

Stability analysis of nano-sized switched domains in ferroelectric lead meta niobate single crystal : an approach to avoid back-switching of domain

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Abstract- Unique ability of a ferroelectric material to maintain its polarization even in the absence of an external voltage makes it very useful as a non-volatile memory device, but sometimes it has seen that the polarized domains are shrinking to zero (back-switching) upon removal of externally applied voltage. Therefore, it is very important to know the stability conditions for a ferroelectric domain before the material is used in the fabrication of ferroelectric random access memory (FRAMs). The intention of this article is to present a stability analysis of polarized domains in ferroelectric lead-meta-niobate (PbNb_2O_6) single crystal, verified by two well reported mathematical formulations i.e. Wang et al and Ingle et al [14, 15]. To ascertain the stability of polarized domain in this grown material, critical parameters viz. critical radius for nucleation (r_c), domain wall energy (α) and critical energy for nucleation ($\Delta\omega_c$), geometrical dimensions of domain (ac_1, ac_2) are calculated for PbNb_2O_6 single crystal with the help of its temperature dependent dielectric behavior by using above mentioned formulations. It has found that in this stability analysis, the ferroelectric domains present in this grown PbNb_2O_6 single crystal are of nano-sized $\{r_c = (5.06 \text{ to } 9.32) \times 10^{-9} \text{ m}\}$ and thermally unstable point domains $\{\alpha = 10^{-6} \text{ J/m}^2, \Delta\omega_c = 10^{-28} \text{ J}\}$. The geometrical dimensions of domains calculated (ac_1, ac_2) are also found low as compared to critical value required to avoid back switching of these domains.

Keywords— FRAMs, back-switching, ferroelectric domains.

INTRODUCTION

The fabrication of high density ferroelectric random access memory (FRAMs) requires stable switched domains of very small size under low voltage or short pulses [1] in ferroelectric single crystals. Sometimes, switched domains are unstable and suffer from significant back-switching (shrinking to zero) upon removal of externally applied electric field [2]. Therefore, it is always desirable to know the stability conditions for a domain in the absence of applied electric field. Domain structures in

anisotropic ferroelectric crystal having a direct influence on the macroscopic properties like the dielectric constant of the material [3]. As the domain-evolution proceeds through the micro-domain nucleation, the increase or the decrease of dielectric constant always associated with the nucleation of domains [4, 5] due to anisotropy of surface of the crystal and back-switching processes can't be denied. Recently, domain back-switching processes have attracted a lot of attention of the researchers [6-10].

In this article, the intention is to find-out the critical value of certain parameters which determine the stability condition of domain structures, will be helpful to avoid the back switching in ferroelectric lead meta niobate (PbNb_2O_6) single crystal. With a view to explain the switching behavior in ferroelectric PbNb_2O_6 crystal, the idea of existence of point domains (thermally stable or unstable) is anticipated and the critical value of their geometrical dimensions, domain wall energy, fraction of domains nucleated, critical energy for nucleation are calculated and verified by two mathematical formulations. This analysis is providing useful information's to ascertain the stability of ferroelectric domains in PbNb_2O_6 single crystal so as to avoid the problem of back switching after the removal of external electric field.

I. MATERIAL AND METHODS

The single crystals of lead meta niobate (PbNb_2O_6) were grown from melt by employing Goodman's technique with useful modifications [11]. The constituent oxides (PbO and Nb_2O_5) are purchased from Merck of analytical reagent grade with 99.4% purity. A Gallenkamp furnace is used to grow the crystal at temperature 1623°K and to perform a special kind of cooling and reheating process for various soaking time so as to avoid the stray nucleation in crystal growth process. It was observed that the grown crystals are of pale yellow color, oxygen-deficient and containing Pt-ion as the main impurity due to use of platinum crucible. The single orthorhombic phase at room temperature and lattice parameters with point group were calculated by XRD-pattern of this grown sample [12]. The experimental details of dielectric-constant measurements,

the evidences of ferroelectric nature at room temperature and phase transition temperature (843°K) were also confirmed and reported with the help of its hysteresis loop studies [12] and microscopic domain structure studies [13] in our previous articles.

THEORY AND FORMULATIONS USED

To carry-out the stability analysis for switched domains in ferroelectric PbNb_2O_6 single crystal, the two established formulations given by Ingle *et al.* [14] and Wang *et al.* [15] have been applied. Theoretical treatment based on statistical mechanics reported by Ingle *et al.* [14], a domain nucleates and expands under an externally applied electric field involves the change in internal energy at the nucleation-sites, whereas the internal energy depends upon the electro-static energy, surface energy of nucleated domain wall, depolarizing energy and strain energy. Specially, the surface energy of nucleated domain depends upon the size and shape of the domain. According to this theoretical treatment [14], the critical radius for nucleation (r_c) of domains can be calculated by

$$r_c = (3N_0V_0/4\pi N)^{1/3} \quad (1)$$

Where V_0 is the volume of domain nucleated, N is the number of domains nucleated per unit volume, N_0 is the number of available sites for nucleation, therefore (N/N_0) will be consider as the fraction of domains nucleated. The value of critical radius for nucleation (r_c) is useful in the calculations of domain wall energy (α) and critical energy for nucleation ($\Delta\omega_c$),

$$\alpha = r_c P_s E \quad (2)$$

$$\text{and } \Delta\omega_c = (4\pi/3).(r_c)^3.P_s.E \quad (3)$$

where ' P_s ' is the spontaneous polarization value and ' E ' is the applied electric field.

Wang *et al.* [15] also presented another general formulation theory by choosing the change in internal energy as the Liapunov function to determine the stability conditions for switched domains. They claimed that their theory is generally applicable to various fields like phase transformation, nucleation, expansion of dislocation loops in thin films etc. Moreover, they considered a spherical shaped domain and assumed unrealistically that it will expand along the radial direction, then established a kinetic equation governing the evolution of domain;

$$da/dt = -M[4\pi a^2\{(2P_s/3C) - 2E^0P_s\} + 8\pi a\alpha] \quad (4)$$

where ' M ' is a material constant, ' a ' is a parameter related to geometrical dimension of domain, ' C ' is the dielectric constant and ' α ' is the domain wall energy. To determine the boundary conditions for domain evolution, Wang defined the stationary points ' a_c ' at which driving force (da/dt) is zero, i.e.

$$[a_{c1} = 0, a_{c2} = 2\alpha/\{2E^0P_s - 2P_s^2/3C\}] \quad (5)$$

Where $aa_{c1} = 0$ is verified as stable equilibrium point and ' a_{c2} ' is a non-stationary point. This means, if the radius of a nucleated domain is in the range of ($0 \leq a \leq a_{c2}$), it will shrink to zero, whereas if ($a \geq a_{c2}$) then nucleated domain will expand to fill the whole sample. Thus, ' a_{c2} ' is the critical value of radius for nucleation in the Wang formulations [15] and it has a congruity with the parameter ' r_c ' reported in Ingle *et al.* [14].

II. RESULTS AND DISCUSSION

A When a switching field is applied, a typical evolution of domains in ferroelectric single crystal during the polarization can be established, which includes;

- (i) arising of new domains, i.e. nucleation,
- (ii) forward growth of domains through the sample thickness,
- (iii) sideways motion of the domain walls,
- (iv) coalescence of residual domains.

Collectively, these complicated phenomena can be reconsidered in the present analysis in such a way that the domains of different orientations of polarization coexisting in one, and sample are none, but the different regions divided by domain-walls, and the switching process is similar to be a first order phase transformation and achieved through arising of nuclei of different dimensionality. In single crystals, so preferable nucleation occurs at the sample surface as well as in the vicinity of defects, thus the nucleation probability at a given place, and consequently, the rate of growth of a domain will depend on the local strength of internal field which is averaged over the volume of the order of nucleus size. In other words, the local electric field is the driving force of switching process and depends upon the size of nucleated domains, that is why we are calculating the various critical parameters viz. critical radius for nucleation (r_c), domain wall energy (α) and critical energy for nucleation ($\Delta\omega_c$) for PbNb_2O_6 single crystal in the present article with the help of its temperature dependent dielectric behavior and obviously to ascertain the stability of a domain.

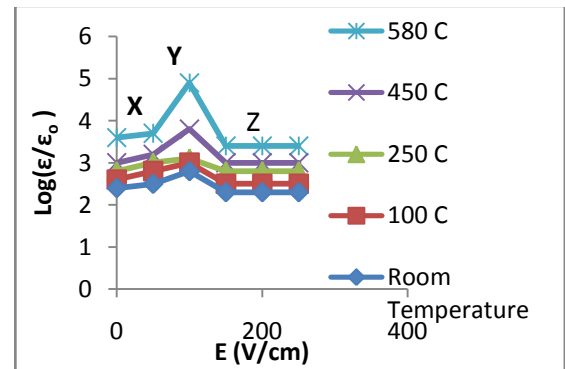


Fig.1. Variation of Log of Dielectric Constant of PbNb_2O_6 single crystal with Electric Field at different Temperatures

Fig.[1] shows the variation of log of dielectric constant of ferroelectric PbNb_2O_6 single crystal with respect to applied electric field at different temperatures. The explanation of increase and decrease of dielectric constant with respect to applied field is thoroughly discussed on the basis of micro-domain nucleation process in PbNb_2O_6 single crystal in our previous article [12]. Summarily, when an electric field is applied to the crystal, certain fresh additional domains nucleated whereas some stable domains were already present. Due to increase of number of nucleated domains per unit volume (N) and more alignment of dipole units, the

polarization value of crystal is increases. Consequently, the dielectric constant also increases from point 'X' to 'Y'; but the nucleation must takes place at the strain sites available in the structure and these strain sites are the outcome of impurities or defects present in the structure. Our microscopic studies of PbNb_2O_6 single crystal [13] reveals that the nature of strain produced by defects is such that it prefers the twinning that nucleates the domain wall rather than nucleating a closed domain. Moreover, as these available nucleation strain-sites (N_0) filled one by one, thus 'N' will go on decreasing due to non-availability of nucleation-sites and consequently the dielectric constant of the crystal decreases from point 'Y' to 'Z'. At this stage of explanation, it would not be wrong to say that all these dielectric mechanism involves a change in internal electric field inside the bulk of the crystal, and depolarizing energy also plays a vital role in it. In a ferroelectric crystal, the internal electric field is determined not only by the potential difference between electrodes but also it has a contribution of the sum of depolarization field produced by bound charges, screening field produced by charges on the electrodes and bulk charges. Particularly in the PbNb_2O_6 crystal, these bound charges can be appearing at several places viz. at polar surface, at the encountering domain walls, or in the bulk. Thus, the bound charges produce so called depolarizing field is opposed to the spontaneous polarization, decreases the nucleation probability and slow the micro-domain nucleation process as well as switching process. In fig.[1], the point 'X' is determine the minimum activation energy for nucleation in PbNb_2O_6 single crystal which means that no nucleation can take place up to an electric field of 50V/cm at room temperature. There is a slight decrease is observed in the value of activation field with the increase of temperature. Thus, domain nucleation requires certain threshold bias at room temperature, corresponding to non-zero activation energy for nucleation. Furthermore in Fig.[1], the position of point 'Y' is also not constant as the temperature of PbNb_2O_6 crystal increases; it indicates the elongation of state at which all available nucleation strain-sites are filled one by one and no further nucleation is possible. By extrapolating 'YZ' parts of Fig. [1], we are determining the fraction of domains nucleated (N/N_0) corresponding to various temperatures in PbNb_2O_6 single crystal, and its variation with temperature has shown in Fig.[2]. The value of ' N/N_0 ' is useful in the calculations of various critical parameters e.g. r_c , α , $\Delta\omega_c$.

Fig.2. Variation of Fraction of domains(N/N_0) of PbNb_2O_6 single crystal with Temperature

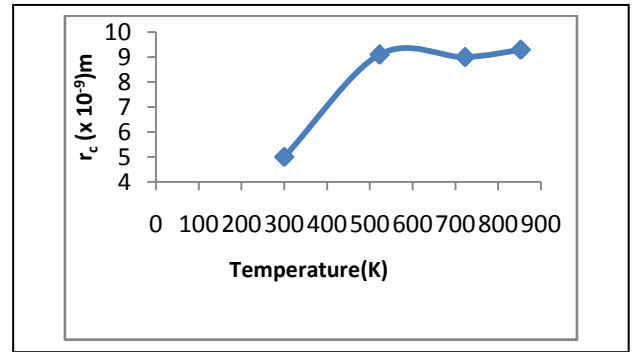


Fig.3. Variation of Critical radius of nucleation of domains in PbNb_2O_6 single crystal with Temperature

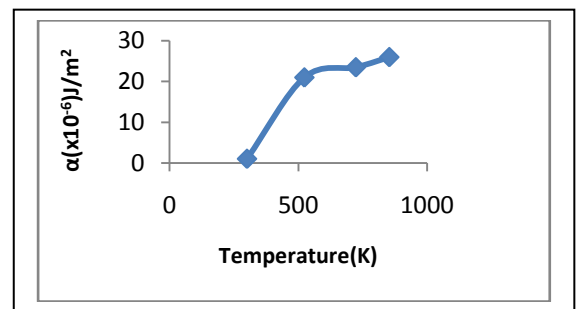


Fig.4. Variation of Domain Wall Energy of PbNb_2O_6 single crystal with Temperature

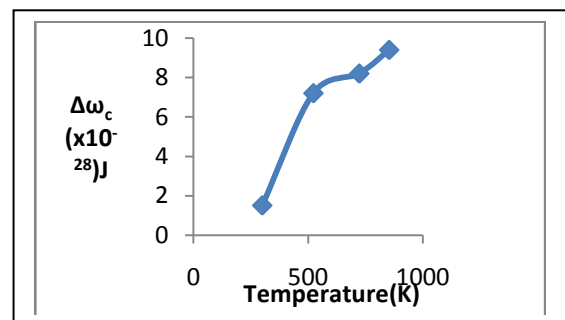
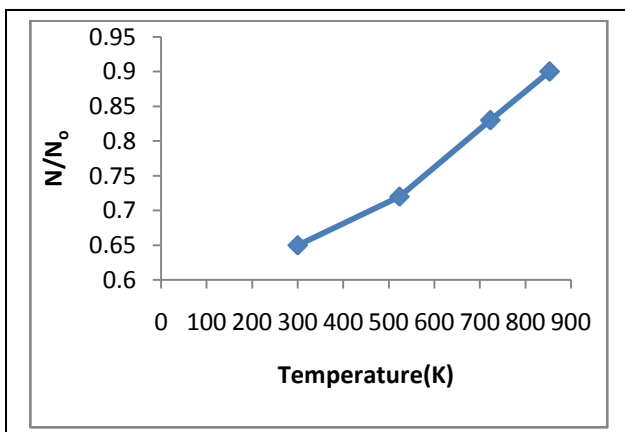


Fig.5. Variation of Critical field for nucleation of domains in PbNb₂O₆ single crystals with Temperature

The formulations presented by Ingle et al. [14], the critical radius for nucleation (r_c) of domain in PbNb₂O₆ single crystal at various temperatures were calculated and found that these values are ordered in nano-scale i.e. from (5.06 to 9.32) $\times 10^{-9}$ m. The variation of ' r_c ' with temperature has shown in Fig. [3]. This parameter (r_c) describes the critical-dimension (size and shape) required for a domain to be nucleated and to be proceeded in growth process. On the other hand, it also represents the information about the critical geometrical dimension for a domain which is to be required avoiding its' back-switching. It is also obvious from Fig. [3], the nano-sized domains are involved in the nucleation process of PbNb₂O₆ single crystal. In addition, the domain wall energy (α) and critical energy for nucleation ($\Delta\omega_c$) are also calculated and there variations with temperature have been studied in Fig. [4] and Fig. [5], respectively. It has found that the wall energy (α) of these domains in PbNb₂O₆ single crystal is nearly hundred times lower (i.e. in the order of 10^{-6} J/m²) than the accepted value for a thermally stable domain [16]. Furthermore, the critical energy for nucleation ($\Delta\omega_c$) of thermally stable domains was reported [16] in order of 10^{-8} J, whereas it has also found very low in our case of PbNb₂O₆, i.e. in order of (10^{-28}) J. With these analytical calculations, it is evident that the physical state of nucleated domains in PbNb₂O₆ is different from that of thermally stable domains, apparently is an unstable state. However, it was reported [17, 18] that both stable and unstable point domains were existing in ferroelectric crystal.

At this moment, it is very important for us to know the stability condition for a domain in this peculiar material. In this regard, the determination of critical geometrical dimensions of a domain may provide an important information to ascertain its stability to avoid the back-switching, and for sure in fabricating the FRAMs with reliable retention properties. We can determine and verify the critical dimension for a domain {equation (5)}, above which it will expand in an unstable manner by the formulations reported by both Ingle et al and Wang et al. [15]. In our case of PbNb₂O₆ single crystal, the value of ' a_{c2} ' parameter is (81.818 $\times 10^{-9}$) m. calculated, which indicates the required critical radius for a domain that can't be back-switched even after the removal of applied electric field. Thus, in case of PbNb₂O₆ single crystal, if the radius of a nucleated domain is in the range of '0' to '(81.818 $\times 10^{-9}$)m', it will shrink to zero and disappear i.e. **back-switching**; whereas if the radius of a particular domain is greater than (81.818 $\times 10^{-9}$)m then only **it will expand to fill the whole sample**. Hence, it again confirms that why the nucleated domains in presently grown PbNb₂O₆ single crystal is unstable in the behavior as the value of ' r_c ' calculated by Ingle et al [14] is (5 $\times 10^{-9}$) m which is considerably less than the value of ' a_{c2} ' = (81.818 $\times 10^{-9}$) m' calculated by Wang et al.[15]. Therefore, it can be suggested here that it must shrink to zero. Moreover, the calculated values of ' r_c ' and ' a_{c2} ' in our case of PbNb₂O₆ also present a complimentary agreement between these two formulation theories [14, 15]. As the parameter values of fraction of domains nucleated (N/N₀), critical radius of domain (r_c), wall-energy (α) and critical energy for nucleation ($\Delta\omega_c$) are increased with temperature, it followed the anticipated idea of existence of unstable nano-sized domains and indicates that it should be present at phase transition temperature as well as at

room temperature under the influence of low electric field. As the electric field changes, these point domains may disappear and appear again, their dimension may also fluctuate as well due to unstable character [13]. The existence of fluctuating state of domains in this grown sample PbNb₂O₆ is excessively quite interesting from the application point of view.

This investigation can be further extended in two ways so that the nucleated domains in PbNb₂O₆ single crystal will maintain them in a stable configuration, as a future scope of work. As discussed earlier, for the expansion process of a domain, the driving force comes from the interaction energy of applied electric field and spontaneous polarization whereas the resistance is provided by depolarization energy, domain wall energy and coercive field. The depolarization field arises due to instantaneous and spatially non-uniform distribution of bound charges during switching. The re-distribution of free charges at the surface as well as in the bulk of the sample can significantly decrease the depolarization field by external and bulk screening to assist the switching in PbNb₂O₆ single crystal. Secondly, scanning near field optical microscopy (SNOM) based methodologies will indeed very promising if this ferroelectric material can be resolved in atomic scale. This SNOM-technology will be helpful not only for tracking and probing the different material properties and dynamical issues in switching ferroelectric devices but also its nano-optical approach supports the capability of even writing and manipulating domains and domain-walls locally at the surface or in the bulk of the sample. Hence, in principle, a fully optically operated memory device becomes possible. congruity with the parameter ' r_c ' reported in Ingle et al. [14].

III. CONCLUSIONS

The stability analysis undertaken in this paper provided very useful information's which can decide whether the particular ferroelectric material is suitable for the use in fabrication of random access memory-device or not. In this study, the domains of ferroelectric lead meta niobate (PbNb₂O₆) single crystal is analyzed, and it is found that the nucleated nano-sized domains of critical radius (81.81 $\times 10^{-9}$)m and above will not be shrink to zero (i.e. **back-switched**) even after the removal of applied electric field at room temperature. It has also found that thermally unstable point domains exist in this PbNb₂O₆ single crystal having the critical radius of nucleation in order of 10^{-9} m, the domain wall energy in the order of 10^{-6} J/m² and the critical energy for nucleation in the order of 10^{-28} J. All these parameters are vary with temperature in this PbNb₂O₆ single crystal.

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