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Physics

PHENOMENOLOGICAL PHASE TRANSITION STUDY ON FERROELECTRIC AND ANTIFERROELECTRIC CERAMICS

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Abstract

The phase transition behavior of the ferroelectric $Pb(Zr_{0.90}Ti_{0.10})ZrO_3$ (PZT10) and antiferroelectric $(Pb_{0.95}Ba_{0.05})ZrO_3$ (PBZ05) has been studied using phenomenological theories. This study is focused to observe the effect of B-site doping in PZT and A-site doping in PBZ of ABO_3 Perovskite structure. It is shown that PBZ05 does not obey Landau second order type phase transition, whereas PZT10 obeys it. The spontaneous polarization so obtained for PZT10 is similar to the reported data but not for PBZ05. However, the Landau- Devonishire theory of first order phase transition is almost applicable for both ferroelectric PZT10 and antiferroelectric PBZ05. The opposite nature of hysteresis curve of PBZ05 to that of PZT10, confirms that PBZ05 should be antiferroelectric in nature and PZT10 should be ferroelectric. The large value of latent heat obtained from this study in PBZ05 confirms the strong first order nature of phase transition but the very small value of latent heat in PZT10, requires further study to confirm the second order nature of phase transition.

Keywords: *Phase transition, phenomenological theories, hysteresis, particle size*

Introduction:

During the past two decades, revolutionary breakthroughs have occurred in the understanding of ferroelectric (FE) and antiferroelectric(AFE) materials, both from the perspective of theory and of experiment. First principles approaches, including the Berry phase formulation (Kittle 1996) of ferroelectric, now allow accurate, quantitative predictions of materials properties, and single crystalline thin films are now available for fundamental studies of these materials. In addition, the need for high dielectric constant, insulators and nonvolatile memories in semiconductor applications has motivated a renaissance in the investigation of these materials. The electronic ceramics such as potassium niobate (KN), lead zirconate titanate (PZT) (Mishra & Pandey 1997), lead barium zirconate (PBZ) (Pokharel & Pandey 2000) with ABO_3 perovskite structure show ferroelectric and antiferroelectric behaviors which are being used in many applications in electronic and optics. As the ferroelectric device elements become smaller and smaller with the dimension of ferroelectrics in the sub-micrometer range or even lower, the physical properties become size dependent and the particle size effect must be taken into consideration for optimizing the properties. Ferroelectric phase transition is a structural phase transition. As a result of transition from the high temperature phase, a spontaneous polarization appears and some symmetry elements of the high temperature phase are lost on cooling below the transition temperature. The ferroelectric and antiferroelectric phase transition in perovskite has been considerable interest due to their wide range of technological applications. They are closely linked with technological application due to possessing useful and valuable piezoelectric, electric and electronic properties. Ferroelectrics are used in acoustic wave devices, electro-optical devices, optical waveguides, mechanical actuators and detectors and non-volatile memory devices. The biggest use of ferroelectric ceramics has been in the areas such as dielectric ceramics for capacitor applications, thin film for non-volatile memories, piezoelectric materials for medical ultrasound imaging and actuators, and electro optic materials for data storage and displays (Mishra & Pandey 1997).

In this paper, theoretically studied using phenomenological theories on the phase transitions behavior of ferroelectric PZT10 and antiferroelectric PBZ05 ceramics is presented using Landau and Landau-Devonshire theories (Landau 1937, Devonshire 1948, Landau & Lifshitz 1980) of ferroelectric phase transitions.

Materials and Methods:

We used the Landau and Landau-Devonshire phenomenological theories to study the phase transitions behavior of ferroelectric and antiferroelectric materials. The coefficients of Landau and Landau-Devonshire coefficients are adopted from the available literature (Cross 1967, Pokharel & Pandey 2002) as listed in table

1. We mainly focused our study on ferroelectric and antiferroelectric polycrystalline samples such as $(Zr_{0.90}Ti_{0.10})3$ (PZT10) and $(Pb_{0.95}Ba_{0.05})ZrO_3$ (PBZ05) using the available literatures. The free energy is plotted with respect to polarization at different temperatures using Landau theory for second order phase transition and Landau-Devonshire theory for first order phase transition. The XMGRACE program was used as a basic tool for the study and results calculations.

Theoretical Survey:

(a) Landau Phenomenological Theory: Second Order Phase Transition

Free energy and spontaneous polarization

Landau developed a theory of phase transition for ferroelectric materials based on order parameter. For the second order phase transition, the Gibb's free energy of the ferroelectric material in terms of order parameter-spontaneous polarization in the absence of external electric field and stress is calculated from the Landau theory as mentioned below (Dhungana 2014);

$$\Delta G = \left(\frac{1}{2}\right)\alpha_0(T - T_0)P^2 + \left(\frac{1}{4}\right)\beta P^4 \quad (1)$$

$$P_S = \left(\alpha_0 \frac{T-T_0}{\varepsilon_0 C\beta}\right)^{\frac{1}{2}} = (\alpha/\beta)^{1/2} \quad (2)$$

Where ε_O = 8.854 X $10^{-12}C^2/Nm^2$ is permittivity of the free space, α and β are the Landau coefficients. The coefficients α for ferroelectric phase is temperature dependent.

$\alpha = \alpha_0(T\text{-}T_0)/\varepsilon_0 C$

Where α_0 is constant and depends on the nature of the materials, C is Curie constant and T_0 is Curie-Weiss temperature. For second order phase transition, there is no latent heat associated and $T_C = T_0$.

(b) Landau-Devonshire Theory

(i) Free energy and spontaneous polarization:

For the first order phase transition, Landau theory is further extended by Devonshire including external electric field where sixth power term of polarization is required where β will be negative. In first order phase transition latent heat is associated where the transition temperature (Tc) is greater than Curie- Weiss temperature (Devonshire 1948).

$$\Delta G = \frac{1}{2}\alpha_0(T - T_0)P^2 + \frac{1}{4}\beta P^4 + \frac{1}{6}\sigma P^6\text{-EP} \quad (3)$$

$$P_S^2 = \frac{-\beta \pm \sqrt{\beta^2 - 4\sigma\frac{(T-T_0)}{(\varepsilon_0 C)}}}{2\sigma} = -3\beta/4\sigma \quad (4)$$

The transition temperature also called Curie temperature is related to Curie-Weiss temperature by the relation;

$T_c = T_0 + 3\beta^2\varepsilon_0 C/16\sigma$ (5)

Other two characteristic temperatures are:

$T_1 = T_0 + \beta^2\varepsilon_0 C/4\sigma$ (6)

$T_2 = T_0 + 9\beta^2\varepsilon_0 C/20\sigma$ (7)

T_1 is called inflexion temperature and above T_2 ferroelectric phase will totally converted into paraelectric phase.

In the graph of free energy as the function of polarization for the first order phase transition different characteristic temperatures are shown:

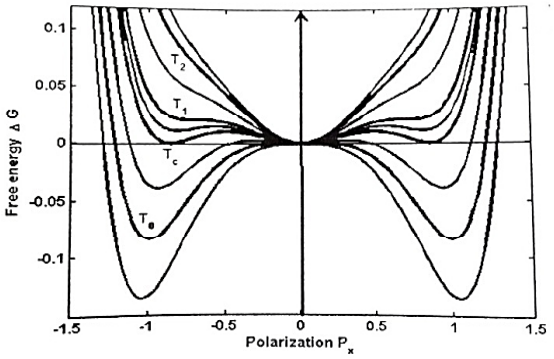

Fig. 1: Free Energy vs polarization Curve for different temperatures

(ii) P-E Hysteresis Loop

The hysteresis loop (P versus E) may be obtained by minimizing Landau –Devonshire free energy with respect to polarization and is given by from equation below (Liang et al 2009, Fukuda et al 1974):

$$E = \alpha_0(T - T_0)P + \beta P^2 + \sigma P^5 \quad (8)$$

The graph so obtained from above equation at various temperatures are as below:

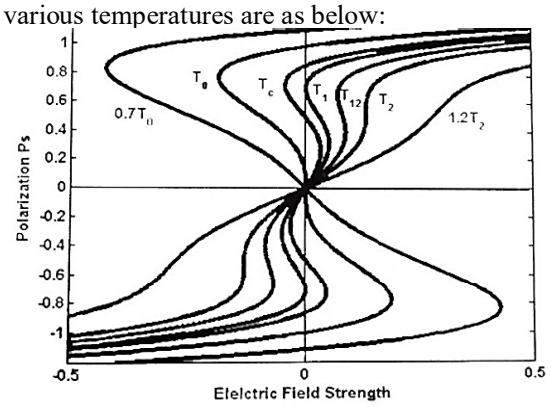

Fig. 2: Polarization vs applied electric field curve

(iii) Latent Heat

The latent heat of the ferroelectric materials depends upon the transition temperature and the spontaneous polarization. The relation between the latent heat, transition temperature and the spontaneous polarization is given by the equation (Benguigui 1970, Arlt 1990).

$$L = Tc\Delta S = -Tc\frac{\partial G}{\partial T} = \left(\frac{1}{2}\right)\alpha_0 T_c P_s^2 \qquad (9)$$

The latent heat can directly be obtained from the maxima of free energy curve at the transition temperature as shown below in fig.3. The value of energy at the middle of two minima polarization is the latent heat as shown in figure below.

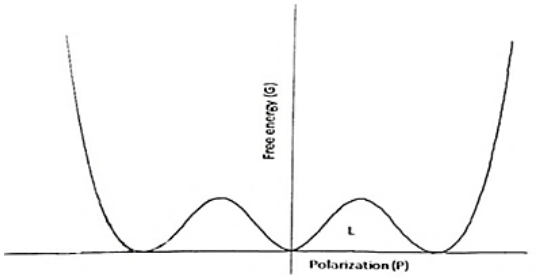

Fig. 3: Free Energy vs Polarization curve at transition temperature

Results and Discussion:

We will present here the result obtained from simulation on the basis of Landau and Landau-Devonshire phenomenological theories for PZT10 and PBZ05:

Landau Phenomenological Theory: Second Order Phase Transition

a) Free energy and polarization

The free energy of the ferroelectric material and spontaneous polarization in the absence of external electric field and stress was calculated from the Landau theory for second order phase transition using Landau coefficients from reported data for PZT10 and PBZ05 (Cross 1967, Pokharel & Pandey 2002). Then the following figures are plotted.

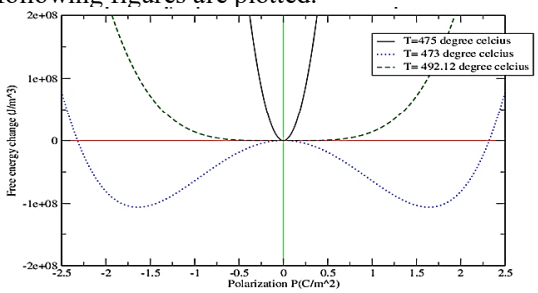

Fig.4: ΔG vs Polarization at different temperatures for PZT10

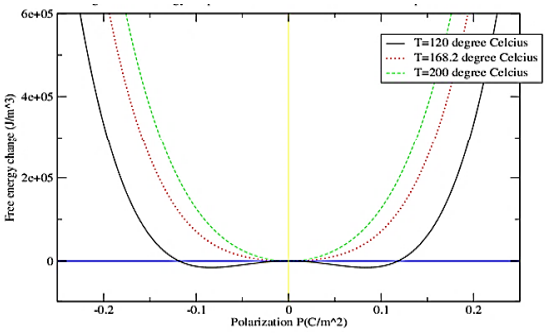

Fig.5: Free energy vs polarization at different temperatures for PBZ05

The fig.4 shows the variation of free energy density ΔG (J/m^3) with polarization P(C/m^2) for PZT10 ceramics. The transition temperature of PZT10 is 492.12^{0}C (Cross 1967) at which the curve of the plot shows flatness at the bottom up to spontaneous polarization P_s=±0.30C/m^2 which is similar to the reported spontaneous polarization 0.33C/m^2 of PZT10 (Cross 1967). Above transition temperature (T_c) the curve is purely parabolic but below it, the material being in ferroelectric phase, contains two cups or minima with maximum free energy at polarization ±P_0 which is thus expected to be in ferroelectric sample.

In PBZ05 (fig.5), the curve is slightly different in comparison to fig.4. It may be due to that the PBZ05 is not ferroelectric materials but it is antiferroelectric in nature up to 168.2^{0}C then converts into ferroelectric phase and above 225^{0}C, it has paraelectric phase. The observed polarization obtained from this figure for PBZ05 is about 0.02 C/m^2 which is far below than the reported value (Pokharel & Pandey 2002).

b) Polarization and temperature

When the graph is plotted between spontaneous polarization with temperature for second order phase transition of PZT10 and PBZ05 then we get for both samples at Curie temperature or transition temperature (Tc), spontaneous polarization drops to zero at transition temperature. Above T_c, the materials convert into paraelectric phase in which elementary dipoles are randomly oriented and below T_c, the dipoles interact with each other. Their interaction gives rise to an internal field, which lines up the dipoles. The nature of the dropping the polarization to zero at transition temperature for PZT10 in fig. 6 and for PBZ05 in fig.7 being slightly different the nature of the phase transition could not be same.

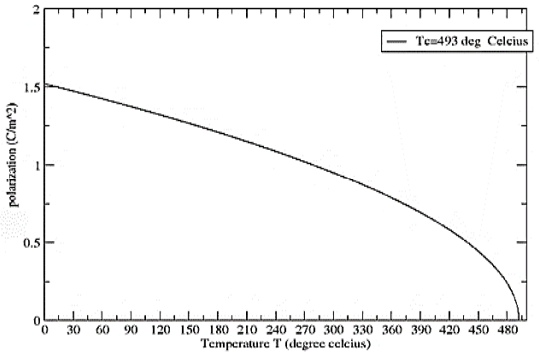

Fig.6: Variation of polarization with temperature for PZT10

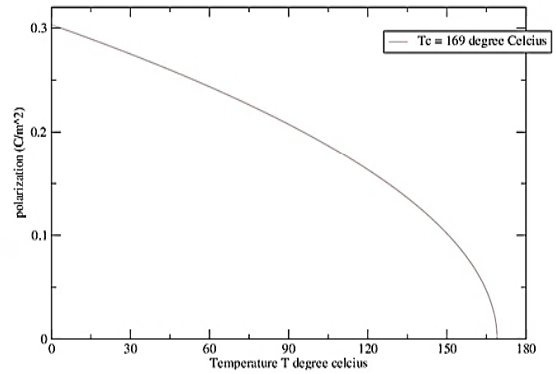

Fig.7: Variation of polarization with temperature for PBZ05

As we know form the theoretical study for the second order phase transition, the curve of polarization should pass continuously and finally meet at T_c along temperature axis corresponding to zero polarization as shown in Fig. 6 and Fig.7. Hence, from the free energy and polarization study with respect to temperature, we conclude that the phase transition behavior of PZT10 should be second order type and PBZ05 is not second order type. It may be first order type, so for further confirmation Landau- Devonshire theory is applied.

Landau-Devonshire Theory: First Order Phase transition

a) Free Energy and Polarization:

Fig.8 and Fig.9 reveal the variation of free energy density ΔG with the polarization for PZT10 and PBZ05 ceramics samples, assuming the nature of phase transition as first order type. In contrast to second order phase type, there is no flat portion of the curve at the bottom at transition temperature Tc rather three minima at P=0 and P = ±Ps are observed as predicted by Landau- Devonshire theory. The height of the minima in the curve along ΔG- axis at P = ±Ps gives the latent heat (L). Such type of behavior is possible only in first order type phase transition.

The values of Ps for PZT10 and PBZ05 as obtained from these graphs are 0.40 C/m^2 and 0.26 C/m^2 where the spontaneous polarization for PZT is slightly different and that of PBZ05 is similar to that of reported data, (Cross 1967, Pokharel & Pandey 2002) confirming the first order type of phase transition in PBZ05 but PZT10 needs further study for confirmation.

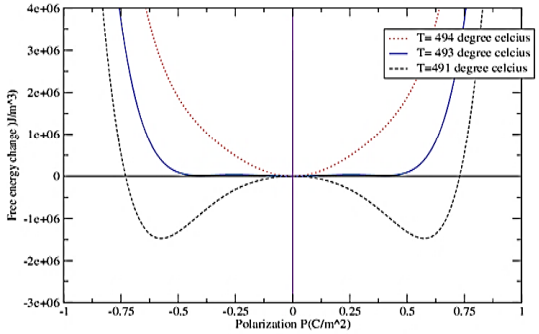

Fig.8: ΔG Vs Polarization different temperatures for PZT10 ceramics.

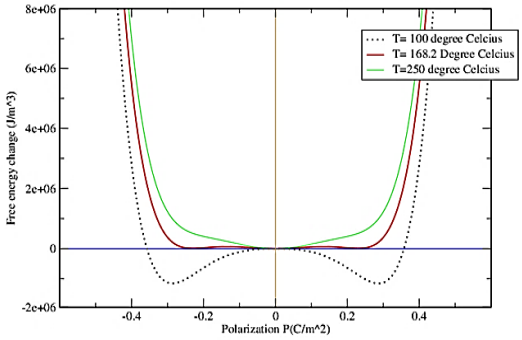

Fig.9: ΔG Vs Polarization at different temperatures for PBZ05

b) Polarization and temperature

The feature of polarization versus temperature graph i.e. fig.10 for PZT10 is similar to the first order nature of phase transition. But the absent of sudden drop of the polarization to zero at transition temperature is the characteristics property of second order phase transition. The phase transition temperatures as obtained from the figures are almost similar to the reported data.

But in PBZ05 sample as shown in fig. 11, the polarization curve is not drop to zero at transition temperature rather decreases linearly with temperature even above 190^0C while its transition temperature is 168.2^0C. It confirms that PBZ05 is not ferroelectric materials but it is antiferroelectric in nature and the ferroelectric theory is not applicable for it. It requires Kittle theory (Pokharel & Pandey 2002) of antiferroelectric phase transition.

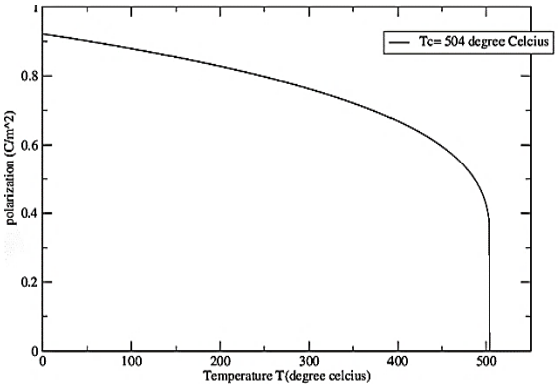

Fig.10: Variation of Polarization with temperature of PZT10 for first order phase transition.

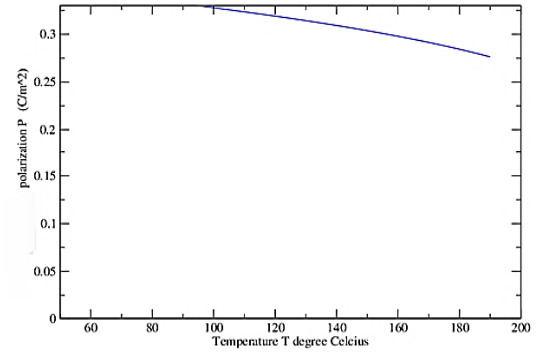

Fig.11: Variation of Polarization with temperature of PBZ05 for first order phase transition.

c) P-E Hysteresis curve

The observation of hysteresis curve i.e. the graph between polarization and applied electric field is the characteristics property of ferroelectric and antiferroelectric materials. The theoretical hysteresis curves of PZT10 is plotted in fig.12. The nature of curve is similar to the nature of ferroelectric materials by comparing it with the hysteresis curve of $KNbO_3$ which is ferroelectric material (Liang et al 2009). As $KNbO_3$ is ferroelectric materials which confirms PZT10 is ferroelectric material. But fig.13 for PBZ05 having opposite nature in comparison to the hysteresis curve of ferroelectric materials. Hence PBZ05 is not ferroelectric material, so it must be antiferroelectric in nature so it should be antiferroelectric material (Pokharel & Pandey 2002). Actually, the ferroelectric materials have single loop hysteresis but an antiferroelectric material shows double loop hysteresis having opposite arrangement of dipoles. It is because the ordering of dipoles in ferroelectric materials is parallel even in the absence of an external electric field and in antiferroelectric, it is antiparallel in nature.

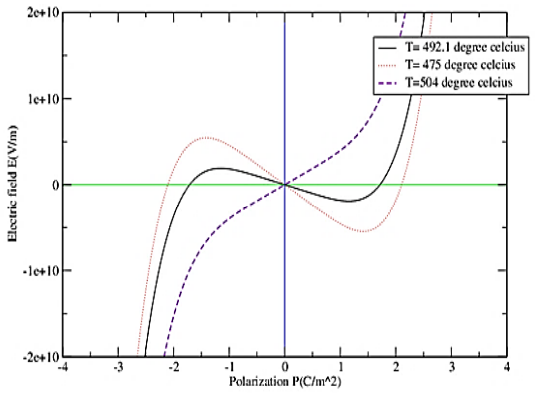

Fig.12: Hysteresis curves of PZT10 at different temperature

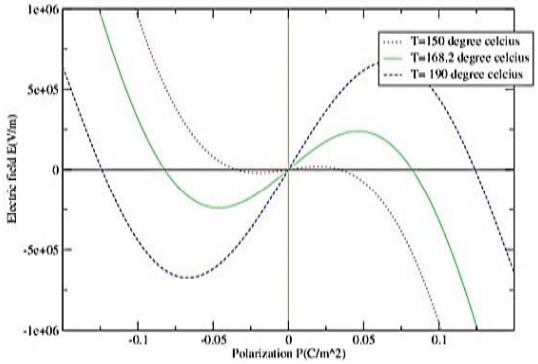

Fig.13: Hysteresis curves of PBZ05 at different temperatures

d) Latent Heat

Fig.14 and Fig.15 reflect the variation of free energy density ΔG with the polarization for PZT10 and PBZ05 ceramic samples at transition temperature respectively in the first order type phase transition. From the graph we observe that there is no flat portion of the curve at the bottom at transition temperature T_c rather three minima at P=0 and P=$\pm P_s$ as per prediction of Landau – Devonshrie theory. The height of the minima curve along ΔG- axis at P=$\pm P_s$ gives the latent heat (L). Such type of behavior is possible only in first order type phase transition because in second order type phase transition there is no minima at T_c but only flat surface. The value of latent heat for PZT10 and PBZ05 as obtained from the graph are similar as that of the reported data (Benguigui 1970) with are listed in the table 1.

From the table, it is observed that the calculated/observed value of latent heat of PBZ05 is similar to the reported data but different for PZT10, which confirms that PBZ05 should be first order type material and PZT10 may be second order type.

Table 1: Reported Calculated and Observed values of latent heat for the samples.

Materials	Reported (J/m^3) L	Observed (J/m^3) L	Tc (^0C)	To (^0C)	$\alpha_0(Nm^2/C^2)$	$\beta(Nm^6/C^4)$	$\sigma(Nm^{10}/C^6)$
PZT10 (Cross 1967)	$7.69x10^4$	$3.87x^4$	493	493	$1.62x10^8$	$-5.84x10^7$	$2.56x10^8$
PBZ05 (Pokharel & Pandey 2002)	$6.0x10^6$	$5.2x10^6$	168/225	145.7	$3.48x10^5$	$-1.28x10^9$	$1.79x10^{10}$

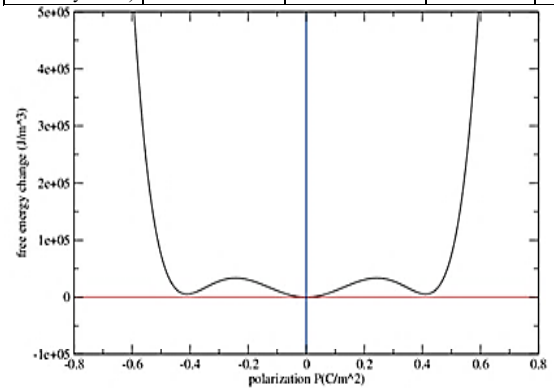

Fig.14: Variation of ΔG with P at Tc for first order phase transition of PZT10.

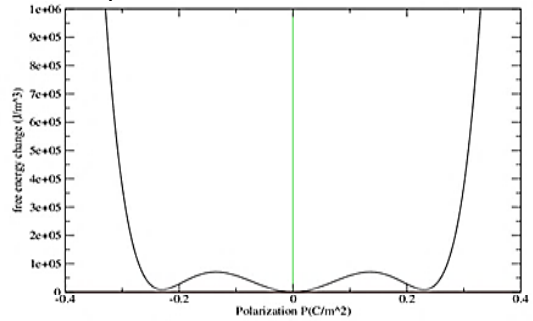

Fig.15: Variation of ΔG with P at Tc for first order phase transition of PBZ05

Conclusions:

1. Landau Phenomenological Theory

- The variation of free energy density ΔG (J/m^3) with polarization P(C/m^2) for second order phase transition is studied for PZT10 and PBZ05. At their transition temperature the spontaneous polarization is recorded 0.30 and 0.02 C/m^2 respectively. The value for PZT10 is similar to reported data but not for PBZ05. Thus PBZ05 do not obey Landau second order phase transition behavior. It also confirms PZT10 may be second order type and PBZ05 should be first order type materials.
- In the graph plotted between spontaneous polarization and temperature of PZT10 and PBZ05, the curves meet at the transition temperature (Tc), which is slightly different from reported value.

2. Landau-Devonshire Theory

- The graph plotted between free energy density ΔG (J/m^3) with polarization P(C/m^2) for first order phase transition of PZT10 and PBZ05 ceramic samples show three minima at P=0 and P=±Ps at transition temperature as per Landau- Devonshire theory. And the value of spontaneous polarization Ps as obtained are 0.40 and 0.26 C/m^2 respectively where the value for PBZ05 is similar to the reported data but slightly different for PZT10 sample. The latent heat of transition for PZT10 and PBZ05 are also observed finite and positive in nature. The latent heat for PBZ05 is similar to the reported data so it should be first order type whereas PZT10 shows very low value of latent heat so it may be second order type material.

- The feature of polarization versus temperature graphs for PZT10 confirms ferroelectric and nearly the first order type nature of the sample. The sudden drop of the polarization to zero at transition temperature is the characteristic property of first order phase transition. But in PBZ05 sample, the polarization curve does not drop at transition rather decreases linearly with temperature even up to 200 ^0C. It shows that PBZ05 is not ferroelectric material, so it may be antiferroelectric.
- The Hysteresis loop plotted for PZT10 confirms that it is ferroelectric material. But for PBZ05 curve is opposite in nature in comparing to ferroelectric materials which confirms that the material should be antiferroelectric innature.

- The latent heat observed in first order phase transition of PZT10 and PBZ05 are listed in table 1 from which, comparatively PBZ05 is more prominent towards first order type nature of phase transition than PZT10.

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