STUDIES ON ELECTRICAL PROPERTIES OF PZTs CONTAINING VARYING AMOUNTS OF RARE EARTHS (Ce, Pr AND Nd) BY IMPEDANCE SPECTROSCOPY

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Introduction

Lead Zirconate Titanate (PZT) [1] ceramics have been extensively used for various device applications, because of their excellent dielectric, pyroelectric, piezoelectric and electro-optic properties [2]. Doping of PZT with rare earths in A/B sites (perovskite ABO₃), has shown significant bearing in its dielectric and ferroelectric characteristics [3].

Conventional method of preparing these ceramic materials is through solid-state reactions [4, 5]. But the advantages of solution-based routes lie in the formation of the product at much lower temperatures with larger surface area and better micro homogeneity as compared to solid state route. Lower synthesis temperature prevents volatilization of the component oxide, facilitating fixing of required stoichiometry. This paper presents synthesis of PZT powders containing 5, 10 and 15 mole % Ce, Pr and Nd by Gel-Entrapment Technique [6]. AC Impedance spectroscopy has been utilized, to study the electrical properties such as dielectric properties and electrical conductivity of the samples at different temperatures.

Experimental

The oxides Pb₁₋ₓRxZr₀.₆₅Ti₀.₃₅O₃, where R = Ce, Pr and Nd and x = 0, 0.05, 0.1 and 0.15, were prepared by Gel-Entrapment Technique. The samples were characterized by room temperature XRD, TG-DTA (Setaram, Model 92-16.18) and DSC (Setaram, Model 131) techniques. The samples were pelletized into 10 mm diameter disks of thickness 1.5 mm, at a pressure of 250 MPa and sintered in air at 1000°C for 2 h. The pellets were then polished and coated with thin layer of Pt paste on flat ends and fired to 800°C for 2 h to have a better contact with the electrode for measurement of electrical properties.

The electrical properties of the samples were measured using a Solatron AC Frequency Analyzer (Model 1260) in the frequency range 10 MHz to 1 Hz. The impedance spectra were recorded in the temperature...
interval of 350 to 800°C with the step of 25°C for all the samples. The temperature was controlled by a microprocessor and measured by a K-type thermocouple placed very close to the sample. At each temperature, the samples were equilibrated for 20 min before recording the spectra.

Results and Discussion

The room temperature XRD analysis of the samples indicated that, the materials were single phase with cubic lattice structure, except for Nd containing samples in which some pyrochlore phases were also observed. The cell parameters of the compounds obtained from least square fitting of the XRD data, were found to be in good agreement with the reported values. Fig. 1 shows the room temperature XRD patterns of these compounds, calcined at 1073 K. The sharp and singlet pattern indicates better phase purity and crystallinity.

**Electrical property measurements by Impedance Spectroscopy**

For impedance measurements, the sintered pellets were polished and coated with a thin layer of Ti paste and heated to 1073K for 2 h, to improve contact with the electrode. The electrical properties of the samples were measured using a Solartron AC Frequency Analyzer (Model 1260) in the frequency range 10 MHz – 1 Hz. Fig. 2 gives the Nyquist plot of the compound Pb$_{0.95}$Ce$_{0.05}$Zr$_{0.65}$Ti$_{0.35}$O$_3$ at various temperatures. The relaxation frequency ($f_o$) of the material, independently of the geometrical parameter of the sample, was found at the apex of the Nyquist semicircle fulfilling the condition $2p f_o R_b C_b = 1$.

From this relation, the bulk capacitance of the material ($C_b$), also called the geometric capacitance, can be calculated and the bulk dielectric constant $\varepsilon_b$ can be determined using $C_b = \varepsilon_b \varepsilon_0 A/l$, where $\varepsilon_0$ is the vacuum permittivity.

The semicircular pattern in the impedance spectrum is representative of the electrical processes taking place in the material, which can be expressed as an equivalent electrical circuit comprising of a parallel combination of resistive and capacitive elements. The

![Fig. 1: Room temperature XRD patterns of PZTs doped with Nd, Ce and Pr calcined at 1073 K. (* = pyrochlore phase)](image)

![Fig. 2: Nyquist plot of Pb$_{0.95}$Ce$_{0.05}$Zr$_{0.65}$Ti$_{0.35}$O$_3$ at various temperatures](image)
The intercept of the semicircle on the real axis, gives the resistance of the corresponding component contributing towards the impedance of the sample. The graph shows that at lower temperature, the resistance offered for conduction is very high. As temperature increases, the conduction becomes easier. This shows typical semiconductor behaviour in these samples. At lower temperature only conduction through grains prevails whereas as at higher temperature grain conduction as well as grain boundary conduction is seen. The Nyquist plot for PZT undoped and doped with 5 mole% of Pr, Ce and Nd is presented in Fig. 3. The impedance of the sample decreased with Pr doping whereas the impedance showed increase with doping of Ce and Nd. The large increase of impedance value in the case of Nd containing samples, may be due to the pyrochlore phase present in them.

The frequency (1 Hz to 10 MHz) dependent dielectric constants ($\varepsilon_r$) of all the compounds were determined from the capacitance values. Fig. 4 shows the variation of $\varepsilon_r$ of PbZr$_{0.65}$Ti$_{0.35}$O$_3$ as well as Pb$_{0.9}$R$_{0.1}$Zr$_{0.65}$Ti$_{0.35}$O$_3$ where R = Ce, Pr and Nd as a function of temperature measured at 1 kHz as well as 10 kHz. It is clear that the $\varepsilon_r$ of all the compounds decrease with increase in frequency as the capacitance value of these compounds decreases with increase in frequency. The dielectric constant of these samples increased with increase in temperature as the polarizability of the oxide system increases with temperature. Also, it can be seen from the figure that the $\varepsilon_r$ increases with Pr doping in the parent PZT sample, whereas the $\varepsilon_r$ value remarkably decreases with Ce as well as Nd doping. The sample Pb$_{0.9}$Pr$_{0.1}$Zr$_{0.65}$Ti$_{0.35}$O$_3$ showed $\varepsilon_r$ of $-22489$ at $710^\circ$C, measured at 1 kHz. The undoped samples (PZT) showed a $\varepsilon_r$ of $\sim 19600$ at this temperature, whereas the $\varepsilon_r$ for Ce and Nd containing samples showed $\varepsilon_r$ values of 5232 and 3002 respectively. Further the dielectric constants of Ce and Nd doped samples were found to decrease with increase in dopant concentration. Qi-Yue Shao et al.
[7] also reported that the dielectric constant of PZT thin films decreased when the film was doped with Ce. The authors attributed this behaviour to the presence of pyrochlore phase in Ce containing thin films. But in the present study, pyrochlore phase was not observed in the Ce containing samples even for 15 mole% of Ce. Ce has almost equal probability to replace Pb\(^{2+}\) at A site or Zr\(^{4+}/Ti^{4+}\) ions at B sites of ABO\(_3\) perovskite lattice. This is feasible, as Ce can exist both in tri and tetra valence states and can replace Pb\(^{2+}\) (rCe\(^{3+}\) = 1.43 Å and rPb\(^{2+}\) = 1.63 Å) or Zr\(^{4+}\) (rCe\(^{4+}\) = 0.86 Å and rZr\(^{4+}\) = 0.73 Å), respectively. It is reported in the literature [8] that tendency of Ce to occupy A site (as Ce\(^{3+}\)) is more if the Ce ion concentration is less than 1 mole% and beyond 1 mole%, both A as well as B sites can be occupied by Ce equally (Ce\(^{3+}\) in A site and Ce\(^{4+}\) in B site). They further reported that the samples containing Ce in the A sites (3+ oxidation state) improve the electrical properties. Similarly, in the present study, 5 to 15 mole % of Ce containing samples, may be occupying a large proportion of B sites in the ABO\(_3\) system which might be responsible for the decreased e value in the Ce containing PZT. Even though Pr also exhibits tri and tetra oxidation states, tri oxidation state is more stable than tetra oxidation states, whereas in the case of Ce ion, extra stability would be attained by Ce\(^{4+}\) ion because of noble gas electronic configuration by removal of 4 electrons. Hence Pr occupancy in B sites in place of Zr\(^{4+}/Ti^{4+}\) is small and high value of e, was observed in the present study. Since A site substitution can reduce oxygen vacancies by forming A site vacancy—oxygen vacancy defect dipoles, increase electric displacements thus increasing the dielectric constant. The donor dopants have been reported to improve the dielectric and ferroelectric properties of PZT thin films [9, 10]. Considering the ionic radius of Nd\(^{3+}\) (1.0 Å) the B site occupancy by Nd should be the minimum. But in our study, the addition of Nd in PZT reduces the dielectric constant. This may be due to the presence of pyrochlore phase in the Nd containing samples. During sintering, pyrochlore forms usually as a transient phase before the PZT formation. The pyrochlore phase is oxygen deficient and so it is a metastable transient phase [11]. Thus, in the Non crystallite PZTs, the presence of impurity phases such as pyrochlore, play an important role in deciding the dielectric constant.

The DC conductivity of the samples was calculated using the relation, \(\sigma = 1/Ra*(l/A)\), where R is the electrical resistance, is the thickness of the sample and A the area of cross section of the sample. The activation energy, \(E_\mu\) for all the samples was calculated from the plot of \(\ln(\sigma T)\) versus 1/T using the conductivity relation \(\sigma T = \sigma_0 \exp (-E/(K_B T))\), where \(\sigma_0\) is the pre-exponential factor, \(E\), the activation energy and \(K_B\) the Boltzmann constant. The DC conductivity increases with increase in temperature. At higher temperature, PZT as well as rare earth doped PZT samples behave as semiconductors and in semiconducting ceramics, free carriers interact with the charged grain boundaries, giving rise to increase in the ionic conductivity. During the course of motion through the solid, the available limited number of mobile carriers get trapped in relatively stable potential wells. Due to a rise in temperature, the donor cations take a major part in the conduction process and the conductivity increases. At 10 mole% and 15 mole% dopant concentration, PCeZT showed maximum conductivity amongst the same class of samples. It was also observed, that in PCeZT samples, the conductivity increases with increase in dopant concentration, whereas for both the Pr and Nd containing samples the conductivity decreases as we increase the dopant concentration. This may be due to the fact that at higher Ce ion concentration, more cationic vacancies are created at A site which contributes more towards the conductivity values. The variation of DC conductivity for PZT and Pb\(_{0.85}\)Zr\(_{0.15}\)Ti\(_{0.36}\)O\(_3\), where R = Ce, Pr and Nd with 1/T is given in Fig. 5. The conductivity in Nd doped samples showed a minimum value among all the samples and decreased with dopant ion concentration. The amount of pyrochlore phase in the Nd containing samples increases with increase in Nd concentration and reduces the conductivity of these samples.
Conclusions

PZT containing 5, 10 and 15 mole% of Ce, Pr and Nd were prepared, by a novel solution-based technique. The dielectric constants of PZT decrease with Ce doping, because of the B site occupancy whereas the polarizability of samples increases with Pr doping. The DC conductivity of the samples increases with increase in Ce concentration, which may be due to the cationic vacancy at A site created. The pyrochlore phase in Nd doped samples is found to be responsible for lower conductivity as well as lower dielectric constant values.

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References

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