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Conduction Studies of $Pb(Zr_{0.35-x}Y_xTi_{0.65})O_3$ (x = 0.00, 0.10 and Y = Mn/Ce) Ceramics

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Abstract

Lead zirconate titanate (PZT), being one of the most widely investigated ferroelectric, plays a crucial role in the development of technologies related to memories, sensors, actuators, etc. In this work, the samples of $Pb(Zr_{0.35-x}Y_xTi_{0.65})O_3$ (x = 0.00, 0.10 and Y = Mn/Ce) composition were synthesized, to investigate their conduction mechanism as a function of frequency and temperature. The temperature response of conductivity of the samples, over selected frequencies, indicated reduction in the barrier properties of the materials. It is observed that the magnitude of conductivity, over a wide range of frequency, is higher for cerium (Ce) modified PZT and lower and manganese (Mn) modified PZT. The negative coefficient of resistance behavior has been observed, from the nature of the variation of the conductivity of samples. Significantly, the conductivity spectra of the compounds is governed by Jonscher's power law.

Keywords: Ferroelectric, PZT, Conductivity

1. Introduction

PZT, belongs to ABO_3 perovskite solid solutions, is an immense and versatile ferroelectric material system [1]. It is used extensively in dielectric capacitors, ferroelectric and/or piezoelectric devices. The lattice of PZT usually consists of lead (Pb^{+2}) ions at A-site, and the zirconium/titanium (Zr+4/Ti+4) ions coexists at B-site in certain proportions by maintaining the neutrality of charge [2-3]. Doping and/or substitution of ions of different elements, of different valences (can be either isovalent or aliovalent or both together), can alter the electrical properties of PZT significantly [2]. The enhanced properties (such as high resistivity, large dielectric constant, high polarization, high piezoelectric coefficients, etc.) and deteriorated properties (such as tangent loss, low conduction, less diffuseness, etc.) determine the applicability of PZT in electronic devices and applications [4]. So, lots of investigations, on the piezo and ferroelectric properties, can be vastly found in the existing literature. Since PZT is also one of the most widely used resistive element in electric circuits and boards, it is required to study and alter the impedance and conduction mechanisms of PZT. The material PZT, in ceramic form, is usually employed as a component of grain-grain boundary-electrode material interface in the above mentioned applications [5].

The process of conduction in ceramic dielectrics, is mainly due to the movement of charge carriers over short or long range distances. When an electric field is applied externally, the charge carriers that are bounded weakly (i.e. electrons/holes and cations/anions) results in conduction [6]. Using the dielectric data parameters, the magnitude of ac electric conductivity can be evaluated as per the following expression [5]:

$\sigma_{ac} = \omega\varepsilon_r\varepsilon_0\tan\delta$

where ε_0 permittivity in free space, and ω angular frequency. The response of ac conductivity with respect to frequency, can be investigated from the following Jonscher's power law expression [7-9]:

$$\sigma_T(\omega) = \sigma(0) + \sigma_1(\omega)$$

$$\sigma_T(\omega) = \sigma_0 + a\omega^n$$

where σ (0) is the conductivity that is independent on frequency and $\sigma_1(\omega)$ is the ac conductivity that is dependent on frequency. An attempt has been made by Jonscher, to understand the mechanism of conduction in dielectric solids [10]. The ratio of magnitudes of steady state current with respect to the externally applied voltage, gives the value of conductivity of a material [11]. The importance of studying conductivity is due to the dependence of electrical of PZT on the conductivity. The response of ac conductivity with respect to temperature, can be investigated from the following expression [12]:

$$\sigma = A\exp.(-\frac{E_a}{kT}) + B\exp.(-\frac{E_b}{kT})$$

where E_a and E_b corresponds to the activation energy for intrinsic and extrinsic conduction process respectively. At higher temperatures, the dominance of intrinsic conduction over the extrinsic conduction reduces the aforementioned expression, as follows [13]:

$$\sigma = A\exp.(-\frac{E_a}{kT}).$$

In this work, a systematic investigation has been done on the electrical conduction mechanism of Mn and Ce modified PZT material. The samples have been prepared through a high temperature solid state synthesis method. The nature of conductivity of the samples, as a function of temperature and frequency, is reported in this paper.

2. Experimental Section

The inorganic oxides of 99.9% purity were used to prepare the samples of $Pb(Zr_{0.35-x}Y_xTi_{0.65})O_3$ (x = 0.00, 0.10 and Y = Mn/Ce). The complete procedure and process parameters are similar to that, which have been reported elsewhere [1, 5].

3. Results and Discussion

3.1 Variation of ac conductivity with frequency

The nature of fluctuation of ac conductivity of $Pb(Zr_{0.35-x}Y_xTi_{0.65})O_3$ (x = 0.00, 0.10 and Y = Mn/Ce) with frequency, is shown in Figure 1.

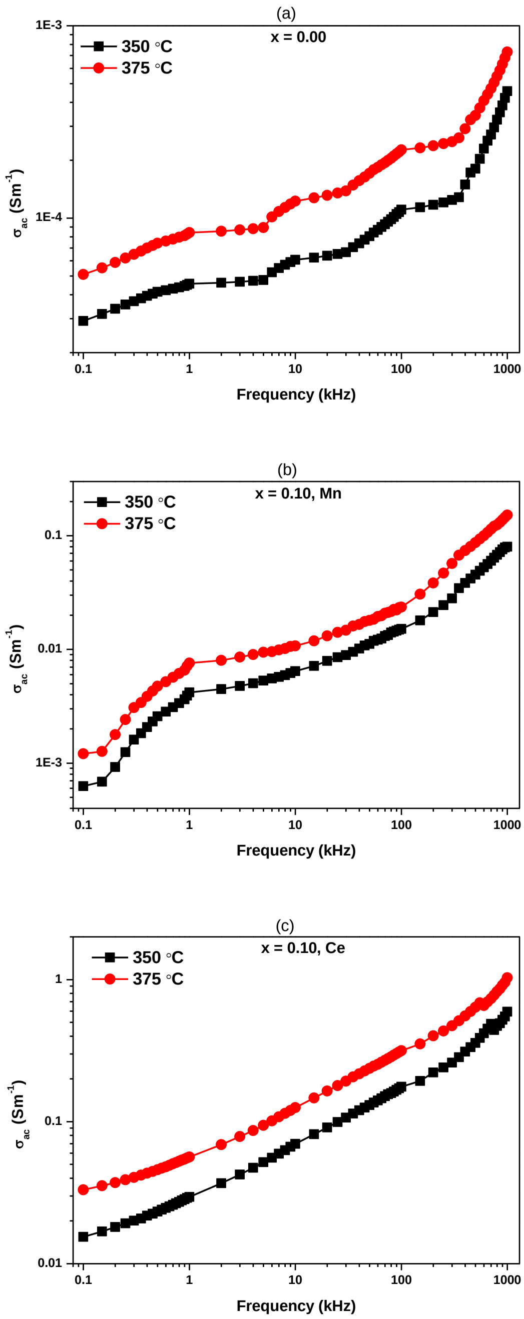
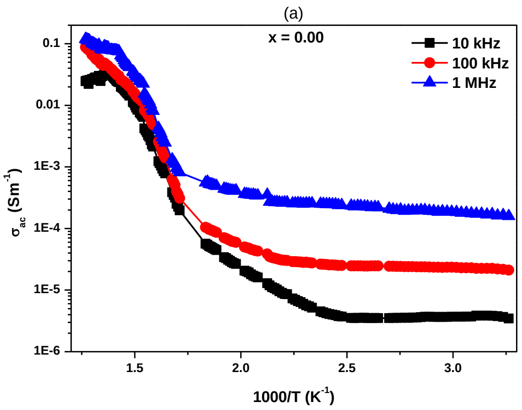


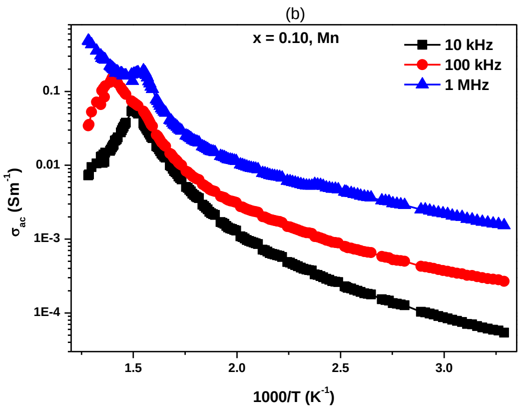
Fig.1 (a-c). Variation of ac conductivity with frequency

The magnitude of σ_{ac}, of all samples, is increasing with increase in both frequency and temperature. All the curves exhibit different slopes. The frequency that indicate the change in slopes of the curves, is generally referred as hopping frequency [14]. The existence of change in slopes of the curves, at hopping frequency, indicate the presence of hopping of charge carriers. The changes in slope takes place, with change in temperature, when grains start dominating the resistance of the material [8]. Further, the increase in ac conductivity, with rise in temperature, suggests the release of space charge in the material. Hence the conduction in the compounds, is a phenomenon that is activated thermally [5]. From the figure, one can also observe that Ce modified PZT possess large values of conductivity whereas pure PZT possess lower values. The conductivity values of Mn modified PZT are intermediate between pure and Ce modified PZT.

3.2 Variation of ac conductivity with inverse absolute of temperature

The information on the fluctuation of ac conductivity of $Pb(Zr_{0.35-x}Y_xTi_{0.65})O_3$ (x = 0.00, 0.10 and Y = Mn/Ce) with temperature, can be further explored from Figure 2.





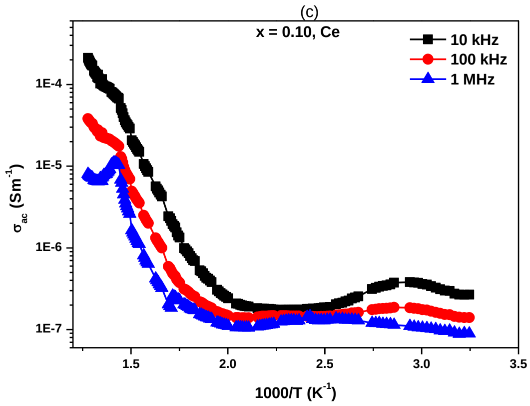


Fig.2 (a-c). Variation of ac conductivity with inverse absolute of temperature

From the entire observation, it is evident that the value of ac conductivity is strongly dependent on temperature. The increase in the magnitude of conductivity, with rise in temperature, suggests that the compounds exhibit negative coefficient of resistance behavior [10]. This is due to increase in the sufficient energy, for charge carriers, to jump over the barrier which results in the increase of ac conductivity. Hence, the conduction phenomenon is thermally activated, and this kind of conduction suggests the possible reduction in the barrier properties of the materials [13]. At low temperature region, the graphs are indicating different slopes for different frequencies. Hence, the activation energies of the compounds are different at different frequencies. Therefore, the conduction mechanism in the compounds is both frequency and temperature dependent. The nature of the spectra suggests that the compounds obey Jonscher's power law. The magnitude of ac conductivity is lower, for all samples, in the region of low temperatures. But the magnitude of ac conductivity is higher, for all samples, in the region of high temperatures.

Conclusions

The ceramics of $Pb(Zr_{0.35-x}Y_xTi_{0.65})O_3$ (x = 0.00, 0.10 and Y = Mn/Ce) composition have been prepared at very high temperatures, using solid state reaction method. The compounds exhibit the hopping mechanism of charge carriers, as indicated from the entire spectra. Also the conduction in compounds is mainly due to the thermal activation of charge carriers. The activation energies of the compounds are different for different frequencies. Hence the process of conduction is both frequency and temperature dependent.

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