International Journal of Emerging Technology and Advanced Engineering
Website: www.ijetae.com (ISSN 2250-2459, ISO 9001:2008 Certified Journal, Volume 6, Issue 10, October 2016)

Investigation of Complex Impedance Properties of Pure and Gd^{3+}-Substituted Lead Zirconate Titanate Ceramics

Subhash Chandra Azad[1], N K Singh[2], Rajiv Ranjan[3]
[1,2]*Department of Physics, Vir Kunwar Singh University, Ara, Bihar, India-802301*
[3]*Department of Physics, Jamshedpur Co-Operative College, Kolhan University, Jharkhand, India-831001*

***Abstract---* The pure and Gd^{3+}-substituted lead zirconate titanate (PZT) ceramics with chemical composition $Pb_{1-x}Gd_x(Zr_{0.56}Ti_{0.44})_{1-x/4}O_3$; x = 0.00 and 0.06 have been prepared using high temperature mixed oxide method at sintering temperature 1200^0C. Using a non-destructive complex impedance spectroscopy (CIS) technique, the impedance properties of the materials have been investigated within wide range of temperatures and frequencies. The real part of impedance (Z') is found to decrease with the increase in frequency as well as temperature and at high frequencies, it acquires a very low constant value and becomes almost independent of both the frequency and temperature. The variation of imaginary part of impedance (Z") with frequency shows some peaks that shift towards higher frequencies with the increase in temperature exhibiting a decreasing trend of peak height. It suggests about the temperature dependent relaxation process in the material. The complex impedance Z' ~ Z" Nyquist plots indicates single semicircle or its tendency which suggests about the presence of bulk resistive contribution in the materials. The bulk resistance exhibits a decreasing trend with the increase in temperature suggesting a typical negative temperature coefficient of resistance (NTCR) type behaviour. These complex impedance plots also suggest the presence of non-Debye type of relaxation phenomenon in the materials.**

***Keywords---* PZT, PGZT, CIS, Impedance analysis, NTCR, Non-Debye type relaxation**

I. INTRODUCTION

With the discovery of ferroelectric property in $BaTiO_3$ in 1945, a revolution has arisen in the field of ferroelectricty which was resulted in the development of a large number of materials of different structural families (such as, perovskite, tungsten bronze, etc.). Among various oxides, materials with perovskite family of general formula ABO_3 (where, A = mono or divalent; B = tri-hexavalent ions) were found useful in different electronic applications. Specially, some lead based perovskites namely $PbTiO_3$, $PbZrO_3$, $Pb(Zr,Ti)O_3$, $Pb(Mg,Nb)O_3$, etc. were found to be better ferroelectric materials [1-2].

Lead zirconate titanate $Pb(Zr,Ti)O_3$ (popularly known as, PZT) [3] is the solid-state solution of ferroelectric $PbTiO_3$ (PT; $T_c = 490^oC$) and antiferroeletric $PbZrO_3$ (PZ; $T_c = 230^oC$) presenting two ferroelectric phases: tetragonal phase in the titanium rich side of the binary system and rhombohedra phase in the zirconium rich side [4-5]. With the change in Zr/Ti ratio, the physical properties of PZT can be modified considerably so that it becomes useful for many device applications.

Its characteristic parameters considerably depend on its compositional fluctuations, particle size, nature of substitution, calcination and sintering temperatures, etc. PZT has tremendous applications in the field of research as well as in industries in the form of computer memory and display, actuators, Pyroelectric detectors, transducers, microphone, sensors, etc [1, 6-8].

This paper reports on the study of impedance properties of pure and Gd^{3+}-substituted PZT ceramics with Zr/Ti ratio 56/44 using complex impedance spectroscopy technique.

II. EXPERIMENT

The Gd^{3+}-substituted lead zirconate titanate (PGZT) ceramics have been prepared through high temperature mixed oxide method with chemical composition $Pb_{1-x}Gd_x(Zr_{0.56}Ti_{0.44})_{1-x/4}O_3$ (where x = 0.00 and 0.06) using 99.9% pure (M/S Loba Chemie, Inc. Bombay, India) ingredients: PbO, ZrO_2, TiO_2 and Gd_2O_3. An extra 3% of PbO was added to the mixture to compensate lead-loss at high temperatures. The well mixed oxides were calcined at an optimized temperature of 1100°C for 10 hours. Using polyvinyl alcohol (PVA) as binder, the calcined powders were converted into pellets and were sintered at an optimized temperature 1200°C for 10 hours so as to get maximum density (97% of theoretical density).

For the study of electrical properties, the smooth flat surfaces of the pellets were painted with high purity air-drying silver paint. Using Phase Sensitive Multimeter (PSM; Model 1735) along with its accessories various electrical data were recorded at different temperatures and frequencies. Using them, complex impedance properties of the materials have been investigated.

III. RESULTS AND DISCUSSION

The complex impedance properties of the materials have been analysed using complex impedance spectroscopy (CIS) technique [9]. This technique is helpful in analysing real and imaginary components of complex electrical parameters so as to get true picture of the material properties.

IJETAE
EXPLORING RESEARCH AND INNOVATIONS

International Journal of Emerging Technology and Advanced Engineering
Website: www.ijetae.com (ISSN 2250-2459, ISO 9001:2008 Certified Journal, Volume 6, Issue 10, October 2016)

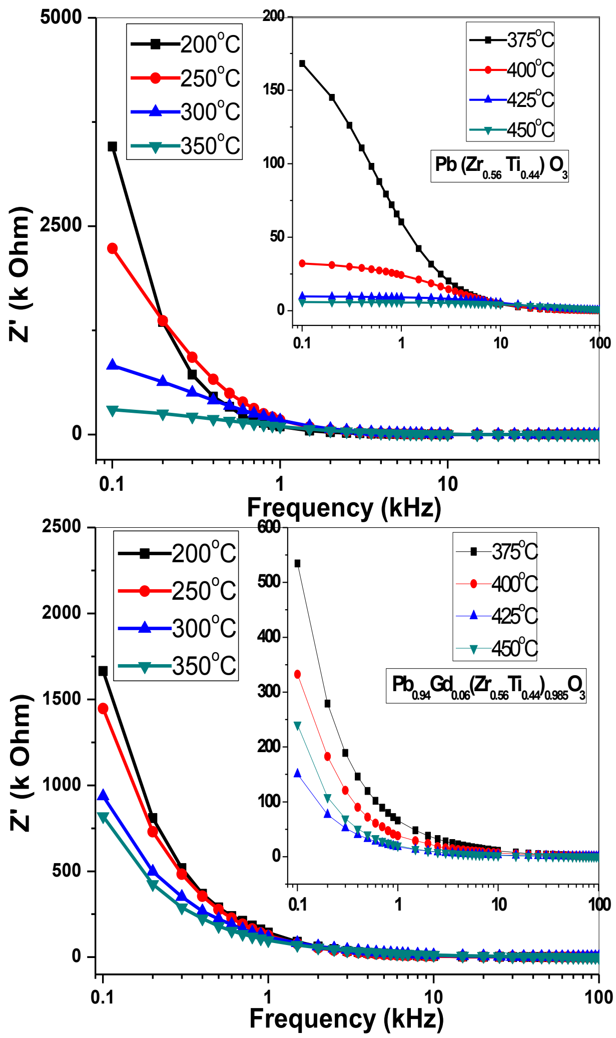

Fig.-1: Temperature-frequency dependence of Z' of PZT and PGZT ceramics

The variation of real part of impedance (Z') of PZT and PGZT samples with frequency at selected temperatures is shown in Fig.-1. Z' shows almost a sharp fall with the increase in frequency in lower frequency range. Z' is also found to decrease with the increase in temperature. At higher frequencies, Z' achieves nearly a very low constant value and becomes almost independent of frequency as well as temperature. It is mainly due to low frequency dispersion at lower frequencies and release of space charge at higher frequencies [10-12].

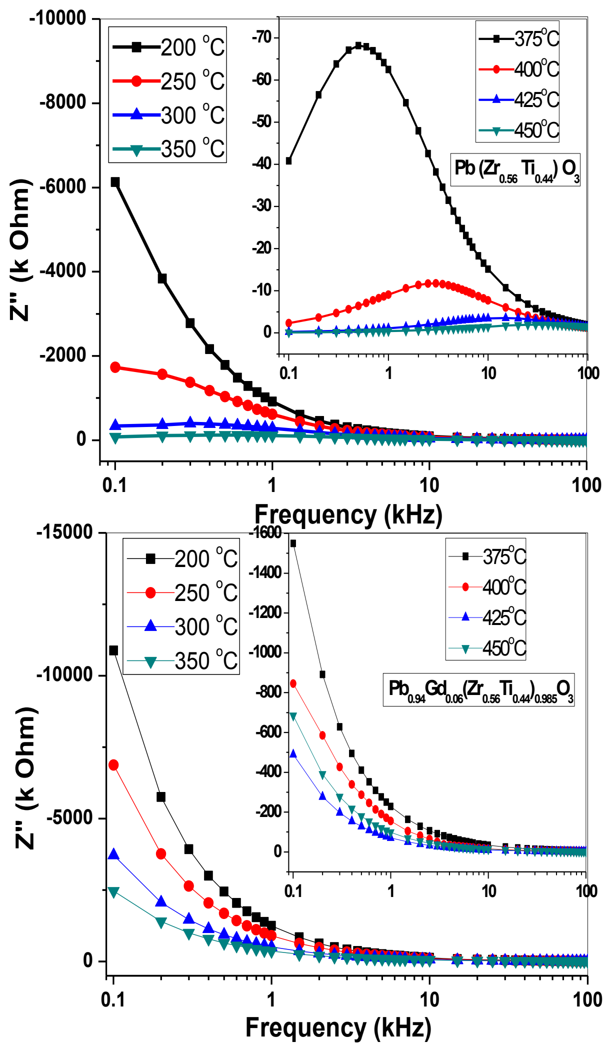

Fig.-2: Temperature-frequency dependence of Z" of PZT and PGZT ceramics

Fig.-2 shows the variation of imaginary part of impedance (Z") of the samples with frequency at different temperatures. At lower temperatures, Z" is found to decrease with increase in temperature as well as frequency and achieves a very low constant value at higher frequencies where it becomes independent of both frequency and temperature. In the higher temperature region, some peaks are observed that shifts towards higher frequencies as temperature increases. The peak height gradually decreases with the increase in temperature and finally merges in the high frequency region.

It shows thermally activated relaxation process in the materials. It may be due to presence of space charge polarization at lower frequencies and its elimination at higher frequencies. The observed asymmetric broadening of peaks indicates about the presence of some electrical processes in the materials with spread of relaxation time. This may be due to the presence of immobile species at low temperature and defects at higher temperatures [13-14].

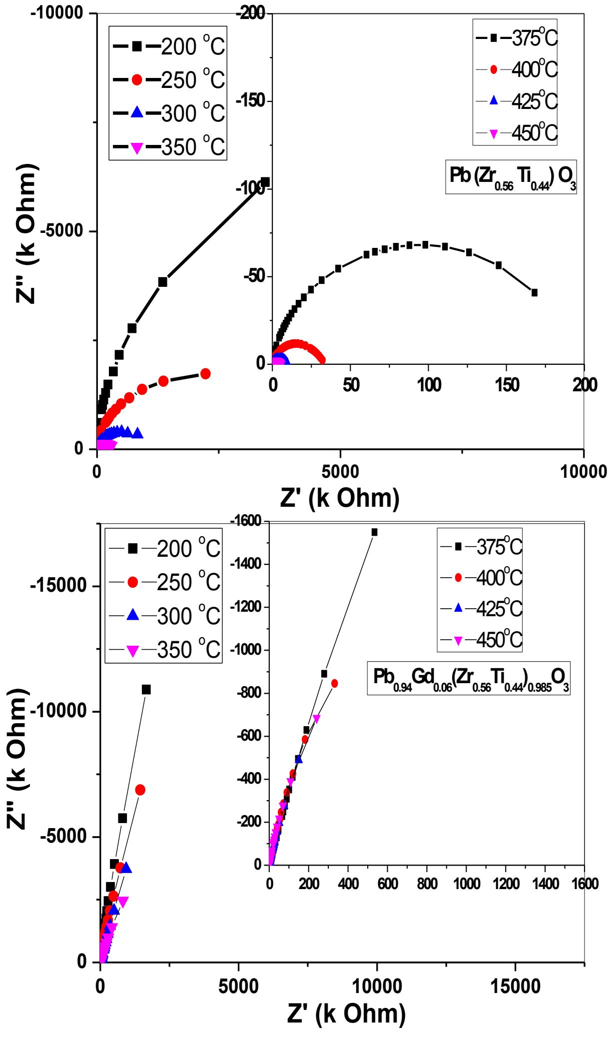

Fig.-3: Temperature-frequency dependence of Z" of PZT and PGZT ceramics

Fig.-3shows the complex impedance spectrum (Z' ~ Z": Nyquist plot) of pure and Gd^{3+}-substituted PZT compound at different temperatures. Appearance of semi-circular arc at different temperature shows that electrical properties in the material arise mainly due to the contribution of bulk effect. At lower temperatures only single arcs are obtained which are transformed into semicircles at higher temperatures.

The formation of full, partial or no semicircles depends on the strength of relaxation and also experimentally available frequency range [15]. The electrical process taking place within the materials may be modelled (as an RC circuit) on the basis of the brick-layer model [9]. In Nyquist plots, intercept of semi-circular arcs on real Z'-axis gives the value of bulk resistance (R_b) which is found to decrease with increase in temperature. It suggests about the negative temperature coefficient of resistance (NTCR) type behaviour of the PGZT compound. These plots exhibit depressed semicircles with centres lying below the real Z'-axis which confirms the presence of non-Debye type of relaxation in the material [16-17].

IV. Conclusion

Polycrystalline samples of PZT and PGZT with chemical composition $Pb_{1-x}Gd_x(Zr_{0.56}Ti_{0.44})_{1-x/4}O_3$; x = 0.00 and 0.06 were prepared by mixed oxide method at 1200°C sintering temperature. Real and imaginary parts of complex impedance properties of the materials were investigated by using complex impedance spectroscopy (CIS) technique. At a particular temperature, the observed single arc in the form of single/double semicircles (or tendency) in the complex impedance plots confirms about the formation of samples in single phase.

The real part of impedance (Z') is found to decrease with the increase in frequency which indicates normal ferroelectric behaviour of the materials. At high frequencies Z' gets a very low constant value and becomes almost independent of both the frequency and temperature. The decrease of Z' with increase in temperature at lower frequencies suggests negative temperature coefficient of resistance (NTCR) type behaviour of the materials. The variation of imaginary part of impedance (Z″) exhibits similar behaviour as that of Z' at lower temperatures. At higher temperatures, some peaks are observed that shift towards higher frequencies as temperature increases with a decreasing trend of peak height. It suggests about the temperature dependent relaxation process in the material. The complex impedance Z' ~ Z" Nyquist plots exhibit single semicircle or its tendency which suggests about the presence of bulk resistive contribution in the materials. It supports NTCR behaviour of the materials. The intercept of these semicircles on real Z' -axis gives the value of bulk resistance which is found to decrease with increase in temperature. The value of bulk resistance (R_b) is found to increase with 6% substitution of Gd^{3+} in the pure PZT sample. These complex impedance plots also suggest the presence of non-Debye type of relaxation phenomenon in the materials.

Acknowledgement

The author Rajiv Ranjan would like to acknowledge University Grant Commission for MRP-PSJ-001/11-12 for financial support.

REFERENCES

[1] Lines, M. E. and Glass, A. M. 1977 Principles and Applications of Ferroelectrics and Related Materials, Oxford University Press, Oxford**.**

[2] Jaffe, B., Crook, W. R. and Jaffe, H. 1971 Piezoelectric Ceramics, Academic Press, New York**.**

[3] Shirane, G. and Suzuki, K. 1952 J. Phys. Soc. Jpn. 7, 333.

[4] Zhong, W. L., Wang, Y. G., Zhang, P. L. and Qu, B. D. 1994 Phys. Rev. B 50, 698.

[5] Mabud, S. A. 1980 J. Appl. Cryst. 13, 211.

[6] Sambasivarao, K., Prasad, T. N. V. K. V., Subrahmanyam; A. S. V., Lee, J. H., Kim, J. J. and Cho, S. H. 2003 Mater. Sci. Eng. B 98, 279.

[7] Neurgaonkar, R. R., Oliver, J. R. and Nelson J. G. 1991 Mater. Res. Bull. 26, 771.

[8] Cross, L. E. 1996 Mater. Chem. Phys. 43, 108.

[9] Macdonald, J. R. 1987 Impedance Spectroscopy, John Wiley and Sons.

[10] Suchanicz, J. 1998 Mater. Sci. Eng. B. 55, 114.

[11] Plocharski, J. and Wieczoreck, W. 1988 Solid State Ionics 979, 28.

[12] Suman, C. K., Prasad, K. And Choudhary, R. N. P. 2006 J. Mater. Sci. 41, 369.

[13] Jonscher, A. K. 1977 Nature. 267, 673.

[14] Behera, A. K., Mohanty, N. K., Behera, B. and Nayak, P. 2013 Adv. Mat. Lett. 4(2), 141.

[15] Garhardt, R. 1994 J. Phys. Chem. Solids 55, 1491.

[16] Sinclair, D. C. and West, A. R.1994 J. Mater. Sci. 29, 6061.

[17] Nobre, M. A. L. and Lanfredi, S. 2003 J. Phys. Chem. Solids 64, 2457.

Corresponding Author--- Tel: +91 657 2340334; fax: +91 657 2228176 (rajivranjan.jcc@gmail.com)