Effective material properties in twinned ferroelectric crystals

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Without external fields, ferroelectric materials will have multidomain configuration in the ferroelectric state. Detailed analysis found that twinning may not be treated as random since the number of orientations for the domain walls are limited in a given symmetry change during a ferroelectric phase transition. In each finite region of a large crystal or in small crystallites, a particular set of twins is favored under certain boundary conditions, which consists of only two of the low temperature variants. Statistic models of random distribution of domains do not apply for calculating the physical properties of such twin structures. However, one could derive the two domain twin properties by using the constitutive equations and appropriate mechanical boundary considerations. This paper presents a theoretical analysis on such a two-domain twin system, including its global symmetry and effective material properties resulting from different twinning configurations. Numerical results are derived for $LiNbO_3$ and $BaTiO_3$. © *1999 American Institute of Physics.* [S0021-8979(99)01214-1]

I. INTRODUCTION

The macroscopic material properties of a multidomain ferroelectric system are the collective average of individual domains. Traditionally, people took statistic average of the properties of all the low temperature variants and used the volume ratio as the weighting factor. However, in reality, different physical properties may follow different averaging rules depending on the geometric configuration. For many properties the contribution of each domain do not always coincide with their volume ratio. For example, the elastic constant of a fiber reinforced composite is much larger in the fiber length direction than in its radial direction, although the volume ratio can be the same. Similarly, in a multidomain system the contribution of each domain not only depends on the volume ratio but also on the relative geometric configuration and on the orientation of the applied external fields. Experimental evidence showed that the domains often appear in a twin band with only two variants in the set.[1,2] Even for a ceramic system, domains observed in each given grain are mostly twin pair sets rather than all the available variants. Such a limited variant twinning pattern is more pronounced in a single crystal system since all orientations must be coherently joined together. Each twin band often occupies a sizable volume in a large single crystal. Generally speaking, two-variant twinning is the basis of all multidomain systems in ferroelectrics.

Recent development in domain engineering of relaxor based single crystal systems (e.g., for single crystals PZN-PT, PMN-PT) produced much enhanced piezoelectric and dielectric properties.[3] Experimental observation showed that many engineered crystal systems have only two variants.[4] Even those nonpoled samples are composed of large regions of two-variant twin band structures. Experimental observation of these relaxor based single crystals revealed that the twinning mostly consists of two variant twins[5,6] (for PZN and for $BaTiO_3$). It is also found that the orientation of the two-domain system and the selection of the variants can significantly influence the effective material properties of multidomain systems. This means that the statistical model or models, based only on the volume ratio, will not give proper prediction of the physical properties in these domain engineered crystals. Roughly speaking, the volume ratio average scheme assumed isotropic distribution of domain walls and ignored the cross coupling between different quantities of the associated domains.

If we utilize the fact that the basic domain structure only consists of two variants and they have a certain orientation relation in domain engineered crystal systems, it is possible to accurately derive the apparent macroscopic property by directly applying external loads to the system. Such a two-variant domain set can then serve as the building block for calculating properties of systems with more complex domain patterns.

The importance of calculating the effective properties of two domains lies in the fact that the macroscopic properties observed experimentally, whether from an ultrasonic method or from a resonance technique, are actually a collective contribution of the *existing* domains, not all *possible* domains. In a given domain engineered single crystal, only some of the low temperature variants can appear.

Because of the importance of predicting the effective material properties, there is vast literature on property averaging of multicomponent systems. For example, the equivalent elastic constants were previously calculated for two layer elastic system[7] by using the volume ratio as the weighting factor for both the stress and strain. This approach allows the calculation of elastic properties in two layer system for materials of any symmetry and any orientation between the two layers. This method was later extended to piezoelectric materials.[8] The dynamic approach for calculating the effec-

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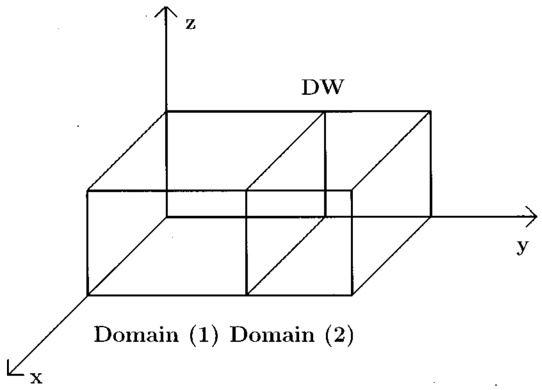

FIG. 1. The two domain system with coordinate systems chosen with the y axis perpendicular to the domain wall (DW).

tive material properties of piezoelectric layered material of arbitrary orientation[9] was based on the nature of acoustic wave propagation in layered material in the long-wavelength limit. It allowed explicit calculation of a complete set of all material properties. Another method for effective material property calculations is the method of effective medium which was applied to calculate the properties of polycrystalline ceramics[10–12] and piezoelectric composites.[13,14] The mechanical stress and electric field were assumed uniform in the matrix and in the inclusion (grains). The average was calculated under a number of assumptions about the space distribution and the shape of inclusions (spherical and elliptical shape). Effective material properties for 1–3 composites were calculated for $6mm$ symmetry as a function of volume fraction.[13] While all of these techniques have advantages and disadvantages in certain aspects, they have provided guidance for many particular applications and for the proper characterization of multicomponent systems of interest to a certain accuracy.

However, it is not appropriate to use the volume ratio average if there are only a limited number of domains in a system. In this paper we will try to eliminate some of those less convincing assumptions used in previous averaging methods and to develop a systematic procedure particularly applicable to a two-domain twin system. We will use different weighting factors for different physical properties based on the relative orientation to the external stress and electric field. Some quantities in each domain can be the same as in the combined twin system rather than all quantities being the weighted average. We will also give the macroscopic symmetry associated with twinning of different pairs of the low temperature variants resulting from cubic to rhombohedral and cubic to tetragonal ferroelectric phase transitions.

II. AVERAGING OF TENSOR PROPERTIES IN A TWIN CRYSTAL

For the twinned structure under study, we assume that the two variants have a volume ratio of $v^{(1)}$ and $v^{(2)}$ and the domain wall (DW) is perpendicular to the y axis. Considering the unit cell of a twin structure as shown in Fig. 1, we can apply static stress and electric field to the system and use the response to derive the effective average property of this twin crystal. For generality, we allow the crystallographic symmetry of both materials to be arbitrary, however the material properties of both domains must be expressed in the same coordinate system before performing the average. For a ferroelectric system, the material properties are represented by the elastic compliance tensor $\mathbf{s}^{(i)}$, piezoelectric constant tensor $\mathbf{d}^{(i)}$ and dielectric constant tensor $\boldsymbol{\epsilon}^{(i)}$, which satisfy the constitutive relations

$$\begin{pmatrix} \boldsymbol{\eta}^{(i)} \\ \mathbf{D}^{(i)} \end{pmatrix} = \begin{pmatrix} \mathbf{s}^{(i)} & \mathbf{d}^{(i)T} \\ \mathbf{d}^{(i)} & \boldsymbol{\epsilon}^{(i)} \end{pmatrix} \begin{pmatrix} \mathbf{T}^{(i)} \\ \mathbf{E}^{(i)} \end{pmatrix} \quad (i=1,2), \tag{1}$$

where the superscripts (1) and (2) represent the quantity for domain 1 and domain 2, respectively. $\boldsymbol{\eta}^{(i)}$ and $\mathbf{D}^{(i)}$ are the elastic strain tensor and the electric displacement vector, $\mathbf{T}^{(i)}$ and $\mathbf{E}^{(i)}$ are the stress and electric field, respectively. The two domains can be of different thickness, which is represented by volume ratios $v^{(1)}$ and $v^{(2)}$ with $v^{(1)}+v^{(2)}=1$. Components of elastic strain $\boldsymbol{\eta}$ are assumed to be symmetric, while the components of elastic stress do not have this symmetry due to the cross domain coupling. The simplified notation is related to the true tensor notation in the following form:

$$T_\lambda = \begin{Bmatrix} T_{ij} & i=j \\ T_{ij}+T_{ji} & i\neq j \end{Bmatrix} \quad (i,j=1,2,3; \quad \lambda=1,\ldots,6). \tag{2}$$

Since the material properties are similar in magnitude for the two domains, unlike the case of polymer–ceramic composite,[15,16] it is reasonable to assume that the mechanical stress, strain, electric field and electric displacement in both domains are homogeneous in the equilibrium state. At equilibrium, the effective stress and strain of the twin system is symmetric and the two domains are required to form a coherent nonseparating boundary (DW) under external applied stresses. For convenience, we will use the shortened notation for all the tensor components of material properties defined by[17]

$$s_{\lambda\nu} = \begin{Bmatrix} s_{ijkl} & i=j,k=l \\ 2s_{ijkl} & i\neq j,k=l \\ 2s_{ijkl} & i=j,k\neq l \\ 4s_{ijkl} & i\neq j,k\neq l \end{Bmatrix} \quad (i,j,k,l=1,2,3; \quad \lambda,\nu=1,\ldots,6), \tag{3a}$$

$$d_{i\mu} = \begin{Bmatrix} d_{ijk} & j=k \\ 2d_{ijk} & j\neq k \end{Bmatrix} \quad (j,k=1,2,3;\mu=1,\ldots,6). \tag{3b}$$

The constitutive relations for each of the domains are

$$\eta_{ij}^{(n)} = d_{kij}^{(n)} E_k^{(n)} + s_{ijkl}^{(n)} T_{kl}^{(n)}, \tag{4a}$$

$$D_i^{(n)} = \epsilon_{ij}^{(n)} E_j^{(n)} + d_{ijk}^{(n)} T_{jk}^{(n)} \quad (i,j,k,l=1,2,3;n=1,2), \tag{4b}$$

where $T_{ij}^{(n)}$ and $E_k^{(n)}$ are the components of the elastic stress tensor and electric field vector, respectively.

Volume ratio averaging conditions can be expressed as[8]

$$\eta_{ij}^{\mathrm{eff}} = v^{(1)}\eta_{ij}^{(1)} + v^{(2)}\eta_{ij}^{(2)}, \tag{5a}$$

$$T_{ij}^{\mathrm{eff}} = v^{(1)}T_{ij}^{(1)} + v^{(2)}T_{ij}^{(2)} \quad (i,j=1,2,3). \tag{5b}$$

These relations cannot hold true simultaneously for both the strain and stress as one can see from the twin structure in Fig. 1. We need to redefine the conditions for such a system for which the orientation and configuration are known. Mechanical equilibrium and nonseparable boundary conditions, i.e., the continuity of the three components of stress: $T_{22}^{(i)}, T_{23}^{(i)}$ and $T_{21}^{(i)}$, six components of strain: $\eta_{11}^{(i)}, \eta_{33}^{(i)}, \eta_{32}^{(i)}, \eta_{13}^{(i)}, \eta_{31}^{(i)}$ and $\eta_{12}^{(i)}$, two components of electric field, $E_1^{(i)}$ and $E_3^{(i)}$, and the electric displacement $D_2^{(i)}$, $(i=1,2)$, lead directly to the following conditions across the domain wall:

$$\eta_{11}^{(1)} = \eta_{11}^{(2)}, \tag{6a}$$

$$\eta_{33}^{(1)} = \eta_{33}^{(2)}, \tag{6b}$$

$$\eta_{32}^{(1)} = \eta_{32}^{(2)}, \tag{6c}$$

$$\eta_{13}^{(1)} = \eta_{13}^{(2)}, \tag{6d}$$

$$\eta_{31}^{(1)} = \eta_{31}^{(2)}, \tag{6e}$$

$$\eta_{12}^{(1)} = \eta_{12}^{(2)}, \tag{6f}$$

$$D_2^{(1)} = D_2^{(2)}, \tag{6g}$$

$$T_{22}^{(1)} = T_{22}^{(2)}, \tag{6h}$$

$$T_{23}^{(1)} = T_{23}^{(2)}, \tag{6i}$$

$$T_{21}^{(1)} = T_{21}^{(2)}, \tag{6j}$$

$$E_1^{(1)} = E_1^{(2)}, \tag{6k}$$

$$E_3^{(1)} = E_3^{(2)}. \tag{6l}$$

These conditions provided different averaging rules for some components of elastic stress, strain, electric field and electric displacement.

Equations (6a)–(6l) give the relations between the elastic stress and electric field in domain 2 and domain 1. For a prescribed stress or electric field to the twinned system, one can first represent the stress and field in domains 1 and 2 using the global quantities. Then, these tensor components can be substituted into Eqs. (5a)–(5b) to find the effective material properties. The linear system of equations, Eqs. (6a)–(6l) can be solved in matrix form

$$\mathbf{b}^{(1)}\boldsymbol{\tau}^{(1)} = \mathbf{b}^{(2)}\boldsymbol{\tau}^{(2)}, \tag{7}$$

where

$$\mathbf{b}^{(i)} = \begin{pmatrix}
s_{11}^{(i)} & s_{12}^{(i)} & s_{13}^{(i)} & s_{14}^{(i)} & s_{14}^{(i)} & s_{15}^{(i)} & s_{16}^{(i)} & s_{16}^{(i)} & d_{11}^{(i)} & d_{21}^{(i)} & d_{31}^{(i)} \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
s_{13}^{(i)} & s_{23}^{(i)} & s_{33}^{(i)} & s_{34}^{(i)} & s_{34}^{(i)} & s_{35}^{(i)} & s_{36}^{(i)} & s_{36}^{(i)} & d_{13}^{(i)} & d_{23}^{(i)} & d_{33}^{(i)} \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
s_{14}^{(i)} & s_{24}^{(i)} & s_{34}^{(i)} & s_{44}^{(i)} & s_{44}^{(i)} & s_{45}^{(i)} & s_{46}^{(i)} & s_{46}^{(i)} & d_{14}^{(i)} & d_{24}^{(i)} & d_{34}^{(i)} \\
s_{15}^{(i)} & s_{25}^{(i)} & s_{35}^{(i)} & s_{45}^{(i)} & s_{45}^{(i)} & s_{55}^{(i)} & s_{56}^{(i)} & s_{56}^{(i)} & d_{15}^{(i)} & d_{25}^{(i)} & d_{35}^{(i)} \\
s_{16}^{(i)} & s_{26}^{(i)} & s_{36}^{(i)} & s_{46}^{(i)} & s_{46}^{(i)} & s_{56}^{(i)} & s_{66}^{(i)} & s_{66}^{(i)} & d_{16}^{(i)} & d_{26}^{(i)} & d_{36}^{(i)} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
d_{21}^{(i)} & d_{22}^{(i)} & d_{23}^{(i)} & d_{24}^{(i)} & d_{24}^{(i)} & d_{25}^{(i)} & d_{26}^{(i)} & d_{26}^{(i)} & \epsilon_{12}^{(i)} & \epsilon_{22}^{(i)} & \epsilon_{23}^{(i)} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix} \quad (i=1,2) \tag{8}$$

and transposed vector $\boldsymbol{\tau}^{(i)}$ is given by

$$\boldsymbol{\tau}^{(i)T} = (T_{11}^{(i)}, T_{22}^{(i)}, T_{33}^{(i)}, \tfrac{1}{2}T_{23}^{(i)}, \tfrac{1}{2}T_{32}^{(i)}, \tfrac{1}{2}(T_{13}^{(i)} + T_{31}^{(i)}),$$
$$\tfrac{1}{2}T_{12}^{(i)}, \tfrac{1}{2}T_{21}^{(i)}, E_1^{(i)}, E_2^{(i)}, E_3^{(i)}). \tag{9}$$

To find out the effective material properties of the two-domain system, we can use matrix calculations. In the examples, however, we will solve them in steps for convenience.

Nine simple loads for the two-domain system were applied to help us derive the independent effective constants. In each case, only one or two components of the load are nonzero.

longitudinal stress

1. $T_{11}^{\mathrm{eff}} \neq 0$
2. $T_{22}^{\mathrm{eff}} \neq 0$
3. $T_{33}^{\mathrm{eff}} \neq 0$

} all other T_{ij}^{eff} are zero and $E_i^{\mathrm{eff}} = 0$;

shear stress

$$\left.\begin{array}{l}4.\;\; T_{23}^{\mathrm{eff}}\neq 0, T_{32}^{\mathrm{eff}}\neq 0\\ 5.\;\; T_{13}^{\mathrm{eff}}\neq 0, T_{31}^{\mathrm{eff}}\neq 0\\ 6.\;\; T_{12}^{\mathrm{eff}}\neq 0, T_{21}^{\mathrm{eff}}\neq 0\end{array}\right\}\ \text{all other } T_{ij}^{\mathrm{eff}} \text{ are zero and } E_i^{\mathrm{eff}}=0;$$

electric field

$$\left.\begin{array}{l}7.\;\; E_1^{\mathrm{eff}}\neq 0\\ 8.\;\; E_2^{\mathrm{eff}}\neq 0\\ 9.\;\; E_3^{\mathrm{eff}}\neq 0\end{array}\right\}\ \text{all other } E_i^{\mathrm{eff}} \text{ are zero and } T_{ij}^{\mathrm{eff}}=0.$$

The constitutive relations become relatively simple for these nine independent loads for calculating the effective material properties. Usually only one kind of material constants for the effective material is involved in each equation.

Putting each of these nine independent loads into Eqs. (6a)–(6l) and using the averaging rules, Eqs. (5a)–(5b) we obtain the linear system of equations

$$\mathbf{A}\mathbf{x}_i=\mathbf{y}_i, \tag{10a}$$

$$\mathbf{A}=\mathbf{A}^{(1)}+\frac{v^{(1)}}{v^{(2)}}\mathbf{A}^{(2)}, \tag{10b}$$

$$\mathbf{A}^{(i)}=\begin{pmatrix} s_{11}^{(i)} & s_{13}^{(i)} & s_{14}^{(i)} & s_{15}^{(i)} & s_{16}^{(i)} & d_{21}^{(i)}\\ s_{13}^{(i)} & s_{33}^{(i)} & s_{34}^{(i)} & s_{35}^{(i)} & s_{36}^{(i)} & d_{23}^{(i)}\\ s_{14}^{(i)} & s_{34}^{(i)} & s_{44}^{(i)} & s_{45}^{(i)} & s_{46}^{(i)} & d_{24}^{(i)}\\ s_{15}^{(i)} & s_{35}^{(i)} & s_{45}^{(i)} & s_{55}^{(i)} & s_{56}^{(i)} & d_{25}^{(i)}\\ s_{16}^{(i)} & s_{36}^{(i)} & s_{46}^{(i)} & s_{56}^{(i)} & s_{66}^{(i)} & d_{26}^{(i)}\\ d_{21}^{(i)} & d_{23}^{(i)} & d_{24}^{(i)} & d_{25}^{(i)} & d_{26}^{(i)} & \epsilon_{22}^{(i)} \end{pmatrix}\ (i=1,2), \tag{10c}$$

$$\mathbf{x}_i=\begin{pmatrix} T_{11}^{(1)}\\ T_{33}^{(1)}\\ \frac{1}{2}T_{32}^{(1)}\\ \frac{1}{2}(T_{13}^{(1)}+T_{31}^{(1)})\\ \frac{1}{2}T_{12}^{(1)}\\ E_2^{(1)} \end{pmatrix}\quad (i=1,2,\ldots,9), \tag{10d}$$

$$\mathbf{y}_1=\frac{1}{v^{(2)}}T_{11}^{\mathrm{eff}}\begin{pmatrix} s_{11}^{(2)}\\ s_{13}^{(2)}\\ s_{14}^{(2)}\\ s_{15}^{(2)}\\ s_{16}^{(2)}\\ d_{21}^{(2)} \end{pmatrix}\quad \mathbf{y}_2=T_{22}^{\mathrm{eff}}\begin{pmatrix} s_{12}^{(2)}-s_{12}^{(1)}\\ s_{23}^{(2)}-s_{23}^{(1)}\\ s_{24}^{(2)}-s_{24}^{(1)}\\ s_{25}^{(2)}-s_{25}^{(1)}\\ s_{26}^{(2)}-s_{26}^{(1)}\\ d_{22}^{(2)}-d_{22}^{(1)} \end{pmatrix}, \tag{10e}$$

$$\mathbf{y}_3=\frac{1}{v^{(2)}}T_{33}^{\mathrm{eff}}\begin{pmatrix} s_{13}^{(2)}\\ s_{33}^{(2)}\\ s_{34}^{(2)}\\ s_{35}^{(2)}\\ s_{36}^{(2)}\\ d_{23}^{(2)} \end{pmatrix}$$

$$\mathbf{y}_4=\tfrac{1}{2}T_{23}^{\mathrm{eff}}\begin{pmatrix} \left(1+\frac{1}{v^{(2)}}\right)s_{14}^{(2)}-s_{14}^{(1)}\\ \left(1+\frac{1}{v^{(2)}}\right)s_{34}^{(2)}-s_{34}^{(1)}\\ \left(1+\frac{1}{v^{(2)}}\right)s_{44}^{(2)}-s_{44}^{(1)}\\ \left(1+\frac{1}{v^{(2)}}\right)s_{45}^{(2)}-s_{45}^{(1)}\\ \left(1+\frac{1}{v^{(2)}}\right)s_{46}^{(2)}-s_{46}^{(1)}\\ \left(1+\frac{1}{v^{(2)}}\right)d_{24}^{(2)}-d_{24}^{(1)} \end{pmatrix}, \tag{10f}$$

$$\mathbf{y}_5=\frac{1}{v^{(2)}}T_{13}^{\mathrm{eff}}\begin{pmatrix} s_{15}^{(2)}\\ s_{35}^{(2)}\\ s_{45}^{(2)}\\ s_{55}^{(2)}\\ s_{56}^{(2)}\\ d_{25}^{(2)} \end{pmatrix}$$

$$\mathbf{y}_6=\tfrac{1}{2}T_{12}^{\mathrm{eff}}\begin{pmatrix} \left(1+\frac{1}{v^{(2)}}\right)s_{16}^{(2)}-s_{16}^{(1)}\\ \left(1+\frac{1}{v^{(2)}}\right)s_{36}^{(2)}-s_{36}^{(1)}\\ \left(1+\frac{1}{v^{(2)}}\right)s_{46}^{(2)}-s_{46}^{(1)}\\ \left(1+\frac{1}{v^{(2)}}\right)s_{56}^{(2)}-s_{56}^{(1)}\\ \left(1+\frac{1}{v^{(2)}}\right)s_{66}^{(2)}-s_{66}^{(1)}\\ \left(1+\frac{1}{v^{(2)}}\right)d_{26}^{(2)}-d_{26}^{(1)} \end{pmatrix}, \tag{10g}$$

$$\mathbf{y}_7=E_1^{\text{eff}}\begin{pmatrix} d_{11}^{(2)}-d_{11}^{(1)} \\ d_{13}^{(2)}-d_{13}^{(1)} \\ d_{14}^{(2)}-d_{14}^{(1)} \\ d_{15}^{(2)}-d_{15}^{(1)} \\ d_{16}^{(2)}-d_{16}^{(1)} \\ \epsilon_{12}^{(2)}-\epsilon_{12}^{(1)} \end{pmatrix} \qquad \mathbf{y}_8=\frac{1}{v^{(2)}}E_2^{\text{eff}}\begin{pmatrix} d_{21}^{(2)} \\ d_{23}^{(2)} \\ d_{24}^{(2)} \\ d_{25}^{(2)} \\ d_{26}^{(2)} \\ \epsilon_{22}^{(2)} \end{pmatrix}, \tag{10h}$$

$$\mathbf{y}_9=E_3^{\text{eff}}\begin{pmatrix} d_{31}^{(2)}-d_{31}^{(1)} \\ d_{33}^{(2)}-d_{33}^{(1)} \\ d_{34}^{(2)}-d_{34}^{(1)} \\ d_{35}^{(2)}-d_{35}^{(1)} \\ d_{36}^{(2)}-d_{36}^{(1)} \\ \epsilon_{23}^{(2)}-\epsilon_{23}^{(1)} \end{pmatrix}. \tag{10i}$$

The mechanical stresses $T_{ij}^{(1)}$ and electric field $E_2^{(1)}$ are different in general for these simple loads. Values of mechanical stress and electric field in domain 2 can be expressed from Eqs. (6a)–(6l) using values of corresponding components in domain 1. We can solve Eq. (10a) and substitute the results into Eqs. (5a)–(5b) to find the effective material properties for the two-domain system. Detailed procedure is illustrated in the example below.

III. EXAMPLES OF TENSOR PROPERTY AVERAGING FOR A TWIN CRYSTAL WITH THE SAME VOLUME RATIOS OF THE TWO DOMAINS

As an example, we calculate the effective material properties of a $3m$ symmetry class single crystal, such as the PZN-PT single crystal, with a set of twins containing equal volume ratios of the two domains. First of all, we need to rotate all tensor components of material properties for both domains from their own material coordinates to the same global coordinate system (material coordinate for the parent cubic structure). Components of material properties for domains 1 and 2 are rotated to the common coordinate system using matrices

$$\mathbf{R}^{(1)}=\begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{3}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{3}} \\ 0 & -\frac{2}{\sqrt{6}} & \frac{1}{\sqrt{3}} \end{pmatrix}$$

and

$$\mathbf{R}^{(2)}=\begin{pmatrix} -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{3}} \\ -\frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{3}} \\ 0 & -\frac{2}{\sqrt{6}} & \frac{1}{\sqrt{3}} \end{pmatrix}. \tag{11}$$

Because the prototype symmetry of the paraelectric phase is cubic, the possible DW orientations[18] for the two domains with polarization $P_S[111]$ and $P_S[1\bar{1}\bar{1}]$ are [010] and [101]. We calculate the effective material properties for the case with DW oriented in [010]. Domains are often observed as periodic twin bands in most ferroelectric materials, therefore it is reasonable to assume the same volume ratios for the two domains, i.e., $v^{(1)}=v^{(2)}=\frac{1}{2}$, the expected symmetry of such a twin structure and its effective material properties is $mm2$.

Independent material properties for the $3m$ symmetry class in its own crystallographic coordinate system with the mirror symmetry plane perpendicular to the x axis can be found in published tables.[17]

Material properties for domain 1 in the chosen coordinate system (as plotted in Fig. 1) are

$$\mathbf{s}'^{(1)}=\begin{pmatrix} s'_{11} & s'_{12} & s'_{12} & s'_{14} & s'_{15} & s'_{15} \\ s'_{12} & s'_{11} & s'_{12} & s'_{15} & s'_{14} & s'_{15} \\ s'_{12} & s'_{12} & s'_{11} & s'_{15} & s'_{15} & s'_{14} \\ s'_{14} & s'_{15} & s'_{15} & s'_{44} & s'_{45} & s'_{45} \\ s'_{15} & s'_{14} & s'_{15} & s'_{45} & s'_{44} & s'_{45} \\ s'_{15} & s'_{15} & s'_{14} & s'_{45} & s'_{45} & s'_{44} \end{pmatrix}, \tag{12a}$$

$$\boldsymbol{\epsilon}'^{(1)}=\begin{pmatrix} \epsilon'_{11} & \epsilon'_{12} & \epsilon'_{12} \\ \epsilon'_{12} & \epsilon'_{11} & \epsilon'_{12} \\ \epsilon'_{12} & \epsilon'_{12} & \epsilon'_{11} \end{pmatrix}, \tag{12b}$$

$$\mathbf{d}'^{(1)}=\begin{pmatrix} d'_{11} & d'_{12} & d'_{12} & d'_{14} & d'_{15} & d'_{15} \\ d'_{12} & d'_{11} & d'_{12} & d'_{15} & d'_{14} & d'_{15} \\ d'_{12} & d'_{12} & d'_{11} & d'_{15} & d'_{15} & d'_{14} \end{pmatrix}, \tag{12c}$$

while material properties for the second domain in the same coordinate system can be derived as

$$\mathbf{s}'^{(2)}=\begin{pmatrix} s'_{11} & s'_{12} & s'_{12} & -s'_{14} & s'_{15} & -s'_{15} \\ s'_{12} & s'_{11} & s'_{12} & -s'_{15} & s'_{14} & -s'_{15} \\ s'_{12} & s'_{12} & s'_{11} & -s'_{15} & s'_{15} & -s'_{14} \\ -s'_{14} & -s'_{15} & -s'_{15} & s'_{44} & -s'_{45} & s'_{45} \\ s'_{15} & s'_{14} & s'_{15} & -s'_{45} & s'_{44} & -s'_{45} \\ -s'_{15} & -s'_{15} & -s'_{14} & s'_{45} & -s'_{45} & s'_{44} \end{pmatrix}, \tag{13a}$$

$$\boldsymbol{\epsilon}'^{(2)}=\begin{pmatrix} \epsilon'_{11} & -\epsilon'_{12} & \epsilon'_{12} \\ -\epsilon'_{12} & \epsilon'_{11} & -\epsilon'_{12} \\ \epsilon'_{12} & -\epsilon'_{12} & \epsilon'_{11} \end{pmatrix}, \tag{13b}$$

$$\mathbf{d}'^{(2)}=\begin{pmatrix} d'_{11} & d'_{12} & d'_{12} & -d'_{14} & d'_{15} & -d'_{15} \\ -d'_{12} & -d'_{11} & -d'_{12} & d'_{15} & -d'_{14} & d'_{15} \\ d'_{12} & d'_{12} & d'_{11} & -d'_{15} & d'_{15} & -d'_{14} \end{pmatrix}, \tag{13c}$$

where

$$s'_{11}=\tfrac{1}{9}(4s_{11}+4s_{13}+4\sqrt{2}s_{14}+s_{33}+2s_{44}), \tag{14a}$$

$$s'_{12}=\tfrac{1}{9}(s_{11}+3s_{12}+4s_{13}-2\sqrt{2}s_{14}+s_{33}-s_{44}), \tag{14b}$$

$$s'_{14}=\tfrac{2}{9}(s_{11}-3s_{12}+s_{13}+\sqrt{2}s_{14}+s_{33}-s_{44}), \tag{14c}$$

$$s'_{15}=\tfrac{1}{9}(-4s_{11}+2s_{13}-\sqrt{2}s_{14}+2s_{33}+s_{44}), \tag{14d}$$

$$s'_{44}=\tfrac{2}{9}(5s_{11}-3s_{12}-4s_{13}-4\sqrt{2}s_{14}+2s_{33}+s_{44}), \tag{14e}$$

$$s'_{45}=\tfrac{1}{9}(-2s_{11}+6s_{12}-8s_{13}+4\sqrt{2}s_{14}+4s_{33}-s_{44}), \tag{14f}$$

$$d'_{11}=\frac{1}{3\sqrt{3}}(2d_{15}-2\sqrt{2}d_{22}+2d_{31}+d_{33}), \tag{14g}$$

$$d'_{12}=\frac{1}{3\sqrt{3}}(-d_{15}+\sqrt{2}d_{22}+2d_{31}+d_{33}), \tag{14h}$$

$$d'_{14}=-\frac{2}{3\sqrt{3}}(d_{15}+2\sqrt{2}d_{22}+d_{31}-d_{33}), \tag{14i}$$

$$d'_{15}=\frac{1}{3\sqrt{3}}(d_{15}+2\sqrt{2}d_{22}-2d_{31}+2d_{33}), \tag{14j}$$

$$\epsilon'_{11}=\tfrac{1}{3}(2\epsilon_{11}+\epsilon_{33}), \tag{14k}$$

$$\epsilon'_{12}=\tfrac{1}{3}(-\epsilon_{11}+\epsilon_{33}). \tag{14l}$$

As an example, let us apply load 1, i.e., $T_{11}^{\rm eff}\neq 0$, other are all zero (the other loads 2–9 can be solved similarly). The corresponding matrices for the linear system are

$$\mathbf{A}=\begin{pmatrix} 2s'_{11} & 2s'_{12} & s'_{15} & 0 & 0 & 0\\ 2s'_{12} & 2s'_{11} & s'_{15} & 0 & 0 & 0\\ 2s'_{15} & 2s'_{15} & s'_{44} & 0 & 0 & 0\\ 0 & 0 & 0 & s'_{44} & s'_{45} & 2d'_{15}\\ 0 & 0 & 0 & s'_{45} & s'_{44} & 2d'_{15}\\ 0 & 0 & 0 & d'_{15} & d'_{15} & 2\epsilon'_{11} \end{pmatrix}, \tag{15a}$$

$$\mathbf{x}_1=\begin{pmatrix} T_{11}^{(1)}\\ T_{33}^{(1)}\\ T_{12}^{(1)}\\ T_{32}^{(1)}\\ T_{13}^{(1)}+T_{31}^{(1)}\\ E_2^{(1)} \end{pmatrix}, \tag{15b}$$

$$\mathbf{y}_1=(2T_{11}^{\rm eff})\begin{pmatrix} s'_{11}\\ s'_{12}\\ s'_{15}\\ -s'_{14}\\ -s'_{15}\\ -d'_{12} \end{pmatrix}, \tag{15c}$$

where we reshaped matrix **A** and vectors $\mathbf{x}_1,\mathbf{y}_1$ for convenience. The solution of Eq. (10a) for our particular case is given by

$$T_{11}^{(1)}=T_{11}^{\rm eff},\quad T_{33}^{(1)}=0,\quad T_{13}^{(1)}+T_{31}^{(1)}=0, \tag{16}$$

$$T_{32}^{(1)}=(-2T_{11}^{\rm eff})\frac{\det\mathbf{B}_1}{\det\mathbf{B}},\quad T_{12}^{(1)}=(-2T_{11}^{\rm eff})\frac{\det\mathbf{B}_2}{\det\mathbf{B}},$$

$$E_2^{(1)}=(-T_{11}^{\rm eff})\frac{\det\mathbf{B}_3}{\det\mathbf{B}}, \tag{17}$$

where

$$\mathbf{B}=\begin{pmatrix} s'_{44} & s'_{45} & d'_{15}\\ s'_{45} & s'_{44} & d'_{15}\\ d'_{15} & d'_{15} & \epsilon'_{11} \end{pmatrix}\quad \mathbf{B}_1=\begin{pmatrix} s'_{14} & s'_{45} & d'_{15}\\ s'_{15} & s'_{44} & d'_{15}\\ d'_{12} & d'_{15} & \epsilon'_{11} \end{pmatrix}, \tag{18}$$

$$\mathbf{B}_2=\begin{pmatrix} s'_{44} & s'_{14} & d'_{15}\\ s'_{45} & s'_{15} & d'_{15}\\ d'_{15} & d'_{12} & \epsilon'_{11} \end{pmatrix}\quad \mathbf{B}_3=\begin{pmatrix} s'_{44} & s'_{45} & s'_{14}\\ s'_{45} & s'_{44} & s'_{15}\\ d'_{15} & d'_{15} & d'_{12} \end{pmatrix}. \tag{19}$$

Mechanical stresses in domain 2 are expressed as

$$T_{11}^{(2)}=T_{11}^{\rm eff},\quad T_{33}^{(2)}=0,\quad T_{32}^{(2)}=-T_{32}^{(1)}, \tag{20}$$

$$T_{13}^{(2)}+T_{31}^{(2)}=0,\quad T_{12}^{(2)}=-T_{12}^{(1)},\quad E_2^{(2)}=-E_2^{(1)}. \tag{21}$$

Now we can substitute these expressions into the averaging conditions Eqs. (6a)–(6l) and obtain some of the effective material properties for the two-domain system. The same procedure can be applied to the other loads 2–9 and a complete set of effective material properties for the twin structure will be obtained and they are explicitly given below:

$$\mathbf{s}^{\rm eff}=\begin{pmatrix} s_{11}^{\rm eff} & s_{12}^{\rm eff} & s_{13}^{\rm eff} & 0 & s_{15}^{\rm eff} & 0\\ s_{12}^{\rm eff} & s_{22}^{\rm eff} & s_{12}^{\rm eff} & 0 & s_{25}^{\rm eff} & 0\\ s_{13}^{\rm eff} & s_{12}^{\rm eff} & s_{11}^{\rm eff} & 0 & s_{15}^{\rm eff} & 0\\ 0 & 0 & 0 & s_{44}^{\rm eff} & 0 & s_{46}^{\rm eff}\\ s_{15}^{\rm eff} & s_{25}^{\rm eff} & s_{15}^{\rm eff} & 0 & s_{55}^{\rm eff} & 0\\ 0 & 0 & 0 & s_{46}^{\rm eff} & 0 & s_{44}^{\rm eff} \end{pmatrix}, \tag{22a}$$

$$\boldsymbol{\epsilon}^{\rm eff}=\begin{pmatrix} \epsilon_{11}^{\rm eff} & 0 & \epsilon_{13}^{\rm eff}\\ 0 & \epsilon_{22}^{\rm eff} & 0\\ \epsilon_{13}^{\rm eff} & 0 & \epsilon_{11}^{\rm eff} \end{pmatrix}, \tag{22b}$$

$$\mathbf{d}^{\rm eff}=\begin{pmatrix} d_{11}^{\rm eff} & d_{12}^{\rm eff} & d_{13}^{\rm eff} & 0 & d_{15}^{\rm eff} & 0\\ 0 & 0 & 0 & d_{24}^{\rm eff} & 0 & d_{24}^{\rm eff}\\ d_{13}^{\rm eff} & d_{12}^{\rm eff} & d_{11}^{\rm eff} & 0 & d_{15}^{\rm eff} & 0 \end{pmatrix}, \tag{22c}$$

where

$$s_{11}^{\rm eff}=s'_{11}-(s'_{14}\det\mathbf{B}_1+s'_{15}\det\mathbf{B}_2+d'_{12}\det\mathbf{B}_3)/\det\mathbf{B}, \tag{23a}$$

$$s_{12}^{\rm eff}=s'_{12}-(s'_{15}\det\mathbf{B}_1+s'_{15}\det\mathbf{B}_2+d'_{11}\det\mathbf{B}_3)/\det\mathbf{B}, \tag{23b}$$

$$s_{13}^{\rm eff}=s'_{12}-(s'_{15}\det\mathbf{B}_1+s'_{14}\det\mathbf{B}_2+d'_{12}\det\mathbf{B}_3)/\det\mathbf{B}, \tag{23c}$$

$$s_{15}^{\rm eff}=s'_{15}-(s'_{45}\det\mathbf{B}_1+s'_{45}\det\mathbf{B}_2+d'_{14}\det\mathbf{B}_3)/\det\mathbf{B}, \tag{23d}$$

$$s_{22}^{\rm eff}=s'_{11}-(s'_{15}\det\mathbf{B}_4+s'_{15}\det\mathbf{B}_5+d'_{11}\det\mathbf{B}_6)/\det\mathbf{B}, \tag{23e}$$

$$s_{25}^{\text{eff}}=s'_{14}-(s'_{45}\det\mathbf{B}_4+s'_{45}\det\mathbf{B}_5+d'_{14}\det\mathbf{B}_6)/\det\mathbf{B}, \tag{23f}$$

$$s_{44}^{\text{eff}}=s'_{44}-(s'_{14}\det\mathbf{B}_7+s'_{15}\det\mathbf{B}_8+s'_{45}\det\mathbf{B}_9)/\det\mathbf{B}^*, \tag{23g}$$

$$s_{46}^{\text{eff}}=s'_{45}-(s'_{15}\det\mathbf{B}_7+s'_{14}\det\mathbf{B}_8+s'_{45}\det\mathbf{B}_9)/\det\mathbf{B}^*, \tag{23h}$$

$$s_{55}^{\text{eff}}=s'_{44}-(s'_{45}\det\mathbf{B}_{10}+s'_{45}\det\mathbf{B}_{11}+d'_{14}\det\mathbf{B}_{12})/\det\mathbf{B}, \tag{23i}$$

$$\epsilon_{11}^{\text{eff}}=\epsilon'_{11}-(d'_{14}\det\mathbf{B}_{13}+d'_{15}\det\mathbf{B}_{14}+\epsilon'_{12}\det\mathbf{B}_{15})/\det\mathbf{B}, \tag{23j}$$

$$\epsilon_{13}^{\text{eff}}=\epsilon'_{12}-(d'_{15}\det\mathbf{B}_{13}+d'_{14}\det\mathbf{B}_{14}+\epsilon'_{12}\det\mathbf{B}_{15})/\det\mathbf{B}, \tag{23k}$$

$$\epsilon_{22}^{\text{eff}}=\epsilon'_{11}-(d'_{12}\det\mathbf{B}_{16}+d'_{12}\det\mathbf{B}_{17}+d'_{14}\det\mathbf{B}_{18})/\det\mathbf{B}^*, \tag{23l}$$

$$d_{11}^{\text{eff}}=d'_{11}-(s'_{14}\det\mathbf{B}_{13}+s'_{15}\det\mathbf{B}_{14}+d'_{12}\det\mathbf{B}_{15})/\det\mathbf{B}, \tag{23m}$$

$$d_{12}^{\text{eff}}=d'_{12}-(s'_{15}\det\mathbf{B}_{13}+s'_{15}\det\mathbf{B}_{14}+d'_{11}\det\mathbf{B}_{15})/\det\mathbf{B}, \tag{23n}$$

$$d_{13}^{\text{eff}}=d'_{12}-(s'_{15}\det\mathbf{B}_{13}+s'_{14}\det\mathbf{B}_{14}+d'_{12}\det\mathbf{B}_{15})/\det\mathbf{B}, \tag{23o}$$

$$d_{15}^{\text{eff}}=d'_{15}-(s'_{45}\det\mathbf{B}_{13}+s'_{45}\det\mathbf{B}_{14}+d'_{14}\det\mathbf{B}_{15})/\det\mathbf{B}, \tag{23p}$$

$$d_{24}^{\text{eff}}=d'_{15}-(s'_{14}\det\mathbf{B}_{16}+s'_{15}\det\mathbf{B}_{17}+s'_{45}\det\mathbf{B}_{18})/\det\mathbf{B}^*, \tag{23q}$$

where

$$\mathbf{B}^*=\begin{pmatrix} s'_{11} & s'_{12} & s'_{15}\\ s'_{12} & s'_{11} & s'_{15}\\ s'_{15} & s'_{15} & s'_{44}\end{pmatrix}\quad \mathbf{B}_4=\begin{pmatrix} s'_{15} & s'_{45} & d'_{15}\\ s'_{14} & s'_{44} & d'_{15}\\ d'_{11} & d'_{15} & \epsilon'_{11}\end{pmatrix}, \tag{24a}$$

$$\mathbf{B}_5=\begin{pmatrix} s'_{44} & s'_{15} & d'_{15}\\ s'_{45} & s'_{15} & d'_{15}\\ d'_{15} & d'_{11} & \epsilon'_{11}\end{pmatrix}\quad \mathbf{B}_6=\begin{pmatrix} s'_{44} & s'_{45} & s'_{15}\\ s'_{45} & s'_{44} & s'_{15}\\ d'_{15} & d'_{15} & d'_{11}\end{pmatrix}, \tag{24b}$$

$$\mathbf{B}_7=\begin{pmatrix} s'_{14} & s'_{12} & s'_{15}\\ s'_{15} & s'_{11} & s'_{15}\\ s'_{45} & s'_{15} & s'_{44}\end{pmatrix}\quad \mathbf{B}_8=\begin{pmatrix} s'_{11} & s'_{14} & s'_{15}\\ s'_{12} & s'_{15} & s'_{15}\\ s'_{15} & s'_{45} & s'_{44}\end{pmatrix}, \tag{24c}$$

$$\mathbf{B}_9=\begin{pmatrix} s'_{11} & s'_{12} & s'_{14}\\ s'_{12} & s'_{11} & s'_{15}\\ s'_{15} & s'_{15} & s'_{45}\end{pmatrix}\quad \mathbf{B}_{10}=\begin{pmatrix} s'_{45} & s'_{45} & d'_{15}\\ s'_{45} & s'_{44} & d'_{15}\\ d'_{14} & d'_{15} & \epsilon'_{11}\end{pmatrix}, \tag{24d}$$

$$\mathbf{B}_{11}=\begin{pmatrix} s'_{44} & s'_{45} & d'_{15}\\ s'_{45} & s'_{45} & d'_{15}\\ d'_{15} & d'_{14} & \epsilon'_{11}\end{pmatrix}\quad \mathbf{B}_{12}=\begin{pmatrix} s'_{44} & s'_{45} & s'_{45}\\ s'_{45} & s'_{44} & s'_{45}\\ d'_{15} & d'_{15} & d'_{14}\end{pmatrix}, \tag{24e}$$

$$\mathbf{B}_{13}=\begin{pmatrix} d'_{14} & s'_{45} & d'_{15}\\ d'_{15} & s'_{44} & d'_{15}\\ \epsilon'_{12} & d'_{15} & \epsilon'_{11}\end{pmatrix}\quad \mathbf{B}_{14}=\begin{pmatrix} s'_{44} & d'_{14} & d'_{15}\\ s'_{45} & d'_{15} & d'_{15}\\ d'_{15} & \epsilon'_{12} & \epsilon'_{11}\end{pmatrix}, \tag{24f}$$

$$\mathbf{B}_{15}=\begin{pmatrix} s'_{44} & s'_{45} & d'_{14}\\ s'_{45} & s'_{44} & d'_{15}\\ d'_{15} & d'_{15} & \epsilon'_{12}\end{pmatrix}\quad \mathbf{B}_{16}=\begin{pmatrix} d'_{12} & s'_{12} & s'_{15}\\ d'_{12} & s'_{11} & s'_{15}\\ d'_{14} & s'_{15} & s'_{44}\end{pmatrix}, \tag{24g}$$

$$\mathbf{B}_{17}=\begin{pmatrix} s'_{11} & d'_{12} & s'_{15}\\ s'_{12} & d'_{12} & s'_{15}\\ s'_{15} & d'_{14} & s'_{44}\end{pmatrix}\quad \mathbf{B}_{18}=\begin{pmatrix} s'_{11} & s'_{12} & d'_{12}\\ s'_{12} & s'_{11} & d'_{12}\\ s'_{15} & s'_{15} & d'_{14}\end{pmatrix}. \tag{24h}$$

The symmetry of these effective material properties is at least $mm2$. Some may show degeneracy in certain components.

Similar calculations can be carried out for any arbitrary material symmetry and arbitrary orientation of domains and DW.

IV. NUMERICAL EXAMPLES FOR $m3m\rightarrow3m$ AND $m3m\rightarrow4mm$ FERROELECTRIC SPECIES

In order to make some comparison between our method and the volume ratio weighted average, we have performed a numerical computation for two systems that have experimental data available in the single domain single crystal state. Unfortunately, the lack of experimental results prevented us from direct comparison to measured data for a two-domain twin band system. The two systems calculated represent domains formed at the ferroelectric phase transitions of $m3m\rightarrow3m$ and $m3m\rightarrow4mm$. ($BaTiO_3$) was chosen as an example for the $m3m\rightarrow4mm$ transition. There are unfortunately no complete data sets available for the $m3m\rightarrow3m$ transition. Therefore we used the numerical data of $LiNbO_3$ in the $3m$ phase and assumed that the domain structures could be engineered to the configurations resulting from a $m3m\rightarrow3m$ transition (the true phase transition of $LiNbO_3$ is $\bar{3}m\rightarrow3m$ and there are only 180° domains in its natural $3m$ phase).

If the effective material properties could be calculated based on volume ratio weighted average,[8] the effective material properties can have a very compact form. In vector notation, the effective material properties of a two-domain system are given by a 9×9 matrix

$$\mathbf{M}=\begin{pmatrix}\mathbf{s} & \mathbf{d}^T\\ \mathbf{d} & \boldsymbol{\epsilon}\end{pmatrix}, \tag{25}$$

where $\mathbf{s}$ is a 6×6 matrix of the elastic compliances, $\mathbf{d}$ is a 6×3 matrix of piezoelectric constants and $\boldsymbol{\epsilon}$ is a 3×3 matrix of the dielectric constant. Because the volume ratio weighting method eliminated the cross coupling between domain 1 and domain 2 and ignored the orientation effect, the effective material properties can be simply expressed as

$$\mathbf{M}=\left(\mathbf{M}^{(1)}(\mathbf{m}^{(1)})^{-1}\mathbf{m}^{(2)}+\frac{v^{(2)}}{v^{(1)}}\mathbf{M}^{(2)}\right)\times\left((\mathbf{m}^{(1)})^{-1}\mathbf{m}^{(2)}+\frac{v^{(2)}}{v^{(1)}}\mathbf{I}\right)^{-1}, \tag{26}$$

where $\mathbf{M}^{(1)}$ and $\mathbf{M}^{(2)}$ are matrices of material properties of both domains and $\mathbf{I}$ is a 9×9 unit matrix. The matrices $\mathbf{m}^{(1)}$ and $\mathbf{m}^{(2)}$ are given by

TABLE I. Effective material properties for two variant twin structure of $LiNbO_3$ and $BaTiO_3$. The coordinate system is chosen in the way that the y-axis is perpendicular to the DW. Zero values of tensor components are listed by dots.

Material property		$LiNbO_3$ DW(010)				$BaTiO_3$ DW(110)			
		$P_S[111]$	$P_S[1\bar{1}\bar{1}]$	This work	Ref. 8	$P_S[100]$	$P_S[010]$	This work	Ref. 8
$S_{\alpha\beta}$ $[10^{-12}\,m^2\,N^{-1}]$	11	5.60	5.60	5.42	5.50	7.92	7.92	7.49	7.92
	12	−1.36	−1.36	−1.10	−1.08	−1.28	−1.28	−1.71	−1.28
	13	−1.36	−1.36	−1.38	−1.46	−3.80	−3.80	−3.47	−3.79
	14	−1.35	1.35	...	...	...	...	...	...
	15	0.26	0.26	−0.49	−0.53	...	...	...	...
	16	0.26	−0.26	...	...	3.83	−3.83	...	...
	22	5.60	5.60	4.65	4.84	7.92	7.92	7.49	7.92
	23	−1.36	−1.36	−1.10	−1.08	−3.80	−3.80	−3.47	−3.79
	24	0.26	−0.26	...	...	...	...	...	...
	25	−1.35	−1.35	1.36	0.87	...	...	...	...
	26	0.26	−0.26	...	...	3.83	−3.83	...	...
	33	5.60	5.60	5.42	5.50	8.05	8.05	7.81	8.05
	34	0.26	−0.26	...	...	...	...	...	...
	35	0.26	0.26	−0.49	−0.53	...	...	...	...
	36	−1.35	1.35	...	...	−2.89	2.89	...	...
	44	15.65	15.65	15.27	15.27	13.62	13.62	11.94	11.94
	45	−0.98	0.98	...	...	4.78	−4.78	...	...
	46	−0.98	−0.98	−0.99	−0.99	...	...	...	...
	55	15.65	15.65	7.92	9.22	13.62	13.62	11.94	13.62
	56	−0.98	0.98	...	...	...	...	...	...
	66	15.65	15.65	15.27	15.27	34.23	34.23	30.63	30.63
$d_{i\alpha}$ $[10^{-12}CN^{-1}]$	11	16.28	16.28	11.84	15.53	−157	157	...	...
	12	−5.83	−5.83	−5.03	−3.74	121	−121	...	...
	13	−5.83	−5.83	−3.14	−6.58	24	−24	...	...
	14	−47.11	47.11	...	...	...	...	...	...
	15	26.44	26.44	23.84	20.40	...	...	...	...
	16	26.44	−26.44	...	...	−85	−85	−127	−127
	21	−5.83	5.83	...	...	121	121	130	121
	22	16.28	−16.28	...	...	−157	−157	−147	−157
	23	−5.83	5.83	...	...	24	24	17	24
	24	26.44	26.44	22.23	22.23	...	...	...	...
	25	−47.11	47.11	...	...	...	...	...	...
	26	26.44	26.44	22.23	22.23	−85	85	...	...
	31	−5.83	−5.83	−3.14	−6.58	...	...	...	...
	32	−5.83	−5.83	−5.03	−3.74	...	...	...	...
	33	16.28	16.28	11.84	15.53	...	...	...	...
	34	26.44	−26.44	...	...	−277	−277	−179	−180
	35	26.44	26.44	23.84	20.40	−277	277	...	...
	36	−47.11	47.11	...	...	...	...	...	...
ϵ_{ij} $[10^{-10}Fm^{-1}]$	11	3.45	3.45	1.68	3.40	135	135	24.1	24.1
	12	−0.44	0.44	...	...	−121	121	...	...
	13	−0.44	−0.44	1.04	−0.50	...	...	...	...
	22	3.45	3.45	1.91	1.92	135	135	133.3	135.5
	23	−0.44	0.44	...	...	...	...	...	...
	33	3.45	3.45	1.68	3.40	256	256	199.6	199.6

$$\mathbf{m}^{(i)}=\begin{pmatrix} s_{11}^{(i)} & s_{12}^{(i)} & s_{13}^{(i)} & s_{14}^{(i)} & s_{15}^{(i)} & s_{16}^{(i)} & d_{11}^{(i)} & d_{21}^{(i)} & d_{31}^{(i)} \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ s_{13}^{(i)} & s_{23}^{(i)} & s_{33}^{(i)} & s_{34}^{(i)} & s_{35}^{(i)} & s_{36}^{(i)} & d_{13}^{(i)} & d_{23}^{(i)} & d_{33}^{(i)} \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ s_{15}^{(i)} & s_{25}^{(i)} & s_{35}^{(i)} & s_{45}^{(i)} & s_{55}^{(i)} & s_{56}^{(i)} & d_{15}^{(i)} & d_{25}^{(i)} & d_{35}^{(i)} \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ d_{21}^{(i)} & d_{22}^{(i)} & d_{23}^{(i)} & d_{24}^{(i)} & d_{25}^{(i)} & d_{26}^{(i)} & \epsilon_{12}^{(i)} & \epsilon_{22}^{(i)} & \epsilon_{23}^{(i)} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \quad (i=1,2). \tag{27}$$

Numerical values for a two-domain system of engineered $LiNbO_3$ and $BaTiO_3$ calculated using this approach[8] are listed in Table I to compare with the numerical values obtained by using the method given in this paper (also listed in Table I).

It is important to point out that the global symmetry of the twin structure is maintained whether or not the intercoupling between the two domains has been considered. For the case of $LiNbO_3$, the symmetry belongs to the $mm2$ class. For $BaTiO_3$ the symmetry of the system is also $mm2$, but there is additional degeneracy for some material properties. They are: $s_{44}^{\mathrm{eff}}=s_{55}^{\mathrm{eff}}$. Using the method of volume ratio average,[8] only two of the degenerate relations $s_{11}^{\mathrm{eff}}=s_{22}^{\mathrm{eff}}, s_{13}^{\mathrm{eff}}=s_{23}^{\mathrm{eff}}$ hold for the elastic compliance tensor.

From Table I, the difference in elastic properties calculated using these two methods is small. This is because the elastic properties of the two variants are very similar, the intercoupling effect is not significant. The difference is much larger in the piezoelectric and dielectric constants for lower symmetry systems. For $LiNbO_3$, the calculated piezoelectric coefficient d_{13} using these two methods differ by more than 100% and the dielectric coefficient ϵ_{13} even have different signs. It appears that the difference becomes smaller for higher symmetry systems. For the $4mm$ symmetry $BaTiO_3$, the difference is within a few percent for most of the quantities. Therefore, the volume ratio averaging method could give good predictions on the effective properties for higher symmetry systems but may run into problems for lower symmetry systems.

V. DISCUSSION AND CONCLUSIONS

In summary, we have reported in this paper a general procedure to calculate the effective material properties of a two-variant twin structure. The method has taken into account specifically all the boundary conditions and used more realistic relations for each individual tensor component, rather than using a unified volume ratio averaging scheme. This procedure requires to solve two sets of linear systems of equations and could be easily implemented using a computer. The equations are all linear and can be solved without much difficulty.

In order to compare our method to the volume averaging scheme, we have calculated two systems with polar symmetries of $3m$ and $4mm$ using both methods. It was found that the new method gives similar results for a $4mm$ system but predicts quite different piezoelectric and dielectric coefficients for $3m$ systems. In some components, the difference can exceed 100%. The elastic properties, however, differ very little for both symmetries because the two types of domains are very similar in elastic properties, therefore the coupling of the two domains does not make a significant difference while performing the property average.

Two variant twins are the basis of all twin structures as revealed by all microscopy works. Properly calculated, the effective property of the two-variant twins will pave the way to calculating more precisely more complicated multidomain single crystal ferroelectric systems.

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