

Dielectric and Electrical Properties of Lead Cadmium Zirconate Titanate Ceramics

^{1*}Balgovind Tiwari, ²T. Babu, ³R.N.P. Choudhary

^{1,2}*Department of Physics, IIIT-RKValley, RGUKT, A.P., India.*

³*Department of Physics, ITER, SOA University, Bhubaneswar, Orissa, India.*

Abstract

A new PZT based material, lead cadmium zirconate titanate (PCZT), was prepared by using solid state reaction method. Systematic study on dielectric and electrical properties of PCZT ceramics has been done by modifying PZT with cadmium in various amounts of 5%, 10% and 15%. Dielectric studies showed that compounds exhibit phase transition generally observed in normal ferroelectric material. Curie temperature (T_c) values of modified PZT samples were less compared to T_c value of pure PZT. Except at 1 kHz frequency, all samples have low tangent loss up to 350°C at all remaining frequencies. Resistivity of every sample is decreased due to temperature effect. Presence of bulk and grain boundary effects in all samples were shown by Nyquist plot, and bulk effect in material is confirmed through modulus spectrum. Impedance studies have indicated semiconductor behavior of PCZT ceramics. Non-Debye electrical relaxation process occurred in material and conduction mechanism is found to be thermally activated process.

Keywords: ceramics; ferroelectric; tangent loss; Nyquist plot; conduction;

1. INTRODUCTION

Synthesis of new material systems is a wide research area till date. So various materials have been synthesized systematically and is still happening, for the industrial and other application purposes. Among them, PZT (lead zirconium titanium) is the one that has received a lot of attention due to its superior dielectric

*Corresponding Author (Balgovind Tiwari).
E-mail: balgovindtiwari@gmail.com

properties [1]. Further, different physical properties of PZT can be varied by means of modification resulting in the synthesis of new ceramic material systems [2]. PZT ($\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$) where x lies between 0 and 1 [3], has ABO_3 perovskite structure allows one to make a proper substitution at A and/or B sites where Pb and Zr/Ti ions reside. Details of ABO_3 structured PZT were already reported by some researchers [4-5]. Donors and /or acceptors are generally used for the substitution [4, 6-7]. Because of the piezoelectric nature of PZT, it is being used in the systems of piezoelectric energy harvesting [8]. In fact, modified material systems of PZT have got their use in the applications like piezoelectric sensors, piezoelectric transducers and actuators [5, 9]. The different structural phases of PZT based on its Zr/Ti ratio [10] made this material to be investigated widely.

Morphotropical phase boundary (MPB) of PZT ceramic is the region where both rhombohedral and tetragonal phases exist together [11-13]. In this work, PZT of MPB composition has been chosen to synthesize. Because, PZT of this composition shows improved dielectric properties [14], high polarization and also the best electrical properties and piezoelectric response [11-12, 15-18]. It is found that the physical properties of PZT can be controlled by making a suitable modification at the A-site [13].

Lanthanum substitution at the Pb-site of PZT has resulted in getting a new material known as lead lanthanum zirconatetitanate (PLZT) which has shown very interesting electrical properties, making it a suitable material for electrical and mechanical devices [19-20]. Even though, lots of work have been reported on PZT and its A-site modification [21-26], our literature review has conveyed that the work on modification of PZT by cadmium (Cd) has not been carried out so far. This has motivated us to carry out the detailed investigation on PZT by substituting Cd at the A-site. Therefore, a new material system (PCZT) has been synthesized using a standard solid state reaction method, and studied the effect of Cd on dielectric and electrical properties of PZT as presented in this paper.

2. EXPERIMENTAL

The chemicals used to prepare the samples of the PCZT ceramics are: lead oxide (PbO), cadmium oxide (CdO), zirconium dioxide (ZrO_2) and titanium dioxide (TiO_2). A solid state reaction method has been used as the experimental synthesis technique. After weighing, above chemicals were mixed through the process of dry grinding for 2h, followed by wet grinding (using acetone) for another an another hour in an agate mortar and pestle. Further, the samples were calcined at a temperature of 950 °C for 6 hours. Pellets were made using a hydraulic press device and the more details of making pellets is reported elsewhere [27-28]. Then the pellets were sintered at a temperature of 1100°C for 4 h. The electrical characterization has been done on PCZT compounds using the LCR-meter, and the details about measurement of dielectric and electrical characteristics has been reported elsewhere [27-28].

3. RESULTS AND DISCUSSIONS

3.1 Dielectric Studies

3.1.1 Study of temperature dependent dielectric constant

Figure 1 shows the variation of dielectric constant (ϵ_r) with temperature at different frequencies. For all samples, ϵ_r value has increased with increase in temperature up to its maximum value called ϵ_{max} and then showed a decrease at all frequencies except at 1 kHz where a further increase has been observed.

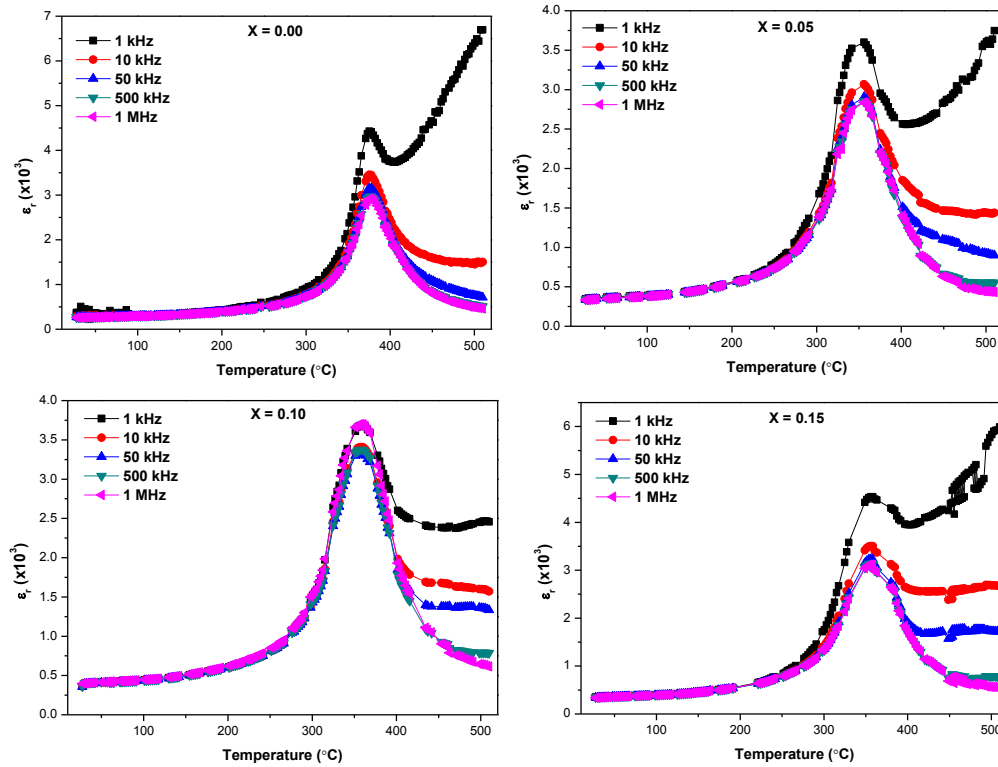


Figure 1: Study of dielectric constant with respect to temperature at chosen frequencies

Space charge polarization (scattering/transportation of space charges due to thermal activation) or some defects may be responsible for the increase of ϵ_r at higher temperatures [29-30]. It is observed from the figure that there is a point of Curie temperature (T_c) at which the transition of phase has been occurred. The occurrence of phase transition is generally from the ferroelectric to non-ferroelectric phase (paraelectric phase). In each composition, identical T_c has been observed at the given frequencies (value of T_c has not changed much with change in frequency). The change in the value of T_c has been observed in the material due to Cd substitution at the Pb-site. Substitution of 5% amount of Cd has decreased the value of T_c from 375 $^{\circ}\text{C}$ to 356 $^{\circ}\text{C}$ where the further increase in the concentration of Cd has not changed much

the value of T_c . The decrease in value of ϵ_{\max} with increase in frequency has been clearly observed in $x = 0.00, 0.05, 0.15$ samples, indicating the presence of normal dielectric behavior of a ferroelectric material [31]. But for $x = 0.10$ sample, an initial decrease followed by constancy in the value of ϵ_{\max} is observed. Widened dielectric peaks were not observed in the samples, suggesting the absence of disordering in the material perovskite structure. At 1 kHz, the value of ϵ_{\max} was decreased due to the substitution of the initial amount of Cd and then from there on, ϵ_{\max} value was increased with an increase in the concentration of Cd showing the maximum of ϵ_{\max} in $x = 0.15$ sample. The detailed particulars regarding the changes in T_c and ϵ_{\max} with respect to the frequency and concentration of Cd are given in table 1.

Table 1: Dielectric properties of PCZT ceramics

Cd concentration	f (kHz)	ϵ_{\max}	T_c ($^{\circ}\text{C}$)	ϵ_r	Tan δ
0.00	1	4428	375	841	0.93
	10	3454	375	723	0.15
	50	3153	375	703	0.05
	500	2965	377	697	0.02
	1000	2921	377	706	0.02
0.05	1	3602	356	1442	0.59
	10	3068	356	1278	0.12
	50	2904	356	1257	0.05
	500	2852	356	1267	0.08
	1000	2838	356	1307	0.15
0.10	1	3686	358	1575	0.57
	10	3408	358	1374	0.12
	50	3329	358	1341	0.05
	500	3374	358	1358	0.04
	1000	3701	358	1471	0.07
0.15	1	4536	358	1543	0.58
	10	3504	358	1307	0.13
	50	3230	356	1270	0.05
	500	3137	356	1267	0.04
	1000	3121	356	1303	0.05

3.1.2 Study of tangent loss with temperature

Figure 2 shows the dependence of tangent loss ($\tan \delta$) on temperature at various frequencies. In all samples, a constancy in the values of $\tan \delta$ has been observed up to a certain temperature at all frequencies except at 1 kHz. At 1 kHz, the value of $\tan \delta$ is invariant up to 150 °C for $x = 0.00$ sample, and 220 °C for the remaining samples. At the remaining frequencies, all the samples including, pure PZT, which has shown very less tangent loss up to 350 °C. So, the substitution of Cd has not changed the values of $\tan \delta$. There is a sharp increase in the loss spectrum of all samples at high temperatures indicating the presence of space charge polarization or existence of oxygen ion vacancies or unidentified defects. Further, conduction process is highly active at higher temperatures resulting in the increase of $\tan \delta$ [30]. The anomalies near the phase transition temperatures indicate the occurrence of relaxations of dipoles.

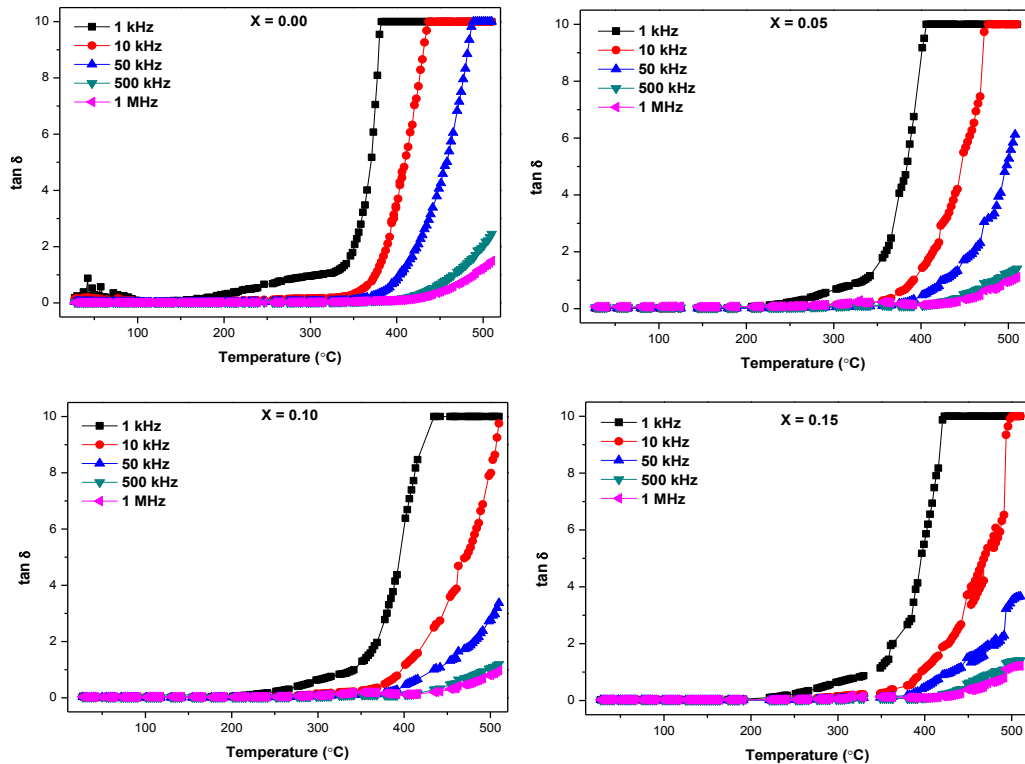


Figure 2: Variation of tangent loss with temperature at chosen frequencies

3.1.3 Study of variation of ϵ_r and $\tan \delta$ with frequency

Figure 3 shows the dependence of ϵ_r and $\tan \delta$ on frequency at 298 °C. It is clearly observed from the figure that the nature of variation of ϵ_r and $\tan \delta$ is very much identical where both are observed to be decreased with increase in frequency confirming the dielectric nature of a normal ferroelectric material [30]. Therefore, Cd

substitution has not made any change in the dielectric behavior of the materials. The high values of ϵ_r are observed in the region of low frequency where the different polarizations (such as atomic, orientational, space charge, ionic, electronic, interfacial, dipolar, etc.) and assemblage of charge carriers at grain boundary or interface contribute to the ϵ_r value [31-32]. But in the region of high frequency, low values of ϵ_r are observed due to the absence of some polarizations except electronic polarization which contributes to ϵ_r even in the high frequency region.

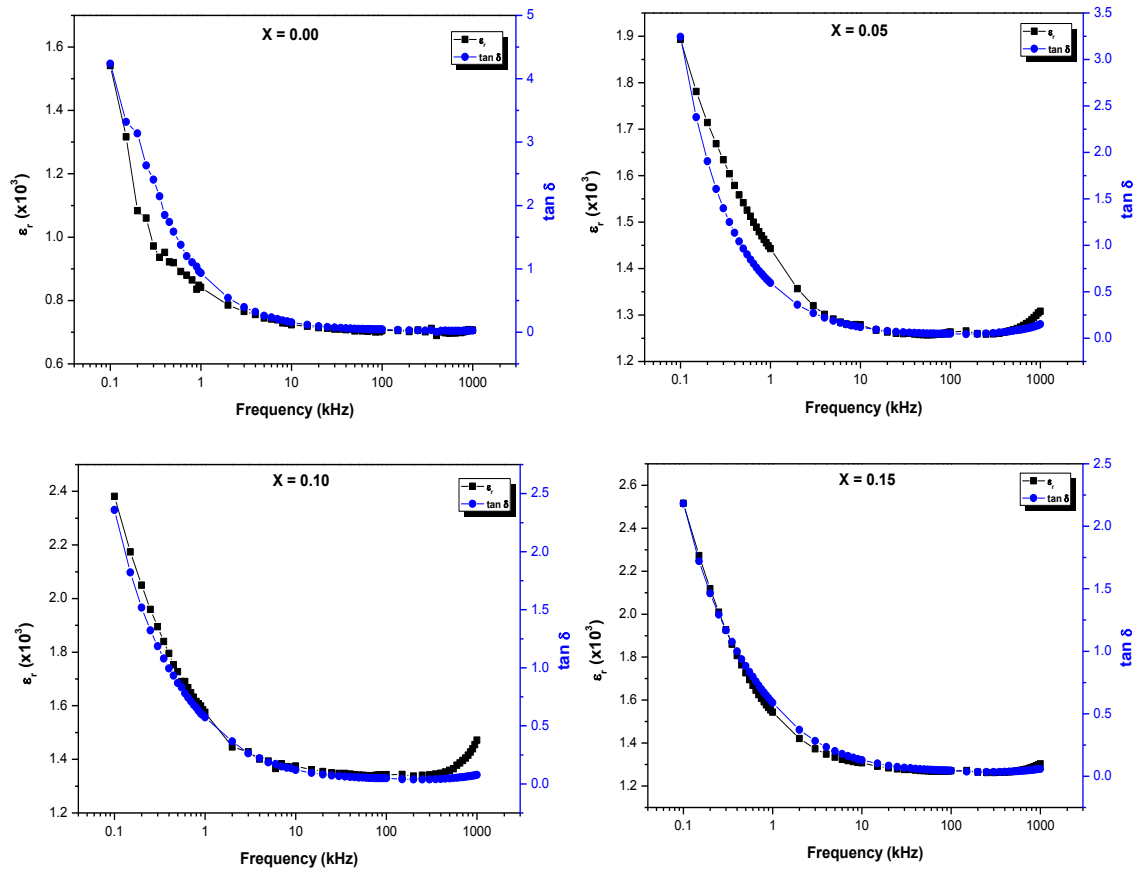


Figure 3: Variation of dielectric constant and tangent loss with frequency

So the charge carriers will have no time to drift due to increase in frequency and this results in the decrease of ϵ_r of the material [34]. With increase in the concentration of Cd, there is an increase in the values of both ϵ_r and $\tan \delta$ of the material. Since the packing fraction is high in the material, the decreasing nature of $\tan \delta$ has been observed with increase in frequency and this again suggested the presence of a mechanism of dipole relaxation. The space charges undergo relaxation because of their incapability to respond to the higher frequencies of applied electric field [35]. The detailed particulars of ϵ_r and $\tan \delta$ at certain frequencies were given in table 1.

3.2 Impedance studies

3.2.1 Nyquist plots

Figure 4 shows the variation of the real part of impedance with the imaginary part of impedance (i.e. Nyquist plot/complex impedance spectrum) at different high temperatures.

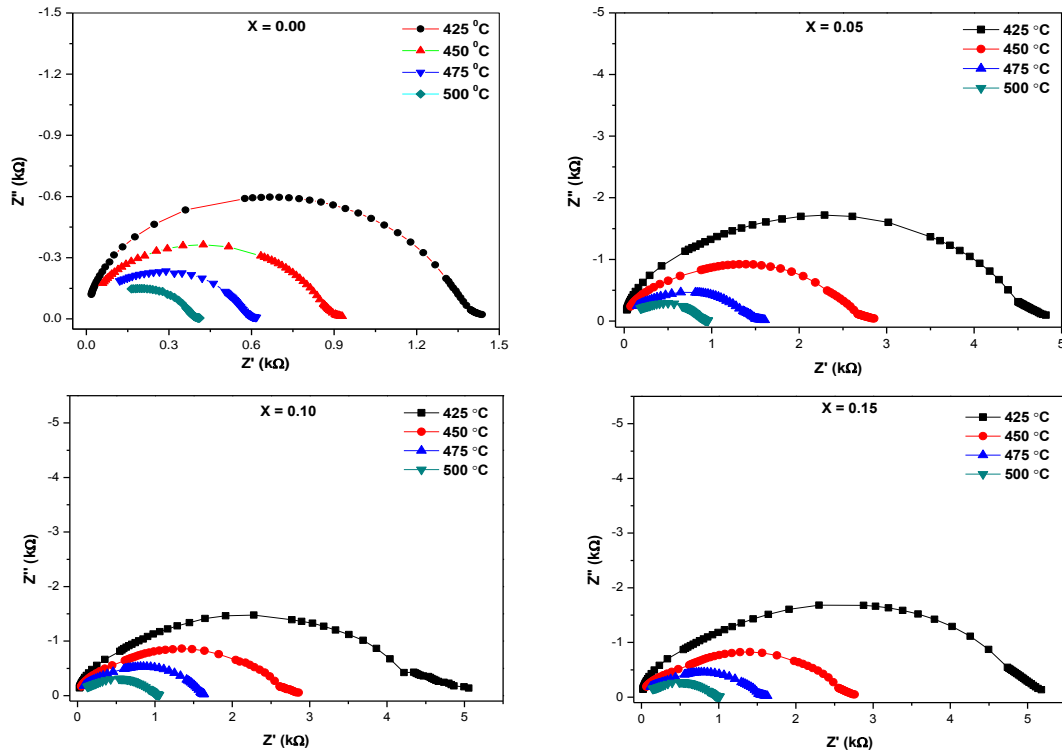


Figure 4: Study of real part of impedance with respect to imaginary part of impedance at selected temperatures

The plots show the semicircles at the selected temperatures of all the samples. The point of intersection (i.e., intercept) of semicircular arc on Z' axis (i.e., x-axis) render the value of bulk resistance of the sample. With increase in temperature, it clearly observes from the figure that the interception points has shifted towards the origin giving the evidence of decrease in resistive property and the increase in ac conductivity of material [30]. For all the samples, the presence of two semicircles is noticed. One is the high frequency semicircle indicating the bulk/grain property of material that results from the parallel combination of bulk resistance and bulk capacitance. Another is the low frequency semicircle which has just a start indicating the effect of grain boundary. The start of low frequency semicircle indicates the presence of poorly resolved grain boundary components (i.e., the partial effect of grain boundary) and non-homogeneous electrical behavior of grain boundaries of samples. Therefore, it can be concluded that the process of conduction/electrical response of material is mainly due to its bulk property. As per the observations made

above, electrical circuit of the material will be the parallel combination of bulk resistance and bulk capacitance in the material. The absence of third semicircle in the Nyquist plots indicate the negligible contribution of ceramic electrolyte-electrode interface effect [40]. But for $x = 0.00$, even the higher frequency semicircle is not clearly formed, but still there is a tail of the low-frequency semicircle. This unclear/badly formed semicircle indicates non-Debye type of relaxation process in the material [34]. The impedance values were changed with changes in the concentration of Cd. Particularly at 425 °C, impedance value has been increased with increase in Cd concentration. It is also very much clear that the substitution of Cd at A-site of PZT has resulted in the higher values of impedance compared to pure PZT. Maximum value of impedance is observed in $x = 0.15$ sample at 425 °C. It is also expected that the value of bulk resistance will show a decrease and an increase with increase in temperature and the amount of Cd respectively. The above observation of bulk resistance with temperature is generally noticed in semiconductors [32].

3.2.2 Study of real part of impedance with change of frequency

Figure 5 shows the nature of the real part of impedance (Z') with respect to the frequency at high temperatures.

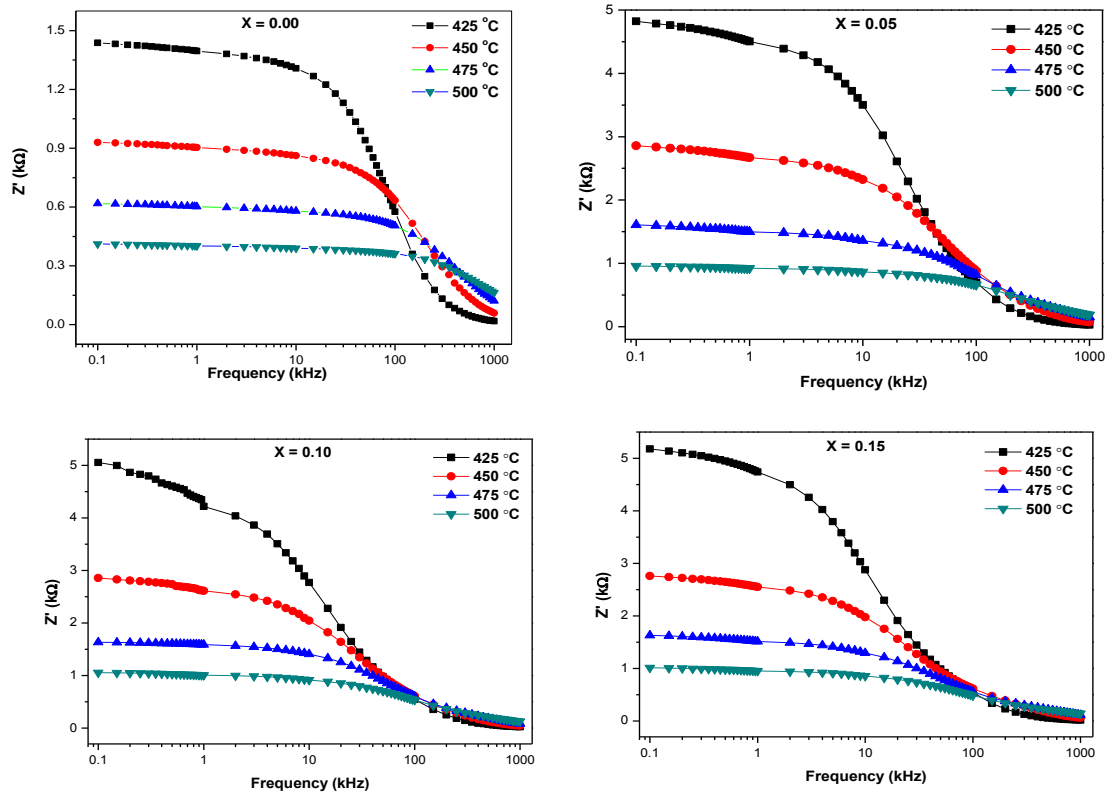


Figure 5: Study of real part of impedance with respect to the frequency at selected temperatures

With the increase in frequency, the value of Z' is found to be decreased in all samples, indicating the increment in ac conductivity with a rise in frequency [29]. With increase in temperature also, there is a decrease in value of Z' showing the negative temperature coefficient of resistance (NTCR) property [2, 3] resembling semiconductor behavior in all PZT samples [35]. A clear dispersion spectrum has been observed for all the samples in the low- frequency region, and the NTCR behavior of material has been changed in the high- frequency region showing the merging of Z' which is still found to be temperature dependent. At higher temperature (i.e. 500°C), an electrical property (i.e., dc conductivity) of the material which is invariant of the frequency was indicated by the lower frequency plateau. At high frequency region, merging of Z' has been observed in material irrespective of Cd substitution. This is possibly because of liberation of space charges as a consequence of the decrease in barrier properties of the materials with increase in temperature [29, 35-36]. Because of little time for the space charges to relax, the recombination might be faster so that the space charge polarization is lessened at higher frequencies resulting in the merging of Z' [37]. Further, it is clearly seen that the merger of Z' has been shifting towards the region of low frequency indicating the liberation of space charges at low frequencies only. There is an enormous increase in the value of Z' due to a small amount of Cd ($x = 0.05$) substitution. With further increase in the amount of Cd, no large changes in the values of Z' are observed. At 425 °C, the values of impedance were increased with increase in concentration of Cd. For $x = 0.15$ sample, the high value of impedance at 425 °C may be due to the space charge polarization and orientation polarization (i.e. inter-grain, intra-grain dipoles orientation) [34].

3.2.3 Study of imaginary part of impedance with change in frequency

Figure 6 shows the nature of the imaginary part of impedance (Z'') with respect to the frequency (i.e., loss spectrum) at high temperatures. In all the samples, Z'' value has reached the maximum value (i.e. Z''_{\max}) at a particular frequency irrespective of the temperature and concentration of Cd. The frequency coinciding with the Z''_{\max} is known as peak frequency or relaxation frequency [34]. Here, the loss spectrum is characterized by the appearance of the peaks, merging of the spectrum, height of the peaks and widening of the peaks. A Debye like peak was observed in all the samples of loss spectrum indicating the existence of space charges and the start of an electrical relaxation process.

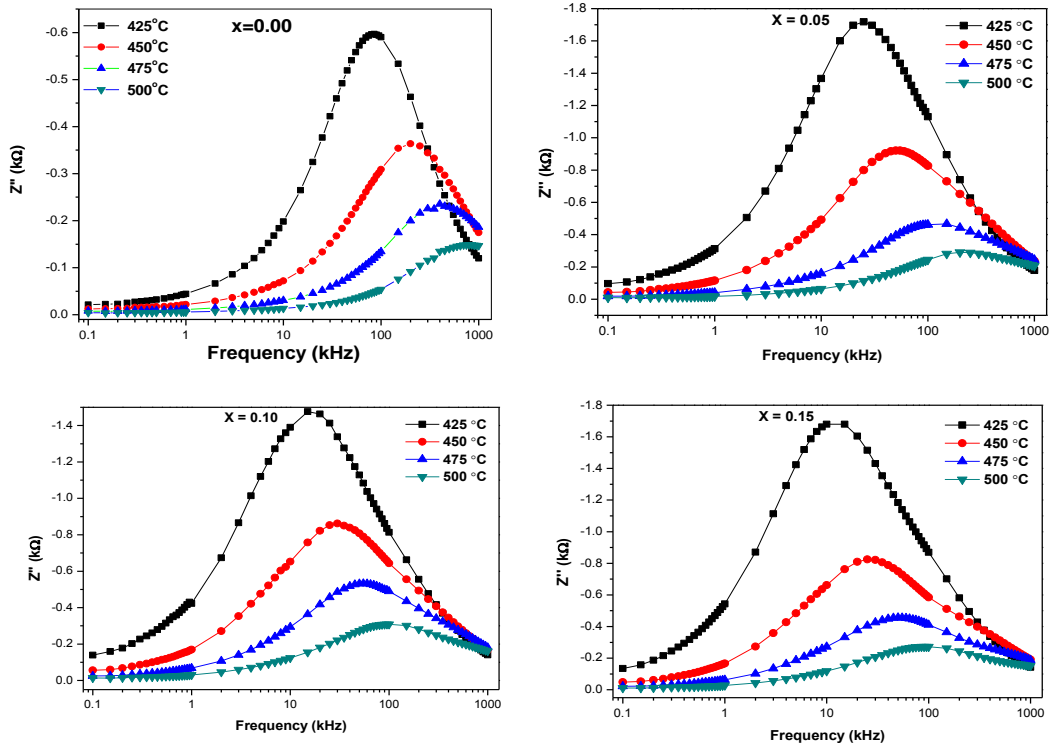


Figure 6: Study of imaginary part of impedance with respect to the frequency at selected temperatures

It is clearly observed that the peaks are found to be very much dependent on temperature. With increase in temperature, it has been observed in all samples that there is a shift in peaks showing the occurrence of the relaxation process. The relaxation is found to be non-Debye type of relaxation process which was indicated by the presence of asymmetric peak. At lower temperatures, presence of immobile species or electrons is responsible for the mechanism of relaxation with the oxygen vacancies or defects holding the responsibility at higher temperatures [33, 35]. Since the peaks are shifting towards the region of higher frequency, there is the minimum capacitive effect on Cd substitution which indicated an improvement in net impedance and barrier properties of the materials. Moreover, the relaxation process is slowed down initially due to the assemblage of space charges. Dispersion at lower frequencies and merging at higher frequencies in loss spectrum of all the samples is due to the space charge polarization (i.e. it is active at lower frequencies and ineffective at higher frequencies). But for $x = 0.00$ sample, merger of Z'' at high frequency region was not clearly observed, which is expected to appear on the further increase of frequency and this goes beyond our measuring limit. The merger of Z'' in the high frequency region provided the information of space charges aggregation in the material, regardless of the concentration of Cd. The peaks were seemed to be broadened with change in Cd concentration, indicating that the process of electrical

relaxation is pure dependent on the concentration of Cd. Hence, the existence of electrical process with the spread of relation time at two points of equilibrium (i.e., multiple relaxation times) has been indicated in material due to the asymmetric broadening of peaks. In all the samples, the peaks were found to be broadened with increase in temperature showing that the process of electrical relaxation is pure dependent on temperature. In high temperature observations, generally the relaxation species like defects might be the reason behind the process of electrical conduction in the material [38-39]. Quick movement (i.e., hopping) of conduction electrons/oxygen ion vacancies/defects between the available localized sites are responsible for electrical conduction/electrical transport process [35].

3.3 Modulus studies

3.3.1 Complex electric modulus spectrum

Figure 7 shows the study of real part of modulus with respect to the imaginary part of the modulus (i.e., complex modulus spectrum) at the selected high temperatures.

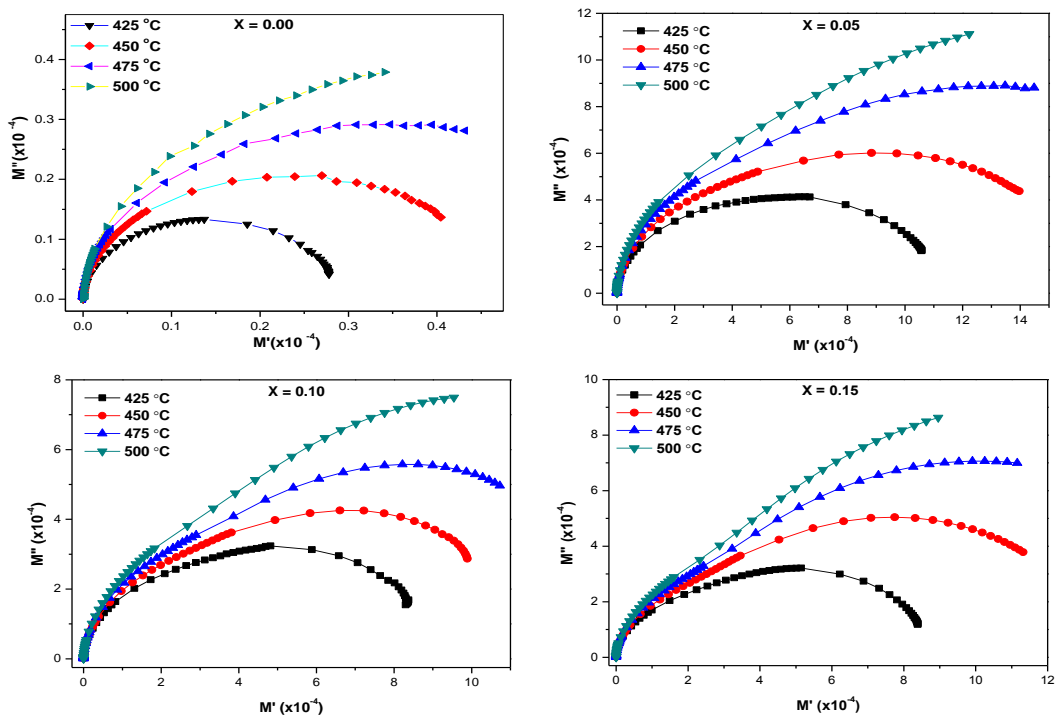


Figure 7: Study of real part of modulus with respect to the imaginary part of modulus at selected temperatures

The complex modulus spectrum has been evaluated from the impedance data because this spectrum can give an indication and analysis of the electrical response of the materials. A single semicircle can be observed in the spectrum of all samples. The

point of intersection (i.e., intercept) of semicircular arc gives the total capacitance due to the bulk/grain property. This again confirms the effect of bulk property in electrical properties of Cd modified PZT samples. With increase in temperature and concentration of Cd, the spectrum is showing a noticeable change indicating the changes in capacitance values of the materials. The distorted semicircles instead of an exact semicircle indicated the presence of non-Debye type of electrical relaxation process with the spread of relaxation with different mean time constants. From the figure, it can be concluded that the grain boundary has shown no effect on the total capacitance and the relaxation process of the material because of the absence of second semicircle. The single semicircular also confirmed that the compounds are in the single phase mode.

3.3.2 Variation of real part of modulus with frequency

Figure 8 shows the nature of the real part of modulus with respect to the frequency at different high temperatures.

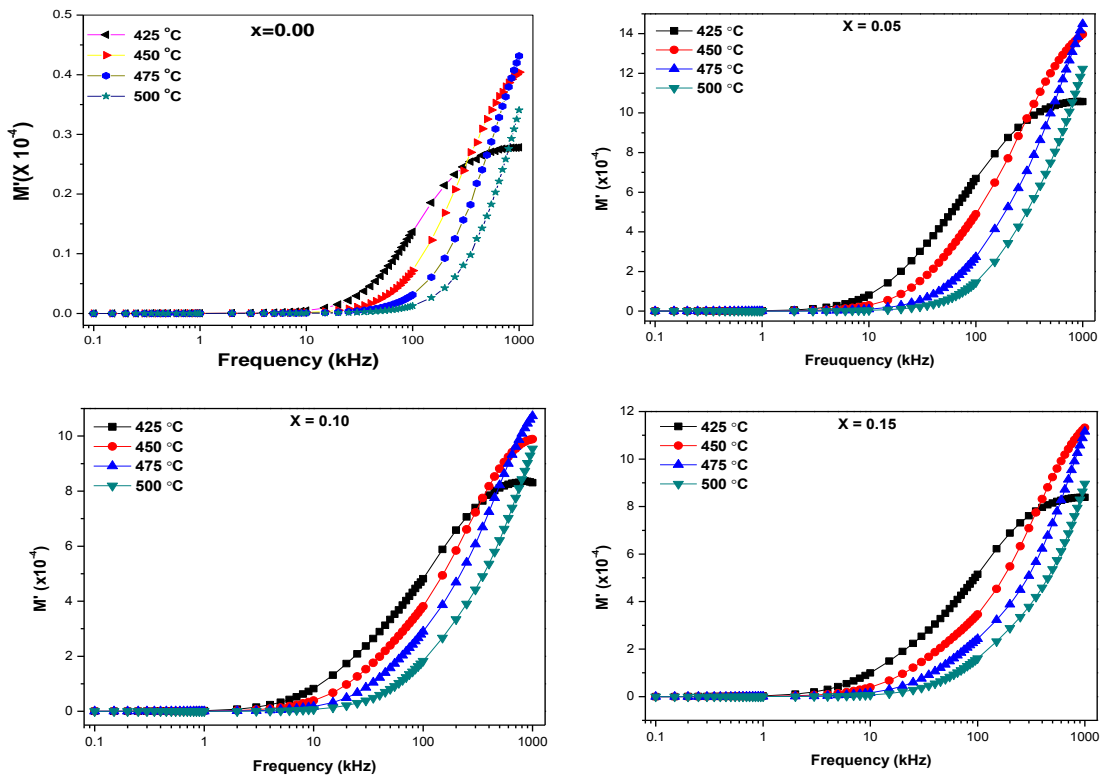


Figure 8: Variation of real part of modulus with frequency at chosen temperatures

For all samples, an identical nature has been observed in which the M' values were seemed to come near to zero in 0 kHz and 1 kHz frequency range (i.e., very low

frequency region). Low values of M' in the low frequency region and its exponential increase in the high- frequency region is due to the unavailability of restoring force of the flow of charges under the influence of steady electric field which again indicated the absence of effect of electrode-interface in the material. It clearly observed in $x = 0.00$ sample that the dispersion was starting to appear after 10 kHz frequency, whereas for the remaining sample dispersion has been observed after 2 kHz frequency. The conductivity relaxation is majorly responsible for the dispersion phenomenon in the material. Further, long range mobility of charge carriers has been confirmed by the increase in dispersion with increase in frequency as well as the indication of M' attaining a maximum value (asymptotic value of M' or M'_{\max}). Hence, it can be concluded that the electrode polarization has not been contributed to M' at higher frequencies, whereas there is considerable contribution of electrode and/or ionic polarization at lower frequencies [34]. Due to the substitution of Cd at A site of PZT, larger values of M' were resulted. With an increase in concentration of Cd, M' values were significantly changed.

3.3.3 Variation of imaginary part of modulus with frequency

Figure 9 shows the variation of the imaginary part of modulus with respect to the frequency at high temperature values. It was clearly observed that the values of M'' are approaching zero in the low frequency region and there is an appearance of peak (i.e. M''_{\max}) in the high frequency region irrespective of temperature except at 600°C in modified samples. At 600°C, a clear peak was not appeared due to our limited measuring capacity, which is expected to appear on a further increase of frequency. This observation indicated the absence of electrode polarization in the material. With increase in temperature, the peaks were observed to be asymmetric and have got shifted to the high frequency region. M'' has increased with increase in frequency and takes a peak value at a particular frequency. These peaks represent the transition from short range mobility to long range mobility on decreasing frequency, where the peak from low frequency side represents the limit of frequencies in which the ions are capable of moving larger distances from one site to the neighboring site by hopping. However, in the high frequency region, the ions are spatially confined to their potential wells and can execute only localized motions [39].

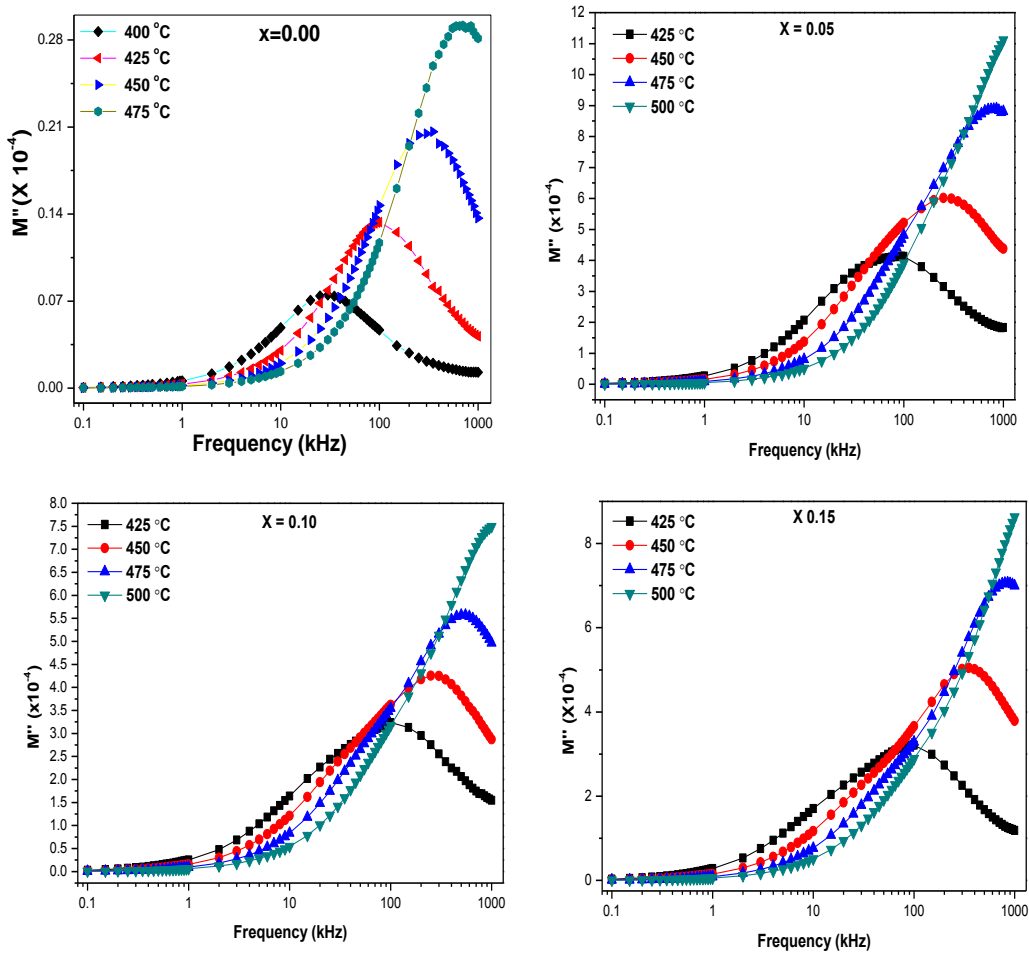


Figure 9: Variation of imaginary part of modulus with frequency at chosen temperatures

For all the samples, it is seen that M''_{\max} has been shifting to the frequency of higher relaxation with increase in temperature showing the correlation among the mobile ions motion. This observation also has given an indication of a thermally activated relaxation process for all samples in which there is a domination of hopping of charge carriers with little polarons. Further, the asymmetric peaks were found to be broadened which suggested the spread of times of relaxation with different time constant and therefore the relaxation in material is non-Debye type of relaxation. In all samples, it has been observed that there is a significant increase in the height of M''_{\max} with increase in frequency which is a general feature observed in real ionic conductors. Also, the frequency corresponding to M''_{\max} has been increased with increase in frequency for all samples. This increase in value of the frequency with increase in temperature is attributed to the conductivity relaxation. Due to the substitution of Cd, larger values of M'' were resulted. $x = 0.05$ sample has shown

very large value of M'' at 600 °C compared to the remaining samples at the same temperature. Because of inverse proportionality relation between the peak height and capacitance of the material [35], it can be concluded for all samples that there are considerable changes in capacitance of the material at all given temperatures due to Cd substitution.

4. CONCLUSIONS

PCZT ceramics were fabricated using solid state synthesis. Results of dielectric studies revealed that the T_c value is decreased initially due to the substitution of 5% Cd and then increased with increase in amount of Cd but still the T_c values were found to be less compared to pure PZT. 10% of Cd substitution (i.e. $x = 0.10$ sample) has resulted in the higher values of ϵ_r compared with other samples. Substitution of Cd+2 ions at the Zr site resulted in lower T_c values and higher values of impedance. Rise in ac conductivity has been indicated in PCZT ceramics due to decrease in their resistive property. Absence of electrode-interface effect has been observed in all the samples of PCZT. Asymmetrically broadened peaks in modulus spectroscopy has confirmed the occurrence of non-Debye type of relaxation process, and the real ionic conductor behavior of material was also indicated from the modulus study.

ACKNOWLEDGEMENT

We (authors) would like to thank IIT Kharagpur for its support to the experimental work. We are also thankful for the partial financial support provided by DST-SERB.

REFERENCES

- [1] Nguyen Dinh Tung Luan, Le Dai Vuong, Truong Van Chuong, Nguyen Truong Tho, Structure and Physical Properties of PZT-PMnN-PSN Ceramics Near the Morphological Phase Boundary, *Advances in Materials Science and Engineering*, 2014 (2014), 821404 (8 pages).
- [2] Sakri Adel, Bouremel Cherifa, Djafri Dhiya Elhak, Bouaziz Mounira, Effect of Cr_2O_3 and Fe_2O_3 doping on the thermal activation of un-polarized PZT charge carriers, *boletín de la sociedad española de cerámica y vidrio*, 57 (2018), 124–131.
- [3] Dariusz Bochenek, Przemysław Niemiec, Microstructure and physical properties of the multicomponent PZT type ceramics doped by calcium, sodium, bismuth and cadmium, *Applied Physics A*, 124 (2018), 775.
- [4] Fares Kahoul, Louanes Hamzioui, Ahmed Boutarfaia, The influence of Zr/Ti content on the morphotropic phase boundary and on the properties of PZT-SFN piezoelectric ceramics, *Energy Procedia*, 50 (2014), 87 – 96.
- [5] Sheng-Yuan Chu, Te-Yi Chen, I-Ta Tsai, Walter Water, Doping effects of Nb

- additives on the piezoelectric and dielectric properties of PZT ceramics and its application on SAW device, *Sensors and Actuators A*, 113 (2004), 198–203.
- [6] Thomas R. Shrout, Shujun, J. Zhang, Lead-free piezoelectric ceramics: Alternatives for PZT?, *J. Electroceram*, 19 (2007), 111–124.
- [7] Pulkit Sharma, Sugato Hajra, Sushrisangita Sahoo, Pravat Kumar Rout, Ram Naresh Prasad Choudhary, Structural and electrical characteristics of gallium modified PZT ceramics, *Processing and Application of Ceramics*, 11 [3](2017), 171–176.
- [8] Mitsuhiro Okayasu, Smart Energy Materials of PZT Ceramics, *International Journal on Smart Material and Mechatronics*, 2 (2015), 102-105.
- [9] H. Ossmer, C. Slouka, L. Andrejs, P. Blaha, G. Friedbacher, J. Fleig, Electrocoloration of donor-doped lead zirconatetitanate under DC field stress, *Solid State Ionics*, 281 (2015), 49–59.
- [10] Pulkit Sharma, Sugato Hajra, Sushrisangita Sahoo, P. K. Rout, R. N. P. Choudhary, Capacitive and resistive characteristics of gallium modified leadzirconatetitanate, *J Mater Sci: Mater Electron*, 28 (2017), 12048–12055.
- [11] J. A. Pérez, M. R. Soares, P. Q. Mantas, H. Amorín, M. E. V. Costa, A. M. R. Senos, Growth of Lead ZirconateTitanate Single Crystals by the High Temperature Solution Method, *Materials Science Forum*, 514-516 (2006), 184-187.
- [12] M. Cerqueira, R. S. Nasar, E. Longo, J. A. Varela, A. Beltran, R. Llusar, J. Andres, Piezoelectric behaviour of PZT doped with calcium: a combined experimental and theoretical study, *Journal of Materials Science*, 32 (1997), 2381-2386.
- [13] S. C. Panigrahi, Piyush R. Das, R. Padheed, R. N. P. Choudhary, Effect of Gd on dielectric and piezoelectric properties of lead zirconatetitanate ferroelectric ceramics, *Ferroelectrics*, 524 (2018), 14-29.
- [14] A. S. Karapuzha, N. K. James, H. Khanbareh, S. van der Zwaag, W. A. Groen, Structure, dielectric and piezoelectric properties of donor doped PZT ceramics across the phase diagram, *Ferroelectrics*, 504 (2016), 160-171.
- [15] Jean-Claude M'Peko, Antonio G. Peixoto, Ernesto Jimenez, Luis M. Gaggero-Sager, Electrical Properties of Nb-Doped PZT 65/35 Ceramics: Influence of Nb and Excess PbO, *Journal of Electroceramics*, 15 (2005), 167–176.
- [16] Rajiv Ranjan, Rajiv Kumar, R. N. P. Choudhary, Effect of Sm Substitution on Structural, Dielectric, and Transport Properties of PZT Ceramics, *Research Letters in Physics*, 2009 (2009), 382578 (4 pages).
- [17] Giulia Montanari, Anna Luisa Costa, Stefania Albonetti, Carmen Galassi, Nb-Doped PZT Material by Sol-Gel Combustion, *Journal of Sol-Gel Science and Technology*, 36 (2005), 203–211.

- [18] Shujun Zhang, Ru Xia, Laurent Lebrun, Dean Anderson, Thomas R. Shrout, Piezoelectric materials for high power, high temperature applications, *Materials Letters*, 59 (2005), 3471 – 3475.
- [19] Sweta Sharma, S.C. Azad, Md. Soaib Khan, Rajiv Ranjan, Banarji Behera, R.N.P. Choudhary, Effect of Gd^{3+} -substitution on structural and electrical properties of lead zirconate titanate (PZT; Zr/Ti=55/45) ceramics, *Journal of Metallurgy and Materials Science*, 56 (2014).
- [20] Kanhaiya Lal Yadav, R.N.P. Choudhary, Synthesis and characterization of PLZT (10/65/35), *Journal of Materials Science*, 28 (1993), 769-772.
- [21] G.H. Haertling, and C.E. Land, Hot-Pressed (Pb, La) (Zr, Ti) O₃ Ferroelectric Ceramics for Electrooptic Applications, *J. Am. Ceram. Soc.*, 54(1971), 1–11.
- [22] Q. Sun, H. Deng, X. Li, P. Yang, and J. Chu, The influence of La content on properties of PLZT thin films, *J. Phys.: Conference Series*, 276(2011), 012186.
- [23] S. Singh, O.P. Thakur, and C. Prakash, Synthesis, Structural and Electrical Properties of Lanthanum-modified Lead-zirconate-titanate System, *Def. Sci. J.* 55(2005), 349–356.
- [24] K. Carl, and K. Geisen, Dielectric, optical properties of quasi-ferroelectric PLZT ceramic, *Proceedings IEEE*, 61(1973), 967–974.
- [25] R. Ranjan, R. Kumar, N. Kumar, B. Behera, and R.N.P. Choudhary, Impedance and electric modulus analysis of Sm-modified Pb (Zr_{0.55}Ti_{0.45})_{1-x}/4O₃ ceramics *J. Alloys Comp.* 509(2011), 6388–6394.
- [26] S.R. Shannigrahi, F.E.H. Tay, K. Yao, and R.N.P. Choudhary, Effect of rare earth (La, Nd, Sm, Eu, Gd, Dy, Er and Yb) ion substitutions on the microstructural and electrical properties of sol-gel grown PZT ceramics, *J. Euro. Ceram. Soc.*, 24(2004), 163–170.
- [27] Balgovind Tiwari, R.N.P. Choudhary, Complex Impedance Spectroscopic Analysis of Mn modified Pb(Zr_{0.65-x}Mn_xTi_{0.35})O₃ Electroceramics, *J of Physics and Chemistry of Solids*, 69(11), 2852-2857.
- [28] Balgovind Tiwari, R.N.P. Choudhary, Frequency–temperature response of Pb(Zr_{0.65-x}Ce_xTi_{0.35})O₃ ferroelectric ceramics: Impedance spectroscopic studies, *Journal of Alloys and Compounds*, 493 (2010), 1–10.
- [29] S. K. Pradhan, S. N. Das, S. Bhuyan, C. Behera, R. Padhee, R. N. P. Choudhary, Structural, dielectric and impedance characteristics of lanthanum-modified BiFeO₃–PbTiO₃ electronic system, *Appl. Phys. A*, 122 (2016), 604.
- [30] Kalpana Parida, Sujit Kumar Dehury, R. N. P. Choudhary, Structural, electrical and magneto-electric characteristics of complex multiferroic perovskite Bi_{0.5}Pb_{0.5}Fe_{0.5}Ce_{0.5}O₃, *J Mater Sci: Mater Electron*, 27 (2016), 11211–11219.
- [31] S. N. Das, A. Pattanaik, S. Kadambini, S. Pradhan, S. Bhuyan, R. N. P. Choudhary, Dielectric and impedance spectroscopy of Ni doped BiFeO₃-

- BaTiO₃ electronic system, *J Mater Sci: Mater Electron*, 27 (2016), 10099–10105.
- [32] Alok Shukla, Nitin Kumar, C. Behera, R. N. P. Choudhary, Structural, dielectric and magnetic characteristics of Bi(Ni_{0.25}Ti_{0.25}Fe_{0.50})O₃ ceramics, *J Mater Sci: Mater Electron*, 27 (2016), 1209–1216.
- [33] Alok Shukla, Nitin Kumar, C. Behera, R.N.P. Choudhary, Structural and electrical characteristics of (Co, Ti) modified BiFeO₃, *J Mater Sci: Mater Electron*, 27 (2016), 7115–7123.
- [34] Niranjana Panda, Samita Pattanayak, R. N. P. Choudhary, Ashok Kumar, Effect of La-substitution on structural, dielectric and electrical properties of (Bi_{0.5}Pb_{0.5}) (Fe_{0.5}Zr_{0.25}Ti_{0.25})O₃, *Appl. Phys. A*, 122 (2016), 823.
- [35] Susmita Nath, Subrat Kumar Barik, R. N. P. Choudhary, Electrical and ferroelectric characteristics of (LaLi)_{1/2} (Fe_{2/3}Mo_{1/3})O₃, *J Mater Sci: Mater Electron* 27 (2016), 8717–8724. 2852-2857.
- [36] S.Sen, P.Pramanik, R.N.P.Choudhary, Effect of Ca-additions on structural and electrical properties of Pb(SnTi)O₃ nano-ceramics, *Ceram.Int.* 33, 579–587.
- [37] R.K.Mishra, Structural electrical and magnetic properties of Yttrium/Neodymium/Manganese modified Bismuth and Lead based multiferroics, Ph.D. Thesis (2008), IIT Kharagpur, India.
- [38] Banarji Behera, P. Nayak, R.N.P.Choudhary, Impedance spectroscopy study of NaBa₂V₅O₁₅ ceramic, *J. Alloys Compd.* 436, 226–232.
- [39] Banarji Behera, P.Nayak, R.N.P.Choudhary, Study of complex impedance spectroscopic properties of LiBa₂Nb₅O₁₅ ceramics, *Mater.Chem.Phys.*, 106, 193–197.
- [40] S.K. Patri, Synthesis and characterization of Bismuth layered multiferroic derivatives, Ph.D. Thesis, IIT Kharagpur (2009), India.