

# Magnetic and Dielectric Properties of Perovskite Oxynitrides and A-site Ordered Spinel Oxides

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by

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# Chapter 1

## 1. Introduction:

Among the thousands of complex structures known, only a dozen or so dominate the entire collection of useful ceramics.<sup>1</sup> Among these, the perovskite and spinel oxides take a lion's share in the collection of useful ceramics and thus are noteworthy. In perovskites, the major research, till now has been focused on chemical control of physical properties by cation substitution.<sup>2</sup> The anion substitutions, like nitride substitution for oxygen, on the other hand, are less explored. Transition metal oxynitrides have strong potential for application as photocatalysts, pigments, phosphors, dielectrics and magnetic materials.<sup>3,4</sup> Nitride substitution for oxides will multilaterally influence on the positions of conduction/valence bands, bond covalency, and structure distortion, ion polarizability, which can help in exploring modified physical properties among existing oxidic materials or novel properties in new materials. For instance, the compound BaTaO<sub>2</sub>N, which shows very high dielectric constant, can only be synthesized in combination of oxygen and nitrogen.<sup>5</sup> On the other hand, spinels are very interesting compounds for studying long range magnetic ordering and geometrical frustration. Various interesting phenomena like Verwey transition in Fe<sub>3</sub>O<sub>4</sub>, a heavy-Fermion state in LiV<sub>2</sub>O<sub>4</sub> and a heptamer formation in AlV<sub>2</sub>O<sub>4</sub> have been observed.<sup>6-8</sup> Chromium containing spinels, ACr<sub>2</sub>X<sub>4</sub> (X = O, S, Se) are important class of materials as a frustrated system.<sup>9</sup> Usually, bond alteration has been observed in one dimension system. Yoshihiko Okamoto found both geometric frustration and bond alteration in three dimensional A-site cation ordered LiGaCr<sub>4</sub>O<sub>8</sub> and LiInCr<sub>4</sub>O<sub>8</sub>.<sup>10</sup> Interesting dielectric feature coupled with magnetism recently observed in these systems.

## 1.1 Structure:

Perovskite and spinel oxides constitute of a large variety of crystals structures. The numerous structures and their respective properties these materials have made their study very rich and vast. Thus, a proper understanding of crystal structure and bonding is required to get an insight of the materials. The different structural characterization techniques that are used at present are various and are dependent on the aspect of the researcher. Though X-Ray and neutron diffraction techniques hold an integral part of the characterization but there are other sensitive and important techniques such as electron microscopy, spectroscopic technique etc.

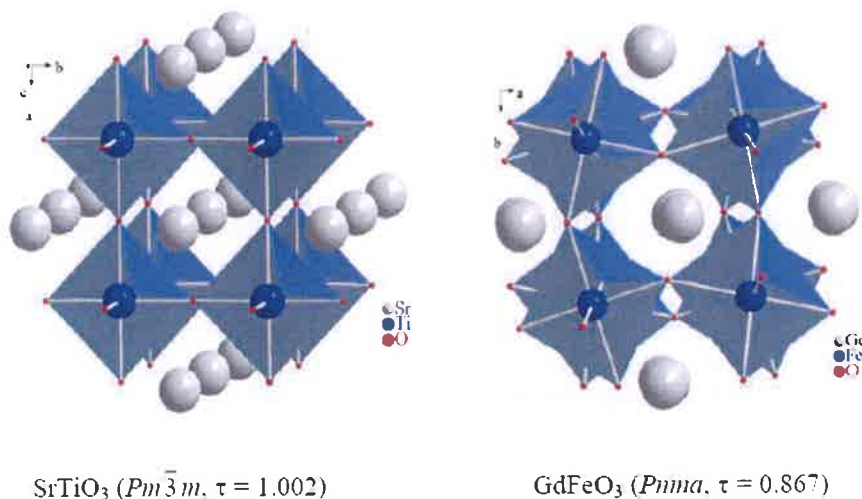
### Perovskite:

A large class of compounds possesses perovskite crystal structures related to the mineral  $\text{CaTiO}_3$ .<sup>11</sup> Crystal structure of cubic  $\text{ABO}_3$  perovskite consists of corner sharing octahedra  $\text{BO}_6$  extended in three dimensions. The A cation occupy the hole formed by eight corner shared  $\text{BO}_6$  octahedra. Thus, A cation has 12 fold co-ordination, and B cation has 6 fold co-ordination. Ideally, perovskite oxide should possess cubic symmetry, but most of the  $\text{ABO}_3$  perovskites exhibit distortion from this symmetry. This distortion often lead to interesting properties, one of which being induction of ferroelectricity ( $\text{BaTiO}_3$ ) in the material.<sup>12</sup> Structural distortion can be understood by Goldschmidt tolerance factor given below.<sup>13</sup>

$$\tau = \frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)}$$

$r_A$ ,  $r_B$  and  $r_O$  are the ionic radii of the cation A and B and oxygen respectively

When  $\tau = 1$ , there will be geometric strain and structure will be cubic. When  $\tau$  differs significantly from 1, cubic structure becomes less stable relative to the lower symmetry ones. When the A cation is too small for the hole provided by  $BO_3$  sub-lattice, it will be in an under-bonded state without lattice distortion. Therefore, perovskites with small  $\tau$  can undergo octahedral tilting such that the overall electrostatic interaction of A is increased.<sup>14,15</sup> From systematic analyses of the octahedral tilting in perovskites, 15 unique tilting systems can be derived with respective space groups.<sup>14-16</sup>

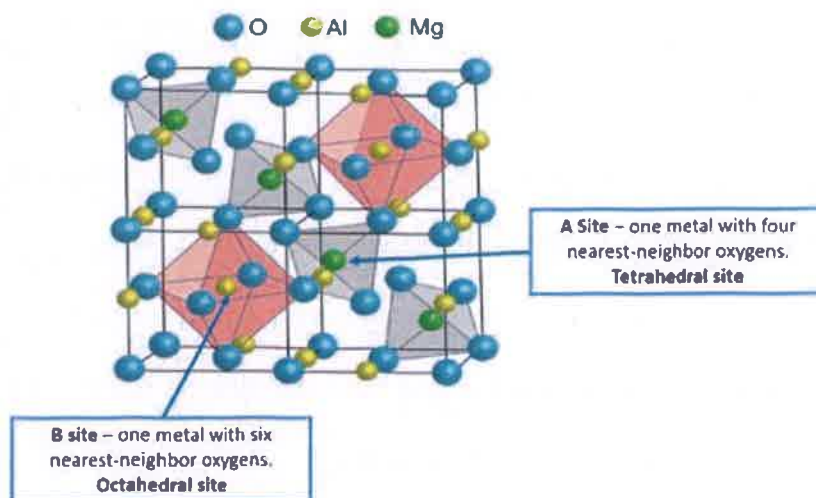


**Figure 1.** Undistorted  $\text{SrTiO}_3$  (left) and distorted  $\text{GdFeO}_3$  structure (right).

Usually, they are found to be distorted towards orthorhombic symmetry; for some extreme situation monoclinic structure also observed e.g.  $\text{GdFeO}_3$  (orthorhombic),  $\text{LaCoO}_3$  (Rhombohedral cubic).<sup>17,18</sup> However, if  $\tau$  differs too much from unity structural distortions cannot be tolerated further, and the perovskite topology collapses. In most of the oxide based perovskite structures,  $\tau$ 's range from  $\sim 0.8$  to 1.1. Generally, people attempt to change in nature of the B cation (size, electronegativity, Jahn-Teller character, etc.), try to manipulate crystal structure and physical property like magnetic, dielectric properties, etc.

## Spinel:

Spinel compounds are well known, diverse and significant in many branches of solid state science. Spinel compounds are named after the mineral spinel ( $\text{MgAl}_2\text{O}_4$ ) and their general formula is  $\text{AB}_2\text{X}_4$ , where A and B are metallic cation and X, represent oxide ( $\text{O}^{2-}$ ) and chalcogenide ( $\text{S}^{2-}$ ,  $\text{Se}^{2-}$ ) ion.<sup>19</sup> The majority of spinel oxides belong to the space group  $Fd3m$ . In a cubic unit cell, 64 tetrahedral sites and 32 octahedral sites are present, But only 8 tetrahedral sites and 16 octahedral sites are occupied by A and B respectively. Spinel structure can be approximated by a cubic close packing of  $\text{O}^{2-}$  ions in which the A and B ions occupy certain interstices. The repeating unit of the conventional unit cell is twice that of the anion lattice. It will be easy to understand the structure if we subdivide a unit cell into 8 octants. Now structure can be described as combination of A and B cubes where A cubes consist of group of  $\text{A}_2\text{O}_4$  (A in 4 coordination) and B cubes a group  $\text{B}_2\text{O}_4$  (B in 6 coordination). In all spinel like substance the anion parameter ( $u$ ) is close to the value of 0.375. Indeed, usually,  $u > 0.375$  resulting oxygen tetrahedron in the A cube is expanded, and the oxygen tetrahedron in B cube is slightly deformed.<sup>20</sup>



**Figure 2.** Crystal structure of normal spinel  $\text{MgAl}_2\text{O}_4$  where  $\text{Mg}^{2+}$  occupy tetrahedral site and  $\text{Al}^{3+}$  occupy octahedral site.

In simple spinels the valency of the cations are  $A = 2+$ ,  $B = 3+$  (e.g.  $MgAl_2O_4$ );  $A = 4+$ ,  $B = 2+$  (e.g.  $MgTi_2O_4$ ) and rarely  $A = 6+$  and  $B = 1+$  (e.g.  $MoLi_2O_4$ ) (reference). In normal spinel, A ions occupy the tetrahedral site, and B ions occupy the octahedral position, but there is another possibility of distribution where half of the B ions occupy tetrahedral position and half of the A ions occupy octahedral position. Later arrangement is denoted as "inverse spinel". In addition to this arrangement intermediate case between normal and an inverse spinel where a fraction of A and B ions are inverted, that is A occupies B positions, and B occupies A positions. They are termed as partial inverse spinels (e.g.  $MgGa_2O_4$ ).<sup>21</sup> Electrostatic potential, cation size, cation valency and crystal field effect are important factors in cation distribution to octahedral or tetrahedral site. Based on Verwey et al. calculation using Ewald's method, it can be said that normal 2-3 spinel is more stable than inverse case, but the inverse 4-2 spinel is more stable than the normal 4-2 spinel.<sup>20</sup>

The Verwey–Heilmann principle states "if neutralization of charge is to be sharply localized around cations, then cations of high valence will have large coordination numbers, so as to be neutralized efficiently by numerous anions in the first coordination shell. So, normal 2-3 spinel, cation occupancy follows the Verwey–Heilmann principle of maximal charge neutralization. According to Pauling first rule cation-anion radius ratio determines the coordination number (C.N.) of the cation, as well as the shape of the coordinated polyhedron of anions. High valence cations generally possess the small radii, indicating lower ratio value which that the high valence cations prefer low coordination numbers.<sup>22</sup> Thus, it explains formation of inverse spinel. In addition, there is a factor called crystal field stabilization (CFSE) which governs in which site (tetrahedral or octahedral) cation will occupy.

## 1.2. Importance of Oxynitrides:

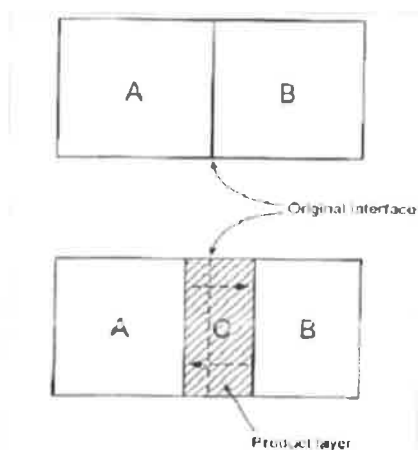
Perovskite oxides have originated various interesting subjects in applied and fundamental areas of solid state chemistry, physics, and materials science. Till now, the chemical control of the physical properties has been done extensively through cation manipulation in oxides while reports on anion substitution are very less. Oxygen and nitrogen show close similarity in electronegativity, coordination numbers and ionic radii. Thus, substitution of nitrogen at oxygen site with retaining the structure is quite a possibility. The resultant compounds, the oxynitrides, are found to be existing in perovskites, also spinels, pyrochlores, baddeleyites, scheelites, apatites and are seen to be showing quite interesting structural and physiochemical properties. When nitrogen is introduced into an oxidic network, it can change the physical property even at minute concentration. Nitrogen is less electronegative than oxygen and this difference between these decreases the band gap of the resultant material compared to the oxide precursor. As a result of the band gap reduction, the optical property changes and photocatalytic activity of semiconductors may be shifted from the UV to the visible light range. Because of the higher polarizability metal, nitrogen bond is more covalent in nature than metal oxygen bond. Larger ionic polarizability of nitride can lead to novel dielectric property in materials. On the other hand, the higher electrical charge of  $N^{3-}$  leads to a larger crystal field splitting in nitride compounds. (3-) charge of nitride may allow deriving new compound. For example, one can think of derivation of  $BaTiO_2N$  from  $BaTiO_3$  [ $BaTiO_3 \rightarrow BaTaO_2N$  ( $Ti^{+4} + O^{-2} \rightarrow Ta^{+5} + N^{-3}$ )]. Xingyi Tan *et al.* experimentally observed weak ferromagnetism in N doped  $BaTiO_3$ .<sup>23</sup> Based on spin-polarized density functional theory calculations, Xingyi Tan *et al.* ascribed the origin of magnetism due to hybridization of the N  $2p$  and Ti  $3d$  states.<sup>24</sup> By N and F co-substitution in  $BaTiO_3$ , Nitesh Kumar *et al.* observed diffused ferroelectric transition<sup>25</sup>



### 1.3. Synthesis:

#### Synthesis of Oxide Materials:

Synthesis of transition metal perovskite and spinel oxides is versatile in terms of concepts and approaches and requires considerable synthetic ingenuity. Deep understanding of principles of thermodynamics, phase equilibrium, kinetics is required to carry out a proper rational synthesis. Most common method in solid state synthesis is ceramic route that includes grinding of precursor materials followed by heating at suitable temperatures in desired atmosphere. Small yet effective modifications are often made like heating in the form of pressed pellet, intermediate grinding and heating. Platinum, silica or alumina boats are used as reaction vessel as they do not interact and



**Figure 3.** Schematic of Solid state diffusion where A and B are precursor materials.

are stable at high temperature. Sometimes the reagents chosen are found volatile or to avoid oxidation of a metal; heating is carried out in evacuated sealed.

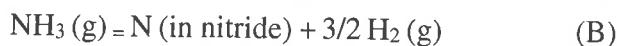
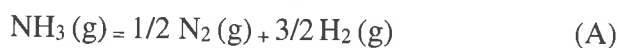
In a typical solid state reaction the, product is formed by thermal diffusion occurs at the interface of two different reactants. At first, nucleation occurs. For nuclei to be stable, they have to several tens of angstroms across (larger than single unit cell). Above a particular size, called critical size of

nuclei, negative free energy of formation of the product, inside the nuclei is greater than the positive surface energy of the nuclei. If the nuclei are too small, the surface area to volume ratio is too large and the nuclei are unstable. Nucleation further leads to agglomeration and increase in the product layer length [figure 2.1.]. For diffusion and nucleation to occur, bonds must be broken, and reform and then only atoms can migrate through interface. This process needs energy barrier. Therefore high temperature necessary to cross the energy barrier and to

proceed the reaction in forward direction. The heating temperature is considered as optimum when at 2/3 of the melting point of the reactants. The diffusion process is usually very slow. Powder of average particle size in the range of nm- $\mu$ m is preferable for proper diffusion to occur and thus, the mixture is ground properly before heating. Area of contact between the particles is an important factor. One of the popular ways to increase contact area and reaction rate by decreasing diffusion length is to make pellet of the powder by compression and then heating it. For an instance,  $\text{ZnCr}_2\text{O}_4$  spinel can be synthesized by mixing  $\text{ZnO}$  and  $\text{Cr}_2\text{O}_3$  and heating at  $1000^\circ\text{C}$  for 24 h in air.<sup>26</sup>

### Synthesis of oxynitride:

According to Darken and Gurry, when metal comes into the contact of  $\text{NH}_3$ , following three reactions are possible:<sup>27,28</sup>



At equilibrium  $\text{NH}_3$  always coexist with  $\text{N}_2$  and  $\text{H}_2$ . But  $\text{N}_2$  is very less reactive towards any oxides and  $\text{N}_2$  need very high temperature (approximately  $1300^\circ\text{C}$ ) to form oxynitride; in some cases beyond the limits of the thermal stability of nitrides. One strategy to encounter this problem is to suppress the dissociation equilibrium of  $\text{NH}_3$  by using high flow rate. Temperature distribution in the furnace should be such that at the center temperature should be high and decrease from center to end. Now suppression of dissociation equilibrium using high flow rate produce unusable  $\text{NH}_3$ , with respect to equilibrium process. If material has tendency to form nitride, then reaction B will proceed in parallel with A. Perovskite oxynitride can be synthesized by mixing of carbonates and

oxides in flowing ammonia. Ruddlesden–Popper (RP) oxynitrides (AO) ( $AMO_2N$ ) ( $A =$  alkaline earth metal and  $M = Nb$ ,  $n=1, 2$ ) have been prepared by using the same method. Low temperature synthesis can be carried out by using nitrogen sources other than  $NH_3$ , based on urea, amide and azide. In the urea method, mixtures of oxides, carbonates and an excess of  $(NH_2)_2CO$  are heated in  $N_2$  gas. The azide and amide routes have been used to prepare oxynitrides of sodium and transition metals as  $Na_3MoO_3N$  from starting material as  $NaN_3$  or  $NaNH_2$  and  $MoO_3$ .<sup>29</sup>

The use of high pressure is expected to be very useful approach in oxynitride synthesis as it suppresses the decomposition to oxides and nitrogen gas. High pressure also assists in stabilization of new phases at moderate temperatures.  $RZrO_2N$  perovskites ( $R = Pr, Nd, Sm$ ) cannot be synthesized in ambient pressure. It can only be synthesized in high pressure–high temperature (1200–1500 °C under 2–3 GPa).<sup>30</sup> Perovskite oxynitride are generally stable in air at room temperature. They may show high thermal stability under  $N_2$  or Ar atmosphere. Most of the oxynitride usually decompose in the presence of oxygen at 300–500 °C to give the corresponding oxides.

## 1.4. Physical properties:

The diverse structures and the variety of properties exhibited by transition perovskite oxynitride and spinels oxides are very much rich in context. External physical parameters like temperature, electric field, magnetic field, mechanical stress, etc. act as external stimuli and have very much impact on the physical properties of the oxides.

### 1.4.1. Magnetic property:

Magnetic moment of a material originates from both orbital angular momenta of the electrons circulating the nucleus and spin of the electrons. A material having all the shell filled with electron usually show negative magnetic susceptibility and the material is defined as diamagnetic.

Interestingly, in N doped  $\text{SrTiO}_3$  and  $\text{BaTiO}_3$ , room temperature ferromagnetism has been observed.<sup>31</sup> This makes the study of oxynitride compounds interesting. In perovskite structure consist of corner sharing octahedra. So, cation – anion – cation angle is  $180^\circ$  which facilitate cation–anion–cation superexchange interaction. In contrast in spinel cation – anion – cation angle is around  $125^\circ$ . Based on geometric and electrostatic potential, Goodenough argued cation – cation is the dominating interaction in spinel oxides.<sup>10,32,33</sup> Study of frustrated magnetism is an important branch magnetism. When antiferromagnetically interacting electrons are arranged in triangular lattice, they cannot satisfy all pairwise interactions simultaneously which make the system frustrated. Cr spinel oxides,  $\text{ACr}_2\text{O}_4$  ( $A = \text{Zn}^{2+}, \text{Mg}^{2+}, \text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ ), exhibit geometrical frustration associated with the pyrochlore geometry of the B-sublattice. It is a Mott insulator with three electron localized in triply degenerate  $t_{2g}$  orbital. Strength of antiferromagnetic are vary significantly with A can be realized from Curie – Weiss temperatures of -390 K, -370 K, -70 K and -32 K for  $A = \text{Zn}^{2+}, \text{Mg}^{2+}, \text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  respectively. Long- range antiferromagnetic ordering of  $\text{ACr}_2\text{O}_4$  take place at 12 K, 12.4 K, 7.8 K and 5.8 K respectively.<sup>10,33</sup> Such low temperature ordering though Curie – Weiss is high indicate presence of magnetic frustration in the systems. Now the question how long-range magnetic order occurring. It is well accepted that a spin–lattice coupling is responsible for magnetic ordering. Distortion of the lattice, in general, makes magnetic coupling non-uniform, which inherently suppresses the geometrical frustration and lifts the spin degeneracy. Such degeneracy lifting can take place cooperatively leading to long-ranged magnetic order, which can be considered as a spin Jahn-Teller transition. Tuning the frustration by applying a magnetic field may help to explore a new phase of the spin–lattice complex in spinel materials. It has been observed that in  $\text{CdCr}_2\text{O}_4$  and  $\text{HgCr}_2\text{O}_4$  the application of a very high magnetic field

changes the initial spin configuration to a collinear three up and one down arrangements for each  $\text{Cr}_4$  tetrahedron thereby leading to the reduction in the magnetic frustration.<sup>33,34</sup>

Y. Okamoto *et al.* has studied magnetic property of  $\text{LiMCr}_4\text{O}_8$  ( $M = \text{Ga}$  and  $\text{Cr}$ ) which contain Both Li and M at A site and the compounds crystalize in  $F\bar{4}3m$ , a subgroup of  $Fd\bar{3}m$ .  $\text{Li}^+$  and  $\text{Ga}^{+3}/\text{In}^{+3}$  are having different ionic radii, which exerts chemical pressures on the  $\text{Cr}_4$  tetrahedra resulting in an alternate arrangement of small and large  $\text{Cr}_4$  tetrahedra in a corner sharing geometry, thereby making a breathing pyrochlore lattice where both Cr-Cr distance alternation and geometrical frustration coexist. For  $M = \text{Ga}$ , Compound they found  $\theta_{\text{cw}}$  (Curie -Weiss temperature) = -658 K while for  $M = \text{In}$ ,  $\theta_{\text{cw}} = -331$  K indicating average interaction is strongly anti ferromagnetic. They observed long-range antiferromagnetic ordering for Ga compound around 13.8 K which while for In compound it is 14 K, evidenced by heat capacity measurement and  $^7\text{Li}$  NMR experiment. Broad maxima for both Ga and In around 45 K and 60 K explained based on short range ordering and spin gap opening. Magnetic transition and structural transition occur simultaneously for Ga compound implying while for In structural transition occur at 15.1 K but magnetic transition occur at 14 K, which imply second order magnetic transition. Recently Rana Saha *et al.* proved the coexistence of two crystallographic phases ( $F\bar{4}3m$  and  $I\bar{4}m2$ ) indicating an incomplete structural phase transformation which is in contrast to  $\text{ZnCr}_2\text{O}_4$  where a complete structural phase transition (cubic to tetragonal) occurs below  $T_N$ . Similar phase transition also found for  $\text{LiInCr}_4\text{O}_8$  from analysis of neutron data .

#### 1.4.2. Dielectric properties:

A dielectric material is a substance that is an electrical insulator while placed in an electric field, electric charges do not flow through the material as they do in a conductor, but only slightly shift

from their average equilibrium positions causing dielectric polarization. Because of dielectric polarization, positive charges are displaced toward the field and negative charges shift in the opposite direction. This gives rise to an internal electric field that reduces the overall field within the dielectric itself. Dielectrics used as capacitors, transducers, infrared imaging, photonic communication, nonvolatile memories, and substrates. For practical use dielectric constant of material should be high. Depending on the specific function of the purposed product, different figures of merit are emphasized in evaluating dielectrics. An important property of a dielectric is the dielectric strength ( $\epsilon_r$ ) - the ability to withstand high voltages without undergoing degradation. Another important factor is dissipating minimal energy in the form of heat, called as dielectric loss. The lower the dielectric loss ( $\tan \delta$ , the proportion of energy lost as heat), the more effective is a dielectric material. In general, high  $\epsilon_r$  is found in oxides of various metals. In addition, it is also important that these properties remain constant over a wide range of temperature. Hence, a material with low temperature coefficient ( $<100$  ppm/K) is also important. The dielectric constant can be obtained by capacitance measurement corresponding energy dissipation can be obtained by loss measurement.

Dielectric constant can be calculated by the following relation:

$$C = \frac{\epsilon_0 \epsilon_r A}{d}$$

Here  $C$  is the capacitance,  $\epsilon_0$  and  $\epsilon_r$  are the permittivity of the vacuum and relative permittivity of the media.

In spite of extensive studies in the past, there is still much to be done to simultaneously achieve high  $\epsilon_r$  ( $>1,000$ ) and low temperature coefficient ( $<100$  ppm/K) in a dielectric material. Perovskite oxynitride are promising candidate for this purpose. In oxynitride substitution of oxide with more

polarizable nitrogen can enhance the dielectric polarization. Besides, less electronegativity of the nitride ion, with respect to the oxide ion increase the covalency of the cation–anion bonds, which may favour the cation displacements through a second-order Jahn–Teller distortion of the  $d^0$  cation. Young et al. reported relative permittivity at room temperature of 4900 and 2900 for SrTaO<sub>2</sub>N and BaTaO<sub>2</sub>N. As both SrTaO<sub>2</sub>N and BaTaO<sub>2</sub>N compound crystalizes in centro symmetric space group local cis ordering of nitrides in the TaO<sub>4</sub>N<sub>2</sub> octahedra together with polar cooperative disorder of N–M–N chains have been suggested. Study of dielectric property coupled with magnetism another area of interest in solid state branch. Mufti observed coupling between the dielectric and magnetic properties at the onset of the magnetic spiral structure ( $T_s$ ) and at the 'lock-in' transition ( $T_f$ ) in MnCr<sub>2</sub>O<sub>4</sub> and CoCr<sub>2</sub>O<sub>4</sub>, and also at the onset of the canted structure ( $T_s$ ) in NiCr<sub>2</sub>O<sub>4</sub>. The strength of the magnetodielectric coupling in this system explained by relative strengths of the spin-orbit coupling in the three materials.<sup>35</sup> Recently Rana Saha et al. observed magneto dielectric effect in A-site ordered LiMCr<sub>4</sub>O<sub>8</sub>.<sup>36</sup>

## 1.5 Bibliography:

- 1 Roy, R. & Muller, O. (Springer-Verlag, New York, 1974).
- 2 Roy, R. Multiple ion substitution in the perovskite lattice. *Journal of the American Ceramic Society* **37**, 581-588 (1954).
- 3 Fuertes, A. Synthesis and properties of functional oxynitrides—from photocatalysts to CMR materials. *Dalton Transactions* **39**, 5942-5948 (2010).
- 4 Xie, R. J. Optical properties of (oxy) nitride materials: a review. *Journal of the American Ceramic Society* **96**, 665-687 (2013).

- 5 Kim, Y.-I., Woodward, P. M., Baba-Kishi, K. Z. & Tai, C. W. Characterization of the structural, optical, and dielectric properties of oxynitride perovskites  $AMO_2N$  (A= Ba, Sr, Ca; M= Ta, Nb). *Chemistry of materials* **16**, 1267-1276 (2004).
- 6 Horibe, Y. *et al.* Erratum: Spontaneous Formation of Vanadium "Molecules" in a Geometrically Frustrated Crystal:  $AlV_2O_4$  [Phys. Rev. Lett. PRLTAO0031-9007 96, 086406 (2006)]. *Physical Review Letters* **96**, 169901 (2006).
- 7 Kondo, S. *et al.*  $LiV_2O_4$ : A heavy Fermion transition metal oxide. *Physical review letters* **78**, 3729 (1997).
- 8 Verwey, E. Electronic conduction of magnetite ( $Fe_3O_4$ ) and its transition point at low temperatures. *Nature* **144**, 327-328 (1939).
- 9 Lee, S.-H. *et al.* Frustrated magnetism and cooperative phase transitions in spinels. *Journal of the Physical Society of Japan* **79**, 011004 (2010).
- 10 Okamoto, Y., Nilsen, G. J., Attfield, J. P. & Hiroi, Z. Breathing pyrochlore lattice realized in A-site ordered spinel oxides  $LiGaCr_4O_8$  and  $LiInCr_4O_8$ . *Physical review letters* **110**, 097203 (2013).
- 11 Buttner, R. & Maslen, E. Electron difference density and structural parameters in  $CaTiO_3$ . *Acta Crystallographica Section B: Structural Science* **48**, 644-649 (1992).
- 12 Schulze, G. F. Jona and G. Shirane, Ferroelectric Crystals. *ZAMM - Journal of Applied Mathematics and Mechanics / Zeitschrift für Angewandte Mathematik und Mechanik* **43**, 512-512, (1963).
- 13 Goldschmidt, V. The laws of crystal chemistry. *Naturwissenschaften* **14**, 477-485 (1926).



- 14 Glazer, A. Simple ways of determining perovskite structures. *Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography* **31**, 756-762 (1975).
- 15 Woodward, P. M. Octahedral tilting in perovskites. I. Geometrical considerations. *Acta Crystallographica Section B: Structural Science* **53**, 32-43 (1997).
- 16 Howard, C. & Stokes, H. Group-theoretical analysis of octahedral tilting in perovskites. *Acta Crystallographica Section B: Structural Science* **54**, 782-789 (1998).
- 17 Kobayashi, Y. *et al.* Structural Phase Transition from Rhombohedral to Cubic in  $\text{LaCoO}_3$ . *Journal of the Physical Society of Japan* **69**, 3468-3469 (2000).
- 18 Coppens, P. t. & Eibschütz, M. Determination of the crystal structure of yttrium orthoferrite and refinement of gadolinium orthoferrite. *Acta Crystallographica* **19**, 524-531 (1965).
- 19 Hosseini, S. Structural, electronic and optical properties of spinel  $\text{MgAl}_2\text{O}_4$  oxide. *physica status solidi (b)* **245**, 2800-2807 (2008).
- 20 Verwey, E. & Heilmann, E. Physical properties and cation arrangement of oxides with spinel structures I. Cation arrangement in spinels. *The Journal of Chemical Physics* **15**, 174-180 (1947).
- 21 Weidenborner, J. E., Stemple, N. & Okaya, Y. Cation distribution and oxygen parameter in magnesium gallate,  $\text{MgGa}_2\text{O}_4$ . *Acta Crystallographica* **20**, 761-764 (1966).
- 22 Pauling, L. *The nature of the chemical bond and the structure of molecules and crystals: an introduction to modern structural chemistry*. Vol. 18 (Cornell university press, 1960).
- 23 Tan, X., Chen, C., Jin, K. & Luo, B. Room-temperature ferromagnetism in nitrogen-doped  $\text{BaTiO}_3$ . *Journal of Alloys and Compounds* **509**, L311-L313 (2011).

- 24 Tan, X., Chen, C., Jin, K. & Gao, Y. Ferromagnetism in dilute magnetic semiconductors through defect engineering: N-doped BaTiO<sub>3</sub>. *Physica B: Condensed Matter* **412**, 91-93 (2013).
- 25 Kumar, N. *et al.* Effect of co-substitution of nitrogen and fluorine in BaTiO<sub>3</sub> on ferroelectricity and other properties. *Journal of Physics: Condensed Matter* **25**, 345901 (2013).
- 26 O'Neill, H. S. C. & Dollase, W. Crystal structures and cation distributions in simple spinels from powder XRD structural refinements: MgCr<sub>2</sub>O<sub>4</sub>, ZnCr<sub>2</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub> and the temperature dependence of the cation distribution in ZnAl<sub>2</sub>O<sub>4</sub>. *Physics and Chemistry of Minerals* **20**, 541-555 (1994).
- 27 Katsura, M. Thermodynamics of nitride and hydride formation by the reaction of metals with flowing NH<sub>3</sub>. *Journal of alloys and compounds* **182**, 91-102 (1992).
- 28 Darken, L. S. & Gurry, R. W. *Physical chemistry of metals*. (McGraw-Hill, 1953).
- 29 Arumugam, N., Hönnerscheid, A. & Jansen, M. A New Oxynitride Compound of Molybdenum, Na<sub>3</sub>MoO<sub>3</sub>N—Synthesis via the Azide Route and Structure. *Zeitschrift für anorganische und allgemeine Chemie* **629**, 939-941 (2003).
- 30 Yang, M. *et al.* Direct solid-state synthesis at high pressures of new mixed-metal oxynitrides: RZrO<sub>2</sub>N (R= Pr, Nd, and Sm). *Inorganic chemistry* **48**, 11498-11500 (2009).
- 31 Liu, C., Xiang, X. & Zu, X. Magnetic properties of Nitrogen doped SrTiO<sub>3</sub>. *Chinese Journal of Physics* **47**, 893-900 (2009).
- 32 Wickham, D. & Goodenough, J. Suggestion concerning magnetic interactions in spinels. *Physical Review* **115**, 1156 (1959).

- 33 Ueda, H., Katori, H. A., Mitamura, H., Goto, T. & Takagi, H. Magnetic-Field Induced Transition to the 1/2 Magnetization Plateau State in the Geometrically Frustrated Magnet  $\text{CdCr}_2\text{O}_4$ . *Physical review letters* **94**, 047202 (2005).
- 34 Ueda, H., Mitamura, H., Goto, T. & Ueda, Y. Successive field-induced transitions in a frustrated antiferromagnet  $\text{HgCr}_2\text{O}_4$ . *Physical Review B* **73**, 094415 (2006).
- 35 Mufti, N., Nugroho, A., Blake, G. & Palstra, T. Magnetodielectric coupling in frustrated spin systems: the spinels  $\text{MCr}_2\text{O}_4$  (M= Mn, Co and Ni). *Journal of Physics: Condensed Matter* **22**, 075902 (2010).
36. Magnetodielectric Effect in A-Site Cation Ordered Chromate Spinels,  $\text{LiMCr}_4\text{O}_8$  (M = Ga and In), Rana Saha, Francois Fauth, Maxim Avdeev, Paula Kayser, Brendan J. Kennedy, and A. Sundaresan, (2016) (submitted).