Investigations of impedance and electric modulus properties of Pb$_{1-x}$Sm$_x$(Zr$_{0.45}$Ti$_{0.55}$)$_{1-x/4}$O$_3$ ceramics

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Received: 06 January 2013, Revised: 20 March 2013 and Accepted: 16 April 2013

**ABSTRACT**

Pb$_{1-x}$Sm$_x$(Zr$_{0.45}$Ti$_{0.55}$)$_{1-x/4}$O$_3$ (PSZT; x = 0.00, 0.03 and 0.06) ceramic samples were prepared by high temperature mixed oxide method. Using complex impedance spectroscopy (CIS) technique, the complex impedance (Z*) and modulus (M*) properties of the materials were analyzed within a wide range of temperature and frequency. Impedance analysis indicates the presence of mostly bulk resistive (grain) contributions which is found to decrease with the increase in temperature. It suggests about the negative temperature coefficient of resistance (NTCR) type behaviour of the materials. Complex modulus plots exhibit the presence of grain (bulk) as well as grain boundary contributions in the materials and also support their NTCR type behaviour. Both the complex impedance and complex modulus plots confirm the presence of non-Debye type of relaxation in the materials. At higher temperatures, bulk resistance is found to increase with the increase in Sm$^{3+}$ concentration in PSZT along with the increase in relaxation phenomenon. Copyright © 2014 VBRI press.

**Keywords:** Ceramics; complex impedance spectroscopy (CIS); impedance; modulus.

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**Introduction**

Now a days, Lead zirconate titanate [PZT; Pb(Zr$_{1-y}$Ti$_{y}$)O$_3$] [1-2] is an interesting dielectric, piezoelectric and ferroelectric material that has tremendous applications in the form of sensor, actuator and transducer [3-5]. It has perovskite ABO$_3$ structure (A = mono or divalent, B = tri-hexavalent ions) in which A-site is occupied by Pb$^{2+}$ and B-site by Zr$^{4+}$ and/or Ti$^{4+}$ [6-8]. It is the solid-solution of ferroelectric PbTiO$_3$ (T$_c$ = 763 K) & antiferroelectric PbZrO$_3$ (T$_c$ = 503 K) presenting tetragonal phase in Ti-rich composition and rhombohedral in Zr-rich composition. Its...
electrical and electromechanical properties rise to a great extent at Morphotropic Phase Boundary (MPB) between these two phases [9-11].

Depending upon specific requirements, physical properties and device parameters of PZT based compounds may be considerably modified with the variations in Zr/Ti ratio, synthesis techniques, particle size, calcination & sintering temperatures, etc [1, 12-16]. With suitable substitution(s) at A and/or B site(s), its material properties can be significantly changed. Interestingly, PZT modified with higher valence additives (like La3+, Sm3+ or Nb5+) results in the increased value of dielectric constant, electromechanical properties, etc. where electroneutrality is maintained by production of Pb-vacancies. On the other hand, PZT modified with lower valence additives (like K+, Fe3+ or Mg2+) results in the reduced value of dielectric constant, electromechanical properties, etc [17-18] by the production of O-vacancies.

Since the past few years, electronic and electro-optic device applications of La-modified PZT ceramics [19-22] have encouraged the research works in this field with others additives. The rare earth element samarium (Sm3+) also fulfils the basic requirements for its substitution to PZT [23-24] such as stability of perovskite phase, appropriate ionic size, high Curie-Weiss temperature, etc. But, only few works have been reported on PZT ceramics modified with samarium [25-29]. Interestingly, it is found that PSZT; Zr/Ti = 45/55 has shown a very high dielectric constant and low tangent loss [30]. In this paper, we report about the analysis of complex impedance and modulus properties of pure and Sm3+-modified PZT ceramics having Zr/Ti ratio 45/55 using complex impedance spectroscopy (CIS) technique.

Complex impedance spectroscopy (CIS) [31] is an effective experimental technique used to characterize micro-structural and electrical properties of polycrystalline electro-ceramic materials. It helps to separate real and imaginary components of complex electrical parameters so as to get the true picture of material properties. It enables us to resolve the relaxation contributions, like, bulk effects, grain boundaries and electrode interface effects in the frequency domain of materials.

In complex impedance spectroscopy, frequency dependent behaviour of the materials may be expressed in terms of complex impedance (Z*), complex electric modulus (M*), complex dielectric constant (ε*) and tangent loss (tanδ), which are related to each other through the relations: Z* = Z' - jZ", M* = 1/ε* (ω) = M' + jM"; ε = ε' - jε" and tanδ = ε"/ε', where (Z*, M*, ε*) and (Z", M", ε") are the real and imaginary components of impedance, modulus and permittivity respectively, j = √-1 the imaginary factor, C₀ = vacuum capacitance.

Experimental

The polycrystalline ceramic samples of Pb₁₋ₓSmₓ(Zr0.45Ti0.55)₁₋ₓO₃ [where x = 0.00, 0.03 and 0.06] were prepared by high temperature mixed oxide method using ingredient oxides; PbO, ZrO₂, TiO₂ and Sm₂O₃ (99.9% purity, M/S Loba Chemie, Inc. Bombay, India) in appropriate stoichiometry. 3% of extra lead oxide was added to the mixture to compensate lead loss at high temperature calcinations and sintering. The oxide powders were mixed thoroughly, first in, dry air and, then, in alcohol (methanol) medium using agate mortar and pestle. The well-mixed oxides were, first, calcined at 950°C for about 10 hr in alumina crucibles. The processes of grinding and calcination were repeated at temperature intervals of 50°C and the formation of desired compounds has been confirmed (through XRD technique) with the mixture calcined at 1100°C for 10 hr. Using small amount of polyvinyl alcohol (PVA) as binder, the calcined powders were cold pressed into thin cylindrical pellets in a steel die punch with the help of a hydraulic press at a pressure of 4x10⁶ N/m². These pellets were, subsequently, sintered at an optimized temperature 1200°C for 10 hr in alumina crucibles so as to get nearly 97% of theoretical density.

For the measurement of electrical properties, smooth flat surfaces of each pellet were electroded with high purity air-drying silver paint. The pellets were, then, dried at 150°C for 4 hr to remove moisture. Now, using computer based arrangements of phase sensitive multimeter (PSM N4L; Model 1735), furnace, variac, etc., a number of electrical data were recorded at different temperatures and frequencies through which various electrical parameters were calculated.

Results and discussion

Complex impedance analysis

The variation of real part of impedance (Z') of the ceramic samples Pb₁₋ₓSmₓ(Zr0.45Ti0.55)₁₋ₓO₃ [x = 0.00, 0.03 and 0.06] with frequency at different temperatures is shown in Fig. 1. Z' is found to decrease with the increase in temperature as well as due to polarization and then monotonous decrease with the increase in temperature and achieves a low value at higher temperatures. It exhibits low frequency dispersion mainly due to polarization and then monotonous decrease with the increase in frequency. This shows increase in material’s ac conductivity with the increase in temperature as well as frequency. At higher frequencies, Z' achieves nearly a very

Fig. 1. Variation of Z' with frequency at different temperatures of Pb₁₋ₓSmₓ(Zr0.45Ti0.55)₁₋ₓO₃; x = 0.00, 0.03 and 0.06.
low constant value and becomes almost independent of frequency as well as temperature. At lower frequencies, $Z'$ decreases with the increase in frequency supporting a slow dynamic relaxation process in the materials probably due to space charge that gets released at higher frequencies [32-36]. It is also observed that $Z'$ exhibits a decreasing trend with the increase in Sm$^{3+}$-concentration in PSZT from $x = 0.00$ to 0.06 up to about 300 $^\circ$C.

Fig. 2 shows the variation of imaginary part of impedance ($Z''$) of the pure and Sm-modified PZT compounds with frequency at different temperatures. At lower temperatures, $Z''$ shows behaviour similar to $Z'$ but some peaks are observed at higher temperatures. These peaks are found to shift towards higher frequencies with the increase in temperature exhibiting a decreasing trend of peak height which finally merge in the high frequency region. It suggests about thermally activated relaxation process in the materials and indicates reduction in bulk resistance with the increase in temperature. 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 [37-38]. Though, these peaks have not been observed at lower temperatures which may be due to the weak current dissipation in the materials or beyond the frequency of measurement. With the increase in Sm$^{3+}$-content from $x = 0.00$ to 0.06, the peak height gradually increases and found to shift towards the shorter frequencies.

Fig. 3 shows the complex impedance spectrum ($Z''$-$Z'$; Nyquist plot) of PSZT compounds at selected higher temperatures. Appearance of single arc or semicircle at a particular temperature shows that electrical properties in the materials arise mainly due to the contribution of bulk effects. At lower temperatures only single arcs (not shown) are obtained which are transformed into semicircles at higher temperatures. The formation of full, partial or no semicircles mainly depends on the strength of relaxation and also experimentally available frequency range [39].

The electrical process taking place within the materials may be modelled (as an RC circuit) on the basis of the brick-layer model [31]. 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 PSZT compounds. These plots exhibit depressed semicircles having centres lying below the real axis (not shown), this confirms the presence of non-Debye type of relaxation phenomenon in the materials [40-41]. At higher temperatures, $R_b$ is found to increase with the increase in Sm$^{3+}$-concentration in the materials.

Complex modulus analysis

The variation of real part of electric modulus ($M'$) of Pb$_{1-x}$Sm$_x$(Zr$_{0.45}$Ti$_{0.55}$)$_{1-x/4}$O$_3$ [x = 0.00, 0.03 and 0.06] with frequency at different temperatures is shown in Fig. 4. $M'$ is found to be very low at lower frequencies and exhibits an increasing trend with the increase in frequency. It shows continuous dispersion on increasing frequency which may be due to short range mobility of charge carriers under the action of an induced electric field. But at higher temperatures, $M'$ increases rapidly with the increase in frequency as well as temperature which attributes temperature dependent relaxation process in the materials. Also it is observed that the dispersion region shifts towards higher frequencies suggesting long-range mobility of charge carriers [42]. The observed plateau region or its tendency indicates about frequency invariant dc behaviour of the materials. With Sm$^{3+}$ substitution to Pb(Zr$_{0.45}$Ti$_{0.55}$)O$_3$ from $x = 0.00$ to 0.06, $M'$ is found to high when $x = 0.03$. 

![Fig. 2](image_url) 

![Fig. 3](image_url)
corresponding to the peaks is maximum in case of PSZT with $x = 0.03$.

![Figure 4](image1.png)

**Fig. 4.** Variation of $M'$ with frequency at different temperatures of Pb$_{1-x}$Sm$_x$(Zr$_{0.45}$Ti$_{0.55}$)$_{1-x/4}$O$_3$: $x = 0.00, 0.03$ and $0.06$.

$M'$ increases with the increase in temperature. It indicates increase in capacitance with the increase in temperature and supports NTCR type behaviour of the materials since the bulk capacitance ($C_b$) is inversely proportional to the bulk resistance ($R_b$). Though, at higher temperatures and lower frequencies, tails are not fully evolved to its true shape which may be due to frequency and temperature limitations.

![Figure 6](image2.png)

**Fig. 6.** Complex modulus plots ($M'$–$M''$) of Pb$_{1-x}$Sm$_x$(Zr$_{0.45}$Ti$_{0.55}$)$_{1-x/4}$O$_3$: $x = 0.00, 0.03$ and $0.06$.

The temperature dependence of complex modulus spectrum (i.e. $M'$ vs. $M''$ spectrum) of PSZT is shown in **Fig. 6**. At higher temperatures, semi-circular arcs are observed in the form of two semicircular arcs (or tendency) which indicates the presence of both grain and grain boundary contributions in the materials. Their centres appear to lie below the real $M'$-axis which supports the non-Debye type of relaxation in the materials. The observed single arc in the form of single/double semicircles (or tendency) in both the complex impedance and modulus plots confirms about the formation of samples in single phase. Impedance analysis indicates the presence of mostly bulk (grain) resistive contributions in the materials whereas complex modulus plots shows the presence of grains as well as grain boundary contributions in the materials. It is due to the fact that impedance plot highlights the phenomenon with largest resistance whereas electric modulus plot highlights the phenomenon with smallest capacitance. Due to the large difference between

**Conclusion**

Polycrystalline samples of Pb$_{1-x}$Sm$_x$(Zr$_{0.45}$Ti$_{0.55}$)$_{1-x/4}$O$_3$: $x = 0.00, 0.03$ and $0.06$ were prepared by mixed oxide method at 1200°C sintering temperature. Real and imaginary parts of complex impedance and modulus 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 both the complex impedance and modulus plots confirms about the formation of samples in single phase. Impedance analysis indicates the presence of mostly bulk (grain) resistive contributions in the materials whereas complex modulus plots shows the presence of grains as well as grain boundary contributions in the materials. It is due to the fact that impedance plot highlights the phenomenon with largest resistance whereas electric modulus plot highlights the phenomenon with smallest capacitance. Due to the large difference between
resistive values of grains and grain boundaries, it is not possible to get two semicircles on the same impedance plot [44]. Both impedance and modulus analysis support the typical behaviour of negative temperature coefficient of resistance (NTCR) of the materials. They also confirm the presence of non-Debye type of relaxation phenomenon in the materials. With the increase in Sm³⁺ concentration in Pb(Zr₀.₄₅Ti₀.₅₅)O₃ upto 6%, the bulk resistance exhibits an increasing trend at higher temperatures along with the increase in relaxation phenomenon in the materials.

Acknowledgements

The author, R. Ranjan would like to acknowledge University Grant Commission for MRP-PSJ-001/11-12 and N. Kumar would like to acknowledge CSIR, New Delhi (India) for financial support.

Reference