International Journal of Researches In Biosciences, Agriculture & Technology | Feb. 2015, Special Issue (2) | ISSN No. (Online) 2347-517X

Improvement in Optical Quality of Surface of Ferroelectric $PbNb_2O_6$ Single Crystal Through Etching and Field Dependent Domain Wall Nucleation

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Abstract

The objective of this study is to achieve the good optical quality of surface of grown ferroelectric lead niobate ($PbNb_2O_6$) single crystal, by employing successive field dependent nucleation and etching process. The mechanism of domain nucleation under the application of external electric field is addressed with the help of surface micrographs of this crystal at every steps of successive study. The comparison of surface micrographs before and after etching shows the improvisation in optical quality of crystal surface, explained through field dependent domain nucleation.

Introduction

As the ferroelectric properties are strongly influenced by domain-movements at surfaces and interfaces, there is an immense interest in exploring how the atomic structure affects the electrical properties of a material. Ferroelectric materials find potential applications in electronic and electro-optical devices including, for example, non-volatile and high-density memories, thin-film capacitors and piezoelectric and pyroelectric devices [1-3]. Ferroelectrics are materials exhibiting spontaneous electric polarization due to dipoles formed by displacements of charged ions inside the crystal unit cell**.** In bulk ferroelectrics, the paraelectric to ferroelectric phase transition is accompanied by the formation of polarization domains to minimize the system energy with respect to the depolarization field and mechanical strain. In case of lead meta niobate ($PbNb_2O_6$) single crystal, the ferroelectric phase persist orthorhombic symmetry at room temperature while it changes to tetragonal symmetry at Curie temperature 570°C [4]. The performance of many electro-optical devices is strongly based on stability of switchable ferroelectric polarization modes which involves the nucleation and growth of domain structures on crystal-surface under an external electric field [5, 6]. To investigate the mechanism involved in switchable polarization modes, the optical quality of crystal-surface highly matters with appropriate instrumental resolution. The present article is an attempt to address such type of mechanism concerning domain wall nucleation and impurity-ion dipole interactions in achieving the preferred optical-quality at the surface of ferroelectric lead meta niobate ($PbNb_2O_6$) single crystal. The main objective of this study is to explore the crystal's surface which will be helpful to understand the domain structures and behavior of impurities in $PbNb_2O_6$ single crystal at microscopic level. For improvisation of the optical quality of surface of $PbNb_2O_6$ single crystal, the domain wall nucleation and etching process is applied with external electric field, and underlying principle and mechanism of this technique is discussed through surface micrographs of crystal.

Material and Methods

The single crystals of lead meta niobate ($PbNb_2O_6$ or PN) grown from melt by employing Goodman's technique in a slightly modified way [7]. The dried constituent oxides in molar composition 1:1 (22.3190gm of PbO and 26.5810gm of Nb_2O_5, Analytical R grade with 99.4% purity purchased from MERCK) grounded together and packed in to a 50cc platinum crucible. Programmable Gallenkamp furnace is set to melt the materials in crucible at temperature 1623K for sufficient soaking time of about twelve hours. To avoid stray nucleation in crystal-growth process, a cooling and reheating process was performed in a suitable rate manner, through a program set in this furnace. It is observed that the obtained $PbNb_2O_6$ crystals are of pale yellow in color, oxygen deficient and containing platinum ions as main impurity due to use of platinum crucible. By XRD-pattern of this grown material, the single orthorhombic phase at room temperature and lattice parameters with point group are calculated, while its ferroelectric nature and phase transition temperature (570°C) is confirmed through hysteresis study [8].

The micro-structure surfaces of grown lead meta niobate ($PbNb_2O_6$ or PN) single crystal studied under reflection by microscope of METZER Company. The domain structure and its evolution during nucleation and polarization reversal processes has been investigated which offer full and direct information on the static and dynamic properties of this grown ferroelectric PN single crystal. The improvised optical quality of surface of PN crystal is observed through surface micrographs after the successive application of external electric field in forward/reverse direction followed by etching with dilute ammonium nitrate, and microscopic changes in domain structures are discussed in the next section.

Results and Discussion

Domain wall dynamics, grain size effect on domain-transition, predominance of crystal-defects under external electric field are already reported by us through the study of surface-micrographs for this ferroelectric $PbNb_2O_6$ single crystal [9, 10]. All these studies require a good optical visualization of crystal's surface, but the stabilized impurities in the form of dipole, cracks as dislocation type of defects, roughness exponent of charges etc. are the practical issues that always hindered the visibility of movements of domain walls. There is a need to purify the surface of the crystal for achieving a good optical quality in microscopic studies while to produce high grade quality crystal is a sophisticated and costly affair. However, less twinned and thin flake of about 0.1mm $PbNb_2O_6$ crystal is chosen for improvement of optical quality of its surface. The viewing direction is along the crystallographic [110] direction in Fig.1, where several impurity-segregation can be easily seen in the form of clusters with 90° and 60° domain walls, marked by arrows. Here, the impurities exist in the form of dipoles (made with nearby vacancies) stabilized themselves by forming micro-domains around the dipole in the crystal structure. The task to remove such type of impurities found difficult as they form dipole-clusters by interacting with electrons freed from the vacancies. Moreover, their behavior can be considered as relaxed dipoles shifting from their ionic states, getting more stabilized by accommodated themselves in various octahedral-voids in the structure when crystal was cooled in the growth process. Although, the impurity-ions (relaxed dipoles) are not visible in Fig.1, the impurity-aggregates and dislocation in the form of cracks present good picture of impurity-content on the surface of the $PbNb_2O_6$ crystal under study.

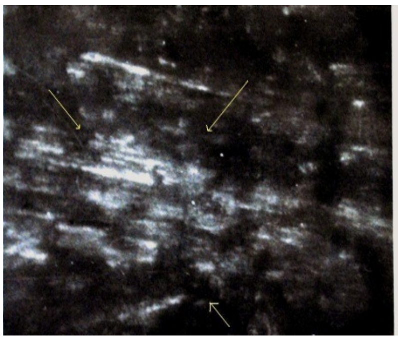

Figure 1. Surface of $PbNb_2O_6$ single crystal without application of electric field and etching

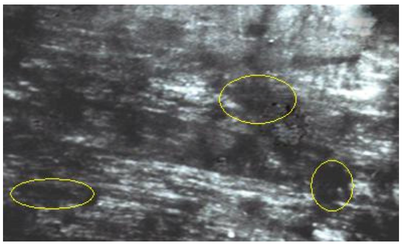

Figure 2. Surface of same piece of $PbNb_2O_6$ crystal after application of electric field 5000V/cm

In order to achieve a good optical surface of crystal, we practiced a simple and cheap method in which field-dependent domain wall nucleation along with etching process is performed to remove this stabilized impurity-content from the structure [11]. This technique is developed by Ingle *etal* [12] in case of ferroelectric $KNbO_3$ crystal, and extended by us in case of $PbNb_2O_6$ crystal. According to this technique, the same piece of $PbNb_2O_6$ crystal whose surface is depicted in Fig.1, poled with d.c.electric field of 5000V/cm for twenty minutes. Fig.2 is the viewed surface of $PbNb_2O_6$ crystal after polling with such electric field of 5000V/cm in which the nucleation of fresh micro-domains of about (4-6) µm around the impurity-content can easily be observed, under the circle. It is pointed out here that the unfavorably oriented relaxed-dipoles in the cluster shown in Fig.1 are diffused in hopping process after the application of electric field, and remaining constituent freed charges are taking part in the nucleation of fresh micro-domains what are appeared in Fig.2. In this way, the relaxed dipoles are re-excited from their ionic state to dipolar state. Further, the d.c.electric field of 15000V/cm in the reverse direction is again applied to same piece of $PbNb_2O_6$ crystal for only four minutes and its surface is shown in Fig.3. It can be observed in Fig.3; that the previously nucleated domain walls (Which were present in Fig.2.) are now evaporated from the viewing surface in Fig.3. This has happened because a large number of dipoles are being freed in this evaporation process of domains. Thus, by the application of forward and reverse electric field, the relaxed-dipoles are continuously excited and de-excited from their ionic state to dipolar state and vice-versa; subsequently a sufficient deposition of impurity-content at the surface of PN crystal can be seen in Fig.3.

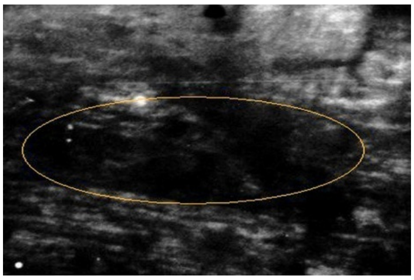

Figure 3. Surface of same piece of $PbNb_2O_6$ crystal after application of electric field 15000V/cm

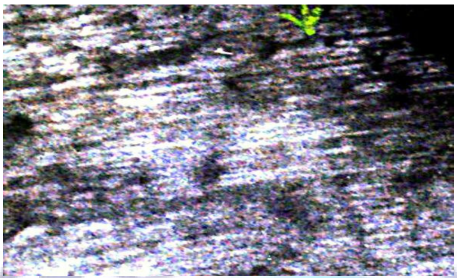

Figure 4. Surface of same piece of $PbNb_2O_6$ crystal after etching by Ammoinium Nitrate

This accumulated deposition of impurities is now removed by washing with dilute ammonium-nitrate and micrograph of washed surface of $PbNb_2O_6$ crystal is shown in Fig.4. We can easily see the improvement of optical quality of surface of $PbNb_2O_6$ single crystal by comparing the Fig.1.and Fig.4. This whole process can be further repeated to achieve more better surface quality of crystal.

Conclusion

Finally, we want to point out that this simple and low-priced technique of purification the surface of $PbNb_2O_6$ single crystal shows that the nucleation and growth of domains under external electric field are helpful to remove the localized impurity from the structure; it also confirms that lattice defects can affect the structure and width of domain walls. This study provides a quantitative basis for possibility of imaging the local polarization dipoles at atomic resolution in future, which will be helpful for the investigation about ferroelectric fatigue and coercive field.

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