Domain Walls in Ferroelectrics

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Abstract

Spontaneous unit-cell deformation accompanies spontaneous polarization in perovskite ferroelectrics, thereby making it energetically favorable for domain walls to form on particular planes that satisfy mechanical compatibility. Historically, domain walls are found analytically, solving for walls with compatible strains within the wall plane. However, analytical solutions do not give any information about relative energetics of non-ideal domain walls. Here, the orientation of the most favorable domain walls and the relative energetics of non-ideal domain walls are predicted by calculating strain mismatch and charge discontinuity over all possible domain wall orientations. This is done for common ferroelectric phase symmetries of tetragonal, rhombohedral, orthorhombic and monoclinic type. In tetragonal and rhombohedral symmetry, the domain walls are independent of any external stimulus as long as the symmetry is maintained. In orthorhombic and monoclinic symmetry, the orientation of certain mechanically permissible domain walls changes with temperature and/or electric field as the unit cell distorts, while others do not. Additionally, in monoclinic systems, domain wall planes are shown to exist that are not perfectly permissible but are very close to permissible, thus these walls were not found by prior analytical methods. The visualization of strain compatibility of all the domain walls makes it easy to see precisely on which planes domain walls are expected or not expected and how the domain walls change their orientation under the effect of external stimulus. Such an analysis can also be used to investigate the relative and changing energetics of non-ideal domain walls in systems under thermal, compositional, electrical, and mechanical stimuli.

Introduction

Domains are regions of a single crystal that exhibit a uniform orientation state. This could include a uniform magnetic moment, uniform strain, or uniform electric polarisation. Domains form to minimise the elastic energy, depolarization energy or demagnetizing energy that all contribute to the total energy of the system(1). The planes that separate two domains within a crystal are called domain walls. In most ferroelectrics, the spontaneous electric dipole is coupled to a spontaneous mechanical strain, and thus a domain in a ferroelectric is a region of uniform electric dipole and mechanical strain. Although the formation of domains in ferroelectrics reduces the elastic strain and depolarization field, this creates a gradient of spontaneous strain and electrical charge between neighbouring domains. In turn, this leads to an increase in energy due to the domain wall, and the resultant domain structure that forms in a ferroelectric material is such that the sum of these energies is minimized. In order to reduce the spontaneous strain gradient, domain walls are ideally mechanically perfect walls occurring on planes for which the spontaneous strain is equivalent for both domains along any direction within the plane of the wall. These walls are called permissible walls(2). Ferroelectric domain walls, in most cases, are also charge free, i.e., the spontaneous electric polarization on either side is such that not only the strain is matched, but also the electrical charge at the wall is zero. Such walls are called neutral domain walls. Thus, domain walls in ferroelectrics are ideally both permissible and neutral.

Domain walls in ferroelectrics contribute to the dielectric and piezoelectric response as well as impart special functionalities that may not exist in the bulk. Domain walls contribute to the extrinsic component of dielectric behaviour through reversible and irreversible domain wall motion(3). Piezoelectric coefficients (d_{33}) have been shown to increase linearly as a function of external stimulus (Electric field or stress) following a Rayleigh type behaviour arising from irreversible domain wall motion (4, 5). Wada *et. al.* showed that piezoelectric properties improved with decreasing domain size in $BaTiO_3$ single crystal. Using a two phase model for the domain wall and tetragonal unit cells, they were able to confirm that a large

proportion of piezoelectric coefficient was contributed to from domain walls(6). In another such work, it was shown that 34% of macroscopic strain in soft $PbZr_xTi_{(1-x)}O_3$ (PZT) under sub coercive field cycling was due to non-180° domain switching(7). It has been shown in $BaTiO_3$, that while in its rhombohedral phase, it has experimental dielectric susceptibility two orders larger than expected when compared to the theoretical (single domain state) demonstrating that the domain walls have a major contribution to dielectric behaviour(8). The high dielectric response at fields lower than the coercive field was argued to be due to the depinning and translation of domain walls. It has also been shown that domain walls in different symmetries around the morphotropic phase boundary contribute differently to the piezoelectric behaviour for PZT(9). This can be related to different domain structure and their relative energetics for different symmetries.

Historically, the domain wall planes separating two neighboring ferroelectric domains are found by calculating walls that have equivalent spontaneous strain along every direction in the plane of the wall(2, 10). According to Fousek et. al.(2), a mechanically permissible wall was one in which every vector changed by the same magnitude in both the domains when transforming from paraelectric to ferroelectric. The change in length was related to the polarization through piezoelectric and electrostrictive coefficients. Solving for planes satisfying the above condition, they found that domains could have permissible walls with arbitrary indices (W_∞), fixed indices (W_f), or indices that are dependent on material coefficients. It is this last one that have been historically called "S walls", where S was indicating "strange" (2, 6, 11-13). Domains for which no permissible wall orientation exists were represented by "R". Erhart(14) calculated the domain walls for all possible paraelectric/elastic – ferroelectric/elastic species using the same process as Fousek et. al.(2), including all the symmetries studied in the current paper. Domain walls were also categorized with respect to charge neutrality. Some of the S walls were even found to have charge neutrality dependent on the spontaneous strain tensor elements i.e., a neutral wall could potentially become charged as a function of temperature. Mathematical relationships of the indices of permissible walls with strain tensor elements were also listed. The study was extensive but was limited in the sense that only the solutions for permissible walls were listed.

In high symmetry systems, for example in a tetragonal ferroelectric with neighboring domains with spontaneous polarization and strain oriented along $[001]$ and $[\bar{1}00]$ (Figure 1(a)), it can be visualized that domain walls will preferentially form on $(\bar{1}01)$ lattice planes to minimize both strain and polarization energetics. As we move to lower symmetries, however, it is not so easy to visualize the planes on which domain walls can be expected to form. Calculation of the wall planes require tensor math(2) and group symmetry knowledge that is not straightforward to apply. Adding further complexity are the S walls mentioned above, wherein the planes on which select permissible and neutral domain walls exist become a function of the lattice parameters, i.e. the domain wall plane changes with lattice parameter variations within a single-phase symmetry. Most common ferroelectrics have tetragonal, rhombohedral and orthorhombic symmetries. More recently however, monoclinic symmetry has been found to exist near the morphotropic phase boundary in the ferroelectric (PZT)(15, 16) and in relaxor ferroelectric solid solutions based on $Pb(Mg_{1/3}Nb_{2/3})O_3$ (for example $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$(17)).

While past calculation methods concentrated on finding the wall planes that are permissible and neutral, non-permissible and/or charged domain walls are also of interest. So called, head-to-head and tail-to-tail domain walls with expected variations in electrical properties due to the uncompensated polarization charge in the wall plane likely exist in many systems(18). Charged domain walls have been observed in $KNbO_3$(19) and $LiNbO_3$(20) single crystals, PZT ceramics(21) and PZT(22) and $BiFeO_3$ thin films.(23). Mobility of charged domain walls change differently compared to neutral domain walls under high and low electrical stimuli(24). Recent works, for example in $BiFeO_3$(25, 26), $BaTiO_3$(27), and $ErMnO_3$(28), have demonstrated that charged domain walls can act as conducting interfaces in a normally insulating material. Such conducting domain walls have led to the possibility of nano-electronic devices(18, 29) and also been shown to influence the bulk dielectric and piezoelectric response of polycrystalline variants of the material(30).

In this paper, we present the relative planar strain and polarization charge variations, that can be related to energy variations through material coefficients, over all possible domain wall orientations in tetragonal, rhombohedral, orthorhombic and monoclinic symmetries. By calculating the residual planar strain and resultant polarization charge over all possible

orientations of domain walls, not only are the most ideal wall planes found, but almost ideal domain wall planes and the relative energy differences for non-ideal walls are also observed.

Method

A stereographic projection is a two-dimensional map representing the normal vectors of the three-dimensional spherical orientation space. The visualization of the domain wall residual planar strain or residual planar polarization charge with a stereographic projection allows us to show the relative variations of the domain wall property, making it possible to see exactly on which planes domain walls are expected and also at what orientations they are energetically unfavourable. **Error! Reference source not found.**(a) shows a set of unit cells from two different domains of a tetragonal system, $[001]$ and $[\bar{1}00]$ oriented spontaneous strain and polarization and demonstrates the relationship between the domain wall orientation and its position on the stereographic projection. In this case, the domain wall can be intuitively imagined as existing on the $(\bar{1}01)$ plane where: 1) the unit cell cross sections intersecting that plane are identical on both sides of the plane, and 2) the perpendicular component of polarization is continuous through the plane (Figure 1(b)).

Two neighboring domains have unique ferroelectric and ferroelastic orientation states. The ferroelectric orientation state is represented by a polarization and coupled strain. The ferroelastic orientation state is represented only by the strain. The symmetry of the crystal structure (that differentiates it from its other equivalent orientation states) is used to calculate a strain tensor for each domain (see Table S1). This strain tensor is then used to calculate planar strain (i.e., shear and tensile components) on any plane (domain wall) passing through a point in the domain. Using the planar strain calculated on either side of the domain wall (i.e., from the orientation states existing on either side), compatibility can be calculated. *This compatibility is represented by residual planar strain values after comparing the individual spontaneous strains of each domain resolved in the domain wall plane.* However, instead of using three quantities (tensile and shear) to define residual strain on a plane, we utilize the Mohr's circle for strain to calculate a radius, which is constant for a plane irrespective of the choice of coordinate axes on that plane (see supplementary equations 14-16). The residual planar tensile and shear strains are used to calculate the radius of the Mohr's circle for strain and is the representative value of the residual strain on the plane lying between two domains. This is given by the following equation,

$$R_M^r = \sqrt{\left(\frac{(\{\varepsilon_{vv}^1 - \varepsilon_{vv}^2\} - \{\varepsilon_{ww}^1 - \varepsilon_{ww}^2\})^2}{4} + \{\varepsilon_{vw}^1 - \varepsilon_{vw}^2\}^2\right)}$$

Where v and w are two carefully chosen perpendicular axes on the domain wall plane being studied. $\varepsilon_{vv}, \varepsilon_{ww}$ represent the tensile strain and ε_{vw} represent the shear strain in that plane. Superscripts differentiates the two domains. R_M^r is the radius of the Mohr's circle for the residual planar strain. The resultant values are related to the elastic energy through the elastic compliance tensor and strain magnitudes for the material. If the material is a ferroelastic, then residual planar strain is sufficient to show the domain wall planes that are most likely to be the domain walls (Figure 1(c)). In this example there are two permissible domain walls. For ferroelectrics, however, this will only give mechanically permissible walls. In order to find if a wall is neutral or charged, an additional calculation of polarisation charge at the domain wall needs to be performed. Each domain is represented by a polarization vector. The comparison of residual charge on the two permissible ferroelastic domain walls visible in Figure 1(c) is shown in Figure 1(b). To calculate the polarization charge on a plane, the difference in the component of polarization vectors along the plane normal is calculated. If the components are equal, the charge is zero, if unequal, then some charge exists. The residual charge in this paper has been normalized by the magnitude of spontaneous polarization (P_S).

$$\begin{aligned} Residual\ planar\ polarization\ charge &= \{(Component\ of\ \hat{P}_A\ along\ \hat{n}_{Plane}) - (component\ of \hat{P}_B\ along\ \hat{n}_{Plane})\} \\ &= \{(\hat{n}_{Plane} \cdot \hat{P}_A) - (\hat{n}_{Plane} \cdot \hat{P}_B)\} \end{aligned}$$

Where $\hat{n}_{Plane}$, $\hat{P}_A$, $\hat{P}_B$ represent the domain wall planar normal unit vector, polarization unit vector of domain A and polarization unit vector of domain B respectively. This calculation is done for all possible domain wall planes and visualized using a stereographic projection as shown in Figure 1(d). It can be seen that only one of the above mentioned permissible ferroelastic domain walls is also neutral. It should also be noted that charged domain walls are possible and have been experimentally observed(18).

Results and Discussion

***Tetragonal symmetry*:** When the material changes phase from cubic to tetragonal, the unit cell elongates along one of the parent-cubic principal axes. This is equivalent to the 4-fold symmetry operation being broken about two <100> axes while it is conserved along the third <100> axis. In the case of tetragonal symmetry, the tetragonal unit cell axes remain aligned to the parent cubic axes. The unit cell has $a = b \neq c, \alpha = \beta = \gamma = 90°$. An example of this type of transition is that in $BaTiO_3$, which undergoes a cubic $Pm\bar{3}m$ to tetragonal $P4mm$ transition on cooling through T_C at approximately 120°C. During such a transition, every vector or plane normal represented using tetragonal axes can be represented without any change relative to the cubic axes (this will not be the case in other symmetries). There are 6 ferroelectric and 3 ferroelastic orientation states in tetragonal symmetry. Refer to Table S2 for a detailed description of all the possible orientation states, their spontaneous strain and polarization directions. As an example, we have shown the residual planar strain and the residual planar charge for domains with polarization orientation along $[\bar{1}00]$ and $[001]$ in Figure 1(c) and 1(d) respectively. Figure 1(c) has two strain-free permissible ferroelastic domain walls. However only one of them overlaps with the residual planar charge minimum of Figure 1(d). In this case, both $(\bar{1}01)$ and (101) are ferroelastic domain walls, while only the $(\bar{1}01)$ is a neutral ferroelectric domain wall. Similarly, all other combinations of polarization vectors are considered. The total number of different combinations is 9. Table 2 list all the orientation state combinations, their residual planar strain and residual planar charge stereographic projections and the resultant most probable ferroelectric domain walls. The residual planar strain has been normalized by a factor of spontaneous tensile strain along the tetragonal axis. All the 90° domain walls are fixed domain walls (W_f) and all the 180° domain walls are non ferroelastic walls but ferroelectric for any arbitrary orientation as long as the domain wall plane is parallel to the polarization vectors. There is a risk calling 180°walls W_∞ (as has been historically called in literature) as that leads to the thinking that they can be of any arbitrary orientation. Therefore, we have renamed 180° walls as $W_{||P}$ implying that domain wall plane is parallel to the polarization vectors.

In the case of tetragonal symmetry, all the strain tensor elements are dependent on a single variable i.e., the tensile strain along the tetragonal axis, $((c-a)/a)$. This common factor can be eliminated, and the ratios' can be used. Any change in lattice parameters has no effect on the relative strain tensor and therefore the preferred domain wall planes remain the same. However, a structure with a very small tetragonal distortion (c/a ratio) will have far less magnitude of variation in the residual planar strain stereographic projection than a structure with a large unit cell distortion, thereby affecting the relative energetics between ideal and non-ideal domain walls. In order to maintain the continuity of material from one domain to another, the domains have to distort depending on the degree of tetragonality. However, this will not affect the permissible domain wall indices.

Rhombohedral Symmetry: We start with the assumption that the polarization direction for this symmetry is along one of the parent-cubic <111> vectors. Here we have used the rhombohedral unit cell whose axes are assumed to be a small distortion from the parent cubic axes. The unit cell has $a = b = c, \alpha = \beta = \gamma \neq 90°$. Miller indices in the following are with respect to the parent cubic axes. In this case, there are 8 ferroelectric and 4 ferroelastic orientation states. Refer to Table S4 for a detailed description of all possible orientation states, their spontaneous strain, and polarization directions. There are a total 16 ferroelectric orientation state combinations possible. Table 2 lists the residual planar strain, residual planar charge and most favourable ferroelectric domain walls for orientation state combinations with [111] as a fixed orientation state for domain 1. Supplementary Table S5 provides a full list of all the 16 orientation state combinations. The strain tensor

of a rhombohedral ferroelectric (with respect to cubic paraelectric) depends on shear strain i.e., the deviation of the parent cubic axes from being perpendicular. The residual planar strain values here have been normalized by the magnitude of this shear strain. All of the 71° and 109° domain walls are fixed domain walls (W_f). All the 180° domain walls are non ferroelastic but ferroelectric for any arbitrary orientation $(W_{||P})$ as long as the domain wall plane is parallel to the polarization vectors.

Similar to the tetragonal case, the ratio of the strain tensor elements in rhombohedral always remains the same irrespective of the value of the tensor element and therefore, changes in lattice parameters are not going to affect the relative strain tensor and therefore the preferred domain wall positions. However, it should be noted again that a lower rhombohedral shear distortion would change the magnitude of residual planar strain variation among domain wall planes on the stereographic projection.

Orthorhombic Symmetry: We start with the assumption that the polarization direction for this symmetry is along the parent cubic <110>. Here we have used orthorhombic unit cell parameters with respect to parent cubic axes. Note, when we do this, we do not rotate the setting of the unit cell to the standard for orthorhombic system, we have, $a = b \neq c$ and $\alpha = \beta = 90° \neq \gamma$. Miller indices in the following are with respect to the parent cubic axes. There are 12 ferroelectric and 6 ferroelastic orientation states. Refer supplementary table S6 for a detailed description of all orientation states, their spontaneous strain, and polarization directions.

As we move to lower symmetry, the calculations increase in complexity as the strain tensor elements are now in terms of two independent variables, the tensile strain and the shear strain. Therefore, as the lattice parameters changes, the strain tensor changes. Thus, to fully understand the permissible and neutral domain walls possible, this case needs to be studied for changing lattice parameters. To do this, we have used data published by Shirane *et. al.*(31) for $NaNbO_3$ at four different tempreatures in the orthorhombic phase space. We calculate the strain tensor elements using the new lattice parameters at all four temperatures. The data and the tensile and shear strain calculated are tabulated in the supplementary information Table S7. The spontaneous strain is calculated with respect to the parent cubic lattice parameters at those temperatures. The results for residual planar strain and residual planar charge are tabulated in Table 3 for $T = 20℃, 150℃, 300℃, 350℃$ for orientation state combinations with [110] as the fixed polarization vector as domain 1. Supplementary Table S8 provides all the possible orientation state combinations.

The 90° and 120° ferroelectric walls do not change their orientation irrespective of changing lattice parameters i.e., they are fixed domain walls (W_f). However, the 60° ferroelectric domain walls change their orientation as the lattice parameters change with temperature. To see this effect, a stereographic projection showing the domain wall orientations for 60° domain walls at all the temperatures investigated are shown in Figure 2. The change in orientation of these walls can be seen through separated markers of different colours for the same wall. These walls have been predicted previously(11) and were aptly termed 'Strange' or 'S' walls. The results in Table 3 are consistent with the previous analytical results(14) (see supplementary Table S8 for comparison). The results in Table 3 and the visualization of 60° domain walls in Figure 2 show that their behaviour is not completely strange as the change in orientation with changing lattice parameters follow high symmetry paths. This means that under changing temperature or any external stimuli capable of inducing a unit cell distortion, a 60° domain wall rotates about a common line of intersection. For example, one can notice 12 separate "S" wall movements in Figure 2 along six separate great circles. Each of these walls, though changing orientation, have one of the <110> directions as a common line. This means that each 60° wall is rotating about one of the <110> axis.

Monoclinic Symmetry: In the case of monoclinic ferroelectrics, there is a mirror plane in which polarization exists. Here we limit our study to one important high symmetry plane: M_A, in which the polarization vector lies on the mirror plane of the {110} family, i.e. the polarisation can rotate from the <001> to <111> cubic unit cell directions within this mirror plane.

Miller indices in the following are with respect to the parent cubic axes. There are 24 ferroelectric and 12 ferroelastic orientation states. Refer to Table S9 for a detailed description of all orientation states, their spontaneous strain, and polarization directions.

The strain tensor in this symmetry for the axes chosen is a function of three independent variables (tensile strain and two different types of shear strain). Therefore, experimental unit cell data is required to study the planes on which strain free domain walls exist in this case. Here, the elements of this strain tensor are populated using the experimental data from the Liu *et. al.* (32) on 0.675 $Pb(Mg_{1/3}Nb_{2/3})O_3$-0.325 $PbTiO_3$. This material is of particular practical interest because of its very large piezoelectric constants, that arise in part due to the distortion of the unit cell with applied electric field. To understand how the domain wall orientations may vary with field, calculations have been made at zero and +3kV/mm electric field values. Details about the lattice parameters and strain tensor elements are listed in the supplementary information Table S10.

Table 4 lists all the orientation state combinations for domain 2 and a fixed monoclinic domain 1 of polarization direction $[P_1, P_2, P_2]$ which is variable but constrained to the $(0\bar{1}1)$ plane. A stereographic projection of residual planar strain is shown for each combination studied. As the polarization direction is a variable, this makes it difficult to calculate the entire stereographic projection of residual planar charge. Due to this, we have analytically solved for the domain wall plane (hkl) that will result in a neutral domain wall for the particular combination studied. For example, the second combination in the second row, the final relationship for a neutral domain wall is $P_1 h + P_2 l = 0$.

In M_A monoclinic symmetry, some combinations have only fixed domain (W_f) walls. Some have both strange (S) and fixed (W_f) domain walls. However, some cases exist in which there are no perfectly permissible domain walls (historically termed as "R") in the sense that the minimum residual planar strain although very small is non-zero. Strange domain walls have been shown to vary as a function of lattice distortion. In previous literature(14), there are three kinds of S-walls in this symmetry that each vary in a unique way as function of lattice distortion that can also be seen here. Refer to supplementary Table S11 for a description of analytically calculated S walls and their comparison with our results. The results are shown to be consistent with the analytical results(14).

Discussion

Dielectric response in a ferroelectric is a function of intrinsic and extrinsic contributions. The extrinsic contribution includes reversible and irreversible domain wall motion. The residual planar strain and charge stereographic projection for each symmetry shows that in the vicinity of a mechanically permissible neutral domain wall, the energy is not discontinuously changing. Thus, a little flexibility in the orientation of domain walls can be accommodated, and in fact is highly likely in complex microstructures(33), where grain boundaries and other defects have an influence on total system energy. Furthermore, in all symmetries, the magnitude of distortion away from the parent cubic unit cell changed the absolute difference in residual planar strain for every possible domain wall plane. Thus, in some cases, the residual planar strain landscape around permissible walls can change, thereby possibly influencing the magnitude of permitted vibration (reversible motion) of domain walls under external stimuli.

Orthorhombic and monoclinic symmetries have domain walls that vary as a function of crystal distortion. This can happen due to temperature as well as an electric field or stress(34). The walls that change as a function of lattice distortion but remain permissible have historically been called as "strange" walls. However, all the strange walls of orthorhombic vary as a function of strain tensor parameters in the same fashion. The relationship was identified by Erhart(14) in 2004 and can be visualized by our results. Therefore, the 60° S walls in orthorhombic symmetry can be predicted once the changed lattice parameters can be identified. For monoclinic symmetry there are three kinds of domain walls that vary differently. Keeping up with the terminology, they are "stranger" in comparison to orthorhombic domain walls. Nevertheless, they are still dependent on the lattice distortion. Thus, once we know the lattice distortion, the domain wall planes can be accurately predicted. Monoclinic symmetries also have domains with non-permissible domain walls, historically also called as R walls.

We would like to point out that here we have only studied one kind of monoclinic symmetry, i.e., the M_A type. Erhart(14) has shown that M_C has even more types of strange walls wherein charge neutrality is dependent on the values of spontaneous polarization/strain.

It should be noted that this study has not considered the relative energetics between the elastic compatibility and electrical neutrality. Here, we have calculated the intersection of minimum residual planar charge and minimum residual planar strain to find the domain walls fulfilling both the mechanical compatibility as well as charge neutrality criteria. We have not mathematically combined residual planar strain and charge at each domain wall to calculate the relative energy. Although this would give a better comparison, this is avoided due to the fear of arbitrarily combining the effect of elastic compatibility and electrical neutrality. Unit cell and mesoscopic modelling of the domain walls would be required to gauge the relative energy differences between the two effects. However, experimental observation of head to head and tail to tail domain walls in literature(18) would suggest that in those systems, the electric charge energy is not as strong as the elastic energy. This could certainly be the case in systems where other conduction mechanisms at the domain walls(25) or local screening effect by charged defects(35) are possible.

This type of analysis can also be used to study the change in domains and domain walls during phase transitions. Consider case 6 in Table 4. Here domain 1 is $[P_1, P_2, P_2]$ and domain 2 is $[P_2, P_1, \overline{P_2}]$ in the monoclinic phase. The plane on which monoclinic polarization vectors lie is $(0\bar{1}1)$ and $(\bar{1}0\bar{1})$ respectively. This can also be considered as a monoclinic phase that occurs as a transition between a tetragonal (domain 1 is $[100]$ and domain 2 is $[010]$) and rhombohedral phase (domain 1 is $[111]$ and domain 2 is $[11\bar{1}]$). In other words the polarization vector can be seen as rotating from tetragonal [100] to rhombohedral [111] via monoclinic $[P_1, P_2, P_2]$ on $(0\bar{1}1)$ for domain 1 and rotating from tetragonal [010] to rhombohedral $[11\bar{1}]$ via monoclinic $[P_2, P_1, \overline{P_2}]$ on $(\bar{1}0\bar{1})$ for domain 2. Using Table 1, this tetragonal phase has a 90° domain wall with (110) as the permissible – neutral domain wall. Using Table 2, this rhombohedral phase has a (71°) domain wall with (110) as the permissible neutral domain wall. Using Table 4 row 6, the monoclinic phase also has (110) as its permissible and neutral domain wall. Therefore, for this particular case, the polarization vectors can rotate from tetragonal (90°) to rhombohedral (71°) via the monoclinic phase while keeping the same domain wall strain free and neutral throughout the rotation. Although the favourable domain wall orientation remains same, it should be pointed out that the strain variation in the stereographic projection around this strain free domain wall orientation changes, thus the extrinsic contribution during this transition potentially changes as well. This may have implications for conventional ferroelectrics with morphotropic phase boundaries separating tetragonal and rhombohedral phases, with such domain walls facilitating interphase switching under external stimulus. These results can provide insights about domain walls during preferentially followed rotation paths by polarization vectors when changing symmetries(36). We would like to acknowledge that here we have only considered a domain structure with just two domain types. The complexity of a domain structure(37) should be taken into account for complete energy analysis. It should also be noted that here we have only considered the strain originating from the ferroelastic distortion accompanying the polarization. Strains from different sources, e.g., strain due to the substrate clamping of thin films, point defects, line defects (misfit dislocations), and grain boundaries(33) can have an impact on the strain around a domain wall. These additional sources may distort the plane on which the permissible domain wall falls.

One drawback of calculating domain walls analytically is that some domains are said to have no mechanically permissible domain walls, for example shown by a superscript "R" in Table 4. These cases have been defined as with no permissible domain wall orientation in previous work(2, 14). However, when the strain is studied for all the potential domain wall planes, domain walls with very low strain are found. These domains are "almost" mechanically permissible walls. They can likely happen if the small amount of strain can be accommodated within the crystal structure.

Finally, we would like to add that this theory is a function of symmetry lost and symmetry maintained which then leads to the polarization vectors and strain tensors and therefore the analysis is not limited to perovskites. It can be extended to different classes of materials including ferroelastics, shape memory alloys, martensitic transformations, and super-elastic materials as long as the symmetry of the phases prior and after domain formation are known (38, 39).

Conclusions

In this paper, we have calculated the most favourable domains walls and the relative energetics of every domain wall plane orientation possible for four common ferroic symmetries of tetragonal, rhombohedral, orthorhombic and monoclinic M_A type. This is done by calculating strain compatibility and charge continuity on every possible domain wall plane. Using stereographic projections to show residual planar strain and residual planar charge makes it easy to identify ideal and non-ideal domain walls and the relative energetics across domain wall orientations. While the domain walls in tetragonal and rhombohedral symmetry do not change with unit cell distortion, some of the domain walls and their relative energetics in lower symmetries change due to changing lattice distortion. This can happen under application of external stimuli such as thermal, mechanical or electrical. Although strange, this change in domain wall orientation with external stimuli follows high symmetry paths and can be predicted with knowledge of the distortion. The change in relative energetics and rotation of domain walls due to external stimuli can be related to the extrinsic piezoelectric contribution and may have significant implications for understanding ultra-high piezoelectric constants and high dielectric permittivity of some ferroelectrics. Analytically non-ideal domain wall situations are shown to have almost ideal ferroelastic domain walls and can therefore exists in systems capable of accommodating some strain. Using one example we have shown how same ferroic domain wall in different symmetries (e.g. tetragonal – monoclinic - rhombohedral) can facilitate preferentially followed rotation paths by polarization vectors when changing symmetries. Understanding the impact on domain wall orientation and their relative energetics due to varying conditions (temperature, electric field, mechanical strain) can aid in comprehending their impact on unique properties of these systems like jumps in piezoelectric behaviour and existence of non-ideal domains in strained thin films. It is hoped that the results shown here, may provide the possibility for others to design compositional variations and/or electrical treatments that engineer specific populations of domain walls in a system, enhancing desired properties.

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List of Captions

Figure 1: (a)Visualisation of two tetragonal domains, their ferroelectric domain wall and its position on the stereographic projection. (b) shows the charge created on the two mechanically compatible domain walls. The left image in (b) shows a neutral domain wall with the component of polarization along domain wall plane normal being continuous, while the right image shows a charged domain wall with discontinuous components of polarization along domain wall plane normal. (c) Stereographic projection of residual planar strain over all possible orientations of the domain wall. (d) Residual planar charge at the domain wall. Combining (c) and (d), it can be observed that only the $(\bar{1}01)$ domain wall is both permissible and neutral.

Figure 1: Stereographic projection showing 60° domain walls at four different temperatures. The blue, red, green, and black markers respectively represent the minimum residual planar strain 60° domain walls at T= 20°C, 175°C, 300°C and 350°C. Strange 60° walls change their orientation as a function of temperature. However, the change in orientation follow high

symmetry paths, i.e., the walls are rotating about a common axis which are of the <110> type. This effect can also be seen in table 3. The lattice parameters used are from experimental data (31) for $NaNbO_3$. The orientation convention of the stereographic projection follows Fig. 1.

Table 1: All the tetragonal orientation states combinations with their residual planar charge and residual planar strain over all possible orientation of domain wall planes. The permissible and neutral domain walls are listed in the right most column preceded by the corresponding domain 2 description. The colour scale is in the last row. The residual planar strain has been normalized by a factor of spontaneous tensile strain along the tetragonal axis. The residual planar charge has been normalized by magnitude of spontaneous polarization. The orientation convention of the stereographic projection follows Fig. 1.

Table 2: All of the rhombohedral orientation state combinations with [111] orientated polarization vector as Domain 1. Residual planar charge and residual planar strain over all possible orientation of domain walls planes is shown. The permissible and neutral domain walls are listed in the right most column preceded by the corresponding domain 2 description. The superscript shows the angle between the polarization vectors: 71°, 109°, and 180°. The residual planar strain has been normalized by the magnitude of shear strain value coming from the deviation of the parent cubic axes from being perpendicular. Colour scale is shown in last row. The orientation convention of the stereographic projection follows Fig. 1.

Table 3: All the orthorhombic orientation state combinations with [110] orientated polarization vector as domain 1. Residual planar charge and residual planar strain over all possible orientation of domain wall planes, along with the permissible and neutral domain walls are shown for four different temperatures. The lattice parameters are used from experimental data(31) for $NaNbO_3$. The superscript shows if the angle between the polarization vectors is 60° or 120°. Colour scale is shown in last row. The orientation convention of the stereographic projection follows Fig. 1.

Table 4: All the monoclinic M_A orientation state combinations with $(0\bar{1}1)$ plane with the polarization vector as domain 1. Residual planar strain for all possible orientation of domain wall planes is shown at 0 and +3kV/mm electric field. The strain tensor elements are derived from experimental data taken from (32) for PMN-PT. Refer supplementary tables 8-11 for more details. The walls with superscript "R" are the analytically non permissible domain walls. The orientation convention of the stereographic projection follows Fig. 1.