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Shape of ferroelectric domains in LiNbO₃ and LiTaO₃ from defect/domain-wall interactions

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The observed orientations and shapes of ferroelectric domains in stoichiometric and congruent LiTaO₃ and LiNbO₃ are explained in terms of the differences in the energetics of domain walls, and the energetics of defect/domain-wall interactions. Density functional theory calculations show that the energy of a Y-wall, parallel to (11 $\bar{2}$ 0), is lower than that of the X-walls, parallel to (10 $\bar{1}$ 0), in both stoichiometric LiNbO₃ and LiTaO₃. As a result the domains are hexagonal and delineated by Y-walls. In congruent LiTaO₃, the interaction of antisite defects with domains walls can reverse this order of stability, leading to triangular domains delineated by one type of X-wall. In congruent LiNbO₃, the interactions of the antisite defects with the domain walls are too weak to reverse the order of stability of the domains walls; as a result the domains remain hexagonal. © 2011 American Institute of Physics. [doi:10.1063/1.3560343]

LiTaO₃ is a ferroelectric material with trigonal structure, similar to LiNbO₃. Stoichiometric LiTaO₃ has a Curie temperature¹ of ~970 K and spontaneous polarization² of ~55 $\mu\text{C}/\text{cm}^2$. Because of its unique optical properties, LiTaO₃ is a candidate for nonlinear frequency converters,³ electro-optic devices,⁴ and holography.⁵ Control of the shape of the ferroelectric domains is a key to good performance for optical applications; different domain shapes can focus or defocus light in the plane and convert the wavelength of incident light in different ways. Congruent LiTaO₃ shows a Li deficient composition with $C_{\text{Li}}/[C_{\text{Li}}+C_{\text{Ta}}] \sim 0.485$,¹ and has a very different Curie temperature from that of stoichiometric LiTaO₃.⁶ The nonstoichiometry results in significant changes in optical, electric, and elastic properties near domain walls, and affects the domain dynamics.⁷ Recent studies^{2,8} show that the threshold field for domain reversal also depends on the stoichiometry. Figure 1 shows the domain wall structures in LiNbO₃ and LiTaO₃ observed in experiments.^{9,10} Under stoichiometric conditions, both form hexagonal domains, entirely delineated by Y-walls, Figs. 1(a) and 1(b); the Y-walls and X-walls are defined to be parallel to the (11 $\bar{2}$ 0) and (10 $\bar{1}$ 0) planes respectively.⁹ The domains in congruent LiNbO₃ remain hexagonal, delineated by Y-walls, Fig. 1(c), while congruent LiTaO₃ forms triangular domains delineated by X-walls, Fig. 1(d). Gopalan *et al.*⁷ explained the hexagonal domain shapes in terms of the anisotropy in shear strain at the walls, and the triangular shapes as a mechanism by which to reduce the high strain points created by X-walls of different orientations. The change in domain shape from hexagonal to triangular under different

electromechanical coupling¹⁰ has been explained by Shur in terms of the effectiveness of screening by the depolarization field during switching process.¹⁰ Since Gopalan *et al.*¹¹ showed that the local structure of domain walls can be altered by defects, it is physically reasonable to seek an understanding of these domain shapes in terms of a defect mechanism. In this study, the differences in domain shape in the two systems are understood in terms of the energetics of the domain walls and their interactions with intrinsic defects. Moreover, the preference for a specific orientation of X-wall in congruent LiTaO₃ is explained.

We first examine the shape of ferroelectric domain in stoichiometric systems. The energetics and structures of Y-walls and X-walls in LiNbO₃ have previously been analyzed with electronic-structure calculations at the level of density functional theory (DFT).¹² There are two X-wall variants, depending on displacements of three sets of oxygen

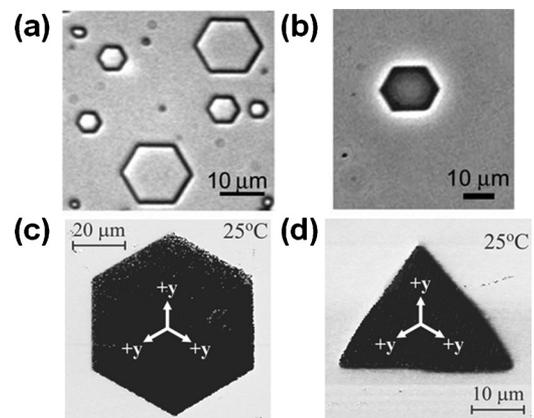


FIG. 1. Domain shapes: (a) stoichiometric LiNbO₃ (Ref. 10), (b) stoichiometric LiTaO₃ (Ref. 10), (c) congruent LiNbO₃ (Ref. 9), and (d) congruent LiTaO₃ (Ref. 9). Optical images: (a) domain revealed by etching, (b) phase-contrast-microscopy, (c) and (d) piezoelectric force microscopy phase contrast images. Reproduced from Refs. 9 and 10 with permission.

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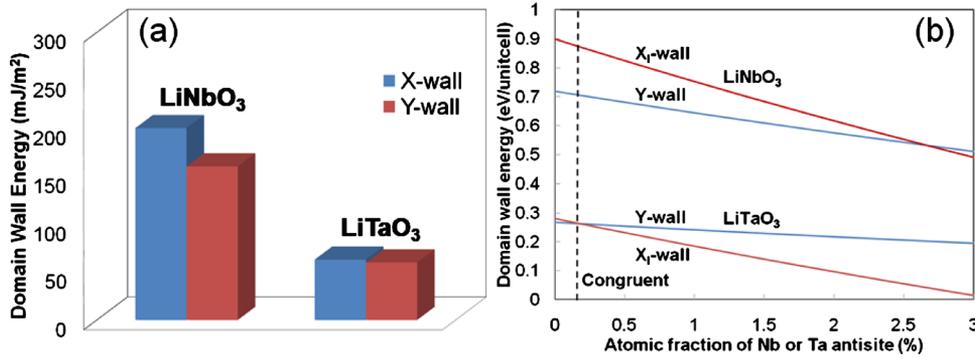


FIG. 2. (Color online) (a) Comparison of domain wall energies in stoichiometric LiNbO₃ and LiTaO₃ calculated with DFT. (b) The predicted domain wall energies as a function of atomic fraction of Nb or Ta antisite defects in LiNbO₃ and LiTaO₃. The stoichiometric composition is at zero atomic fraction; the congruent composition is shown as a dotted line.

atoms near the X-walls: perpendicular movement of oxygen pointing into the X-wall (X_I-wall) and the perpendicular movement of oxygen pointing out of the X-wall (X_{II}-wall). As summarized in Fig. 2(a), these calculations showed that the energy of the Y-wall in stoichiometric LiNbO₃ is 160 mJ/m² while the average of the two X-walls is 200 mJ/m². Although it is not possible to distinguish the energy of two X-walls from DFT, a study with empirical potentials¹² found that they have almost identical domain wall energies. Thus, we concluded that the Y-wall has an energy 40 mJ/m² (0.18 eV/unitcell) less than that of X-walls. Consistent with the results for LiNbO₃,¹² DFT also predicts that in stoichiometric LiTaO₃ the energy of the Y-walls (60 mJ/m²) is less than that of the X-walls (63 mJ/m²); however, this energy difference is only 3 mJ/m² (0.0135 eV/unitcell). These DFT results are thus consistent with the experimental observation that the ferroelectric domains in both stoichiometric LiNbO₃ and LiTaO₃ are hexagonal, delineated by Y-walls.

To explain the shapes of domains in congruent systems, it is necessary to understand the defect energetics and the defect/domain-wall interactions. A previous DFT study in LiNbO₃ showed that Nb_{Li}^{••••} compensated by four V_{Li}^{••••} is the most energetically stable defect complex in the congruent system.¹³ Corresponding DFT calculations also predict that Ta_{Li}^{••••} compensated by four V_{Li}^{••••} is the energetically stable defect cluster in congruent LiTaO₃.

DFT calculations show that the interactions of a lithium vacancy with either Y- or X- walls are weak¹⁴ and do not depend significantly on its distance from the domain wall. By contrast, the interactions of the cation antisites with the domain walls are strongly attractive. In particular, the formation energy of Ta_{Li}^{••••} at an X_I-wall in LiTaO₃ is 0.33 eV/defect less than in the bulk. Similarly the Ta_{Li}^{••••} is attracted to both a Y-wall and an X_{II}-wall by 0.09 eV/defect. The small differences in the domain wall energies and the relatively large differences in the association energy of the antisite defect to the domain walls offer the possibility for the order of the stability of the walls to change with the increased defect concentration in the congruent system. As Fig. 2(b) shows, LiTaO₃ requires only ~0.18% atomic fraction of Ta_{Li}^{••••} to overcome the energy difference between the Y-wall and the X_I-wall. The actual concentration of Ta_{Li}^{••••} in the congruent system is ~0.2% atomic fraction. Hence, the defect/domain wall interactions can lead to a change in the preferred domain wall orientation from the Y-wall to the X_I-wall, as is indeed observed in going from stoichiometric to congruent LiTaO₃.

The corresponding analyses for LiNbO₃ also predict the attraction of Nb_{Li}^{••••} to an X_I-wall (0.51 eV/defect) is stronger than to a Y-wall (0.26 eV/defect) or to an X_{II}-wall (0.05 eV/defect).¹⁴ However the difference in the X- and Y- wall energies is so large that, as we can also see from the Fig. 2, ~2.65% atomic fraction of Nb_{Li}^{••••} antisites would be required to overcome the energy difference between the X_I-wall and the Y-wall: a more than ten times greater concentration of Nb_{Li}^{••••} than actually present in the congruent material. Thus, the Y-wall is energetically preferred in both stoichiometric and congruent LiNbO₃, and the domains in congruent LiNbO₃ remain hexagonal.

These differences in the strength of the defect/domain-wall interactions can also be understood in terms of the changes in the associated local polarizations. In particular, when the defect and domain wall manifest components of polarization of the same sign, in the same spatial direction, there is a tendency for them to attract each other; this is analogous to the elastic interaction between a dislocation and a point defect.¹⁵

Figure 3 compares the uniaxial polarization when a Ta_{Li}^{••••} is placed ~0.75 Å on the down polarization side of an X_I-wall (blue diamonds) and X_{II}-wall (green triangles) with the polarization in the absence of an antisite defect (red circles). It can be seen that the Ta_{Li}^{••••} has a very different effect in the two cases: the X_I-wall shows a significant change in the polarization only on very close to the antisite

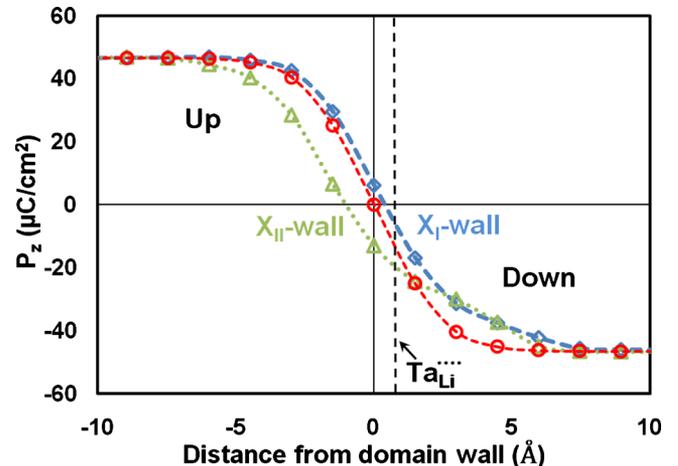


FIG. 3. (Color online) The uniaxial polarization (P_z) around the domain wall when Ta_{Li}^{••••} defect is placed at 0.75 Å away from the wall on the down polarization side. For comparison, the essentially identical P_z for an isolated X-wall are shown in circles; the profiles of the isolated X_I- and X_{II}-walls are essentially identical.

defect, while the X_{II} -wall shows variations over a much wider range. Indeed, fits of the polarization profiles to the usual hyperbolic tangent function^{12,16} show that the domain wall width of the X_{II} -wall increases from 2.48 to 3.64 Å by the addition of the Ta_{Li}^{4+} , while that of X_I -wall only increases from 2.37 to 2.80 Å. That is, the antisite defect distorts the polarization profile of the X_{II} -wall much more than the X_I -wall; as a result the Ta_{Li}^{4+} interacts much more strongly attractive with the X_I -wall than with the X_{II} -wall. A detail analysis of the nonuniaxial components of the polarizations associated with X-walls and the Ta_{Li}^{4+} confirms this physical picture.^{14,17}

With this information on the energetics of defect/domain-wall interactions, it is now possible to understand the change in the shape of domains from hexagonal to triangular. For stoichiometric $LiTaO_3$, all six edges are delineated by same type of Y-wall. Because of the strong Ta antisite/ X_I -wall interactions in the congruent composition, the Y-wall is no longer energetically favored and the X_I -wall is more stable. A domain delineated purely by X_I -walls is triangular. This result is consistent with the experimental preference for the X_I -wall in congruent $LiTaO_3$.⁹ In contrast, the interaction between a Nb antisite and X_I -wall is not strong enough to overcome the large energy difference between the X- and Y-walls in $LiNbO_3$; thus the Y-wall is energetically most stable for both stoichiometric and congruent compositions.

It is possible that the preferred domain wall in $LiNbO_3$ might be different if appropriate dopants could overcome the energy difference between the preferred (Y-) and nonpreferred (X-) domain wall orientations. Therefore, we can expect that the control of the shape of domains might be

achieved by choosing dopants that tune the energy of interaction between a defect and a domain wall.

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