**CHAPTER III**

**PROPERTIES OF PEROVSKITE MATERIALS**

1. **Introduction**

Perovskite materials with general chemical composition ABO3 are value added materials used for several applications like capacitors, non**-**volatile memories, actuators and sensors,(including biosensing) piezoelectric, ultrasonic and underwater devices, high temperature heating element applications, frequency filters for wireless communications, solar cells, superconductors, photochromic, electrochromic, image storage, switching, surface wave signal processing, as active catalyst for many oxidation reactions including photoelectrochemical water splitting applications and many more. In these device applications perovskites can be employed in bulk form, nano-crystalline state, thin films and in various shapes depending upon the application for which these materials are required.

The properties of perovskite**-**type materials are due to the possibility of sustaining extensive non-stoichiometry in both cation and anion positions and also the distortion of the cation configuration and also the possibility of mixed and variable valence and substitutions in both cationic and anionic positions and the void volume generated in various co-ordinations. It has been stated already that almost all the metallic elements of the periodic table can be accommodated in the perovskite structure. (Refer chapter 1). In ABX3 composition both A and B cations can be substituted as A A’ and B B’ and thus one can generate many complex compounds that can be examined as materials for device fabrication. In practice, it appears that nearly all kinds of devices can be based on perovskite-based materials. The vast and great tunability of the properties of perovskite systems make them amenable for use in any kind of devices either in consumer products or sophisticated gadgets. In fact, the life style in recent years becomes comfortable with the devices like remote control, or self-control of energy in put (in the form of heat) devices or hand held communication devices.

Among the various kinds of perovskites, ABO3 systems find wide application. This is because these systems exhibit the extreme properties like insulating to superconducting and some of them exhibit magnetic property. This wise variation is exemplified in the data given in Table III.1. Similarly, other systems that crystalize in perovskite related structures show variety properties.

Table III.1. Varied Properties of ABO3 Type Perovskites

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| Insulating Applications | Metallic Property | Magnetic behaviour | Superconducting behaviour |
| WO3 | ReO3 | PbCrO3 | SrTiO3 (n type) |
| NaTaO3 | NaWO3 | LaCrO3 | NaxWO3(t) |
| SrTiO3 | KMoO3 | LaMnO3 | KxWO3(t) |
| BaTaO3 | SrNbO3 | LaCoO3 | KxWO3(h) |
| KTaO3 | LaTiO3 | LaFeO3 | RbxWO3(h) |
| LiNbO3 | LaWO3 | CaMnO3 | CsxWO3(h) |
|  |  |  | Many layered perovskites YBa­2Cu3O9-δ |

1. **Catalytic Property**

Normally noble metal catalysts are employed extensively for converting air pollutants (e.g., Pt, Pd, and Rh) and electrocatalysis of oxygen reduction (e.g., Pt) in fuel cells and many other electrochemical cell applications. Inorganic, noble metal–free materials that have high activity, selectivity, and stability are essential to meet global environmental and energy needs. The anxiety to use earth-abundant and cheap catalysts has brought perovskites to the forefront for catalyzing relevant reactions such as the oxidization of toxic hydrocarbons and CO, reduction of NOx for the overall treatment of automotive gas exhaust, and oxygen and hydrogen electrocatalysis to electrochemically enable efficient generation and use of sustainable fuels.

Catalytic studies on the oxidation of CO at metal surfaces have been used to understand the fundamental aspects of catalysis. It is generally believed that CO oxidation on metal surfaces proceeds by the Langmuir-Hinshelwood mechanism, in which both surface-adsorbed CO and dissociative adsorbed O2 react on the surface to form CO2. Therefore the surface-adsorbate binding is critical for observed catalytic activity of perovskites.

In the structure of perovskites, the B-site metal ion binds with six Oxide ions in an octahedral coordination. The transition metal d and oxygen 2p atomic orbitals hybridize, or mix, to form σ orbitals and π orbitals. The concept of crystal field stabilization can be applied to decide the electronic structure of perovskites. At the surface layer, exposed B ions are in coordination environment BO5, with the apical oxide ions. This geometry further breaks symmetry, splitting the eg and t2g states into distinct energy levels.

Specifically, eg-parentage orbitals of the active transition-metal B-site ion in the BO5 coordination capture surface-adsorbate bonding well because of their favorable vertical orientation toward surface-bound intermediates. The occupancy of eg states decides the binding strength of the surface adsorbed species. When CO, NO, or O2 adsorb on the surface B sites end-on, the relevant adsorbate molecules interact with vertically oriented eg-like orbitals, which allows for stronger overlap.

For the adsorption of the CO molecule, a lone-pair σ orbital can donate electrons to the perovskite eg-orbital while the CO π\* orbital receives back electrons from the t2g orbitals. NO and O2 molecules prefer a tilted configuration, allowing their π\* orbital to overlap with the B-site eg orbital. As a result, the eg occupancy decides the strength of adsorbate binding to the surface, with decreased eg filling corresponding with increased adsorbate binding.

The surface interactions of CO, NO, and O2 can be extended to three highly relevant model reactions encompassing clean air and electrochemical energy storage applications—namely, CO and hydrocarbon oxidation, NO oxidation, and oxygen electrocatalysis.

The basis for understanding CO oxidation kinetics on oxides originates from the Langmuir-Hinshelwood scheme for metal surfaces, on oxide surfaces, adsorbed CO on a metal site combines with a neighboring oxide O to form CO2 and a surface O vacancy, resulting in a vacancy-mediated mechanism referred to as the Mars–van Krevelen mechanism. Density functional theory (DFT) calculations for Co-substituted SrTiO3 show that low oxygen vacancy formation can trigger the Mars–van Krevelen–type mechanism for perovskites. Energetically, the reaction kinetics are controlled by the binding strength of oxygen and CO on the surface, which depends on the eg filling of the transition metal ion. Voorhoeve et al. showed that the CO oxidation activity trend for perovskites exhibits a volcano shape as a function of B-site eg filling.

Such observations lend support to subsequent catalyst research centered on Mn- and Co-based perovskites. Metal substitution on the A and B site can alter transition metal oxidation state on the B site, modifying the eg filling and CO oxidation activity. For example, Chan et al. have shown that the CO oxidation activity of LaxSr1–xMnO3 and LaxSr1–xCoO3 increases as nominal eg filling increases from 0.2 to 0.8 from La0.2Sr0.8MnO3 to La0.8Sr0.2MnO3.

Additionally, because CO oxidation serves as a template reaction for oxidation of complex and toxic hydrocarbons, the energetics of surface-carbon and surface-oxygen bonding can similarly dictate the activity of these reactions. A similar volcano-type dependence of propylene (C3H6) and isobutylene (C4H8) oxidation as a function of eg filling was observed, where the maximum activity was approximately centered on eg ≈ 1.

NO oxidation on perovskites has emerged as an area for perovskite catalyst development, because NOx emissions in automotive and industrial exhaust necessitate catalysts that are cheaper and more earth-abundant than commercial platinum catalysts. NO oxidation on perovskites commonly proceeds similarly to CO oxidation on oxides through the vacancy-mediated Mars–van Krevelen mechanism; oxygen and NO first adsorb on the oxide surface, where NO reacts with O to create an O vacancy. The resultant NO2 can then desorb from the surface.

It has been reported in literature that the NOx conversion rate with perovskites such as La0.9Sr0.1CoO3 and La0.9Sr0.1MnO3 was higher than with commercial state-of-the-art Pt catalysts, demonstrating that perovskite chemistries could offer practical alternatives in NOx abatement technologies. These observed trends highlight the immense opportunities in tuning oxide electronic structure to enhance the activity of NO oxidation and, possibly, related nitrogen-based chemical reactions.

Both ORR and OER reaction kinetics are primarily determined by the surface-oxygen binding; in ORR specifically, too weak of an oxygen binding energy results in the first OH-to-OO displacement step becoming rate-limiting, whereas too strong of an oxygen binding energy results in O-to-OH formation being the rate-limiting step. ORR activity on perovskites in basic solution exhibits a volcano trend as a function of eg-like filling of transition metal ions (BO5); low eg filling in LaCrO3 (eg0) can result in B–O2 bonding being too strong, whereas high eg filling in LaFeO3 (eg2) can lead to too weak of an O2 interaction. These effects on ORR activity are well captured over four orders of magnitude, with a peak in perovskite ORR activity at an eg filling of ~1 for LaMnO3, LaCoO3, and LaNiO3, whose activities compare well with those of the state-of-the-art Pt-based catalysts.

Bulk electronic structure of perovskites in a crystalline band theory framework has emerged as a useful perspective for explaining (electro)catalytic activity trends and mechanistic details of (in)stability, because the bulk electronic structure dictates surface adsorption energetics and surface and bulk stability. This relationship between bulk and surface properties allows the use of electronic structure as a guiding principle for catalyst design. The metal-oxygen bonds in perovskites have mixed ionic-covalent character because of the energetic similarity (covalency) and spatial overlap (hybridization) of metal 3d orbitals and O 2p states, which has been shown to influence catalytic activities. Metal 3d bands consist primarily of the σ\* and π\* (eg and ) antibonding states, whereas O 2p states consist mostly of σ, π, and pure nonbonding oxygen states from the coordination chemistry treatment. The DOS of perovskites have been studied extensively by x-ray absorption and emission spectroscopy and DFT studies. The metal electronegativity on the B site, through the choice of transition metal and the design of its oxidation state, can be used to tune the covalency and hybridization of metal 3d and O 2p states. In practice, replacing the B site with a more electronegative atom (e.g., replacing manganese with cobalt) or oxidizing the B site from Bn to Bn+1 lowers the metal 3d states into the O 2p states, which increases the metal-oxygen covalency and hybridization. As the Fermi level moves down toward the O 2p states, the energy penalty to create O vacancy is reduced, allowing for electronic and/or oxygen ion conduction in perovskites, a property that has found applications in gas sensors and SOFCs.

Metal-oxygen covalency has also been useful for understanding mechanistic aspects of OER in aqueous alkaline solutions. Attempts at predicting OER activity from the computed binding energy of oxygenated species (OH, O, and OOH) on the metal site in the conventional mechanism (four electron-proton coupled transfer reactions) have shown limited agreement with activity values.

These observations suggest that a more complex interplay exists between oxide electronic structure and catalytic activity.

 The catalytic properties of perovskite oxides are associated with the oxide ions and hence they can be considered oxygen activated systems for promoting oxidation reactions. These systems can sustain considerable oxygen deficiency and still they are stable. This ability to sustain oxygen vacancies is the main reason to promote oxygen activation reactions. The systems containing Mn, Fe, Co and Cu are mainly used for No decomposition and as auto exhaust environmental catalysts. The ability to undergo oxidation and reduction sequence can also be employed for dispersing noble metals effectively on these systems.

 Even with numerous successes in applications related to electronics and oxygen permeability, however, perovskites have yet to find recognition in environmental catalysis, with few exceptions. Despite this history, the one single reason that can rejuvenate the potential of perovskite-based catalysts in environmental applications is the substantially decreasing sulfur content in fuels. Diesel sulfur content has already been lowered drastically in many parts of the world. This may renew the possibility of using perovskite-based catalysts for vehicle exhaust applications, especially in direct diesel soot oxidation.

A possibility may emerge for catalytic combustion of producer gas generated through biomass gasification. This mixture typically contains very high concentrations of carbon monoxide and hydrogen with traces of sulfur. Photocatalytic water splitting is yet another area where perovskites, heterojunction-based, and other composite materials show good potential for application in the future.

1. **Dielectric Properties**

Dielectric or electrical insulating materials are identified as the materials in which electro**-**static fields can persist for a long time. The dielectric materials offer resistance to the electric current under an applied d.c. voltage. Layers of such substances are inserted into capacitors and the term dielectric refers specifically to this application. The properties inherent to dielectric materials are ferroelectricity, piezoelectricity, electrostriction and pyroelectricity. Typical ferroelectric perovskite compounds are BaTiO3 (temperature dependent and cubic phase is not ferroelectric)

 

Fig. (Top) Chemical and electrochemical reactions namely CO2/CO, N2/NH3, H2O/H2 as a function of electrochemical and absolute scale. (Bottom) Typical chemical and electrochemical reactions on perovskite oxides [Figure reproduced from Hwang et al., Science 358, 751-756 (2017)]

and PdZrO3 and their doped variations. BaTiO3 exhibit high value of dielectric constant due to its anisotropy in its crystal structure.

High dielectric permittivity or ferroelectric materials are of importance as Electro-ceramics for engineering and electronics industry. Perovskites, e.g. titanium or niobium perovskites, BaTiO3 and KNbO3, have been studied in the past. The dielectric constant is the ratio of the permittivity of a substance to the permittivity of free space. A large dielectric constant (*ε*) is based on collective polar displacements of the metal ions with respect to the oxygen sublattice. The phase transition that causes ferroelectricity is usually described by a soft**-**mode model. To tailor the dielectric and mechanical properties several methods have been proposed from the simple BaTiO3 by the solid solution route. These routes take into account the flexibility for chemical manipulation or substitution and submissiveness of the perovskites. One of them is called the relaxor ferroelectric. It is based on a multi**-**element substituted lead titanate (PbTiO3) with the composition A(B’B’’)O3 with a random occupation of the A and B sites by metal cations of different valence states and ionic radii. Relaxor ferroelectrics have large dielectric constant values, a frequency dispersion and variation in dielectric constant as a function of temperature. These effects are due to slow relaxation processes for temperatures above the glass transition. The length scales of fluctuating composition and spontaneous polarization are 2**-**5 nm, i.e. the effects are based on electronic inhomogeneities and the existence of polar nano-regions. The lattice part of the response is considered to be a local softening of transverse-optical phonon branch that prevents the propagation of long-wavelength phonons. It is interesting to note that the fundamental limit, the super-paraelectric state, is still not reached for such small length scales. Generic examples for relaxor ferroelectrics are PZT and PMN. Incipient ferroelectrics or quantum paraelectrics

can be regarded as almost ferroelectric crystals (eg. SrTiO3). High dielectric constant and low dielectric loss make perovskites (eg. BaTiO3) as one of the promising candidates for dynamic random-access memory (DRAM) and tunable microwave device applications

1. **Superconductivity**

Perovskites have been examined for high temperature superconducting behavior from the first report on La-Ba -Cu-O system. Super conductivity is a phenomenon that the material show electrical resistivity tending to or exactly zero and expulsion of magnetic flus fields at certain temperature usually termed as critical temperature denoted as Tc. In cuprate perovskites, the superconductivity is associated with the B site Cu ion and many superconducting oxides have been reported with different A site ions, some of them are Y Ba2Cu3O7, Bi2Sr2Ca2Cu3O10 and HgBa2Ca2Cu3O8+δ which showed superconducting transitions in the range 90-130 K which was the highest Tc at that time. The superconducting behavior among these perovskites are associated with Cu-O layers and also the oxygen non-stoichiometry.

There are other perovskites like LaCoO3 and LaMnO3 which show electrical conductivity similar to that of copper and this behavior is exploited as electrode materials in solid oxide fuel cells.

These discovered superconducting “perovskites” metal**-**oxide ceramics normally contain a ratio of 2 metal atoms to every 3 oxygen atoms. The mechanism of these high temperature superconductors (the so-called Type 2) has not yet been fully understood. The first perovskite oxide namely Ba(PbBi)O3 was introduced with a transition temperature of 13 K in 1973.

1. **Ferroelectricity**

Ferroelectricity is a phenomenon wherein a spontaneous electric polarization occurs in materials by an external electric field. In 1880, Pierre and Paul**-**Jacques Curie discovered the existence of piezoelectricity in various crystals like quartz, and Rochelle salt. Joseph Valasek made systematic study of the magnetic properties of ferromagnetic and the dielectric properties of Rochelle salt. The discovery of ferroelectricity in barium titanate (BaTiO3) and other perovskite**-**based materials was made in 1940s.. A distribution of ferroelectrics (FE) and anti-ferroelectrics (AFE) in the perovskite family were determined by Ven'skev and Zhdanov. The AFEs are found to have a limited range of values of tolerance factor while ferroelectrics span over the whole range of tolerance factor. The ferroelectric materials have dielectric constant larger than those in ordinary dielectrics of about two orders of magnitude. BaTiO3 is a well-known ferroelectric material with relative dielectric constant of over ~2000. There must exist in ferroelectric materials permanent electric dipoles, the origin of which is explained for barium titanate, one of the most common ferroelectrics. The spontaneous polarization is a consequence of the positioning of the B2+, Ti4+ and O2- ions in the unit cell. Ba2+ ions are at the body corners, the O2- anions are at the face centers and the Ti4+ ion is in the octahedral void at the body centre. Only one out of four octahedral voids in the unit cell is occupied. Above 392 K, barium Titanate is a cubic crystal. In this situation, the centres of the negative and the positive charges coincide and there is no spontaneous dipole moment. If the crystal is cooled to below the Curie temperature of 392 K, the Ti4+ ion shifts to one side of the body centre. There is also a displacement of the neighbouring oxygen anions. The crystal transforms from a cubic to tetragonal phase at room temperature. The *c*/*a* ratio of the tetragonal cell is near to 1.012. The centres of the positive and the negative charges do not coincide any longer and local dipoles are created throughout the crystal. The dipoles of neighbouring unit cells are all aligned resulting in a large polarization in the solid. At room temperature, a BaTiO3 crystal exhibits no net polarization, in the absence of an external field, even though the dipoles of adjacent unit cells are aligned. This can be understood by visualizing ferroelectric domains, in the same way as ferromagnetic domain behaviour. The application of the electric field tends to align the domains in the direction of the field and one observes all the phenomena associated with the hysteresis loop such as domain rotation and domain growth Ferroelectric property is used to make sensors, capacitors, memory devices. Tunable capacitors use the non-linear property of ferroelectric material to change the capacitance through tuning. The ferroelectric capacitor has two electrodes sandwiched by a layer of ferroelectric material. The ferroelectric capacitors are tunable and very small in size compared to non**-**tunable dielectric capacitors. The hysteresis of the ferroelectric materials during spontaneous polarization is useful to make memory devices such as ferroelectric RAM and RFID cards. Ferroelectric material is used as the input devices in ultrasound imaging devices, infrared cameras, fire sensors, vibration sensors etc.

1. **Piezoelectricity**

Piezoelectricity is the ability of some materials to generate an electric charge in response to applied mechanical stress. The piezoelectric effect was discovered in 1880

by Pierre Curie and Jacques Curie. They found that if certain crystals were subjected to mechanical strain, they became electrically polarized and the degree of polarization was proportional to the applied strain. The Curies also discovered that these same materials deformed when they were exposed to an electric field. This has become known as the inverse piezoelectric effect. In ferroelectric materials, there is spontaneous alignment of electric dipoles by their mutual interaction, but in piezoelectric materials it requires some external impetus. Therefore, all ferroelectrics are piezoelectric but all piezoelectric are not ferroelectric. An important group of piezoelectric materials are the piezoelectric ceramics, of which PZT is an example. These are polycrystalline ferroelectric materials with the perovskite crystal structure - a tetragonal/rhombohedral structure very close to cubic. They have the general formula A2+B4+O2-3, in which A denotes a large divalent metal ion such as barium or lead, and B denotes a tetravalent metal ion such as titanium or zirconium.

1. **Magnetism and electronic correlations**

Magnetism or orbital (electronic spin) ordering phenomena of various kinds are observed in perovskites with transition metal ions (TMI) that have unfilled 3*d* electron shells. Electronic correlations of such 3*d* states are generally strong, as the ratio of the Coulomb repulsion energy versus the bandwidth is larger compared to other electronic states, *i.e.* they have a more local character and a tendency for insulating states or metal**-**insulator transitions. Hopping and super exchange of these electrons take place via oxygen sites due to the overlap of the respective wave functions. The properties and phase diagrams of a perovskite strongly depend on non-stoichiometries and even more on tilting or distortions of the [BO6] octahedra. Further aspects rely on order/disorder processes of the orbital part of the 3*d* wave function, charge doping and charge/orbital inhomogeneous states that lead to colossal response, *e.g.* to external magnetic fields. Before, however, considering such effects the properties of the system are given by a hierarchy of energies based on the electronic structure, *i.e.* the number of 3*d* electrons, the Hunds Rule coupling, the crystalline electric field or Jahn**-**Teller splitting of the 3*d* electron states and finally due to exchange energies.

1. **Multiferroicity**

Multiferroics symbolize an extraordinary class of materials exhibiting simultaneous ferromagnetic, ferroelectric and ferroelastic ordering. The term multiferroic was first used by H. Schmid in 1994. The distinctiveness of these materials lies on the possibility of simultaneous utilization of both their magnetization and polarization states, a massive potential which would make them outstanding candidates for new generation memory devices and sensors. Many multiferroics are transition metal oxides with perovskite crystal structure, and include rare-earth manganites and ferrites (e.g. HoMn2O5, TbMnO3, LuFe2O4),Ba2CoGe2O7, Ca2CoSi2O7 , TbFe3(BO3)4 , CoCr2O4, FeCr2O4 , MnCr2O4 NdFe3(BO3)4 are the materials which show multiferroicity even at room temperature .Among the various explored multiferroics, bismuth ferrite (BiFeO3), a rhombohedrally distorted perovskite, is receiving attentions since it possesses both ferroelectric order and anti-ferromagnetic order for a widespread temperature range. A ferroelectric material must be an insulator and most of the ferromagnetic materials are generally metals. Hence, the absence of ferromagnetic insulators limits the simultaneous occurrence of ferromagnetic and ferroelectric ordering. However, even when one considers antiferromagnetic systems, there remains a rareness of multiferroics. The conventional requirement for ferroelectricity is a structural distortion from the high symmetry phase that removes the center of inversion and allows an electric polarization. reversal and spatial inversion in ferroelectricity and ferromagnetism. Magnetic ordering of any kind takes place due to the presence of unpaired *d* electrons, here as ferroelectric materials such as common perovskite oxides (ABO3) have a *d0* configuration on the small B cation. If the *d* shell on the small cation is partially occupied, the tendency for it to make a distortion that removes the center of symmetry is strongly suppressed. Thus, magnetoelectric multiferroic materials should have some distortion in the crystal structure with some unpaired electrons in the *d* orbitals. Recently, it has been found that even in the absence of any structural distortion, magnetic spin ordering can produce ferroelectricity. This greatly expands the number of potential ferroic materials.

The achievability of multiferroicity in transition metals doped BaTiO3 has been a new era, both from experimental and theoretical studies . The chemical and physical

properties of these materials can be enhanced through the introduction of extrinsic and intrinsic dopants such as transition metal cations doping, excess oxygen vacancies

 (unpaired electron spin motion) Perovskites with transition metal ions (TM) doped on the B site show an enormous variety of fascinating electrical or magnetic properties. This variety is not only related to their chemical flexibility, but also and to a larger extent related to the complex character that transition metal ions play in certain co-ordinations with oxygen or halides. While magnetism and electronic correlations are usually related to unfilled 3*d* electron shells of the TM, pronounced dielectric properties are connected with filled 3*d* electron shells. Multiferroicity, a coexistence of spontaneous ferroelectric and ferromagnetic moments, is a rare phenomenon due to the small number of low symmetry magnetic point groups that allow a spontaneous polarization. All multiferroic materials can be classified into one of two categories. Type I and type II multiferroics multiferroics. Type I undergo a structural, nonpolar-to-polar phase transition (usually involving the breaking of inversion symmetry) leading to ferroelectricity at high temperatures, whereas the onset of magnetic order occurs below a separate phase transition at lower temperatures. In type II, the staggered (antiferromagnetic) magnetization is the primary order parameter. Magnetic ordering below a given temperature lowers the symmetry group from a nonpolar parent phase to a polar magnetic phase, and magneto-structural coupling to the crystal structure gives rise to an electrically polar state, inducing improper ferroelectricity. In this case, magnetic and ferroelectric order parameters are closely coupled; however, polar non-centrosymmetric magnetic structures tend to result from the complex magnetic ordering of geometrically frustrated states or from competing interactions.

1. **Optical properties**

Perovskites have emerged as a revolutionary class of materials having excellent optical and photoluminescence properties. Merz studied the optical properties of single domain crystals of BaTiO3 at various temperatures. The refractive index of the crystal was nearly a constant value of ~2.4 from 293 to 363 K and reached a maximum value of ~2.46 at 393. Lawless and De Vries also measured the index of refraction of BaTiO3 at 5893 Å in the range 293 to 378 K and above Curie point the index increased 1.3 % to 2.398 and remained constant up to 433K. The single crystal of BaTiO3, was found to transmit from 0.5 μ to 6 μ. Complete absorption was found for wavelengths greater than 11 μ and a feeble absorption band existed near 8 μ. Transmission of better than 70% was measured from 0.55 μ to 5 μ. The index of refraction of these SrTiO3 crystals is 2.407 at 5893 Å, the dielectric constant is 310 and the loss tangent 0.00025. The optical density of CaTiO3 was reported by Linz and Herrington. The absorption characteristics are quite similar to those of SrTiO3 crystals with the exception that the absorptions are shifted to shorter wavelengths. BaTiO3 and SrTiO3 have been considered for high temperature infrared windows. SrTiO3 is considered as an excellent material for use with optically immersed infrared detectors. For many applications the detector-lens combinations are cooled to solid CO2 and liquid N2 temperatures to increase the sensitivity. The electro-optic properties of KTaO3, K(Ta0.65Nb0.35)O3, BaTiO3 and SrTiO3 in the paraelectric phase were measured by Geusic et al. The electro-optic coefficients of these perovskites are nearly constant with temperature and from material to material when the distortions of the optical indicatrix are expressed in terms of the induced polarization. These studies showed that the KTN has a large room temperature electro-optic effect. In the recent years, there has been considerable interest in materials to be used for laser application. The ion Nd3+ appears to be the most popular for introduction into relatively large crystallographic sites. However, except when LaF3 is used as a host, compensating ions are required in these substitutions. Divalent Tm2+ and Dy2+ can be substituted in CaF2 without compensating ions but these divalent rare earth ions are relatively unstable. For crystallographic sites for the Al3+ , Cr3+ proved to be ideal for substitution. Recently, investigations were focused on luminescent properties of rare earth ions doped perovskite-type oxides. Perovskite-type oxides phosphors are very stable and can steadily work in various environments. Moreover, Perovskite type oxides phosphors have been found to be probable candidates in field emission display (FED) and plasma display panel (PDP) devices because they are sufficiently conductive to release electric charges stored on the phosphor particle surfaces. Thus a great deal of perovskite-type oxide phosphors, such as A2+ B4+ O3 (A = Ca, Sr, Ba; B= Ti, Zr, Si, Hf, ) activated by rare earth ions, including Sm3+ , Tm3+ , Pr3+ ,Eu3+, Tb3+ and so forth have been prepared and their luminescent properties were investigated. There are few studies of photoluminescence (PL) in zirconates; especially those with visible emission region. Phosphors of rare earth ions doped perovskite type oxides, such as SrHfO3:Ce and CaTiO3:Pr could be widely used in displays, X-ray phosphors, therefore, many researches focused on luminescent properties of these phosphors recently. Eu3+ is a good activator ion with red or red-orange emission in many hosts, such as borates, niobates and molybdates. Now a days, host BaZrO3 is known as an environmentally friendly photoluminescence (PL) material which emits light in the visible region and can be prepared at low cost. The PL property makes this material promising for applications such as field emission displays, plasma displays, solid state lightning, green photocatalyst and scintillators.

1. **Colossal magnetoresistance (CMR)**

Colossal magnetoresistance (CMR) is a property of some materials that enables them to dramatically change their electrical resistance in the presence of a magnetic field

(mostly manganese-based perovskite oxides). G. H. Jonker and J. H. van Santen discovered CMR in mixed-valence perovskite manganites in the 1950s. The discovery of colossal magnetoresistance (CMR) effect in divalent alkaline-earth ion doped perovskite manganites RE1-*x*AE*x*MnO3, where RE is trivalent rare-earth (La, Pr, Sm, etc.) and AE represents divalent alkaline earth ions (Ca, Sr, Ba), has aroused tremendous interest due to their rich fundamental physics and great potential application in spintronics devices. Depending on the orbital occupancy of the manganese ions and the associated orbital order, different magnetic phases are observed: insulating antiferromagnetic phases with several orbital orders, or a ferromagnetic, metallic, orbitally disordered phases. In these compounds, spins and orbitals are strongly coupled leading to ordering temperatures of similar magnitude for both degrees of freedom. The main spin exchange paths take place via nearly 180˚ TM-O-TM bounds in a three-dimensional lattice. On the other hand, considering only spins, low dimensionality, magnetic frustration, and quantum effects can also lead very peculiar phase diagrams with or, more surprisingly, without magnetic long range order. In fact, in frustrated lattices the degeneracy of the magnetic ground state can be frequently lifted by quantum fluctuations or a second order energy scale. It is generally believed that the underlying origin of CMR effect is closely related to the nature of CMR manganites which are strongly correlated electron systems with interplay among the lattice, spin, charge and orbital degrees of freedom, such as double exchange interaction, Jahn-Taller effect, electronic phase separation as well as charge ordering *etc*., and has been extensively described in some review papers.

Perovskite materials with the same crystal structure as calcium titanate (CaTiO3) exhibit intriguing and extraordinary physical properties that have been extensively studied for both theoretical modeling and practical applications. Inorganic perovskite type oxides are fascinating nanomaterials for wide applications due to its very stable structure, large number of compounds, variety of properties and many practical applications. These solids are currently gaining considerable importance in the field of electronics, geophysics, astrophysics, nuclear, optics, medical, environment,].

Perovskite-phase metal oxides exhibit a variety of interesting physical properties which include ferroelectric, dielectric, pyroelectric, piezoelectric, superconductivity, multiferroic, Proton conducting, Colossal Magnetoresistance (CMR), giant magnetoresistance (GMR), Mixed conduction, catalyst behavior, etc. Depending on these distinct properties. perovskites are useful for several various applications as stated before such as Thin film capacitors, Non-volatile memories, Photo-electrochemical cells, Recording applications Read heads in hard disks, Spintronics devices, Laser applications, For windows to protect from high temperature infrared radiations. High temperature heating applications (Thermal barrier coatings), Frequency filters for wireless communications, Non-volatile memories, Sensors, actuators and transducers, Drug delivery, Catalysts in modern chemical industry, Ultra-sonic imaging, ultrasonics and underwater devices.

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