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Surface micro structuring of ferroelectric domains in PbNb2O6 single crystal

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***Abstract**:*

Surface micro-structuring of a ferroelectric material is such a startling process in which the artificial development of domain- defect-field interactions is achieved to obtain the desired results in device applications. Present microscopic study is an attempt to stipulate the domain distributions is whether dislocation dependent, impurity dipole dependent or the predominant interaction of both these imperfections are involved in ferroelectric lead meta niobate (PbNb2O6) single crystal. Microscopic study of interactions between domains and present defects with response to externally applied electric field has been carried out first time for PbNb2O6 crystal, so as to achieve the surface micro structuring of domains in the requisite manner for device applications using this peculiar material. The ferroelectric PbNb2O6 single crystals were grown by using flux technique and its polarization surfaces were studied under reflection microscope. The nature, alignment, movements and character of dislocations, dipolar impurities, their mutual interactions with respect to externally applied electric field have been discussed with micrographic evidences in this ferroelectric single crystal. The pragmatic results and conclusions of this paper are constructive for emergent the high aspect ratio domain surfaces by micro structuring of domains, necessary to produce optical waveguides in crystal for designing the ridge waveguide photonic circuits.

***Keywords:**-Ferroelectric domains, crystal-defects, impurity-dipole, dislocation, E-field.*

1. Introduction

Ferroelectric domain engineering [1-4] provided a remedy to many problems aroused in optical non-linear device applications such as frequency conversion, domain inversion, polarization reversal etc. by offering the possibility for quasi-phase-matching (QPM) [5]. Surface micro structuring of a ferroelectric material is basically a type of domain-engineering which have been used for the performance improvement of electro-optic [6] and acousto-optic devices [7, 8]. Conventionally, an external electric filed (E-field) of sufficient amplitude is applied to exceed the coercive field of a ferroelectric materials, and differential etching of this domain engineered crystals offer the capability for improved surface micro-structuring [9-12]. Recently, it was reported that the effective coercive field can be modified locally by irradiating the crystal with a laser beam where a photo-induced space charge field played an imperative role with the externally applied E-field [13, 14].

In this article, the surface micro structuring of polarized regions of ferroelectric lead meta niobate ($PbNb_2O_6$ or PN) single crystal studied systematically by using differential etching techniques with the application of external electric field under reflection microscopy. Compared to other microscopic methods, the crystal under reflection is appropriate to determine the domain structures unambiguously, and to study their behavior with defects such as dislocations or cracks or dipolar impurities in the range of nano scale. The objective of this work is to determine the predominance of defects like dislocation and dipolar impurities present in the $PbNb_2O_6$ crystal, and to determine their influence on the nucleation, evolution and evaporation processes of micro domains with the application of externally applied electric field (E-Field). These objectives are helpful in determining the suitable way of surface micro structuring of ferroelectric domains in this peculiar material. Some significant particulars such as; the effect of applied electric field on domain-defect interaction, movements of domain walls, stress and electrostatic energy involvement in the mechanism of domain formation, mutual competition between imperfections during micro structuring of domain etc. is also discussed in this paper. The alignment, presence and character of a particular type of defect are the three intricate issues which have been addressed in this article, because they might have some supportive or adverse effects on the surface micro structuring of domains of this PN single crystal.

2. Materials and methods

The single crystals of lead meta niobate ($PbNb_2O_6$) were grown from melt by employing Goodman's technique in a slightly modified way [15]. The dried constituent oxides in molar composition 1:1 (22.3190gm of PbO and 26.5810gm of Nb_2O_5, AR

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grade with 99.4% purity purchased from MERCK) were grounded together to make a homogeneous mixture and packed in to a 50cc platinum crucible, then introduced into a Gallenkamp furnace at temperature 1623K for a sufficient soaking time of about twelve hours. To avoid stray nucleation in growth process, a special kind of cooling and reheating process were performed. It was observed that the obtained crystals are pale yellow in color, oxygen deficient and containing platinum ions as main impurity. The single orthorhombic phase at room temperature, calculated lattice parameters with point group, ferroelectric nature of this grown $PbNb_2O_6$ and phase transition temperature were confirmed by its XRD-pattern and hysteresis loop studies [16]. The disappearance of hysteresis loop at temperature 843K was also reported with photographic evidences which confirm the phase transition temperature of the grown PN single crystal [16].

Since the investigation of domain structure and its evolution during nucleation and polarization reversal processes offer full and direct information on the static and dynamic properties of the material, we have been used reflection microscope of METZER to study the micro structure surfaces of lead meta niobate ($PbNb_2O_6$ or PN) single crystal as this method found useful for nano scale domain control via highly localized polarization charges, for direct investigation of domain wall interaction with micro structural features such as defects and grain boundaries [17], and for local spectroscopy measurements. Furthermore, this approach offers extremely high resolution, and potentially allowing us the investigation of the microscopic mechanism of the domain wall motion and electrical and mechanical coupling between adjacent grains [17].

3. results and discussion

Various workers [18-21] reported that the dominant contribution in domain formation was of “dislocation”. The basic notion to undertake this study is that since the impurity dipoles and dislocations have nearly the same value of activation energy as well as of critical field for nucleation of domain for a particular ferroelectric material [22], that is why it may possible for both should equally facilitate in the process of nucleation of domains, or there should be subsist a competition between these two defects during this process. Therefore it was thought desirable to undertake a methodical surface study of PN crystal to investigate these points. One more realization towards this study is that, it is quiet natural to be getting the domain structures that are partly nucleated by dislocation and partly nucleated by impurity dipoles. Indeed, some interesting interactions between dislocations and impurity dipoles might be existed in the process, and without the knowledge of these interactions present in the process of micro domain nucleation can’t be completely understood in this peculiar ferroelectric $PbNb_2O_6$ crystal.

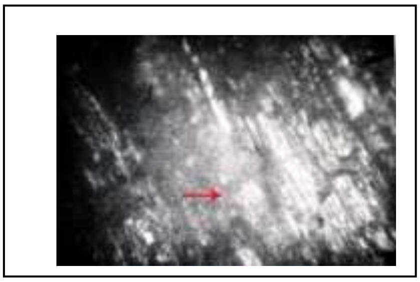

Figure 1. Surface of $PbNb_2O_6$ single crystal before application of electric field and etching.

Fig.1. shows the photomicrograph of fresh surface of $PbNb_2O_6$ single crystal (i.e. before the application of external electric field and etching) in which impurity dipoles are more effectively visible in the domain structure, it are revealed by the presence of impurity segregates near the 90^o domain lines between ‘A’ and ‘B’. These impurity dipoles have been seen as cooperatively arranged. This very same crystal is then subjected to d.c. electric field of 2000 Vcm^{-1} for 5 minutes and etched with the mixture of hydrogen per oxide and ammonium acetate, and it’s photomicrograph is depicted in Fig. 2. It has been observed here;

(1) The 90^o domain pattern has completely evaporated which was present in Fig.1. (shown by under circled),
(2) The dislocations (shown by etch pits between arrows) are appeared in the domain structure and it are randomly arranged.

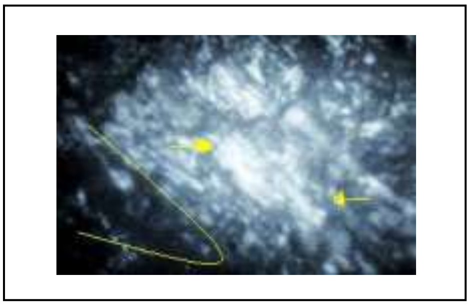

Figure 2. Same crystal's surface of $PbNb_2O_6$ after application of forward bias electric field of 2000Vcm^{-1} for 5 minutes and then etched by CH_3COONH_4.

These disordered (randomly arranged) distributions of dislocations can’t initiate the nucleation because if it will do so, there would be a sufficient increase in strain energy; therefore the crystal has preferred here the micro domain nucleation through impurity dipoles

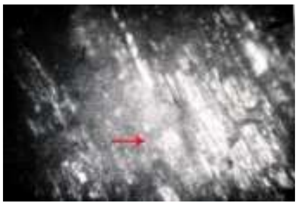

Figure 3. Same crystal's surface of PN after application of 4600 Vcm^{-1} in forward direction for 5 minutes.

Now, this same crystal was further subjected to d.c. electric field of 4600 Vcm^{-1}, its surface micrograph has shown in Fig.3; then again etched with the same liquid mixture (surface photomicrograph has shown in Fig.4.). By the inspection of these two photomicrographs, it is perceive that randomly distributed dislocations have started to arrange themselves in arrays while the impurity dipoles that were cooperatively arranged in Fig.1; being started distribute themselves in the form of clusters. So, from the state of affairs of orderly arranged impurity dipoles and randomly arranged dislocations, a new domain pattern is achieved here in which the dislocations are orderly arranged and impurity dipoles are randomly distributed in the form of cluster. Two more facts are also evident from these micrographs; cooperatively ordered impurity dipoles can be broken down and dislocation moves with response to applied electric field. The straight forward conclusion is that impurity dipoles subsist and involved here in the nucleation and evaporation process by minimizing its self electrostatic energy, while the basic reason of inducing nucleation by ‘dislocation’ is to alleviate the stress of the polarized region. Moreover, the dislocation must possesses the charged character as it moves with response to applied electric field in this PN single crystal; Cerva et al [21] confirmed this fact in case for other ferroelectric material. It means, some mutual interactions definitely existed during the nucleation process between dislocations, impurity dipoles and polarized regions (i.e. ferroelectric domains) in such a way that at a time only one category (either impurity dipoles or dislocations) exists in orderly pattern while other one is distributed randomly at the same time and its all depend on externally applied electric field to this $PbNb_2O_6$ single crystal. This can be a useful way of micro structuring the surfaces of the domains as per the prerequisite of device application in general.

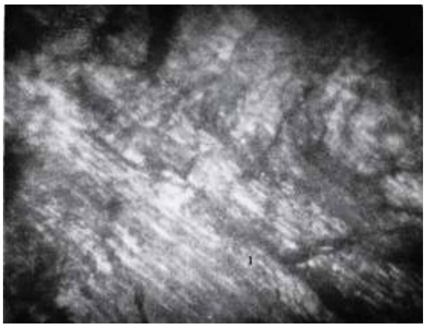

Figure 4. Same crystal's surface of $PbNb_2O_6$ after etching (H_2O_2+CH_3COONH_4).

It is also visible that there exist a number of line defects at the Y-junction and T-junction between two domain walls in Fig.4. Perhaps, the arrangement of atoms along these defects is highly disordered here, and therefore domain walls must be pinned by these defects. This may restrain the occupied polarization when the external electric field is applied to this PN crystal. Consequently, multi domain structure in this crystal possibly leads to lower saturated spontaneous polarization. It is also seen that the domain width increases as forward electric field increases, may be due to a reduction in domain wall energy. The crossover of domain walls of different types put a ceiling on the domain switching under applied field which can also produce fallout in smaller saturated polarization value in this PN crystal. These two observations explain the influence of domain-defects interaction on the P-E behavior of PbNb2O6 single crystal. Further, this very same crystal is again subjected to d.c. electric field of 5800 Vcm^{-1} in *reverse direction* for 5 minutes and etched to reveal the dislocation sites (surface photomicrograph is shown in Fig.5.). It is apparent in this micrograph, the previous domain structure (which was present in Fig.4.) is now evaporated, dislocations are seen randomly arranged revealed by etch pits, and a new domain structure is formed by impurity dipoles which is very similar to Fig.2. It means, the application of forward bias field produces domains associated with dislocations while reverse bias field produces domains by impurity dipoles. This result is again confirmed in Fig.6; which is the micrograph taken after application of forward bias field of 7800 Vcm^{-1} to this very same crystal surface and etched.

After confirm these particulars, again a d.c. electric field in order of 9000 Vcm^{-1} is applied in the reverse direction for 5 minutes to that same crystal, its surface is depict in Fig.7. It is noticeable in Fig.7. and Fig.6; the dislocation sites that were regularly arranged in Fig.6. are now randomly arranged in Fig.7; and small aggregates present at the sites of dislocation are intended for the proof that nucleation proceeds through impurity dipoles. This successive etching study reveals

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that the ferroelectric domains in $PbNb_2O_6$ crystal have a correlation with dislocation substructure in the bulk. These dislocations are in the form of small or elongated loops where walls of domain are terminated along with these loops

Figure 5. Same crystal's surface after applying d.c. electric field of 5800Vcm^{-1} in reverse direction and etched.

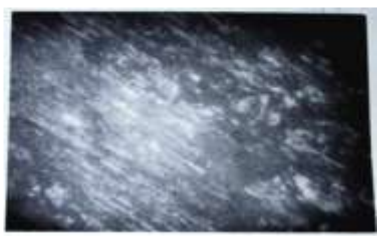

Figure 6. Same crystal's surface after the application of electric field of 7800 Vcm^{-1} in forward bias.

Figure7. Same crystal's surface after the application of d.c. electric field of 9000Vcm^{-1} in reverse direction.

The repeated application of reversal of d.c. electric field results the nucleation of domain proceeds alternately by impurity dipoles and dislocations, it means there is a competition or mutual interaction present between these two defects as well as their interaction exists with the domain structure too in this $PbNb_2O_6$ single crystal. The defects whether induced or permanent (i.e. impurity dipoles or dislocations), reduce the strain energy of the crystal and it is done by nucleation of domains (arising of fresh domains) under the influence of externally applied electric field. As per the need in switching or electro-optic device application, these findings are definitely helpful in domain engineering and micro structuring of ferroelectric domains in $PbNb_2O_6$ crystal.

Recently, it was found that the defect modes inside the photonic band gap (PBG) could bring about tunability for Ag/LiNbO3/Ag photonic crystals structure sandwiched between TiO2 and one other suitable material [22], this attracted much attention for their peculiar properties used in many potential applications, such as filters, optical switches, diode laser etc. [1–6]. In the present study of PN, the existence an innovative defect mode is unmistakably demonstrated which is significantly tunable with the voltage range of external electrical field (from -9000Vcm^{-1} to +7800 Vcm^{-1}). By applying the electric field on this $PbNb_2O_6$ crystal, this defect mode can be modified, and thus a tunable defect state involving two different defects is realized here. The defect mode is tunable means that the two types of involved defects are shifting their role with each other in the nucleation process and their tuning is achieved by a novel electro-optic scheme, i.e., by applying electric field through the crystal in z-direction. It can be concluded that our proposed Ferroelectric Crystals defect mode design is viable and promising for practical applications

4. Conclusion

This domain-defect-field interactions study clearly indicates that the elastic energy considerations have an upper hand over the electrostatic energy considerations in ferroelectric $PbNb_2O_6$ single crystal. The process of micro domain nucleation in ferroelectric lead meta niobate ($PbNb_2O_6$) single crystal is entirely defect dependent in which domains are nucleated or evaporated involving either impurity dipoles or dislocations. Under the effect of externally applied electric field, the dislocations and impurity dipoles are interact with each other, results the alignment of either type of defect at a time. The movements of a single or a pair of domain walls nucleated at the sites of dislocation array indicate the charged character of dislocation. The E-field govern domain-defects interaction has a significant influence on polarization mechanism. In general, the suggest conclusions will be able to initiate a new approach in micro-structuring of domains, domain engineering, switching and other electro-optic device applications where the mechanism of nucleation of domains is operative.

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