2^{3+} B_2^{4+} O_7$ and $A_2^{2+} B_2^{5+} O_7$ pyrochlores.

1.3 STRUCTURE AND STABILITY

The defect pyrochlore can be described in different ways similar to the stoichiometric pyrochlores. In terms of defect-fluorite lattice the defect pyrochlore structure is obtained by removing 8 b oxygen (O') from the unit cell of the stoichiometric pyrochlore structure. There are 8 O' oxygens (8b) per unit cell and removal of all the O' oxygens will lead to the formula $A_2 B_2 O_6$ or ABO_3 . The removal of 8b oxygens however exposes the A cations to each other across the 8b vacancy and the resulting electrostatic repulsion would tend to destabilize the structure. During the case of (8a) vacancy of a normal stoichiometric pyrochlore the electrostatic repulsion between the exposed B cations is reduced by a partial screening due to the displacement of the 48 f oxygen's towards the exposed B cations. In the case of (8b) vacancy of the defect pyrochlores, there is no such movement of the anions and the stability of the defect structure has been explained mainly due to the bonding between A cations through the oxygen vacancy (17) many $A_2B_2O_{7-x}$ type oxides formed with the defect pyrochlore structure have weakly basic ions like Ti^{2+} , Pb^{2+} , Bi^{3+} with a polarisable $6S^2$ lone pair of electrons as the A cation. This leads to an explanation based on the involvement of the $6S^2$ electrons in the structure. According to Longo et al (18) the virtual energy levels of the vacancy are comparable in energy to the 6S and 6P levels of the A ions. The latter are hybridised and are mixed with the virtual levels of the vacancy, forming band states involving the A cations. This results in bonding between the A cations through the vacancy 'trap mediated bond'. In effect this implies polarization of the A cations by the oxygen vacancy resulting in the stabilization of the A-A bonds. When this stabilization is greater than the

loss in medulung energy, a defect pyrochlore structure can be stabilized in preference to the perovskite structure. According to this model, it has been demonstrated that in case of $Pb_2Ru_2O_5$, the 8b vacancy site must have significant electron density. The existence of the defect pyrochlores can also be rationalised from the network model of the stoichiometric pyrochlores. A corner shared BO_6 octahedron or $B_{4/2}O_6$ is the basic unit. The A_2O' chains do not interact strongly eventhough it is an interpenetrating network. The A and O' ions are not very essential for the stabilization of the basic structure and hence the vacancies at both anion and cation site exist leading to the formula $A_2B_2O_6$ or $A_4B_2O_6$. we may now note that perovskite and Pyrochlore structure both posses cornershared BO_6 octahedral network, the essential difference being that in perovskite the Cornershared octanedra are arranged in a simple fashion and occur in linear strings; running parallel to the cube axes. In the pyrochlore structure, however the chain of octahedra are zig-zag lying along the $[110]$ direction with BoB angle 130° when both the 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 the A atom. However if the A and B cations are reasonably electropositive the perovskite structure is found where oxygen will be in 6- fold coordination ($4A + 2B$). It is noted that the pyrochlore-to-perovskite transformation on the application of pressure becomes increasingly difficult to achieve with decreasing charge on the A cation. For both $(3+, 3+)$ and $(2+, 4+)$ combinations, the pyrochlore structures has more negative electrostatic energy than the perovskite for 48f oxygen x parameter

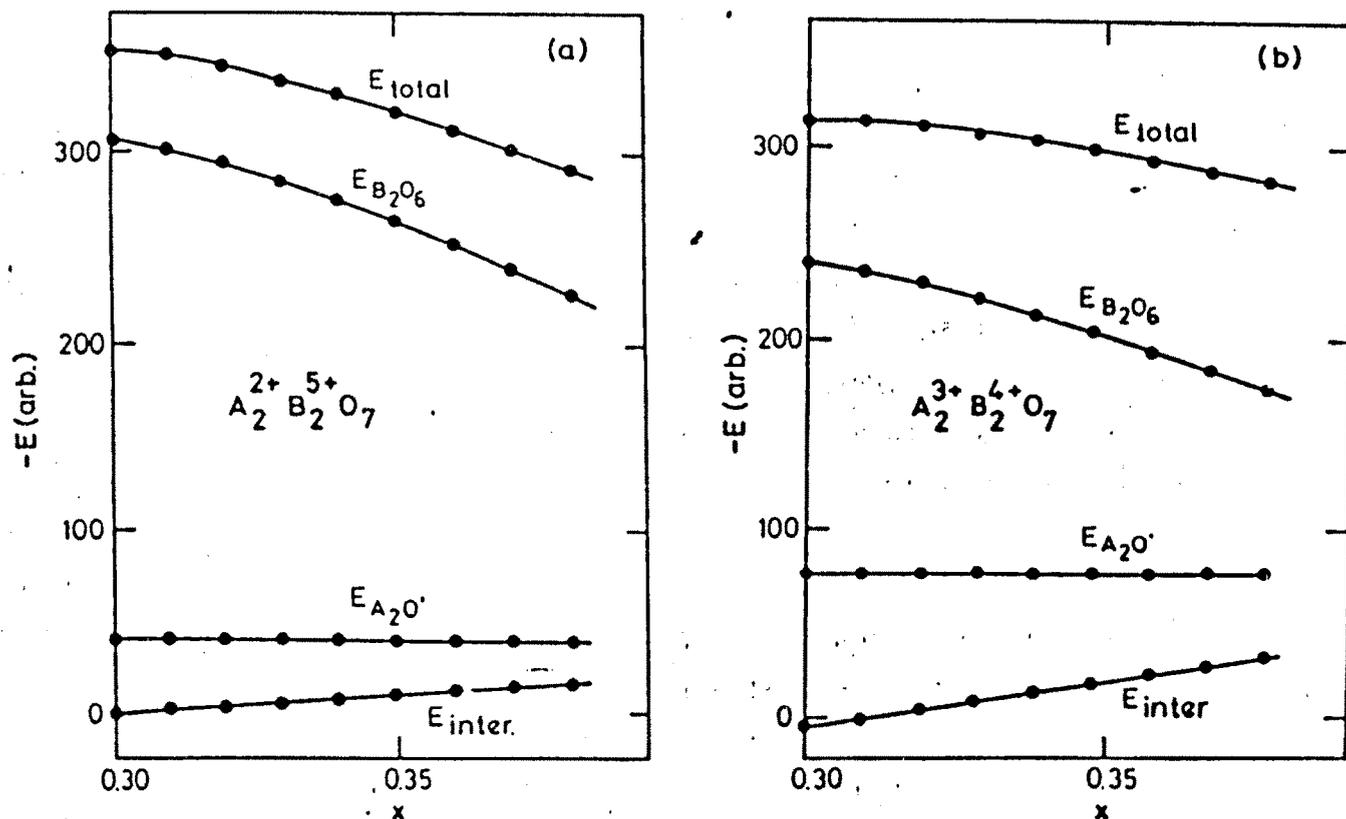


Fig.1.6 Variation of electrostatic energy (E) vs (48f) oxygen x parameter for various $(2+, 5+)$, $(3+, 4+)$ oxide pyrochlores based on Madelung energy and site potential calculations using the network model. $E_{(B_2O_6)}$ is always more negative than $E_{(A_2O')}$ for the respective networks. The internetwork interaction energy (E_{inter}) is only 2-3% of the total energy (E_{total}). After Pannetier (21).

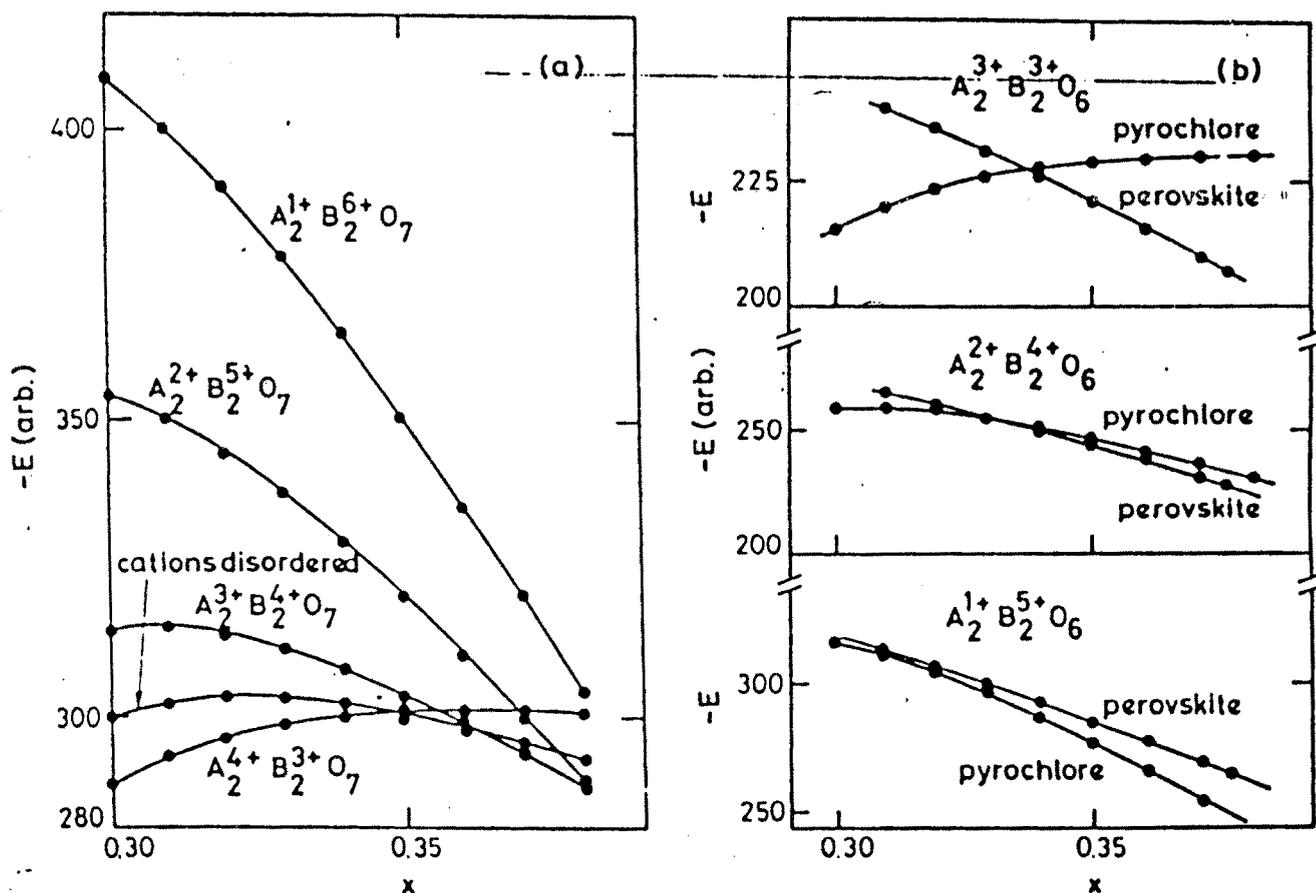


Fig. 1.6 Variation of electrostatic energy (E) vs (48f) oxygen x parameter for various oxide pyrochlores based on Madelung energy and site potential calculations using the network model. (a) (m^+, n^+) and cation disordered defect fluorite of the formula $A_2^{m^+}B_2^{n^+}O_7$. (b) (m^+, n^+) compositions of the formula $A_2B_2O_6$. For discussion see text. After Pannetier (21).

≥ 0.33 . For the given A cation, the radius of the 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 $A_2^{1+}B_2^{5+}O_6$ compositions the calculations show that the perovskite structure is more stable than that of the pyrochlore for values of X (48f oxygen) ≥ 0.32 . Fig.1.6d. For $x \cong 0.30 - 0.32$ the curves are overlapping indicating the borderline nature of the perovskite - pyrochlore stability. In such a case the pyrochlore structure may be stabilized if, there exists an additional contribution to the stability by way of relative sizes of A and B ions. For X values nearer to an ideal 0.3125 (0.30- 0.32) the A and B cations with large and small ionic radius respectively may stabilize the pyrochlore structure.

1.4 $A_2^{3+} B_2^{4+} O_7$ (3+ 4+) PYROCHLORES

Many of the pyrochlore oxides known in the literature are of the (3+ 4+) type $A_2^{3+} B_2^{4+} O_7$. This is due to the fact that a large number of A^{3+} and B^{4+} cations have suitable ionic radius for the formation of pyrochlore structure. where A^{3+} can be a rare earth where as B^{4+} can be a transition metal or any of the group IV elements. shown in fig 1.7.

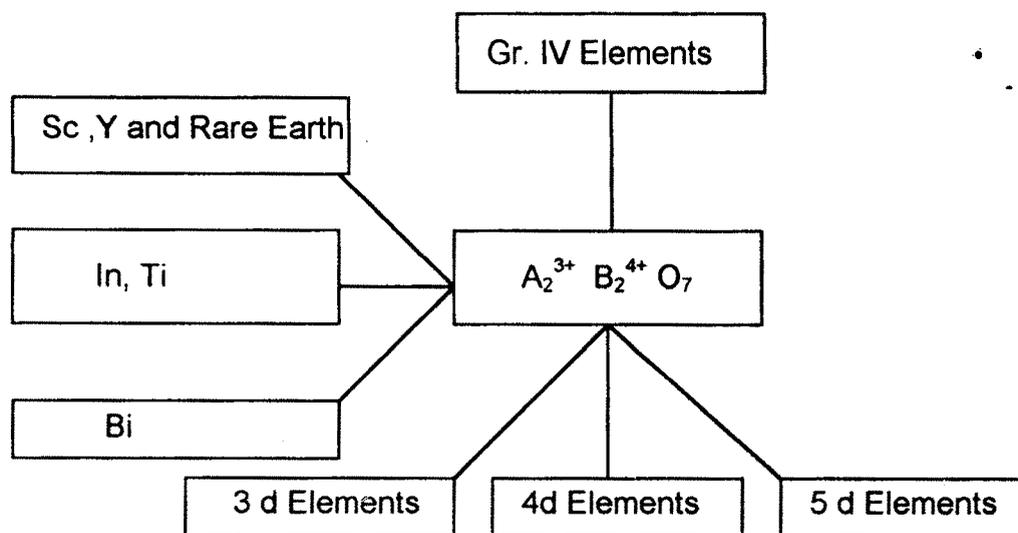


Fig. 1.7 Possible substitutions at the A and B sites of $A_2^{3+} B_2^{4+} O_7$ pyrochlores

A study of $Ln_2 B_2 O_7$ compounds may be expected to throw light on the stability range of pyrochlores because of the systematic changes in the ionic radius of Ln^{3+} ion due to the Lanthanide contraction

Fig 1.8 shows stability field diagram for $A_2^{3+} B_2^{4+} O_7$ pyrochlores obtained by plotting $r_{Ln^{3+}}$ (8-fold coordination) Vs $r_{B^{4+}}$ (6-fold coordination) from shanon ionic radii data (19). From the above fig. it is clear that relative ionic radii or the ionic radius ratio $RR = (r_A^{3+} / r_B^{4+})$ and the oxygen parameter (X) govern the formation and stability of the oxide pyrochlores. Pyrochlores can form for $RR = 1.46$ to 1.48 ($r_{Gd} / r_{Zr} = 1.46$) to ($r_{Sm} / r_{Ti} = 1.78$) at one atmosphere. The work of shanon and sleight (3) Reid et. al. (20) and Chateue and Loriers (21) on the high pressure high temperature synthesis of pyrochlore germanates and silicates has shown that the RR can be extended up to 2.3 it should be pointed out that, in few cases high pressures may be necessary for the synthesis of (3+4+) pyrochlores eventhough the RR may

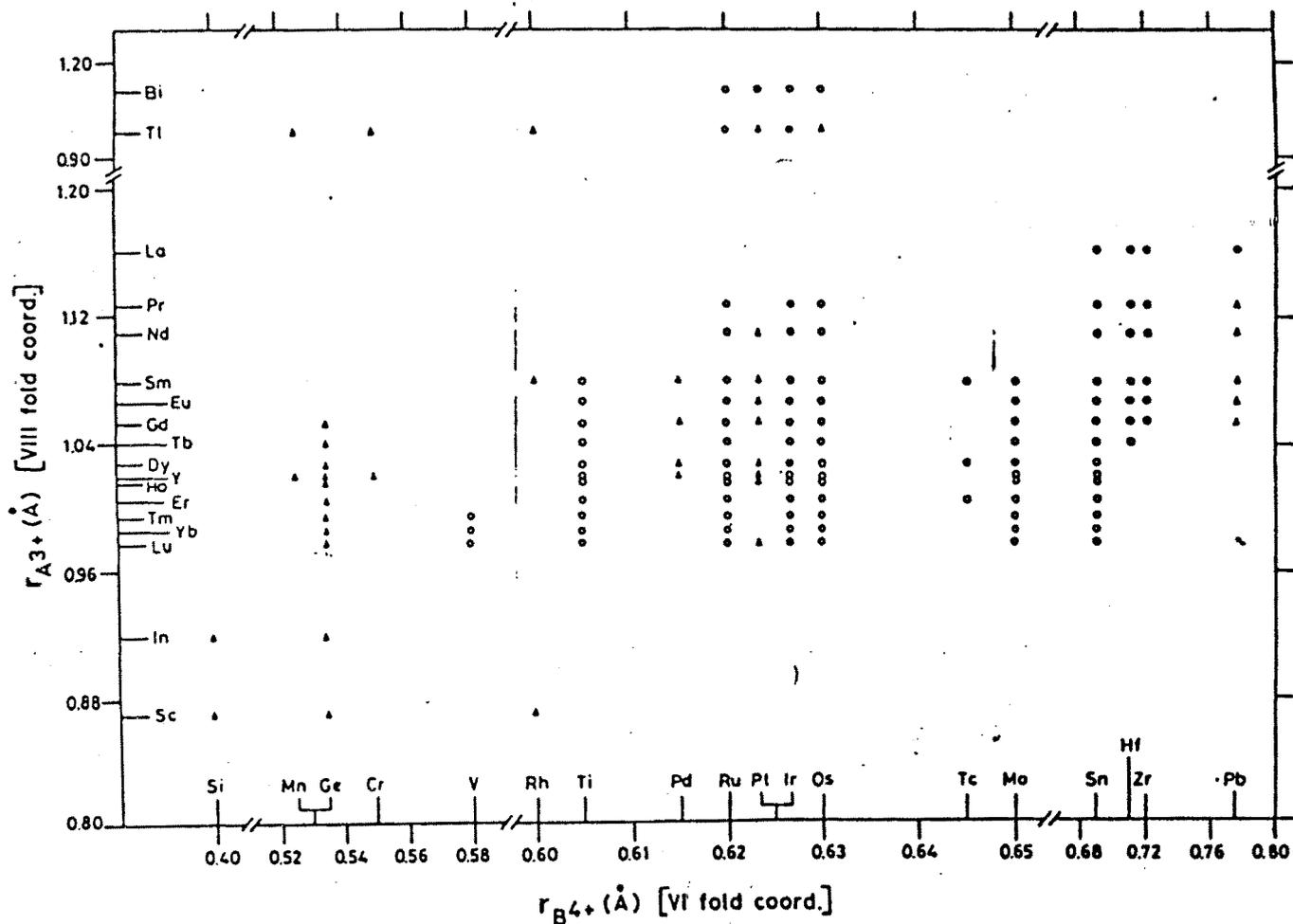


FIG. 1-8 Stability field diagram for $A_2^{3+}B_2^{4+}O_7$ pyrochlores. Ionic radii data taken from Shannon (37). For Bi^{3+} the value of 1.10_f (8 fold) is used as discussed in detail by Shannon. (○ - one atmosphere and △ high pressure synthesis).

fall within the range 1.40 - 1.55. In some cases the oxidation - reduction thermodynamic parameters govern the formation of (3+ 4+) pyrochlores as is shown by the non. existence of $\text{Ln}_2 \text{B}_2\text{O}_7$ with $\text{B}=\text{w}^{4+}$ and Re^{4+} pyrochlores (22,23). Ionic size, RR and charge neutrality criteria are however satisfied for the formation of the above at one atmospheric pressure.

Mc Cauley (24) has attempted a correlation between the stability field and oxygen positional parameter in the (3+ 4+) pyrochlores using Nikiforov's equation (25). However it is questionable significance since r_A^{3+} chosen by him was that for 6-fold coordination and fails miserably when the proper r_A^{3+} is considered (VIII coordination) for larger A ions.

1.5 APPLICATIONS OF OXIDE PYROCHLORES

Usefulness of pyrochlore-type oxides in various devices and other applications is due to their wide spectrum of properties such as electrical, magnetic, dielectric, optical and catalytic behavior. These properties are normally controlled by the parameters such as ionic size, polarizability of the ions electronic configuration and occasionally on the preparative conditions (e.g. particle size etc.). Pyrochlores have also refractory nature. However superconductivity has not yet been observed for any compound with the pyrochlore structure (26). Some of the pyrochlore oxides have nuclear potential applications as neutron absorbers and radioactive waste forms for final disposal. (27) some of these compounds are also good oxide ionic conductors (28) many of the applications involve high

temperatures and an understanding of the physical properties of these compounds such as thermal expansion will be useful.

The electronic behavior of pyrochlore oxides vary widely from insulating through semiconducting to metallic with a few compounds exhibiting semiconductor- to-metal transition. Hence this group of materials can be used in solid state devices. They are used as high permittivity ceramics, thermistors, thick film resistors and switching elements. Stable low resistivity oxide pyrochlores have also been used for screen printing on the dielectrics for capacitor application (29). Stable oxide pyrochlores too have good chances of finding use as electrical heating elements provided suitable compositions are chosen and fabrication and evaluation procedures are standardized.

However it is gratifying to note that oxide pyrochlores find application in wide variety of fields ranging from electronic materials, radioactive disposal to solar energy conversion. Realization of good and stable solid electrolyte through the defect pyrochlores will go a longway in solving the problem of high energy density rechargeable batteries.

In addition some nonferroelectric pyrochlores may serve as technologically useful dielectrics in application such as temperature stable and temperature compensating dielectrics or microwave dielectrics (30) eg - $\text{pb (cd) Bi M SbO}_7$ (where $M=\text{Ti, Zr, Sn}$) pyrochlore compounds in the $\text{Bi}_2\text{O}_3 - \text{ZnO-Nb}_2\text{O}_5$ system and lead - based nonferroelectric pyrochlores ($\text{pb}_{1.83} \text{Mg}_{0.29} \text{Nb}_{1.71} \text{O}_{6.39}$ and $\text{Pb}_2 \text{Fe Wo}_{6.5}$).

1.6 ORIENTATION OF THE PROBLEM

The pyrochlore is one that has received a considerable amount of attention because of its ferroelectric nature (31). Pyrochlore compounds have a wide range of possible applications such as high permittivity ceramics, thermistors, thick film resistors and switching elements. Some nonferroelectric pyrochlores are also used as temperature stable and temperature compensating dielectrics or microwave dielectrics.

The general formula of the oxide pyrochlore can be written as $A_2B_2O_6O'$ with four crystallographically non-equivalent kinds of atom. By interchanging A,B and oxygen atoms and substituting A and B elements, a number of interesting physical properties can be obtained. Thus the electrical nature of the pyrochlore varies from highly insulating through semiconducting to metallic behavior, with a few compounds exhibiting a semiconductor to metal transition. The electrical conductivity of various pyrochlore phases and their solid solutions has been measured (32). The electrical conductivity behavior is also explained generally on the disordered structure of pyrochlore, oxygen vacancies and interstitial positions. In order to understand the conduction mechanism in pyrochlores, we have undertaken the following work.

1. Preparation of pyrochlore by ceramic method using chemical formula $A_2B_2O_7$,
where A = Y, Ce and Sm and B = Ti, and Sn.
2. X-ray diffraction study for confirmation of single phase formation and determination of pyrochlore structure.

3. Electrical properties; DC resistivity and Thermo emf measurements.
4. Dielectric measurements; variation of dielectric constant and loss tangent with frequency, variation of dielectric constant with temperature.

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