

## LETTER TO THE EDITOR

## Domain geometry engineering and domain average engineering of ferroics

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### Abstract

Multidomain samples of ferroics (ferroelectrics, ferroelastics, and related materials) with *fixed* geometrical distribution of domains can offer new macroscopic properties required for particular applications. Two extreme cases of such applications are defined. In *domain-geometry-engineered* samples of ferroic crystals, the spatial distribution of domains and thus the spatial distribution of tensorial properties is tuned to correspond to the  $k$ -vectors of applied electric, optical or acoustic fields. For a given wavelength, the size, geometry, and distribution of domains give rise to a qualitatively new kind of response specified by the symmetry of the multidomain system. In *domain-average-engineered* samples of ferroic crystals, the specimen is subdivided into a very large number of domains, representing  $\mu$  domain states where  $\mu$  is smaller than the theoretically allowed maximum number, and forming a regular or irregular pattern. Its response to external fields is roughly described by tensorial properties averaged over all of the domain states involved. The effective symmetry of the domain-average-engineered system is given by a point group  $H$  and we show how it can be determined. As an example, all groups  $H$  are specified for domain-average-engineered samples which can arise in a material undergoing the phase transition with symmetry change from  $m\bar{3}m$  to  $3m$ .

Ferroic materials (and here we concentrate on non-magnetic materials, i.e. on ferroelectrics, ferroelastics, and higher-order ferroics) play an essential role in a number of technical applications. In some of them, dynamic domain processes are essential (e.g. thin-film memories, electron emitters) while in others the static distribution domains in the sample play the crucial role. In this contribution we concentrate on the latter case and wish to specify a clear distinction between two kinds of such static multidomain system.

We have in mind materials undergoing a structural phase transition from the parent phase of point group  $G$  into the ferroic phase of symmetry  $F \subset G$  (such a material is referred to

as belonging to the species  $G - F$ ). This leads necessarily to the possibility of a coexistence of  $\nu$  domain states [1];  $\nu = |G|/|F|$  where  $|A|$  is the order of the group  $A$ . Assuming that domain walls are of negligible thickness compared with the size of the domains, there are two different ways of specifying—and utilizing—properties of a multidomain sample with a *fixed* distribution of domains; we propose to refer to them as *domain geometry engineering* and *domain average engineering*, respectively. It is the purpose of this contribution to give their definitions and in particular to specify symmetry properties of domain-average-engineered multidomain samples.

First, we consider *domain geometry engineering*. Consider a multidomain sample for which the geometry of the spatial distribution of domains and therefore that of the tensorial material coefficients is specified. Macroscopic responses of such samples to external fields (forces) of defined frequency are determined by this distribution. If the applied fields are static, the response of a multidomain sample is primarily determined by the spatial distribution of tensorial properties (domains) and of the applied field, and codetermined by the boundary conditions along domain walls. (Only in cases of the simplest geometry of domains, namely a single system of parallel domain walls in the case of ferroelastic species, can the latter be eliminated.) As an example, consider a multidomain piezoelectrically active sample. The spatial distribution of strain is

$$\varepsilon_{jk}(\mathbf{r}) = d_{ijk}(\mathbf{r})E_i(\mathbf{r}) \quad (1a)$$

$$d_{ijk}(\mathbf{r}) = d_{ijk}^{(\alpha)} f^{(\alpha)}(\mathbf{r}) \quad (1b)$$

where  $d_{ijk}$  stands for the piezoelectric tensor, the factor  $f^{(\alpha)}(\mathbf{r}) = 0$  or  $1$ , and  $\alpha$  denotes the domain state:  $\alpha = 1, 2, \dots, \mu$  with  $\mu \leq \nu$ . Domain geometry engineering related to *dynamic external fields* is of particular interest. The  $k$ -vector of the applied fields defines the wavelength whose magnitude is chosen to be appropriately related to the size of domains and whose direction is correlated with the domain geometry. For a given wavelength, the size, geometry, and distribution of domains give rise to a qualitatively new kind of response specified by the symmetry of the multidomain system. In the example specified above, we expect the presence of new piezoelectric resonance frequencies. It was this case which was suggested by Newnham *et al* [2], offering new resonance modes of a two-domain sample. Recently, more involved multidomain piezoelectric systems were suggested and realized [3] in crystals of  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$ . Referred to as acoustic superlattices, they can be used to generate and detect ultrasonic waves with frequencies in the range up to several hundreds of MHz. Another example, which has received unusual attention, is quasi-phase-matched optical multipliers. When the conventional phase-matching condition ( $n_{2\omega} = n_{\omega}$ ) cannot be realized in a particular material because of unsuitable dispersion of refractive indices, often a quasi-phase-matched system can be constructed which offers a high integrated non-linear optical response leading to frequency doubling [4]. This requires that a periodic domain pattern be fabricated with a period twice the coherence length  $l_c$ . Such domain-shape-engineered systems are now widely used. An even more intricate geometry-engineered domain pattern has been designed [5] in which two geometrically different building blocks A, B, each containing two domains with antiparallel spontaneous polarizations, are arranged to form a Fibonacci sequence. This leads to the possibility of second-harmonic light generation simultaneously for several optical frequencies.

While domain-geometry-engineered systems have been repeatedly realized and theoretically analysed, the alternative approach to studying and utilizing multidomain ferroic samples with static chaotic distribution of domains has only recently become extremely attractive. By the term *domain average engineering* we mean a situation in which the ferroic sample is subdivided into a very large number of domains, representing  $\mu$  domain states where

$\mu < \nu$ , and forming a regular or irregular pattern. Ideally, the domain size is expected to be much smaller than the wavelength of externally applied fields. Here, in contrast to the case for domain shape engineering, the spatial distribution of tensorial material coefficients is not defined or is irrelevant. The response of the sample can be to some approximation described by tensorial properties averaged over all domain states involved. Considering, as an example, again a sample consisting of piezoelectrically active domains, we expect for the multidomain sample

$$\bar{\varepsilon}_{jk} = \bar{d}_{ijk} \bar{E}_i \quad (2a)$$

$$\bar{d}_{ijk} = \frac{1}{V} \sum_{\alpha=1}^{\mu} d_{ijk}^{(\alpha)} V^{(\alpha)} \quad \mu < \nu. \quad (2b)$$

Both equations (1), (2) can be easily generalized for tensors of higher order.

Recently, a case of this character was considered [6–8] to allow discussion of piezoelectric properties of PZN-PT single crystals poled along one of the  $\{001\}$  directions. Assuming that the material went through the phase transition from  $G = m\bar{3}m$  to  $F = 3m$ , poling along  $[100]$  supports the coexistence of four domain states with spontaneous polarization along the directions  $[111]$ ,  $[1\bar{1}1]$ ,  $[11\bar{1}]$ , and  $[1\bar{1}\bar{1}]$ , with equal probability. In this statement, it is assumed that the domain wall orientation (i.e. mechanical compatibility) aspects can be neglected. In fact, in samples of ferroelastic crystals, strictly speaking, only one set of mechanically permissible parallel domain walls is allowed [9] while in real samples walls of various orientations coexist connected with additional elastic strains, paid for by increased elastic energy [10].

We now discuss the symmetry of *domain-average-engineered* samples in which the volumes of the domain states represented are identical, i.e.  $V(\alpha) = V/\mu$ . Such situations can be achieved by cooling samples through their phase transition temperatures under properly oriented stresses, electric fields or combinations of these. We introduce a classification of domain-average-engineered ferroic samples and determine their average point symmetries. This average symmetry is taken to be the symmetry of the subset of domain states contained in the multidomain ferroic sample.

Consider the phase transition from  $G$  to  $F$ . The symmetry analysis is based on the coset decomposition of the point group  $G$  with respect to its subgroup  $F$ , i.e.

$$G = F + g_2 F + g_3 F + \dots + g_\nu F$$

where the elements  $g_i$  are the coset representatives of the decomposition and  $g_1 = 1$ . We denote the  $\nu$  domain states which may arise at the transition as  $S_1, S_2, \dots, S_\nu$ . The symmetry groups  $F_i$  of the domain states and the relative orientations of the domain states and their polarizations  $P_i$  are all determined by the coset representatives, i.e.  $F_1 = F$ ,  $F_i = g_i F_1 g_i^{-1}$ ,  $S_i = g_i S_1$ , and  $P_i = g_i P_1$ ,  $i = 2, 3, \dots, \nu$ . The closure of the group  $G$  under multiplication implies a permutation of the cosets of the coset decomposition and in turn a permutation of the domain states  $S_i$  under elements  $g$  of  $G$ . The action of an element  $g$  of  $G$  on  $S_i$  is defined as  $g S_i = g g_i S_1 = g_j f S_1 = g_j S_1 = S_j$ , where  $f$  is an element of  $F$ , and the domain state  $S_i$  is transformed by the element  $g$  into the domain state  $S_j$ . The action of an element  $g$  of  $G$  on a subset of domains is denoted by  $g\{S_1, S_2, \dots, S_\mu\} = \{g S_1, g S_2, \dots, g S_\mu\}$ .

Two subsets of domains  $\{S_1, S_2, \dots, S_\mu\}$  and  $\{S'_1, S'_2, \dots, S'_\mu\}$  are said to belong to the same class of subsets of domains if there exists an element  $g$  of  $G$  such that  $g\{S_1, S_2, \dots, S_\mu\} = \{g S_1, g S_2, \dots, g S_\mu\} = \{S'_1, S'_2, \dots, S'_\mu\}$ . The symmetry group  $H$  of a subset of domains  $\{S_1, S_2, \dots, S_\mu\}$  is defined as the group of all elements  $g$  of  $G$  which leave the set invariant, i.e.  $g\{S_1, S_2, \dots, S_\mu\} = \{S_1, S_2, \dots, S_\mu\}$ . The group  $H$  represents the effective symmetry of the domain-average-engineered system consisting of the subset of domains  $\{S_1, S_2, \dots, S_\mu\}$ .

As an example, we consider the phase transition from  $G = m\bar{3}m$  to  $F = 3_{xyz}m\bar{x}y$ . Here  $\nu = 8$ . The indexing of the domain states, the corresponding coset representatives of the coset decomposition of  $G$  with respect to  $F$ , the symmetry groups, and the corresponding polarizations in each domain state are given in table 1.

**Table 1.** Domain state index, coset representative, symmetry group, and polarization.

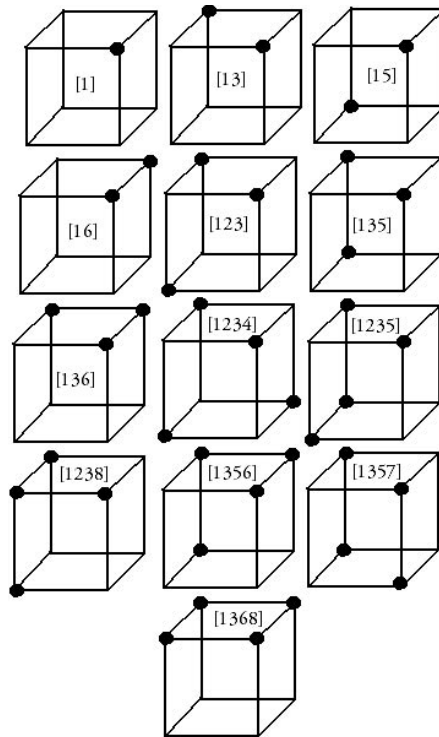
Index $i$	Coset representative $g_i$	$F_i = g_i F_1 g_i^{-1}$	$P_i = g_i P_1$
1	1	$3_{xyz}m\bar{x}y$	(A, A, A)
2	$2_x$	$3_{\bar{x}yz}m\bar{y}z$	(A, -A, -A)
3	$2_z$	$3_{xy\bar{z}}m\bar{x}y$	(-A, -A, A)
4	$2_y$	$3_{x\bar{y}z}m\bar{x}z$	(-A, A, -A)
5	$\bar{1}$	$3_{xyz}m\bar{x}y$	(-A, -A, -A)
6	$m_x$	$3_{\bar{x}yz}m\bar{y}z$	(-A, A, A)
7	$m_z$	$3_{xy\bar{z}}m\bar{x}y$	(A, A, -A)
8	$m_y$	$3_{x\bar{y}z}m\bar{x}z$	(A, -A, A)

All subsets of these domain states have been classified into classes as defined above. In table 2 we list one subset of domain states from each class. Each subset is denoted by listing, between square brackets, the indices of the domain states contained in that subset, the indices having been given in table 1, e.g. the subset  $\{S_1, S_3, S_5\}$  is denoted by [135]. In the right-hand column is the subgroup  $H$  of elements of  $G$  which leave the corresponding subset invariant. This table, in fact, represents the list of domain-average-engineered systems which can arise in a material undergoing a phase transition from  $m\bar{3}m$  to  $3m$ .

**Table 2.** Representative subsets of domain states for the species  $m\bar{3}m - 3m$  and the subgroups of  $m\bar{3}m$  which leave them invariant.

Representative subset	Symmetry $H$ of the subset
[1] or [2345678]	$3_{xyz}m\bar{x}y$
[13] or [245678]	$m_{xy}m\bar{x}y2_z$
[15] or [234678]	$\bar{3}_{xyz}m\bar{x}y$
[16] or [234578]	$m_xm\bar{y}z2_{yz}$
[123] or [45678]	$3_{xyz}m_{xz}$
[135] or [24678]	$m\bar{x}y$
[136] or [24578]	$m_{xy}$
[1234]	$\bar{4}3m$
[1235]	$m\bar{x}z$
[1238]	$3_{x\bar{y}z}m\bar{x}z$
[1356]	$2_{\bar{x}z}$
[1357]	$m_{xy}m\bar{x}y m_z$
[1368]	$4_z m_x m_{xy}$

In figure 1, for each subset listed in table 2, we schematically represent the array of domain states and their polarizations associated with the domain states of each subset. Each domain state is denoted by a heavy dot at a corner of the cube. This represents a polarization from the centre of the cube to that corner—that polarization given in table 1 associated with the corresponding domain state. Subfigure [1] denotes the single-domain state with polarization



**Figure 1.** Graphical representation of the subsets of domain states whose symmetries are specified in table 1. Points at the cube vertices represent spontaneous polarization vectors; the origin is in the centre of the cube. The numbering is that of the indices of the domains and polarizations given in table 1.

in the  $[111]$  direction. The figure denoted by  $[1368]$ , e.g., denotes a multidomain sample in which the following polarization vector directions are equally represented:  $[111]$ ,  $[\bar{1}\bar{1}1]$ ,  $[1\bar{1}1]$ , and  $[\bar{1}11]$ . The corresponding symmetry groups of all these multidomain systems are listed, as already pointed out, in the right-hand-side column of table 2.

Taking into account the distribution of polarization vectors and corresponding strain tensors, one can determine which external forces should be applied in order to obtain any of the domain-average-engineered systems listed in table 1. The trivial example is the system  $[1]$  produced by the electric field  $E$  along  $[111]$ . The system  $[1368]$ , discussed above (see references [6–8]) will be produced by the field along  $[001]$  while the system  $[16]$  requires the application of the field along  $[011]$ . The combination  $[15]$  requires the application of a uniaxial stress along  $[111]$  while the system  $[13]$  calls for the application of both an electric field along  $[001]$  and a uniaxial stress along  $[\bar{1}10]$ .

It is understood that in this symmetry approach we leave behind problems of coercive fields and stresses as well as, as already mentioned, problems of domain coexistence connected with their mechanical compatibility. It seems obvious that domain average engineering can successfully lead to the formation of crystalline systems with new desired properties, in particular in crystals where the domain size is small.

Each of the methods of domain engineering specified above can open a new vista of materials research possibilities in the area of ferroic materials and lead to multidomain assemblies with new desired properties.

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