STUDIES ON STRUCTURAL, DIELECTRIC AND PIEZOELECTRIC PROPERTIES OF LEAD FREE CERAMICS SYNTHESIZED BY SEMI-WET METHOD

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SYNOPSIS

Everlasting desire of human to improve his livelihood, kept him working for the development of technology. They are always in hunt of better and smarter materials to meet these technological endeavors. For the use of a material in a specific application, several researchers are putting notable efforts to expand a material that may lead to momentous progress in the miniaturization of electronics. Perovskites having ABO_3 type structures have received great attention in the field of science and technology in past few decades, because a large number of materials of this class and related structures show fascinating functional properties for industrial applications [1-5]. Piezoelectric materials is one of the unique class of perovskites, in which, these materials play an immense role due to their electronic versatility. 'Piezoelectric materials' are those materials which have the ability of generating an electric potential in response to an applied mechanical stress or vice versa. This phenomenon is known as "Piezoelectricity". The conversion from mechanical energy to electric energy exhibited by a piezoelectric material is known as the "direct piezoelectric effect". This effect was first discovered by brothers "Jacques and Pierre Curie" in 1880. Later on, conversion from electric energy to mechanical energy, demonstrated by Gabriel Lipmann in 1881 is identified as the "converse piezoelectric effect". These materials have tremendous applications in global market. The commercially dominating piezoelectric ceramic especially PZT based materials are extensively utilized in sensors, actuators, transducers, medical ultrasound and many more electronics devices because of their superior dielectric, piezoelectric and electromechanical coupling properties [6-7]. The foremost shortcoming of PZT is that it contains lead, which is toxic in nature [8]. For example, a typical composition of PZT i.e. $Pb(Zr_{0.53}Ti_{0.47})O_3$ contains more than 60 wt % of lead. Lead gets into the environment by two major sources: (i) the evaporation of lead oxide during the processing of lead-based materials (due to its low melting point at 888°C) and (ii) the disposal of discarded lead-contained devices. Most of the wastes are disposed of by the landfill process, in which, lead-containing devices are buried in the ground. The toxic lead can dissolve into the underground water, which contaminating the water source that people need for daily life. Thus, even after losing some of its lead content, not only creates hazard in the atmosphere but also environmentally toxic during disposal of electronic devices. The toxicity of lead creates serious risk to human health. Once, lead is absorbed by a human body, it occupies the bonding sites where calcium is supposed to be. Calcium is believed as a crucial messenger to nerve pulse transmission, heart activity and blood clotting, the replacement of calcium by lead disrupts the functioning of brain neurotransmitter and the central nervous system is fatally jeopardized. In addition, accumulation of lead in human organisms is difficult to remove [9]. Moreover, in the biosensing applications where the biosensor requirements to be operated inside human body, it's essential that the sensing materials, for example the piezoelectrics, need to be biocompatible with the inside environment of human body. Lead-based piezoelectrics are evidently not suitable for these applications.

In view of the above concerns, there are several legislations and regulations against lead-based materials have been increasingly enacted throughout the world. In 2003, European Union (EU) issued the judgment of "Waste Electrical and Electronic Equipment Directive" (WEEE), in which restriction of the hazardous substance directive (RoHS) and End of Live Vehicles (ELV), strictly banned the use of the six materials during the manufacturing of electronic equipment [10-13]. From July 2006, the new electrical and electronic product set in the market, can not have lead [10]. Consequently, to control the usage of lead-containing materials, similar legislation and policies have also been enacted in Asia, China [14], Japan [15] and South Korea [16]. Nevertheless, currently PZT ceramics are exempted due to the lack of suitable replacement in electronic industry. In order to circumvent the drawback of lead toxicity and environmental and safety concerns with respect to the utilization, recycling, and disposal of lead based piezoelectric materials have induced a quest for alternate piezoelectric materials. However, it may be a temporary respite, but the legislation certainly impressed the researchers to increase their research interest in developing lead-free piezoelectric materials that can eventually replace the current lead-based ones. Therefore, a surge of suitable new lead free material is going on rapidly as no single composition has been proposed so far to replace PZT. Intensive research on the related studies has been carried out all around the world for over two decades and search for suitable alternative of lead-free piezoelectric material has been increasing around the globe. Generally, lead-free piezoelectric materials can be classified into two categories; (i) Non perovskite, i.e., bismuth layer structured ferroelectrics (BLSF), i.e.$Bi_4Ti_3O_{12}$, and tungsten-bronze type ferroelectrics, i.e. $BaNb_2O_6$ and (ii) Perovskite, i.e. $BaTiO_3$ (BT), $KNbO_3$, $NaTaO_3$ and $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT), etc. The perovskite family of lead free piezoelectrics is suitable for actuators and high power applications.

The Bismuth Sodium Titanate, having a standard formula unit $(Bi_{0.5}Na_{0.5})TiO_3$ i.e. BNT is ABO_3 type perovskite material. BNT show a rhombohedral R3c crystal structure at room temperature [17]. It is being studied because of its high temperature dielectric constant, as well as its ability to work well without the addition of lead [18]. The BNT is a candidate material for future dielectric and piezoelectric applications that cover large temperature ranges. The large temperature range is advantageous for use in the oil and natural gas industry for down-hole drilling tools, automotive, aerospace and military for applications directly on or near hot engine surfaces. BNT based materials are being studied to create an alternative of PZT that can meet the current industry standard.

Hill et al. (1999) [19] suggested that the origin of large piezoelectric response in PZT materials resulting from the stereo-chemical activity of the $6s^2$ lone pair on the lead ion, is due to large structural distortions from the cubic perovskite phase that produces strong coupling among the electronic and structural degrees of freedom. Baettig et al. (2005) [20] proposed that Bi-based materials have similar or larger ion off centering of cations as compared to Pb-based compounds like PZT. The stereo chemically active $6s^2$ lone pairs in the Bi^{3+} ion are the driven force, which leads to large ferroelectric polarizations. Moreover, Bismuth is non-toxic in its oxide forms. Therefore, BNT is considered to be a favorable and promising candidate in the field of lead-free Piezo-ceramics because of its large remnant polarization ($P_r \sim 38\mu C/cm^2$) and high Curie temperature ($T_c \sim 320°C$) among various lead-free piezoelectric ceramics [17]. Most significantly, it can be prepared under ordinary processing conditions. Though, it is difficult to use this material in electronic industry due to its large coercive field ($E_c \sim 73$ kV/cm) and high conductivity, which causes difficulty in poling process. In addition, BNT has the depolarization temperature T_d (ferroelectric – antiferroelectric transition temperature) and T_m temperature of maximum dielectric constant (antiferroelectric – paraelectric transition) around 185 and 340 °C respectively. Therefore, a lot of studied have been carried to modify electrical properties of BNT either by the doping of some suitable rare earth dopants at A- sites or A and B- sites both, [21-23] or by making of some solid solutions with other ABO_3 type compounds, such as $(Bi_{1/2}K_{1/2})TiO_3$ (BKT) [24-25], $BaTiO_3$ [26-27], $(K_{0.5}Na_{0.5})NbO_3$ (KNN) [28], $NaNbO_3$ [29], $SrTiO_3$ [30]. It has been proved that these compositional modifications in BNT show improved dielectric, ferroelectric, piezoelectric properties and easier treatment in the poling process by reducing coercive field and dielectric loss compared with pure BNT ceramics.

The major research work of the present thesis is focused around synthesis and characterization of BNT based lead free ceramics along with a small piece of work on Zr modified Barium calcium titanate (BCT) ceramics. The challenges for lead-free materials to replace lead-based families are generally low Curie temperature, high coercive field and low relative densities which creates problems in poling treatments. Various dopants are used to overcome the abovementioned problems and tailor the properties of lead free materials as well, depending on applications.

In present work, an attempt has been made to synthesize BNT ceramics by a new processing technique known as Semi-Wet (SW), which has been found worth full in making A-site cation distribution more homogeneous and hence to improve the properties of lead free piezoelectric ceramics. After optimizing the system of pure BNT, it has been used to prepare several BNT based and other ceramics. In BNT ceramics, where A- site contains Bi^{3+} ions as well as Na^{+1} ions (50:50), the processing technique often encountered many uncertainties. One of the very serious problems is the deviation from the stoichiometry. In general, the dielectric as well as piezoelectric properties greatly suffers due to the lack of homogeneity. Hence, A- site of BNT has been prepared by wet chemical route using ethylene glycol by drying followed and TiO_2 addition by solid state method. This has been done to avoid the defects formation from the deviation from stoichiometry. Nevertheless, it is worth mentioning here that the fabrication of homogeneous powders and high quality ceramics has not been an easy task. Thus we can say that semi-wet technique has been proved to be a promising technique (in view point of more easy, convenient and low cost) among other available techniques by means of reproducibility, performance, reliability and economy, to obtain dense and optimum electrical properties.

With this background and the objectives in mind, studies on the effect of substitution on structural, dielectric, ferroelectric and piezoelectric properties of BNT as well as BCT ceramics have been carried out. In this thesis, literature survey, experimental procedure for synthesis and characterization of samples, results and discussion of research work have been organised into seven chapters. Chapter wise discussions are summarized as below:

Chapter 1: This chapter describes a concise introduction of perovskites, ferroelectricity, piezoelectricity and Lead free piezoelectrics along with the literature survey for last 15 years. The origin, history and phase diagram have been discussed. Moreover, current progress and motivation to carry out research in lead free piezoelectrics have been illustrated in details.

Chapter 2: This chapter demonstrates the details of sample preparation method (semi-wet technique) and details of experimental techniques used to characterize specimen samples in the present work.

Chapter 3: In this chapter, synthesis and effect of Gadolinium/Neodymium (Gd/Nd) substitution on the structural, morphological, dielectric, ferroelectric and piezoelectric properties in the systems $(Bi_{1-x}RE_x)_{0.5}Na_{0.5}TiO_3$, where RE = Gd & Nd; abbreviated as BGNT and BNNT respectively have been carried out. The key conclusions are followed as below:

- Compositions $x \leq 0.04$ in the system $(Bi_{1-x}RE_x)_{0.5}Na_{0.5}TiO_3$ have been prepared by semi-wet technique. All the compositions in BGNT and BNNT have shown single phase rhombohedral structure with R3c symmetry at RT.
- Microstructures of these ceramics are found to be more homogeneous and dense. The average grain size is decreased with increasing x, which may be due to inhibition of grain growth as a result of Gd and Nd doping in BNT.
- Dielectric measurements of all the samples have been carried out from room temperature to 500^oC at few frequencies. The temperature dependence of dielectric plots of the compositions in $(Bi_{1-x}RE_x)_{0.5}Na_{0.5}TiO_3$ ceramics exhibit two phase transitions, one at low temperature 'T_d', corresponding phase transition from ferroelectric (FE) to antiferroelectric (AFE) state of polarization and other at high temperature 'T_m', corresponding phase transition from AFE to paraelectric (PE) state. All the compositions of $(Bi_{1-x}RE_x)_{0.5}Na_{0.5}TiO_3$ ceramics show diffuse phase transition,

which may be due to micro-heterogeneity caused by compositional fluctuations and cation disordering. A typical composition with x = 0.02 in BGNT as well as in BNNT has shown relatively high dielectric constant and low loss as compared to other compositions in respective ceramic system. BGNT sample with x = 0.02 has shown relatively superior dielectric properties (For Gd; ε_{r} = 1186, tan δ = 0.021 & For Nd; ε_{r} = 816, tan δ = 0.036 @10kHz).

- All the compositions in BGNT ceramics (i.e. x ≤ 0.04) have shown nearly saturated hysteresis (P-E) loop whereas, BNNT ceramics have shown nearly saturation polarization upto x≤ 0.03. Remanent polarization (P_r) has been found to be more for BNNT as compared to BGNT.
- Temperature dependence hysteresis loop reveals that hysteresis loops are found to be slim with increasing temperature for all the samples in these ceramic systems. With increasing temperature above T_d, the volume % of polar region reduces, which is leading to the deformed P-E loop. Deformed P-E loop behavior around T_d clearly indicates the coexistence of polar and non polar regions in these samples which indicate the co-existence of ferroelectric and antiferroelectric phases.
- Further, a typical composition with x = 0.02 has shown optimum piezoelectric properties in these ceramics (For BGNT; d_{33} = 55 μC/N, k_p= 16% and for BNNT; d_{33}= 40μC/N, k_p = 18 %).

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Chapter 4: This chapter illustrates the synthesis of La/Li co-substitution in BNT i.e. $(Bi_{1-x}La_x)_{0.5}(Na_{1-y}Li_y)_{0.5}TiO_3$; and La/Li/Ba co-substitution in BNT i.e. $[1-z(Bi_{1-x}La_x)_{0.5}(Na_{1-y}Li_y)_{0.5}TiO_3-zBT]$ which are abbreviated as BLNLT & BLNLT-BT system respectively. Studies on the structural, microstructural, dielectric, ferroelectric and piezoelectric properties have been carried out. The key conclusions are followed as below:

BLNLT system

- Composition with x/y = 0.00/0.00, 0.04/0.025, 0.04/0.050, 0.04/0.075 and 0.04/0.10 in the system $(Bi_{1-x}La_x)_{0.5}(Na_{1-y}Li_y)_{0.5}TiO_3$ (i.e. BLNLT) ceramics have been synthesized by semi-wet technique. All the samples show single phase rhombohedral structure with R3c symmetry at RT. Lattice parameters, determined by using FULLPROF software (Rietveld refinement), are found to decrease with increasing concentration, which may be due to small ionic radii of Li^+ ion as compared to Na^+ ions.
- Microstructures of BLNLT ceramics are homogeneous and dense. The average grain size is decreased with increasing x/y = 0.04/0.075 and thereafter leads to anomalous grain growth for $y \geq 0.10$.
- Dielectric measurements of all the samples have been carried out from room temperature to 500°C at few frequencies. The temperature dependence of dielectric plots exhibits a broad maximum whose position (T_m) is frequency dependent up to $y \leq 0.075$. A switching from frequency dependent to frequency independent dielectric behavior is observed with increasing Li concentration. It reveals relaxor type characteristic up to x/y = 0.04/0.075 which may be ascribed to the micro-heterogeneities due to atomic disorder at A-sites in these materials. A broad, however non-relaxer type transition is observed for compositions y = 0.10, which may be caused by localized liquid phase formation due to higher concentration of lithium leading to anomalous grain growth. The dielectric parameters for composition with x = 0.025 have shown the optimum properties in the BLNLT ceramics ($\varepsilon_r = 1365$, tan $\delta = 0.07$ @100kHz).
- Compositions with $y \leq 0.10$ in BLNLT system have shown nearly saturated hysteresis (P-E) loop at room temperature ($P_r = 29.26$ µC/cm^2, $E_c = 28.81$@50Hz). Thus, electric field induced switching of domains becomes more easy by the substitution of Li ion.
- The composition with x/y = 0.04/0.025 has shown the optimum piezoelectric properties in BLNLT ceramics ($d_{33} = 70$ µC/N, k_p= 25%).

BLNLT-BT system

- Composition with x/y/z = 0.04/0.025/0, 0.04/0.025/0.02, 0.04/0.025/0.04 and 0.04/0.025/0.06 in the system [1-z$(Bi_{1-x}La_x)_{0.5}(Na_{1-y}Li_y)_{0.5}TiO_3$-zBT] i.e. (1-z)BLNLT-zBT] have been synthesized by semi-wet technique. All the compositions show single phase rhombohedral structure with R3c symmetry. No structural phase transition has been observed upto x/y/z = 0.04/0.025/0-0.06. Lattice parameters, determined by using Rietveld refinement are found to decrease with increasing concentration, which may be due to the mismatch of ionic radii.
- Microstructures of (1-z)BLNLT-(z)BT ceramics are uniform, dense and homogeneous. The average grain size is decreased with increasing x, which indicates that grain growth is also inhibited with increasing z (i.e. Ba).
- Dielectric measurements of all the samples have been carried out from room temperature to 500^{o}C at few frequencies. The temperature dependence of dielectric plots of these compositions exhibit two phase transitions, one at low temperature, T_d, and other at high temperature, T_m. All these compositions show diffuse phase transition, which may be due to compositional fluctuations. A typical composition with 0.04/0.025/0.06 has been found to show optimum dielectric properties ($\varepsilon_{r\,=}$ 1496, tan δ = 0.06 @100kHz).
- Compositions with x/y/z = 0.04/0.025/0.00 has shown nearly saturated hysteresis (P-E) loop at room temperature ($P_{r\,=}$ 29.26 μC/cm^2, E_c = 28.81@50Hz), while hysteresis loops are getting slim with increasing concentration of Ba. It reveals that remnant polarization (P_r) decreases with increasing B at A- sites. The piezoelectric properties (d_{33} and k_p) have also been found to be decreased with increasing Ba concentration.

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Chapter 5: In this chapter, an attempt has been made to synthesize the $(Bi_{0.96}La_{0.04})_{0.50}Na_{0.5}TiO_3$-$Ba_{0.90}Ca_{0.10}TiO_3$ abbreviated as (1-x)BLNT-(x)BCT solid solutions by semi-wet technique. It is expected that the solid solution system may exhibit MPB region and hence interesting structural, morphological, dielectric, ferroelectric, piezoelectric and electromechanical properties. The key points are illustrated as below:

- (1-x)BLNT-(x)BCT solid solutions ceramics with compositions $x \leq 0.20$ have been synthesized by semi-wet technique in the temperature range (950ºC -1050 ºC). XRD patterns of all these samples confirm phase formation without any traces of secondary phases. Structural phase transition from rhombohedral to tetragonal phase has been identified by Rietveld refinement using FullProf program, which is confirmed by Raman spectroscopy. Further, phase existence of rhombohedral for $x \leq 0.08$, rhombohedral-tetragonal (MPB region) for $0.10 \leq x \leq 0.15$ and tetragonal for $x \geq 0.20$ has been investigated in these ceramics. A slight variation in lattice parameters has been observed, which may be due to mismatch of ionic radii, leading to the strain developed in the lattice of BLNT-BCT solid solutions. For rhombohedral structure, volume of the unit cell has been found to increase, while volume of the unit cell is decreased for tetragonal structure. Moreover, the crystallite size and microstrain have been calculated from Williamson-Hall (W-H) equations and their variation with the doping of BCT is discussed.
- Micrographs of (1-x)BLNT-(x)BCT ceramics show homogeneous, uniform and dense microstructure. Some long and small grains are observed in the specimen for $x = 0.04$. Homogeneous grain growths with relatively smaller grains have been observed with further increasing the concentration of x, which indicates that grain growth is inhibited with increasing x. EDX spectra of a typical composition for $x = 0.12$ indicates that the arbitrarily selected region contains Bi, La, Na, Ba, Ca, Ti, and O elements supporting the diffusion of BCT into BLNT lattice.
- Dielectric measurements of all the samples have been carried out from room temperature to 500^{o}C at few frequencies. Both phase transition temperatures (T_d and T_m) shift towards lower temperature with increasing x and a switching from frequency dependent to frequency independent with x has been observed in these ceramics. It exhibits a broad maximum whose position (T_m) is frequency dependent up to $x \leq 0.12$. It reveals relaxor type characteristic which may be attributed to the micro-

heterogeneities due to atomic disorder at A-sites in these materials. The composition with x = 0.15 has shown the optimum dielectric properties (ε_{r} = 1356, tan δ = 0.07 @10kHz) among these ceramics.

- All the specimen samples with $x \leq 0.20$ have shown saturated hysteresis (P-E) loop at room temperature. These loops have revealed that remnant polarization attain maximum value (P_r = 30 $\mu C/cm^2$) and low coercive field (E_c = 27.28 kV/cm) for x = 0.12 near the MPB.
- The specimen with x = 0.12 (a compositions near MPB) exhibits excellent piezoelectric and electromechanical properties with values of d_{33} = 165 pC/N, k_p = 39%, and a high bipolar strain of 0.12% is achieved for x = 0.10. The enhanced piezoelectric properties may be explained in terms of large number of possible domain states between the rhombohedral and the tetragonal phases at MPB. As a consequence, they favor more crystallographic directions suitable for polarization, which facilitates piezoelectricity.

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Chapter 6: In this chapter an attempt has been made to synthesize the Ca and Zr co-substituted $BaTiO_3$ i.e. $Ba_{1-x}Ca_xTi_{1-y}Zr_yO_3$ (abbreviated as BCTZ) solid solutions by semi-wet technique and tailored the structural, morphological, dielectric, ferroelectric, piezoelectric and electromechanical properties. The key conclusions are illustrated as below:

- Ca and Zr co-substituted BT ceramics with compositions x = 0.13 & $y \leq 0.15$ have been synthesized in the form of solid solution. XRD patterns of these samples have shown single phase with tetragonal structure. Rietveld refinement of XRD data has confirmed tetragonal structure with P4mm symmetry for all samples. The lattice parameter ratio (c/a) increases up to y = 0.10 thereafter, it decreases and volume of the unit cell has been found to increase with increasing y. Raman spectra of all these compositions have also confirmed tetragonal symmetry.
- The relative density of specimen samples has been found to be increased with increasing concentration of Zr up to y = 0.10 thereafter, it decreases. Microstructures of all these samples are homogeneous, uniform and dense except for y = 0.15. For y = 0,

micrograph is highly dense, homogeneous and pore free with larger grain (~28μm). The average grain size has been found to decrease with y, indicating inhibition of grain growth with increasing Zr concentration.

- Temperature dependence of dielectric measurements of all the samples has been carried out from room temperature to 250^{o}C at few frequencies. Dielectric plot (ε_r vs T) with x = 0.13 and y = 0 exhibits sharp transition from FE to PE at T_c, which is further diffused with increasing y. The composition with x/y = 0.13/0.10 in this system exhibits high dielectric constant (ε_r) with low value of dielectric loss (tan δ) (ε_r = 1946, tan δ = 0.012 @10kHz).
- All these compositions with y ≤ 0.15 have shown saturated hysteresis (P-E) loop at room temperature, which reveals that remnant polarization (P_r) increases upto y = 0.10 while coercive field is significantly reduced with increasing y. It indicates that electric field induced switching of domains becomes easy for the compositions with higher Zr concentration.
- The specimen with x = 0.10 exhibits excellent piezoelectric and electromechanical properties with values of d_{33} = 367 pC/N, k_p = 39% and a high bipolar strain of 0.12% is achieved for x = 0.08.

(The manuscript covering above results is under preparation)

Chapter 7: This chapter demonstrates a summary of the results and discussions along with suggestions for further work.

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Papers in International SCI Journals

1. **Pal V.**, Thakur O.P. and Dwivedi R.K., "*Investigation of MPB region in lead free BLNT-BCT system through XRD and Raman spectroscopy*", Journal of Physics D: Applied Physics, vol. 48, 055301, 2015 (**Thomson Reuters I. F.** = 2.521, **H-index** = 121, **H5-index** = 61, **Published by** Institute of Physics, **Indexed** in SCI and SCOPUS).
2. **Pal V.** and Dwivedi R.K., "*Effect of Processing on Synthesis and Dielectric Properties of Lead free $(Bi_{0.98}R_{0.02})_{0.5}Na_{0.5}TiO_3$ Ceramics*" IOP Conf. Series: Materials Science and Engineering, vol. 73, 012121, 2015 (**H-index** = 4, **H5-index** = 13, **Published by** Institute of Physics, **Indexed** in SCI and SCOPUS).
3. **Pal V.**, Dwivedi R.K. and Thakur O.P., "*Synthesis and Ferroelectric Behavior of Gd doped BNT Ceramics*" Current applied physics, vol. 14, pp. 99-107, 2014 (**Thomson Reuters I. F.** = 2.026, **H-index** = 44, **H5-index** = 40, **Published by** Elsevier, **Indexed** in SCI and SCOPUS).
4. **Pal V.**, Dwivedi R.K. and Thakur O.P., "*Effect of Neodymium Substitution on Structural and Ferroelectric properties of BNT ceramics*" Material research bulletin, vol. 51, pp. 189–196, 2014 (**Thomson Reuters I. F.** = 2.105, **H-index** = 68, **H5-index** = 35, **Published by** Elsevier, **Indexed** in SCI and SCOPUS).
5. **Pal V.**, Dwivedi R.K. and Thakur O.P., "*Dielectric and Ferroelectric Properties of Lead-Free$[1-z\{(Bi_{1-x}La_x)_{0.5}(Na_{1-y}Li_y)_{0.5}TiO_3\}-zBaTiO_3]$ Ceramic System*" Advances in Materials Science and Engineering, vol. 2013, Article ID 125634, 7 pages, 2013 (**Thomson Reuters I. F.** = 0.897, **H-index** = 5, **H5-index** = 8, **Published by** Hindawi Publishing Corporation, **Indexed** in SCI and SCOPUS).

Papers in National SCI Journals

1. **Pal V.**, Thakur O.P. and Dwivedi R.K., "*Effect of La/Li on structure, microstructure, dielectric and piezoelectric behavior of BNT ceramics*", Indian journal of Physics, vol. 89 (2),

pp. 123–130, 2015 (**Thomson Reuters I. F.** = 1.785, **H-index** = 17, **H5-index** = 18, **Published by** Springer, **Indexed** in SCI and SCOPUS).

Paper Presented in International Conferences

1. **Pal V.** and Dwivedi R.K., "*Structural and piezoelectric properties of Li modified BLNT Ceramics*", International Conference on Emerging Materials and Applications, 2014, (ICEMA- 14), I.I.T. Roorkee, Saharanpur Campus, April 05-06, 2014. **(**Oral presentation**)**
2. **Pal V.** and Dwivedi R.K., "*Crystal structure and FTIR vibrational spectroscopic studies in complex* $(1-x)(Bi_{0.96}La_{0.04})_{0.5}(Na_{0.975}Li_{0.025})_{0.5}TiO_3$-$(x)BaTiO_3$ *ceramics system*", International Conference on Science & Engineering of Materials (ICSEM-2014), Sharda University, Greater Noida, January 6-8, 2014. (Poster presentation)
3. **Pal V.**, Thakur O.P. and Dwivedi R.K., "*Structural, Microstructure and Ferroelectric Properties of Environmental friendly Lead free* $(Bi_{1-x}Nd_x)_{0.5}Na_{0.5}TiO_3$ *Ceramics*", International Union of Materials Research Society-ICA (IUMRS ICA-2013), IISC, Bangalore, December 16-20, 2013**. (**Oral presentation**)**
4. **Pal V.** and Dwivedi R.K.,"*Dielectric and Piezoelectric Properties of Lead free* $(Bi_{1-x}Nd_x)_{0.5}Na_{0.5}TiO_3$ *Ceramics*", International Conference on Multifunctional Materials , Energy and Environment (ICMFMEE-2013), Sharda University, Greater Noida, August 21-23, 2013. (Poster presentation)
5. **Pal V.** and Dwivedi R.K., "*Effect of Rare Earth Gadolinium Substitution on the Structural, Microstructure and Dielectric Properties of Lead free BNT Ceramics*", Advances in Materials and Processing: Challenges and Opportunities (AMPCO-2012), IIT Roorkee, November 2-4, 2012. **(**Oral presentation**)**
6. **Pal V.** and Dwivedi R.K.,"*Structural and Dielectric Properties of Environmental friendly Lead free* $(Bi_{0.96}La_{0.04})_{0.5}(Na_{0.975}Li_{0.025})_{0.5}TiO_3$ *Ceramics*", Chemical Constellation Cheminar-2012 (CCC-2012), NIT Jalandhar, September 10-12, 2012. (Poster presentation)
7. **Pal V**. and Dwivedi R.K.,"*Effect of Processing on Synthesis and Dielectric Properties of Lead free* $(Bi_{0.98}R_{0.02})_{0.5}Na_{0.5}TiO_3$ *Ceramics*", International Conference on materials Science and Technology (ICMST-2012), St. Thomas College, Pala (Kerala), June 10-14, 2012. (Poster presentation)

8. **Pal V.** and Dwivedi R.K.,"*Dielectric properties of La modified BNT Ceramics for MEMS Applications*", International conference on Smart Structures and Smart Systems (ISSS-2012), IISc Bangalore, January 04-07, 2012. **(**Oral presentation**)**

Paper Presented in National Conferences

1. **Pal V.** and Dwivedi R.K., "Crystal Structure, Ferroelectric and Piezoelectric Properties of Lead Free 1-xBLNT-xBCT Solid Solution Ceramics", 26th Annual General Meeting Materials Research Society of India (26th AGM MRSI-2015), University of Rajasthan, Rajasthan, February 09-11, 2015. **(Poster)**
2. **Pal V.** and Dwivedi R.K.,"*Dielectric and Ferroelectric Properties of Lead Free* $(Bi_{1-x}R_x)_{0.5}Na_{0.5}TiO_3$ *Ceramic*" 17th National Seminar on Ferroelectrics and Dielectrics (NSFD XVII -2012), Siksha 'O' Anusandhanh, Orrisa, December 17-19, 2012. (Poster presentation)
3. **Pal V.** and Dwivedi R.K.,"*Structural, Dielectric and Ferroelectric Behavior of Lead free BRNT Ceramics*", National Seminar on Futuristic Material for Device Applications", Sharda University (Greater Noida), July 27, 2012. (Poster presentation)
4. **Pal V.** and Dwivedi R.K., "*Dielectric Behavior of Nd doped BNT Ceramics*", National Seminar on Futuristic Materials, Sharda University (Greater Noida), September 15-17, 2011. (Poster presentation)
5. **Pal V.** and Dwivedi R.K., "*Effect of La doping on the dielectric behavior of* $(Bi_{1-x}R_x)_{0.5}Na_{0.5}TiO_3$ *ceramic*", National Seminar on Advanced Material and Devices, G.V.M. Girls College, Sonepat (Haryana), July 3-4, 2011. (Poster presentation)
6. **Pal V.** and Dwivedi R.K., "*Ferroelectric and piezoelectric behavior of lead free BNT ceramic*", National Seminar on Functional and Smart Materials, Sharda University (Greater Noida), January 11, 2011. **(**Oral presentation**)**
7. **Pal V.** and Dwivedi R.K., "*Ferroelectric Behavior in* $(Bi_{1-x}La_x)_{0.50}Na_{0.50}TiO_3$ *Ceramics*", 16th National Conference of Dielectrics and Ferroelectrics (NSFD-XVI-2010), GGU Bilashpur (C. G.), December 02-04, 2010. **(**Oral presentation**)**
8. **Pal V.** and Dwivedi R.K.,"*Effect of Chemical Precursors on Structure and Dielectric Properties of Lead free Piezoelectric Ceramic*", National conference "RAMSE" 2010, JUIT Guna (M.P.), October 23-24, 2010. **(**Oral presentation**)**

Participation in Workshop

1. **Pal V.,** **"***Workshop on Nano Probe Techniques***"** held at department of Physics IIT, Delhi, July 14, 2014.
2. **Pal V.,** **"***NRC-M Summer Workshop on Principle and Techniques of X-ray Diffraction***"** held at the Department of Materials Engineering, Indian Institute Science (IISc), Bangalore, from June 10-21, 2013.
3. **Pal V.,** **"***Fundamentals of Quantum Mechanics and Applications***"** workshop held at department of Physics IIT, Delhi, during March 6 -7, 2010.

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