Volume : 09 | Issue : 08 | August 2024 | e-ISSN : 2456-5040

RECENT SYNTHESIS OF MODIFIED ABO_3 TYPE FERROELECTRIC MATERIALS

Yogeshri S. Kokare[1], **B. M. More**[2]

[1] School of Physical Sciences, Punyashlok Ahilyadevi Holkar Solapur University, Solapur (M.S.) Indian (Corresponding Author)
[2] Brahmdevdada Mane Institute of Technology, Solapur. (M.S.) India.

ABSTRACT

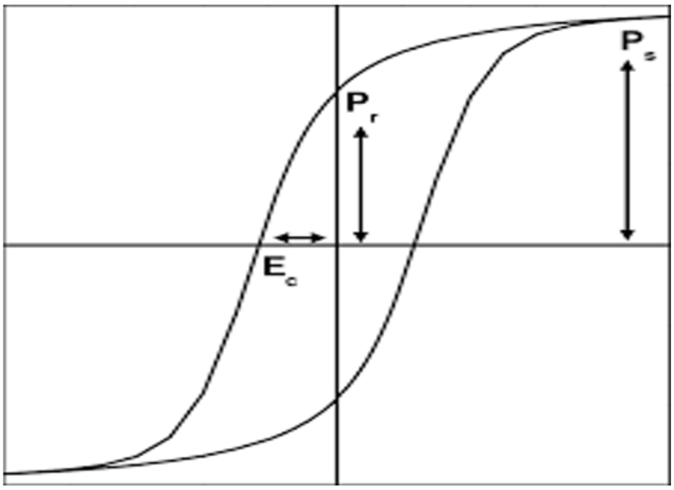
Materials are so important for making human life more healthy, happy and easy. This is the only reasons to look into the newer materials for better future and ferroelectric materials are one of them. There are many types of ferroelectric materials considering their properties but one important way of classification is on the basis of atomic arrangement of atoms in unit cell. These classification is generalized in the form of ABO_3, $A_2B_2O_3$ and so many, where A and B are positions of atoms and O is number of Oxygen atoms. ABO_3 type is one of the type of ferroelectric materials which are widely synthesized and characterized worldwide by many research groups. This review article of one attempt study and take review of work done by various groups.

KEYWORDS: Ferroelectric Materials, Barium Titanate, Piezoelectric Materials, Pyroelectric Materials

1. INTRODUCTION

If we look into the history of discoveries then there are some discoveries which doesn't know its importance at the time of discovery. But in future these discoveries are so great in nature that they received a greatest Nobel prize also, e.g. for a discovery of light ray changes its energy when they scatter's, Scientist C.V. Raman received the Nobel prize in 1930 and the property of light is known as Raman effect. Later the Raman spectroscopy becomes the very valuable tool in material research. Similarly, when Scientist Rongen was performing the experiment in his dark room, few unknown rays were affecting his photographic plats. He was unable to identify these unknown rays, so called it as X-rays. Later the properties of X-rays were understood and the importance of X-rays are so widely spread that it acquires almost every part of human life.

In 1920 Joseph Valasek student of Ph.D. degree working with Prof. William Swann for the developed Seismograph, use to measure the vibration of earthquake. During his work he questioned himself that, does it possible to create an electrical signal with some crystal when they are squeezed? This is the birth of concept of piezoelectricity. The first synthesized piezoelectric crystal was made by a pharmacist named as Pierre Signette in 17th century at a French Seaport, La Rochelle. This piezoelectric crystal is known as Rochelle salt or Signette salt and it is the chemical formula of Potassium, Sodium Tartrate Tetrahydrate ($KNaC_4H_4O_6.4H_2O$). When this Rochelle salt sample was placed in an electric field, he noticed that it results into electric polarization which was quite unusual at that time. Later he tuned up the electric field and measured the polarization. The graph of polarization (P) versus electric field (E) gives the hysteresis loop, which is in figure below.



This unusual observation was presented in a meeting of the American Physical Society gathered at Mary Land in April 1920. The title of the paper was piezoelectric and allied phenomena in Rochelle salt. It is interesting to note that the freshly admitted Ph.D. degree student Valasek did not attended the meeting. At the initial stage Swann and Valasek did not know the cause of hysteresis. But three decades ago, it was known that magnetic moment depends on the magnetic field. Similarly, Valasek discovery has directed the researcher towards the new class of material known as ferroelectric materials and the electric dipole moment or the polarization depends on the change in electric field.

During the Second World War the research on ferroelectric (earlier known as seignetto electric effect) was boosted and the first water insoluble and chemically stable at a room temperature. First Ferroelectric material was invented as a Barium titanate ($BaTiO_3$). Barium titanate has much better Electrical and Mechanical properties than the Rochelle Salt. Later in late 1950 hundreds of various Oxide base ferroelectric materials have been synthesized in the various laboratories. All these materials belong to about 30 different structural types. In the late 1960 the materials having the hysteresis loop are classified in three types such as ferroelectric, ferromagnetic and ferro elastic.

2. IMPORTANCE OF FERROELECTRIC MATERIALS

About a century after the discovery of ferroelectricity more than 20000 research papers have been published, giving the details of application from macroscopic scale to nanoscale. It has also been used in Biology, e.g. for the preparation of wall of aortic blood vessels in pigs and to make the sensor like human multifunctional sensory system. The ferroelectrics are become so important due to its wide range of applications. As the ferroelectric material has very high dielectric constant, which means these materials are able to store large amount of energy, so the high energy density capacitor and compact batteries are being fabricated. Ferroelectric material has very high electrical resistance due to which it becomes the insulator, however Physicist Alex Muller invented the new ferroelectric material with zero resistance in mid of 1980 and this has become high temperature superconducting material. The ferroelectric material which has sufficiently high Pyroelectric coefficient are used in cameras that can see the object at night. Such cameras are used in night vision devices to observe the animal's night behavior in the forest. These types of cameras are also used in medicine and security.

In medical science the ultrasound machineries used for observation of fetus are based on the property of Piezoelectricity. This material generates an electrical voltage when they put under pressure by an object and this voltage can be used to create an image of object. Thus, the image of unborn babies is useful to check how they are growing inside the mother's womb.

Above principle of piezoelectricity is widely used in understanding the topography of Ocean floor. In 2014 there was an evil incidence happened in the Southern India Ocean. An airbus of Malaysian airlines MH370 on the way from Kulalumpur to Beijing was disappeared. The underwater acoustic device was successfully used to locate the disappeared airbus.

When we apply an electric field, the material changes in its dimensions along one or more axis depending upon its basic crystal structure. Though these change in size is few picometres per volt, it plays a very important role in the technique of Atomic Force Microscopy (AFM) used for detection of individual atoms in the materials. In 1986 Gard Binning and Henrich Rohrer own the Nobel Prize for their Scanning Tunneling Microscopy (STM) wherein the ferroelectrics materials are used. The ferroelectric material like Lead Magnesium Niobate or Lead Titanate was the part of a device that NASA has used in Hubble space telescope for correcting the mirror.

In the medical field, there are many devices in which a very small energies are required, for example battery power for mechanical pacemakers to keep horse pumping requires the recharging of batteries. To recharge or to replace the battery only way was to operate the patient but now a days such batteries are recharged by the voltage generated in ferroelectric material due to the thrust of heartbeat.

3. FUTURE OF FERROELECTRIC MATERIALS

The most important advantages of these materials are that it produces an electric field, due to which it acquires an ability to store the data without power source. Along with this it has several other benefits such as high writing speed, high storage density and low operating power. Prof. Andrew Wee from department of Physics under and NUS faculty of science, China. with his other collaborators discovered a material known as 2D Black Phosphorus like Bismuth (BP-Bi) which Demonstrate the ferroelectric properties. The detailed findings of this novel ferroelectric material were published in Nature on 5 April 2023. Through the experimental methods they observed a new form of ferroelectricity within the structure of BP-Bi. This form of ferroelectricity will have implication for future Quantum electronic devices. According to Professor Wee single element ferroelectricity in BP-Bi would open a new perspective to study and design of Novel ferroelectric materials in the future

In the transistor technology like Ferroelectric Field Effect Transistor (FFETs) is also important future semiconducting device made up from ferroelectric material. Recently Scientist S. Kumar has shown that the material surfaces like ferroelectric or piezoelectric surfaces are used as a antibacterial surfaces. Memory devices made up on the ferroelectric material are more compatible with today's Silicon computer. So, this is one more wing of future of ferroelectric material.

Depending upon the crystal structure and the atomic arrangement in a unit cell the ferroelectric materials are classified in different general ways, e.g. ABO_3, $A_2B_2O_3$, -------- etc. The present review article is only devoted to the ABO_3 type of ferroelectric materials.

4. ABO_3 TYPE FERROELECTRIC MATERIALS

Ferroelectric perovskites are one of the most promising functional materials due to the pyroelectric and piezoelectric effect. In the practical applications of ferroelectric perovskites, it is often necessary to meet the requirements of multiple properties. In this work, a metaproperties machine learning strategy was proposed to accelerate the discovery and design of new ferroelectric ABO_3 – type perovskites.

4.1 Historical Survey of ABO_3 type materials:

$LaNiO_3$ type materials have, to date, not received detailed analysis that specifically considers the benefits and challenges of these particular systems. Barium titanate is the first ferroelectric ceramics and a good candidate for a variety of applications due to its excellent dielectric, ferroelectric and piezoelectric properties. Barium titanate is a member of a large family of compounds with the general formula ABO_3 which is called perovskite. (1) Ferroelectric ceramics were born in the early 1940's with the discovery of the phenomenon of ferroelectricity as the source of the unusually high dielectric constant in ceramic, e.g. Barium titanate capacitors. Since that time they have been the heart and soul of several multibillion dollar industries, ranging from high dielectric constant capacitors to later developments in piezoelectric transducers, positive temperature coefficient devices, and electrooptic light valves. (2)

To date the highest bulk Lithium ion- conducting solid electrolyte is the perovskite, (ABO_3) type. Lithium Lanthanum Titanate (LLT) $Li_{3x}La_{(2/3)-}X_{(1/3)-2x}TiO_3$($0 < x < 0.16$) and its related structure materials. (3) Survey of few ABO_3 type ferroelectric material are given below.

4.1.1 $BaTiO_3$ Materials: Barium titanate is one of the most important ferroelectrics. It can be synthesized from the reaction of a mixture of $BaCO_3$ and TiO_2 sintered at 1250°C. The product is powdered and then worked by means of common ceramic techniques. This material shows a permittivity maximum at around 130°C and the permittivity values change largely in the temperature range of 0 – 120°C. (4) Barium titanate ($BaTiO_3$) ceramics were discovered independently during World War II in three countries: In the US by Ogawa in 1944, and in Russia by Vul in 1944. (5) It should be pointed out that the original discovery of $BaTiO_3$ was not related to its piezoelectric properties.

Barium titanate ($BaTiO_3$) which is a ferroelectric with a Curie temperature of 120^0C is known to become electrically conductive when 'polycrystalline' samples are doped with rare-earth ions. Multilayer actuators consisting of alternating layers of undoped resistive $BaTiO_3$ and the $BaTiO_3$ based semiconducting composition doped with 0.15at % La have been fabricated by the tape – casting process. The main advantage of using these materials is that atomic diffusion across the interface between layers are compositionally similar, resulting in a well-defined interface between the actuator and electrode layers. (6)

The dielectric and piezoelectric properties of ferroelectric ceramic $BaTiO_3$ can be affected by its own stoichiometry, microstructure and by dopants entering into the A or B site in solid solution. Modified ceramic $BaTiO_3$ with dopants such as Pb or Ca ions have been developed to stabilize the tetragonal phase over a wider temperature range and have been used as commercial piezoelectric materials. (7)

4.1.2 $PbTiO_3$ Materials: Lead titanate ($PbTiO_3$) is an inorganic compound and it is insoluble in water. At high temperature Lead titanate adopts a cubic perovskite structure. At 750 K the material undergoes a second order phase transition to a tetragonal perovskite structure which exhibits ferroelectricity. Lead titanate is toxic, like other lead compounds. It irritates skin, mucous membranes and eyes. It may also cause harm to unborn babies and might have effects on fertility. Pure $PbTiO_3$ is not commercially used as a piezoelectric material due to practical problems of making a sintered pellet or single crystal. $PbTiO_3$ has more tetragonal distortion than $BaTiO_3$. In tetragonal $PbTiO_3$ phase, the position of the ions may be described by keeping the Pb ion at the origin (0, 0, 0), Ti ions (0.5, 0.5, 0.5+dz_1), O1(0.5, 0.5, dz_2), and O2(0.5, 0, 0.5+dz_3) for Rietveld refinement.

The most relevant difference between $PbTiO_3$ and other perovskite ferroelectrics is a low anisotropy of permittivity and relatively low shear piezoelectric coefficient in $PbTiO_3$.

$PbTiO_3$ has high Curie temperature, high pyroelectric coefficient, low dielectric constant and high spontaneous polarization. $PbTiO_3$ samples were prepared by solid state reaction processing using high purity oxides and carbonates as the starting materials, involving several steps such as mixing, wet grinding, calcination and sintering along with intermediate grinding at each stage. The experimental results on electrical properties indicate that the material exhibits conduction due to bulk and grain boundary effects at high temperature.

$PbTiO_3$ along with $BiScO_3$ was also studied from last two decades for device application like high temperature transducer, sensors and actuators. This $BiScO_3$ - $PbTiO_3$ (BS-PT) composite has sufficiently high Cirie temperature and large piezoelectric constant also. The details review of this material is given by Zhiyong Zhou et al (8)

4.1.3 $SrTiO_3$ Materials: Strontium titanate is an oxide of Strontium and Titanium with the chemical formula $SrTiO_3$. At room temperature it is a centrosymmetric paraelectric material with a perovskite structure. $SrTiO_3$ has an indirect band gap of 3.25 eV and a direct band gap of 3.75eV in the typical range of semiconductors. Synthetic Strontium Titanate has a very large dielectric constant (300) at room temperature and low electric field. It has specific resistivity of over $10^9\Omega$ cm for very pure crystals. It is also used in high voltage capacitors. Strontium Titanate is both much denser (specific gravity 4.88 for natural, 5.13 for synthetic) and much softer (Mohs hardness 5.5for synthetic, 6 – 6.5 for natural) than diamond. At temperatures lower than 105 K, its cubic structure transforms to tetragonal. Its monocrystals can be used as optical windows and high-quality sputter deposition targets.

Now a days most important issue in the field of materials research is energy harvesting and storages. This has very urgent need of society and which requires immediate attention of Researchers of this field. Fabrication of supercapacitors are one of the important step in this direction. Ultimately materials used for such supercapacitors are important to study. The very recent study has shown that the transition metal oxides those having the perovskite structure becoming the good candidate for energy storage device. (9, 10, 11) $SrTiO_3$ nanoparticles is also one of most useful material and this material is widely studied by (12) They synthesized the material by sol-gel method and found typical ABO_3 type structure with average crystalline size of 22 nanometer (nm). The electrode gives maximum specific capacitance of 208.47 Fg^{-1} at the scan rate of 1 mV_s^{-1}. Large conductivity and sufficient high cycling stability nearly 1500 cycles are observed. This is also cost, nonhazardous and gives greater advantages over other ABO_3 type material.

4.1.4 $CaTiO_3$ Materials: Calcium /titanate Powder is a basic inorganic dielectric material with excellent dielectric, temperature, mechanical and optical properties. Calcium titanate Powder is a ceramic material with a main crystal phase. It has a cubic system and perovskite structure. It can be used to make high-frequency temperature compensation capacitors etc. $CaTiO_3$ powders were synthesized using both a polymeric precursor method (CT_{ref}) and a microwave – assisted hydrothermal (CT_{HTMW}) method in order to compare the chemical and physical properties of the perovskite – based material as a function of the synthesis method. Their crystallization and optical properties were carefully investigated and compared to powders synthesized by means of the polymeric precursor method. Using X-ray diffraction, Raman spectra, ICP-AES spectroscopy and FE-SEM microscopy, it was verified that the HTMW process is an efficient method to obtain $CaTiO_3$ single – phase compounds in a short processing time at low temperature. (13) Calcium titanate ($CaTiO_3$) a multi-metal oxide has received extensive attention in recent years, due to its unique structural features, high chemical stability, optimum band edge positions, strong catalytic activity, inexpensiveness, low toxicity and easy synthesis. Among titanium-based perovskite type oxide photocatalysts, $CaTiO_3$ 'the founding father' of the perovskite family has attracted increasing attention from researchers. $CaTiO_3$ is a n-type chemically stable semiconductor with a wide bandgap of 3 – 3.5 eV belonging to the space group Pm- 3m, with Ca ions placed at the corners (1/2, ½, ½), Ti at the body centered (0,0,0) and oxygen at face centered (1/2,0,0; 0,1/3,0; 0,0,1/2) $CaTiO_3$ has many applications, such as light-emitting diodes(LEDs), phosphors, solar cells, capacitors, biodiesel production, drug delivery, chemical/biological sensors, and catalysts. (14)

4.1.5 $MgTiO_3$ Materials: Magnesium titanate ($MgTiO_3$) has been successfully synthesized via the sonochemical method by using TiO_2(P25) and Magnesium nitrate $(MgNo_3)_2.6H_2O$ as precursors without any additional phases such as $MgTi_2O_5$ and Mg_2TiO_4.The synthesized nanoparticles were well characterized by optical methods using UV- VIS diffuse reflectance spectroscopy (DRS) and photoluminescence spectroscopy (PL). The morphology of $MgTiO_3$ nanoparticles is irregular in shape with serious agglomerations were confirmed through SEM analysis. XRD confirms crystal structure and phase purity of $MgTiO_3$ nanoparticles calcinated at 700^0 C for 2 hours. The calculated band gap energy of $MgTiO_3$ nanoparticles has been found to be 3.05 eV. (15) Synthesis of high grade $MgTiO_3$ with low cost and superior dielectric properties is of great importance due to its applications in various technologies including global positioning system, radar, direct broadcasting satellites, telecommunication industry, integrated optical devices and optical waveguides [[1], [2], [3], [4]]. $MgTiO_3$ is usually prepared by conventional mixed oxide route involving milling of oxide powders followed by calcination and sintering. In order to investigate the influence of raw materials on properties of magnesium titanate based compounds, solid solutions of $MgTiO_3$ and $Mg(Ti_{0.95}Sn_{0.05})O_3$ were prepared using two different starting materials MgO and $Mg(OH)_2$. Pure $MgTiO_3$ and Mg $(Ti_{0.95}Sn_{0.05})$ O_3 ceramics were successfully synthesized by conventional solid state mixed oxide route at a sintering temperature of 1400°C using Mg $(OH)_2$ as one of the raw material. The formation of single-phase compounds was confirmed by X-ray diffraction and microstructure identification was performed by scanning electron microscopy (SEM). (16)

4.1.6 $NaTiO_3$ Materials: $NaTiO_3$ is (Cubic) Perovskite structured and crystallizes in the cubic Pm-3m space group. The structure is three-dimensional. Na is bonded to twelve equivalent O atoms to form NaO_{12} cuboctahedra that share corners with twelve equivalent NaO_{12} cuboctahedra, faces with six equivalent NaO_{12} cuboctahedra, and faces with eight equivalent TiO_6 octahedra. (17) The main structure of $NaTiO_3$ catalyst consists of a 4A element (Ti) and a 5A element (Nb, Ta) (11,12). $NaTiO_3$ is excellent activity in the photocatalyst water decomposition without any cocatalyst or additive. Among the metals loaded on the perovskite-type oxides, excellent catalytic activity could be achieved upon Ni and Ru loading. (18)

4.1.7 $LiNaO_3$ Materials: $LiNO_3$ is recognized as an effective additive, forming a dense, nitrogen-rich solid electrolyte interphase (SEI) on lithium's surface, which safeguards it from parasitic reactions. However, its use is limited due to the poor solubility in carbonate electrolytes. Herein, we introduce a bilayer separator designed to release $LiNO_3$ sustainably. (19) The dissolution of $LiNO_3$ in carbonate electrolytes is achieved by introducing pyridine as a new carrier solvent owing to its higher Gutmann donor number than NO_3^-. The Li metal anode in $LiNO_3$-containing carbonate electrolyte demonstrates a much enhanced reversibility due to the preferential reduction of $LiNO_3$ and the formation of an inorganic-rich SEI. (20)

4.2 Importance of ABO_3 type materials:

ABO_3 type oxides form an important class of materials of great technical value in several device applications. ABO_3 type oxides display a wide spectrum of physical properties of technical importance such as ferroelectricity, antiferroelectricity, piezoelectricity, insulating behaviors, semi conductivity, ferromagnetism, antiferromagnetism etc. The ferroelectric properties are mostly controlled by the relative sizes of the ions. The electrical and magnetic properties are mainly dependent on the electronic configuration of the ions. Dopants and substituents have a profound influence on the properties of the ABO_3 oxides. (21)

ABO_3 type compound mainly contains perovskite structure material and ilmenite structure material. It is widely used in energy storage device (22) solar battery (23) ceramic capacitors (24), because of its physical and chemical properties such as ferroelectricity (25), dielectric constant (26) thermoelectricity etc. (27) With the increasing application of electronic devices in engineering, dielectric materials have begun to play a key role in industries such as automobiles, shipping and aerospace.

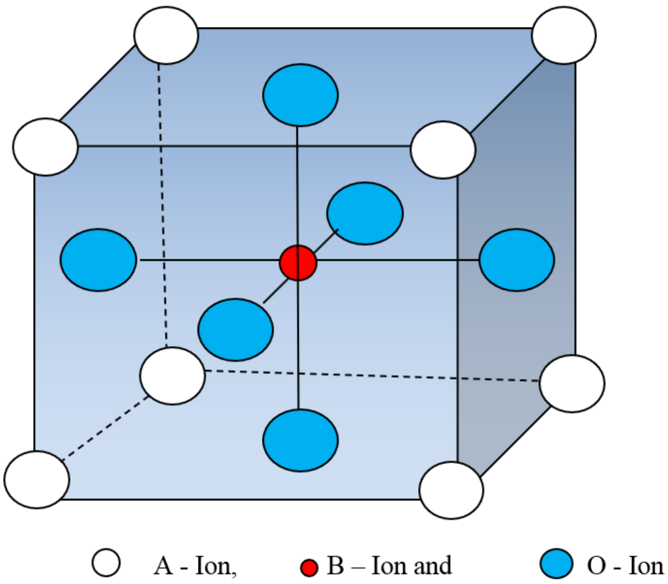
Perovskite oxides with formula ABO_3 are a very important class of functional materials that exhibit a range of stoichiometries and crystal structures. Because of the structural features, they could accommodate around 90% of the metallic natural elements of the periodic table that stand solely or partially at the A and/or B positions without destroying the matrix structure, offering a way of correlating solid-state chemistry to catalytic properties. (28)

Perovskite and perovskite related materials are important crystal structure also due to their diverse physical/chemistry properties (29) over a wide temperature range, e.g. perovskite ceramics with ferroelectric and/or piezoelectric properties, such as BaTiO3 and $Pb(ZrTi)O_3$ plays a dominant role in the electro ceramics industry. Other industry interests of perovskites are: colossal magnetoresistance electrooptical modulator [(PbLa)(ZrTi)O_3 $BaTiO_3$], optical switch ($LiNbO_3$), battery material ($Li_{0.5-x}La_xTiO_3$) etc. (30)

4.3 Future of ABO_3 type materials:

ABO_3 type perovskite oxides have great potential for application due to their rich and diverse chemical and physical properties. Owing to the continuous progress of materials engineering, significant achievements in perovskite growth and implementation of various device demonstrations have been made (31) Perovskite type oxides with general stoichiometry ABO_3 constitute a rich materials playground for application as resistive type gas sensing layers. Immense interest is triggered by among other factors, stability of abundant elements (≈ 90% in the periodic table) in this stoichiometry stability upon doping. Moreover, their capability to host cationic and abundant oxygen vacancies renders them with excellent electrical and redox properties and synergistic functions that influence their performance. (32) On the basis of the bond-valence model (BVM) and structure-map technology, the structural stability and formability of ABO_3 type perovskite compounds were investigated in 376 ABO_3 type compounds. A new criterion of structural stability for ABO_3 type perovskite compounds has been established by the bond-valence calculated tolerance factors which are in the range 0.822 – 1.139. The future work may enable novel perovskite and perovskite related compounds to be explored by screening all the possible elemental combinations in future crystal engineering. (33)

5. MODIFICATION IN ABO3 TYPE OF MATERIALS



The ferroelectric material of the type abo3 is schematically shown above. In this case 'A' is divalent atom and 'B' is a tetravalent atom. Atom 'A' is at the lattice point of a unit cell while the oxygen atom is at a face centered and atom 'B' is at the body centered.

Looking to the Insite of unit cell, it is clear that the interatomic distance between A and B atom causes the change in properties of the material. Thus, to change this interatomic distance, the ways is to either increase or decrease the size of A or/and B site ions. Valency is important factor to be considered to get stable compound and ionic Radii of parent and dopant atoms should be relatively closer to each other. This closer ionic Radii of parent and dopant atoms decides the easiness of product process.

Further B-site atom is body centered and A is at lattice point. The slight distortion of ionic radii of B site ion causes the change in ferroelectric properties. The increased or decreased interatomic distance changes the mode of vibration in unit cell. So, one can easily calculate or whether the sterling mode is changed or bending mode is changed.

5.1 A- Site Modified Materials:

Rongzi Hong Feng Gao et.al. studied the fabrication of $(BaNa)_{0.5}TiO_3$ – $BaTiO_3$ textured ceramic by tape casting. With the plate like $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ (BINNS) particles as template. They concluded that with increasing sintering temperature the density and the size of the grains also increases. The texture fraction has a maximum value (0.61) at the sintering temperature of 1225^0 and the optimal content of template is 20 wt%. (34) Lead free piezoelectric (100-x) $Na_{1/2}Bi_{1/2}TiO_{3-x}BaTiO_3$ solid solution ceramics are investigated by Raman Spectroscopy and X-ray diffraction over a composition range 0 < x > 10g by Dibyaranjan ROUT, Kyoung – Seok MOON et.al. The rhombohedral – tetragonal morphotropic phase boundary in NBT – xBT solid solution ceramics was investigated by Raman spectroscopy in this study. (35) Piezoelectric and ferroelectric properties of Bismuth Sodium Titanate $(B_{1/2}Na_{1/2})TiO_3$(BNT) based solid solution, that is $(Bi_{1/2}Na_{1/2})_{(1-x)}$ $(Pb_{ba}B_{ab})_xTiO_3$ (a + b = 1) are studied from the viewpoint of a new group of Lead free or low Lead content piezoelectric ceramics with a rhombohedral (F_α) tetragonal (F_β) morphotropic phase diagrams were obtained by evaluating the x-ray diffraction patterns, Temperature characteristics, dielectric properties and D-E hysteresis loops and it was found that the morphotropic phase boundary (MPB) exists in the region where the concentration of $[Bi_{1/2}Na_{1/2}]TiO_3$ (BNT) is high. In each mode of ceramic, the piezoelectricity is the highest when the composition is close to MPB. Coercive field of BNPB ceramics is relatively high (20-25 kV/cm) and is regarded as a stable material. The mechanical strength becomes higher as the replaced amount of $BaTiO_3$ increases. (36)

5.2 B-Site Modified Materials:

By Tadashi Takenaka et.al. they also studied a Bismuth Sodium Titanate $(BiNa)_{1/2}TiO_3$(BNT) based solid solutions (1-x) $(BiNa)_{1/2}Ti_3$ + x(a. $SrTiO_3$ + b. PbTiO-3 + c. $CaTiO_3$) (a + b + c = 1) for their dielectric piezoelectric and pyroelectric properties. X-ray diffraction data at room temperature show a rhombohedral (F_α) tetragonal (F_β) phase boundary) MPB) exists at x = 0.13. (37)

6. MODIFICATIONS IN ABO_3 TYPE MATERIALS DURING LAST DECADE

In 2011 Soon Jong Jeong et.al. synthesized the material $Bi_{0.5}Na_{0.5}TiO_3$ and studied the deformation behaviour due to the induced electric field. They found the hysteresis loop of polarization versus electric field. Similarly the same group has studied the above material with $BiAlO_3$ composite. (38) Andre Prado–espinose et.al. studied the piezoelectric activity of $BiNaTiO_3$ with $BaTiO_3$ composites. Using the Raman spectroscopy they found out a relationship between a phase transition at room temperature and the functional properties (39) The same material was synthesized by K. Seevakan and S. Bharanidharan to identify the morphotropic phase of boundary region. He used the method of confocal Raman Microscopy (40). The conventional solid state ceramic synthesis was applied to synthesize $Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}Ti_{0.96}Sn_{0.04}O_3$ ceramics by Nguyen Truong Tho and Le Dai Vuong in 2020. The effect of sintering temperature on the dielectric and ferroelectric properties has been studied by braying the sintering temperature from 1000°C to 1200°C. They have been used sintering time of 2 hr. The density is found to be increased from 4.89 gm/cm^3 for 1000°C and it becomes larger as 5.88 gm/cm3 for 1100°C. Further the density was observed to be decreasing which indicates that the sintering temperature for this case was optimized to be 100°C. As for as the dielectric constant is concern it becomes higher for 100°C and expectedly dielectric loss becomes low. However, the particle size becomes 1µm for 1100°C. P-E hysteresis loop was also studied. The compilation of few physical properties for the ferroelectric ceramics investigated by different groups ae given in the table below. (41)

Table: Table shows the sintering temperature, maximum relativity, coercive field and remnant polarization for various ceramics synthesized by research groups.

Ceramics	Ts (°C)	ε max	Ec (kv/cm)	Pr (µC/cm^2)	Ref
$0.97Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO_{3}$- $0.03(Ba_{0.7}0Sr_{0.30})O_3$	1100	4318	20.7	12.7	42
$0.97Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO_{3}$- $0.03(Ba_{0.70}Sr_{0.30})O_3$	1125	4982	17.85	16.7	42
$Bi_{0.5}(Na_{0.84}K_{0.16})_{0.5}TiO_3$	1125	4930	42.4	29.3	43
$0.97Bi_{0.5}(Na_{0.84}K_{0.16})_{0.5}TiO_{3}$- $0.03Ba(Nb_{0.01}Ti_{0.99})O_3$	1125	5350	16.7	23	43
$Bi_{0.5}(Na_{0.5}K_{0.5})_{0.5}TiO_3$	1150	3500	18.0	23.0	44
$0.98Bi_{0.5}(Na_{0.5}K_{0.5})_{0.5}TiO_{3}$-					
$0.02Ba_{0.9}Ca_{0.1}Ti_{0.9}Zr_{0.1}O_3$	1150	3500	18.0	23.0	44
$Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}(Ti_{0.96}Sn_{0.04})O_3$	1100	4335	14.3	9.5	45

As sintering temperature is a very crucial issue to optimize the high performing properties, the sintering time is also to be taken care of. J. Camargo et.al. studied the influence of sintering time on ferroelectric properties of $Bi_{0.5}(Na_{0.8}K_{0.2})TiO_3$ ceramics. This group of scientists has studied the ferroelectric properties of above material sintered for the time from 2hr. to 8hr. As the time of sintering is increasing, they found that the material density is also increasing. Similarly, the ferroelectric properties are also enhanced. So, the optimum sintering temperature and maximum sintering time is the key factor for enhanced ferroelectric properties. (46)

7. CONCLUSION

The investigations in material synthesis and their characterization in ABO_3 type perovskite shows that at present stage there are enough number of groups over the globe who are actively engaged in this area. If we consider the range of applications, it is clear that there exist a sufficient space to involve many researchers in future also. So in coming decades still more Solid solutions with more enhanced physical, chemical and electric properties for device fabrication will be available from various groups of researchers in this fine focused area of Research in material science.

8. ACKNOWLEDGEMENT

Authors would like to thank the authorities of Brahmdevdada Mane Institute of Technology. Dr. Shrikant Kokare, Former Director, Board of Examinations and Evaluations, Punyashlok Ahilyadevi Holkar Solapur University Solapur for moral support and valuable discussions during the preparation of this paper.

9. REFERENCES

1. M.M. Vijatovic Petrovic, J.D. Bobic, B.D.Stojanovic (Jan 2008) History and Challenges of Barium Titanate : Part II - Science of Sintering 40(2)
2. Gene H. Haertling; B.M. kilwieki (Dec 2004) - Ferroelectric ceramics: History and Technology - Journal of the american Ceramic Society/Volume 82
3. S.Stramare, V. Thangadurai and W. Weppner (Sep 2003) - Lithium Lanthanum Titanates: A review - Chemistry of materials - Chem. Mater. 2003, 15, 21, 3974-3990
4. Tomonari Takeuch, et. al (2005), Preparation of composite dielectric ceramics by Spark plasma sintering method-. In Novel Materials processing by Advanced Electromagnetic Energy Sources,
5. K.Uchino (2012) Piezoelectric ceramics for transducers in Ultrasonic Transducers,
6. Multilayer technologies for piezo-ceramic materials
7. K. Uchino 2010- Piezoelectric materials and the new perspective –, in advanced piezoelectric materials,
8. Zhiyong Zhou et al, (Feb. 2023) Progress in Materials Science, Vol.132, 1010-26
9. S.H.Han et al, (2007) Electrochemical Communication pp. 1805-1809.
10. K.M.Razeeb et al. (2015) Ionics, 21, pp. 2623-2631.
11. X. Zhang et al, (2015) Electrochemical Acta 174pp. 41-50
12. V.V.Deshmukh et al, (2021) Environmental Chemistry and Ecotoxicology Vol. 3, pp. 241-246
13. Mario L. Moreira, Elaine C. Paris et.al. (Oct 2009) Structural and optical properties of $CaTiO_3$ perovskite – based materials obtained by microwave – assisted hydrothermal synthesis: An experimental - Volume 57
14. Manjusha Passi, Bonamali Pal (Aug 2021) A review on $CaTiO_3$ photocatalyst: Activity enhancement methods and photocatalytic applications-Powder Technology- Volume 388
15. Ujwala. Bhagwat, Jerry J.Wu et.al.(Jan2019) Synthesis of $MgTiO_3$ Nanoparticles for Photocatalytic Applications - Volume 4
16. Jasdeep Singh, Shalini Bahel (March 2020) Synthesis of single phase $MgTiO_3$ and influence of Sn4+ Substitution on its

structural, dielectric and electrical properties. -Journal of Alloys and Compounds Volume 816

17. Materials Data on $NaTiO_3$ by Materials Project - 36 MATERIALS SCIENCE - Lawrence Berkeley National Lab. (LBNL), Berkeley, CA (United States). LBNL Materials Project. (July 2020)
18. Baedi, F. Mircholi, H. Gerami Moghadam Study of electronic and optical properties of $Bi_{0.5}Na_{0.5}TiO_3$, $BiTiO_3$, $NaTiO_3$ crystals using full potential linear argumented plane wave method.
19. Siyu Li, Yuhang Liu (2024) Sustainable release of $LiNO_3$ in carbonate electrolytes for stable lithium metal anodes. - Chemical Communication.
20. Dongdong Liu, Xunhui Xiong (2021) An inorganic-rich SEI induced by $LiNO_3$ additive for a stable lithium metal anode in carbonate electrolyte - Chemical communication
21. N. Ramadass (December 1978) ABO_3 – type Oxides- Their structure and properties – A birds eye vie- Material Science and Engineering - Volume 36
22. C.E. Huang et al (2017) cerum.Int Effect of CaO/SnO_2 additives on the microstructure and microwave dielectric properties of $SrTiO_3$- $LaAlO_3$.
23. J.M.Kweun et.al, (2016), Appl.Surf.Sci. Bulk – surface relationship of an electronic structure for high – throughput screening of metal oxide catalysts.
24. H.Liu et.al. (2020) Screening stable and metastable ABO3 perovskites using machine learning and the materials project – comput. Mater. Sci
25. X. Zhai et. al (2018) Accelerated search for perovskite materials with higher curie temperature based on the machine learning methods – Compit. Mater. Sci.
26. W.Li.et.al (2018) Predicting the thermodyanamics stability of perovskite oxides using machine learning models – comput. Mater. Sci.
27. C.E.Calderon et.al (2015) The AFLOW standant for high – throughput materials science calculations – compt. Mater. Sci.
28. Junjiang Zhu, Hailong Li, Linyun Zhong et. al Perovskite Oxides: Preparation, Characterizations and Applications in Heterogeneous Catalysis
29. O. Muller, R.Roy, (1975) The Major Ternary structural Families, springer – Verlag, New Y
30. Z.L.Wang, Z.C.Kang,(1998) Functional and smart Materials, plenum press, New York, - Functional and Smart Materials
31. Chonghe Li, kitty chi kwan soh, Ping Wu (June 2004) Formability of ABO_3 perovskites - Journal of Alloys and Compounds- Volume 372
32. Haoming Wei, Chao Yang, Yangging Wu, Binggiang Cao, Michael Lorenz and Marius Grundmann(2020) Journal of Materials Chemistry – from energy harvesting to topologically insulating
33. Peresi Majura Bulemo (2020) Recent advances in ABO_3 perovskites: their gas – sensing performance as resistive type gas sensors –, - Journal of Korean ceramic Society 57, 24-39,
34. Huan Zhang, Na Li Keyan Li, Dong Feng Xue(2007) Structural stability and formability of ABO_3 – type perovskite compounds-
35. Rongzi Hong, Feng Gao, et.all.(2008) Fabrication of (BiNa)0.5TiO_3 $BaTiO_3$ textured ceramics by tape casting - Journal of Material Science - Volume 43
36. Dibyaranjan ROUT, Kyoung-Seok MOON, et.al Study of the morphotropic phase boundary in the lead-free $Na_{1/2}Bi_{1/2}TiO_3$-$BaTiO_3$ system by Raman spectroscopy
37. Tadashi Takenaka, Yuichi Naitou et.al.) Piezoelectric Ceramics of $(Bi_{1/2}Na_{1/2})TiO_3$-$PbTiO_3$ System
38. T.Takenaka and K.Sakata)Dielectric, piezoelectric and pyroelectric properties of $(BiNa)_{1/2}TiO_3$- based ceramics
39. Dae Su Lee, Dong Hwan Lim et.all Electric field – induced deformation behavior in mixed $Bi_{0.5}Na_{0.5}TiO_3$ and $Bi_{0.5}(Na_{0.75}K_{0.25})_{0.5}TiO_3$-$BiAlO_3$.
40. Andrea Prado – Espinosa, Javier Camargo Et. al.) Exploring new methodologies for the identification of the morphotropic phase boundary region in the $(BiNa)TiO_3$-$BaTiO_3$ lead free piezoceramics: Confocal Raman Microscopy-
41. K.Seevakan and S. Bharanidharan New methodologies for the identification of the morphotropic phase of boundary region in the $(BINA)TiO_3$-$BaTiO_3$ lead free piezoceramics
42. Nguyen Truong – Tho, Le Dai Vuong) Effect of Sintering Temperature on the Dielectric, Ferroelectric and energy storage properties of SnO_2-doped $Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO_3$ Lead – free Ceramics
43. P.Jaita, S. Manotham and N. Lertcumfu, (2018) Influence of Sintering Temperature on Structure and Electrical Properties of Modified-BNKT Lead-Free Piezoelectric Ceramics, Trans. Tech. Publ., E, 55
44. S. Manotham, P. Butnoi, P.Jaita, N. Kumar, K. Chokethawai, g. Rujijanagul and D.P. Cann, (2018) Large electric Field – induced Strain and Large Improvement in Energy Density of Bismuth Sodium Potassium Titanate – based Piezoelectric Ceramics, J.Alloy.Comp., 782,270
45. D.K.Kushvaha, S.K. Rout and B. Tiwari, (2018)Structural, Piezoelectric and Highdensity Energy Storage Properties of Lead-free BNKT – BCZT Solid Solution, J.Alloy.Comp.,782,270
46. Nguyen Truong – Tho, Le Dai Vuong Effect of Sintering Temperature on the Dielectric, Ferroelectric and energy storage properties of SnO_2-doped $Bi_{0.5}(Na_{0.8}K0_{.2})_{0.5}TiO_3$ Lead – free Ceramics
47. J.Camargo, A.Prado Espinosa et.al. Influence of the sintering process on ferroelectric properties of $Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO_3$ lead-free piezoelectric ceramics.