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# Domain characteristics and chemical bonds of lithium niobate

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## Abstract

Domain characteristics such as domain shape, domain switching, and etching rate at Z-surfaces of lithium niobate (LN) single crystals are comprehensively studied from the chemical bonding viewpoint. The present work shows that the domain characteristics are closely correlated to anisotropic bonding behaviors of constituent ions, which may be regarded as a microscopic reflection of detailed conditions of the chemical bonding geometry and strength of $Li^+$ and $Nb^{5+}$ cations in the LN crystallographic frame.

*Keywords:* Domain switching; Domain shape; Etching rate; Chemical bonds; Lithium niobate

## 1. Introduction

Lithium niobate ($LiNbO_3$, LN) is a typical ferroelectric crystal that can be grown into large single crystals, which is of great interest for material scientists due to its excellent physical properties, such as good optical, electric, electro-optical, acousto-optical, piezoelectric, pyroelectric and electro-mechanical properties, etc., which thus lead to wide technical applications. Recently, the domain characteristic in ferroelectric crystals such as LN crystals has attracted much attention and becomes an interesting topic in the field of LN crystals, because the domain structure in bulk LN crystals possesses very important influences on various chemical and physical properties of crystals [1].

The ferroelectric LN phase belongs to a rhombohedral system (with the point group $3m$ and the space group $R3c$) with $a = 5.4944$ Å and $\alpha = 55°52'$. In the hexagonal representation, one unit cell contains six molecules with lattice constants $a = 5.1483$ Å, $c = 13.863$ Å, $c/a = 2.693$ [1]. The ferroelectric domain of LN crystals is oriented with its polarization in either $+c$ $[0\,0\,0\,1]$ or $-c$ $[0\,0\,0\,\bar{1}]$ direction, which is also called the 180° domain. The domain structure of LN crystals has been extensively studied since 1960s [2], a number of techniques are also reported for the domain switching in LN crystals, which include the high-voltage atomic force microscope (HVAFM) [3], titanium in-diffusion [4,5], Li ion out-diffusion [6], electron beam (EB) [7], and thermal polarization [8], etc.

Xue et al. [9] investigated the mono-domain switching of near-stoichiometric Z-cut LN wafers and concluded that the domain reversal at the −Z surface was much easier and more stable than that at the +Z surface. Additionally, the domain shape is an uniform and regular hexagon at the −Z surface comparing with that (an irregular domain shape) at the +Z surface, as shown in Fig. 1 (by scanning force microscopy, SFM. The detailed procedures are described in [9]). Such work leads to an interesting topic concerning the domain engineering by employing surfaces of bulk LN crystals.

The etching technique is widely used to study the ferroelectric domain structure and its distribution in bulk crystals. Etch hillocks on the −Z surface and etch pits on the +Z surface have been observed in LN crystals by Niizeki et al. [10]. Ohnishi and Iizuka [11] studied etching behaviors of the multi-domain LN crystal and found that the top surface of the hillock on the negative surface (−Z) is etched by the same etch rate as the positive surface (+Z). Additionally, etch patterns on the Y-surface indicate that positive needlelike domains range from 200 to 400-μm long and less than about 5 μm wide, which are distributed around domain boundaries

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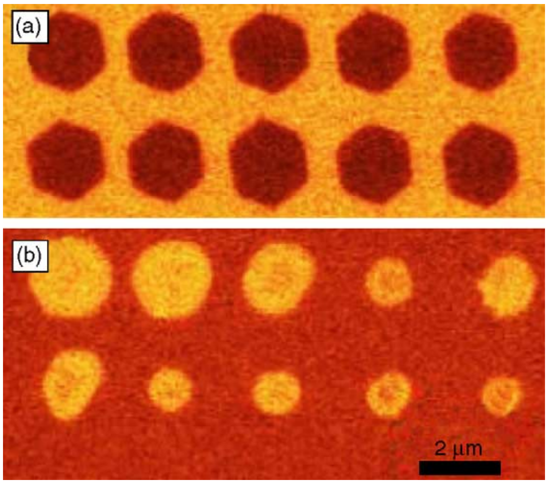

Fig. 1. SFM piezoresponse images of both −Z (a) and +Z (b) surfaces of the LN crystal. Both images are produced by the ±150 V bias voltages, and by the pulse width fixed at 0.05 and 0.5 s at both surfaces. Black pits (a) and white hillocks (b) are inverted domains.

lying nearly perpendicular to the *c* axis on the Y plate. These etch features may be explained by the presence of the microdomain in LN crystals.

Although some different properties between +Z and −Z surfaces of LN crystals have ever been observed during the domain inversion and etching, however, the reason why domain characteristics exist in a huge difference between both surfaces has not yet been investigated. The present work attempts to study domain shape, domain switching, and different etching rates between +Z and −Z surfaces of LN single crystals, on the basis of chemical and physical properties of constituent chemical bonds in the LN crystallographic frame.

## 2. Domain characteristics

Domains represent volumes of the ordering transition with respect to atomic/ionic displacement or spin in the mesoscopic scale. And the dipoles have the same orientation in respective domains. Domain characteristics in this work include domain switching, domain shape, etching rate and so on.

The domain reversal or poling of a ferroelectric crystal is a rather straightforward procedure and involves the application of a suitable electric field across its polar axis. For the domain reversal to occur in any reasonable time, the applied field must be sufficient in magnitude to overcome the coercive field of the crystal. In fact, the domain evolution in LN crystals may be separated into several stages after the partial poling. The first stage is the domain nucleation at the +Z polar surface along electrode edges or at surface defects in the center, when the external field exceeds the threshold value (i.e., the coercive field). At the second stage, domains grow forward and in sideways directions, but the forward growth velocity for LN crystals is always much higher than the sideways one, which leads to the formation of laminar domains under electrodes. Finally, the laminar domains are merged, the new domain that nucleates and grows at domain walls make domain walls spread out of the electrode area.

In the current work, we propose a schematic mechanism for the domain switching in LN crystals. The domain nucleates around the charged probe, the nucleation velocity at this point is the fastest one due to its highest voltage, as shown in Fig. 2(a). The ionic migration during the domain inversion is also shown in Fig. 2(b). The domain reversal difference between −Z and +Z cuts can be explained by the respective surface composition in both cuts [9]. A Z-cut mono-domain LN crystal may be regarded as three constituent parts with different compositions i.e., the +Z surface layer, the inside part, and the −Z surface layer. The Li/Nb ratio is closer to the stoichiometry at the −Z surface layer than that at the +Z

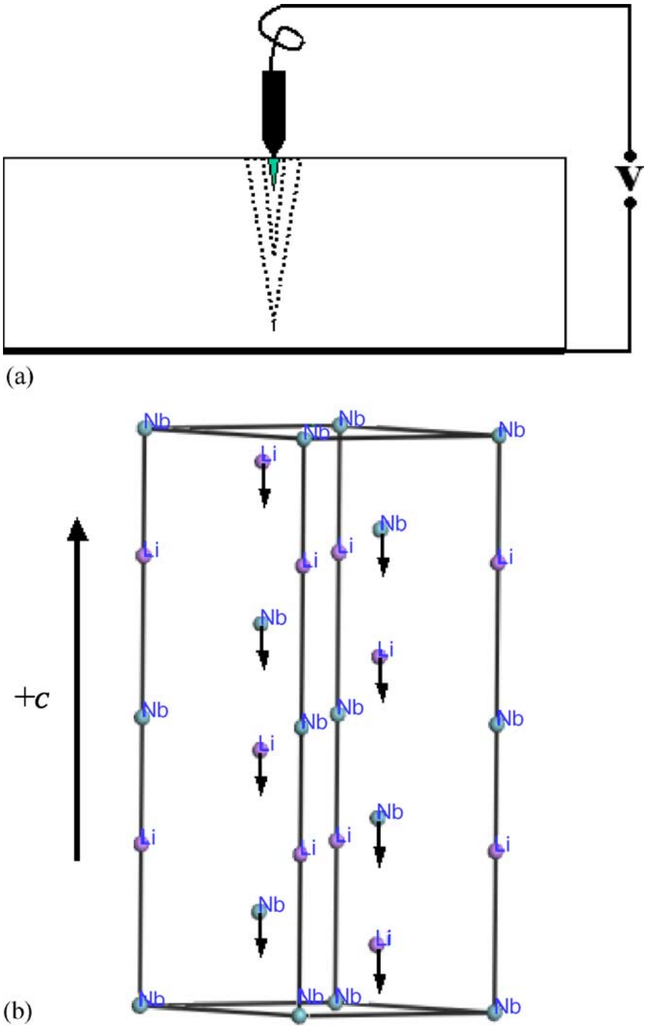

Fig. 2. The domain growth and ionic transfers during the domain inversion. (a) Stages of domain evolution for switching with scanning probe microscope (the Z-cut gold-coated LN surface is adhered to a mental substrate, and then an appropriate bias voltage is applied between the probe and mental substrate). (b) The displacement of Li and Nb ions along the polarization direction (*c*-axis) when the external field is applied.