

Mechanism of electrical conduction in Gadolinium doped Lead Zirconate Titanate (PZT)

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Abstract- Electrical conductivity was investigated in PGZT for the composition $Pb_{1-x}Gdx(Zr_{1-y}Tiy)_{1-x/4}O_3$ into three groups on different Zr/Ti ratio 50/50,60/40 and 65/35 for different concentration of gadolinium substitution as 3%, 6% and 9%. It was observed that electrical conduction followed a typical semiconductor behavior and Gd^{3+} significantly affected the conduction process. ac conductivity measurement was carried on using phase sensitive multimeter for PGZT under ambient atmosphere in order to investigate the defect chemistry by identifying the charge carrier. Activation energy was calculated in the temperature range $T < T_c$ and $T > T_c$ where T_c ranging (365 0C to 415 0C) in order to see the amount of energy required to jump from donor level to the conduction band. The tolerance factor was also calculated for different composition to confirm the Perovskite structure. PGZT under investigation showed a NTCR (Negative temperature coefficient resistance) behavior.

Keywords – PGZT; ac conductivity; NTCR

I. INTRODUCTION

Although ceramics are commonly known for their insulating properties, in actually they exhibit an extensive range of electrical properties competing with metal and liquid electrolytes for the highest electronic and ionic conductivities respectively. Fast ionic conducting ceramics and solid electrolyte are beginning to find applications in various electrochemical devices, thermistors etc. Thermistors or thermal sensitive resistors are a class of semiconducting ceramics which exhibits a steep change in electrical resistivity with changing temperature. Practical thermistors have their electrical resistivity between 100 and 106 Ωm . It is generally categorized into three main categories

- a) NTC (negative temperature resistance) thermistors whose electrical resistivity decreases with increasing temperature
- b) PTC (positive temperature resistance) whose resistivity increases with increasing temperature.
- c) CTC (critical temperature resistance) thermistors which exhibit a drastic change in electrical resistivity at a critical temperature.

Both NTC [1] and PTC units can be used to indicate changes in ambient conditions. PTC units have the advantage that they are unlikely to overheat since an increase in temperature cuts down the power that they need to dissipate. Precautions needs to be taken for NTC [1] units as increase in their temperature increases the power that they can draw from a constant voltage source. In ceramics a large temperature coefficient of resistivity arises from three causes,

- a) The intrinsic characteristics of a semiconductor which leads to an exponential fall in resistivity over a wide range of temperature
- b) A structural transition which is generally accompanied by a change in the conduction mechanism from semiconducting to metallic (this usually results in a large fall in resistivity over a small range in temperature.
- c) A rapid change in dielectric properties in certain ceramics which usually affects the electronic properties.

The electrical conduction mechanism in PZT has been studied by many authors (Kulcsar 1959, Gerson 1963, Dih1978, [2] Takahashi1971). Gerson [3] in 1963 proposed that the p-type conduction in undoped PZT resulted from vacancies on the lead sites, and these vacancies were caused by the loss of PbO during sintering. As also reported by Northrop1967, [4] Atkin1971, [5] and Holman1972 [6]). In 1959 Kulcsar [7] reported that the resistivity was increased by the addition of Nb2O5, but decreased with the addition of Sc2O3. In 1971 Takahaski [8] classified the effect of impurities on resistivity into different groups, For undoped PZT, a high concentrations of interstitials is not possible because the perovskite unit cell is already closely packed and the possible interstitials site are bounded by positive and negative ions. The p-type conduction is due to the volatility of PbO while sintering. According to Goldschmidt rules, the dopant ion enters into the site (A or B) in the ABO3 perovskite structure if the ion and the substituted ion do not differ by more than 15%(Jaffe 1971 [9]). When higher valence ions enter into the lattice site ,

the excess charge must be compensated by vacancies in the perovskite lattice. Depending on the preparation such vacancies can be created when lower valence ion enters into the lattice sites, the charge deficit is compensated mostly by oxygen vacancies. According to Murakami 1973, Henning 1974, Wu 1982 [10] trivalent ion substitution in PZT is a very special case, because for most trivalent ions, the ion size is smaller than Pb^{2+} (A site) but larger than Zr^{4+} (B site). In 1982 Long Wu and Tien Shou Wu (Republic of China) carried out an experiment in which distribution of dopants into A and B site with 0.5% and 0.1% of trivalent ions was done with the help of XRD analysis of cell parameters and tolerance factors 't' he concluded that larger ions such as La^{3+} or Nd^{3+} increases its concentration and act as donor as it favors the A site due to which the resistivity increases. Smaller ion such as Er^{3+} , Dy^{3+} favor the B site so the concentration of O site vacancies was increased the impurities act as acceptors and contribute holes to the conduction process, as a result the resistivity is decreases. However other ion such as Sm^{3+} , Ti^{3+} and Gd^{3+} corresponds to the 50% occupation. so their resistivity is nearly unchanged. In the present paper study of the frequency dependent electrical behavior of PGZT for the composition $Pb_{1-x}Gd_x(Zr_{1-y}Ti_y)_{1-x/4}O_3$ where $x = 0.03, 0.06, \text{ and } 0.09$ and $y = 50, 40 \text{ and } 35$ has been done through the ac conductivity.

II. PROPOSED ALGORITHM

2.1 Material Preparation

The polycrystalline ceramic samples of gadolinium modified PZT with chemical composition is $Pb_{1-x}Gd_x(Zr_{1-y}Ti_y)_{1-x/4}O_3$ with ($x = 0.03, 0.06 \text{ and } 0.09$) were prepared by a mixed oxide method. The ingredient raw materials used were PbO , Gd_2O_3 , ZrO_2 and TiO_2 (99.9% purity, M/S Loba Chemie, Inc. Bombay, India). The ingredient oxides were taken in suitable stoichiometry along with 3% extra lead oxide to compensate lead loss at high temperatures. These oxides were mixed thoroughly in a dry condition for 2h in air, and then, in methanol medium for 2h using agate mortar and pestle to get homogenous mixture of the materials. Now, the well mixed oxides were calcined, first, at 950°C for about 10 h in an alumina crucible. The calcined materials were grinded well and then their XRD patterns were taken. Now the fine and homogeneous powder of the compounds were pressed into cylindrical pellets of 10 mm diameter and 2-3 mm thickness under a uniaxial pressure of $4 \times 10^6 \text{ N/m}^2$ using a hydraulic press. Polyvinyl alcohol (PVA) was used as a binder to reduce the brittleness of the pellets. These pellets were sintered at an optimized temperature of 1210°C for about 10 h in alumina crucibles in order to get maximum density. The binder was burnt out during this high sintering temperature.

2.2 Measurement of ac conductivity

The sintered pellets were then polished with fine emery paper in order to make both the faces flat and parallel. The flat polished surfaces of the pellets were then coated with high-purity air-drying conducting silver paste. The pellets were dried at 150°C for 4 h to remove moisture (if any) before taking any electrical measurements. The ac conductivity of all the PGZT ceramic samples with the chemical composition were calculated in a wide range of temperature (room temp. to 500°C) and frequencies (1kHz and 1MHz) from the data obtained by using the experimental systems containing 'Phase sensitive Multimeter (PGD N4L; Model 1735), laboratory made sample holder and variac with heating arrangement' at a potential difference of 1V and ac signal level of amplitude 1.5V. The dielectric parameters (capacitance, dissipation factor) were measured using Hioki 3532 LCR High Tester, which is an impedance meter, where a touch panel and user interface are used. The frequency can be freely adjusted with four-digit precision in a wide range (102-106 Hz). Moreover, this widely applicable impedance meter can be set, not only in a floating voltage setting but also in a constant voltage setting or a constant current setting mode. In the present study, the ac conductivity was calculated using the formula: $\sigma_{ac} = \omega \epsilon_0 \epsilon_r \tan \delta$ where, ϵ_0 is the vacuum dielectric constant, ϵ_r the relative dielectric constant, ω the angular frequency and $\tan \delta$ the dielectric loss of the materials. The sample was heated above the room temperature with the help of a laboratory - made furnace connected with a variac. The temperature was recorded by thermocouple (chromel-alumel) connected with a dc micro voltmeter (Sysonics Ltd. India) with accuracy of 0.01 mV (equivalent to accuracy in temperature $\pm 0.25\text{K}$). The readings were taken when the sample attained the steady temperature. The temperature interval of the measurement was about 2-3 min. All the samples after Electroding kept at 1500°C for few hours before taking any electrical measurements to remove moisture of the sample, if any. To remove moisture, during experiment silica gel is used inside the sample holder.

III. EXPERIMENT AND RESULT

Figure 1, 2 and 3 shows the AC conductivity (σ_{ac}) with $10^3/T$ at 1 and 1 MHz for PGZT ceramics. In fig 1, for the composition Zr/Ti ratio 50/50 at the frequency 1 kHz, the graph is well distinct for the different composition $x = 0.03, x = 0.06 \text{ and } x = 0.09$, it is seen that conductivity increases at high temperature and at lower temperature the curves tends to merge.

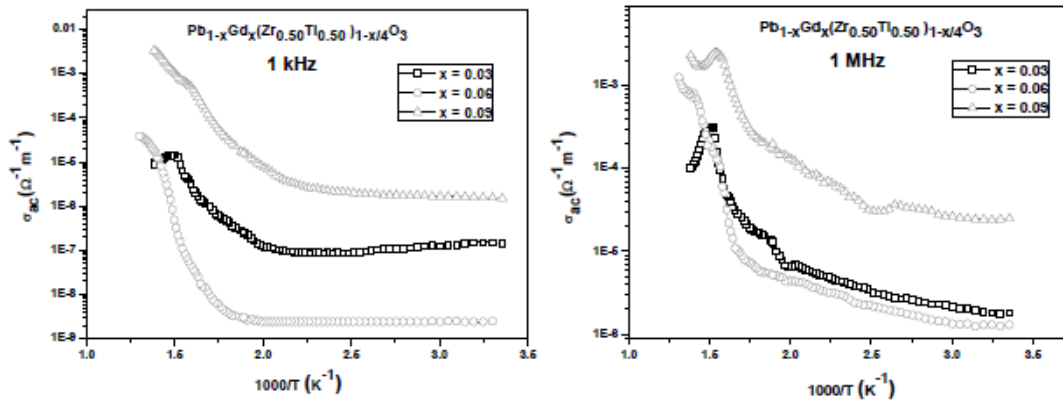


Fig 1: Frequency-temperature dependence of σ_{ac} of $Pb_{1-x}Gd_x(Zr_{0.50}Ti_{0.50})_{1-x/4}O_3$

In figure 2, for the Zr/Ti ratio as 60/40, it is seen that at lower frequency the curves merges but at higher frequency the curves are distinct, for $x=0.09$. This shows increase in Gd^{3+} concentrations increases the conductivity.

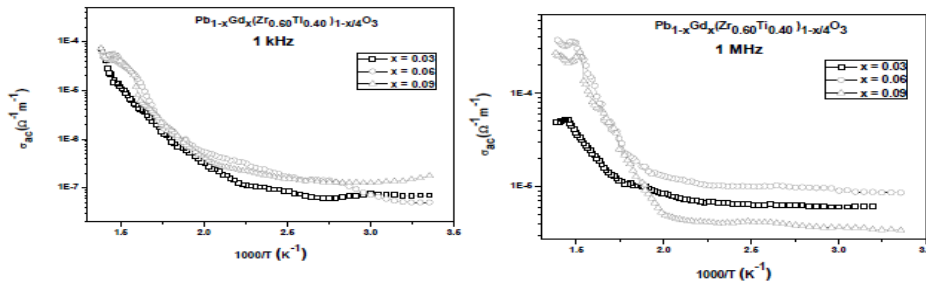


Fig 2: Frequency-temperature dependence of σ_{ac} of $Pb_{1-x}Gd_x(Zr_{0.60}Ti_{0.40})_{1-x/4}O_3$

In figure 3, for Zr/Ti ratio as 65/35 it is seen that for higher temperature, a sharp maximum is observed at a particular temperature, which is nearly independent of the change in frequency.

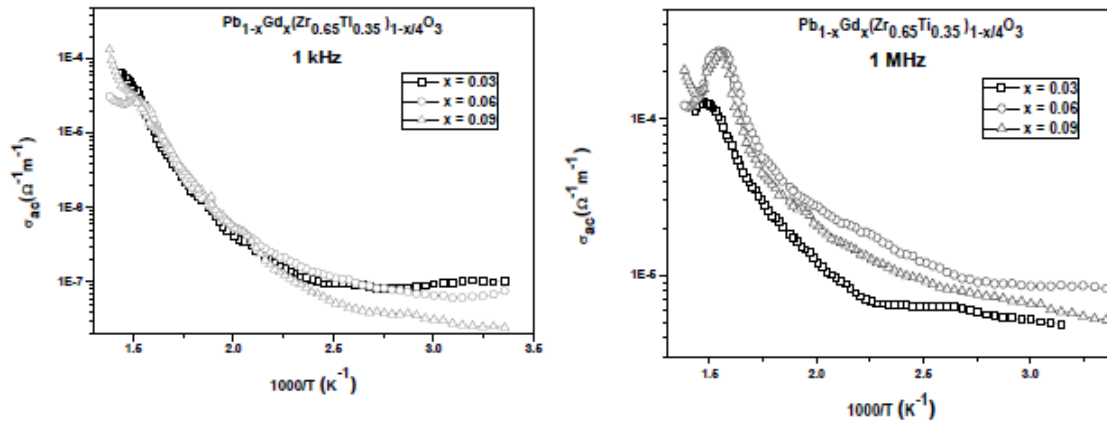


Fig 3: Frequency-temperature dependence of σ_{ac} of $Pb_{1-x}Gd_x(Zr_{0.65}Ti_{0.35})_{1-x/4}O_3$

Table 1: Activation Energy

Gd Content	Frequency	Ea ($\leq T_c$)	
		in eV	
$Pb_{0.95}Gd_{0.05}(Zr_{0.5}Ti_{0.5})_{1-x}O_3$			
3.50.50	1 kHz	0.41	0.34
	1 MHz	0.16	0.12
6.50.50	1 kHz	0.15	0.71
	1 MHz	0.51	0.14
9.50.50	1 kHz	0.97	0.38
	1 MHz	0.63	0.71
$Pb_{0.90}Gd_{0.10}(Zr_{0.5}Ti_{0.5})_{1-x}O_3$			
3.60.40	1 kHz	0.95	0.19
	1 MHz	0.67	0.71
6.60.40	1 kHz	0.14	0.27
	1 MHz	0.58	0.24
9.60.40	1 kHz	0.17	0.33
	1 MHz	0.42	0.74
$Pb_{0.85}Gd_{0.15}(Zr_{0.5}Ti_{0.5})_{1-x}O_3$			
3.65.35	1 kHz	0.15	0.30
	1 MHz	0.20	0.47
6.65.35	1 kHz	0.18	0.19
	1 MHz	0.28	0.49
9.65.35	1 kHz	0.19	0.38
	1 MHz	0.31	0.53

Table 2 : Tolerance Factor

Table for Tolerance Factor (t)			
$Pb_{0.95}Gd_{0.05}(Zr_{0.5}Ti_{0.5})_{1-x}O_3$			
Gd Content	0.03	0.06	0.09
t	0.97532	0.976416	0.977529
$Pb_{0.90}Gd_{0.10}(Zr_{0.5}Ti_{0.5})_{1-x}O_3$			
Gd Content	0.03	0.06	0.09
t	1.007596	1.008725	1.00987
$Pb_{0.85}Gd_{0.15}(Zr_{0.5}Ti_{0.5})_{1-x}O_3$			
Gd Content	0.03	0.06	0.09
t	1.024548	1.025694	1.026857

As the Zr/Ti ratio is increased, then at higher temperature and lower frequencies all the curves tend to merge, this indicates the occurrence of frequency independent dc conduction phenomenon in the PGZT materials. A maximum is observed in ac conductivity at around 410 K for both frequencies, which is closely related to the ferroelectric-paraelectric phase transition (T_c). This is the normal behavior of a ferroelectric material. This behavior can be attributed to the relaxation process associated with the domain reorientation, domain wall motion, and the dipolar behavior [11]. There are distinct region of conduction mechanisms in different temperature ranges: (i) n and /or p-type hopping charge (corresponding to low temperatures), (ii) small polarons and oxygen vacancy conduction (at intermediate temperature regions), and (iii) intrinsic ionic conduction (at high temperature region) [12]. The nature of variation of σ_{ac} over a wide temperature range supports the thermally activated transport properties of the ceramics obeying Arrhenius equation $\sigma = \sigma_0 \exp(-E_a/kT)$ (where σ_0 = pre-exponential factor, k = Boltzmann's constant). The value of activation energy (E_a) of the ceramics at 1 and 1 MHz in given in Table 1, which is quite consistent with that of other complex perovskites [13, 14]. Structural stability and possible distortion in ABO₃ structure perovskite PGZT have been estimated using Goldschmidt's tolerance factor (t); $t = (r_A + r_B) / \sqrt{2} (r_B + r_O)$, where r_A , r_B , r_O , are the ionic radii. For ideal perovskite, $t = 1$ representing an ideal close packing [15]. The estimated values of t is given in table 2, which suggests that the compounds are in distorted perovskite structure. It agrees with the expected range of normal distorted perovskite. The value obtained below the transition temperature ($T \geq T_c$) is in good agreement with those of PGZT single crystals [16]. The activation energy was found to decrease on increasing frequency. This behavior suggests that the conduction mechanism may be due to the hopping of charge carriers (i.e., n and /or p-type) from one site to the other. Therefore, very small amount of energy is required to activate the charge carriers /electrons for electrical conduction. It has been shown by Ang et al. [17] and Moretti and Michel-Calendini [18] that the value of activation energy depends on ionization level of the oxygen vacancy. Usually, activation energy less than 1.0 eV is connected to singly ionized vacancies [17] and/or electronic mobility in space charge regions [19]. Thus, the conduction process within this temperature range may be due to the hopping of charge carriers and/or singly ionized oxygen vacancies of the ceramics.

From the variation of ac conductivity (σ_{ac}) of all the PGZT compounds under consideration with temperature at selected frequencies we get that the value of σ_{ac} exhibits an increasing trend with the increase in temperature. It supports the thermally activated transport properties of the materials obeying the Arrhenius equation;

$\sigma_{ac} = \sigma_0 \exp(-E_a/KBT)$. Also it shows the decrease in bulk resistance of materials with the increase in temperature and thus supports NTCR behavior of the PGZT materials [20]. At a particular temperature in the higher temperature region, a sharp maximum concerning to σ_{ac} has been observed which appears to be nearly independent of the change in frequency [21]. This temperature is transition temperature (T_c) around which marked dispersion takes place. It may be caused due to the increase in polarizability in the PGZT materials. Above T_c , the values of σ_{ac} appear to fall on a straight line which indicates a typical behavior of the dc component [22]. This linear variation of σ_{ac} over a wide range of temperature also supports the existence of thermally activated transport properties [23].

At higher temperatures and lower frequencies, all the curves appear to merge [24]. It indicates the occurrence of frequency independent dc conduction phenomenon in the PGZT materials. The values of activation energy (E_a) of the PGZT compounds above and below T_c are given in Table 1 which indicates the dependence of activation energy on ionization level of oxygen vacancy. At low temperature, the value of activation energy of the samples less than 1 eV indicates the ferroelectric region which may be caused due to the presence of singly ionized oxygen vacancies in the conduction process. On the other hand, the activation energy greater than 1 eV may be caused due to double ionized oxygen vacancies [25-26].

IV. CONCLUSION

For different Zr/Ti ratio with different composition, study of electrical conduction is done for frequency variation and temperature change. Occurrence frequency independent dc conduction phenomenon is being observed for PGZT. The activation energy is less than 1 eV for different composition and is consistent with other reported work. Moreover PGZT shows NTCR behavior which will find its application in thermistors, sensors and other electronic etc.

V. REFERENCES

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