Appendix B

Tensor Representation of Crystals

B.1 Tensor Notation

Many of the physical properties that we study in nature are oftentimes reduced to simple, linear relationships. For example, the conductivity within a material is usually written as:

$$j = \sigma E \tag{B.1}$$

where "j" is the current density, σ is the conductivity, and "E" is the electric field. However, for a complete analysis of real materials in three-dimensions, these simple, one-dimensional representations are inadequate. Many of the properties in nature (the electro-optic effect, piezoelectricity, ferroelectricity, index of refraction, conductivity, etc.) require a full, three-dimensional representation of the response of materials to external forces and fields. The requires a tensorial representation of the physical properties of crystals [79]. Going back to the case of conductivity, an accurate representation of this property is given by:

$$\begin{bmatrix} j_1 \\ j_2 \\ j_3 \end{bmatrix} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} \tag{B.2}$$

where $\sigma_{ab} \equiv$ conductivity in the "a" direction of a material from a field in the "b" direction. Further, the matricies can be represented by:

$$j_i = \sum_{h=1}^{3} \sigma_{ih} E_h \rightarrow j_i = \sigma_{ih} E_h \tag{B.3}$$

This is the Einstein Summation Notation for a second-rank tensor and will be used throughout

the rest of this thesis. Taking this one step further, representing piezoelectricity in a crystal requires a third-rank tensor. As was mentioned in Section 2.2.2, the direct piezoelectric effect occurs when a stress is applied to the crystal and an electric field results. The converse piezoelectric effect occurs when an electric field is applied to the crystal and a strain results. This effect is represented by:

$$P_i = d_{ijk}\sigma_{jk} \tag{B.4}$$

where P is the polarization of the crystal, d is the piezoelectric coefficient of the crystal, and σ is the stress applied to the crystal. The polarization of the crystal is given by P_1, P_2, and P_3 in the x-, y-, and z-directions respectively, and there is a corresponding 3x3 σ-tensor associated with each polarization. As a result, this gives the third-rank tensor:

$$P_1 = \begin{bmatrix} d_{111}\sigma_{11} & d_{112}\sigma_{12} & d_{113}\sigma_{13} \\ d_{121}\sigma_{21} & d_{122}\sigma_{22} & d_{123}\sigma_{23} \\ d_{131}\sigma_{31} & d_{132}\sigma_{32} & d_{133}\sigma_{33} \end{bmatrix} \tag{B.5}$$

$$P_2 = \begin{bmatrix} d_{211}\sigma_{11} & d_{212}\sigma_{12} & d_{213}\sigma_{13} \\ d_{221}\sigma_{21} & d_{222}\sigma_{22} & d_{223}\sigma_{23} \\ d_{231}\sigma_{31} & d_{232}\sigma_{32} & d_{233}\sigma_{33} \end{bmatrix} \tag{B.6}$$

$$P_3 = \begin{bmatrix} d_{311}\sigma_{11} & d_{312}\sigma_{12} & d_{313}\sigma_{13} \\ d_{321}\sigma_{21} & d_{322}\sigma_{22} & d_{323}\sigma_{23} \\ d_{331}\sigma_{31} & d_{332}\sigma_{32} & d_{333}\sigma_{33} \end{bmatrix} \tag{B.7}$$

which are the 1st, 2nd, and 3rd layers of the tensor.

This approach utilizes the full tensorial representation of crystal properties; however, in many cases, there are a significant number of these elements that are either equivalent or are zero. To that end, we can reduce the number of elements in the previous matricies as follows. Because of the fact that, for a given polarization these tensors are symmetric, we can reduce the number of elements in each layer of the tensor by half. For each layer of the previous tensor we have:

$$\begin{bmatrix} d_{11} & d_{12} & d_{13} \\ d_{21} & d_{22} & d_{23} \\ d_{31} & d_{32} & d_{33} \end{bmatrix} \rightarrow \begin{bmatrix} d_{11} & \frac{1}{2}d_{16} & \frac{1}{2}d_{15} \\ & d_{12} & \frac{1}{2}d_{14} \\ & & d_{13} \end{bmatrix} \tag{B.8}$$

and using this conversion from tensor notation to matrix notation, we can also reduce the stress matrix:

$$\begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix} \rightarrow \begin{bmatrix} \sigma_1 & \sigma_6 & \sigma_5 \\ \sigma_6 & \sigma_2 & \sigma_4 \\ \sigma_5 & \sigma_4 & \sigma_3 \end{bmatrix} \tag{B.9}$$

At this point, we can represent the polarization of the crystal in the x-direction as: $P_1 = d_{11}\sigma_1 + d_{12}\sigma_2 + d_{13}\sigma_3 + d_{14}\sigma_4 + d_{15}\sigma_5 + d_{16}\sigma_6$. Using this notation and putting each layer of the tensor in a row, we can more concisely write the equations for the direct (B.10) and converse (B.11) piezoelectric effects as:

	σ_1	σ_2	σ_3	σ_4	σ_5	σ_6
P_1	d_{11}	d_{12}	d_{13}	d_{14}	d_{15}	d_{16}
P_2	d_{21}	d_{22}	d_{23}	d_{24}	d_{25}	d_{26}
P_3	d_{31}	d_{32}	d_{33}	d_{34}	d_{35}	d_{36}

(B.10)

	ϵ_1	ϵ_2	ϵ_3	ϵ_4	ϵ_5	ϵ_6
E_1	d_{11}	d_{12}	d_{13}	d_{14}	d_{15}	d_{16}
E_2	d_{21}	d_{22}	d_{23}	d_{24}	d_{25}	d_{26}
E_3	d_{31}	d_{32}	d_{33}	d_{34}	d_{35}	d_{36}

(B.11)

This is the traditional way that these tensors are represented. At this point, we can take advantage of Newmann's Principle which states that:

> "The symmetry elements of any physical property of a crystal must include the symmetry elements of the crystal."

Using this fact we can reduce the number of non-zero elements in the matrix. As an example, we take the case of the ABO_3 perovskites discussed in Section 2.2.2. For clarity, we will temporarily revert back to the expanded tensor form to illustrate the process.

$$\begin{bmatrix} d_{111} & d_{112} & d_{113} \\ & d_{122} & d_{123} \\ & & d_{133} \end{bmatrix} \begin{bmatrix} d_{211} & d_{212} & d_{213} \\ & d_{222} & d_{223} \\ & & d_{233} \end{bmatrix} \begin{bmatrix} d_{311} & d_{312} & d_{313} \\ & d_{322} & d_{323} \\ & & d_{333} \end{bmatrix} \tag{B.12}$$

In the tetragonal 4mm symmetry group, we have: 4 mirror planes and a 4-fold rotation axis. For the x mirror plane:

$$1 \rightarrow 1, 2 \rightarrow -2, 3 \rightarrow 3$$

which means that any element with an odd number of "2's" will not be invariant under the transformation. Therefore, these elements are necessarily zero. Similarly, for the y mirror plane:

$$1 \rightarrow -1, 2 \rightarrow 2, 3 \rightarrow 3$$

which means that any element with an odd number of "1's" will not be invariant under the transformation. For the xy mirror plane

$$1 \rightarrow 2, 2 \rightarrow 1, 3 \rightarrow 3$$

which means $d_{311} = d_{322}$ and $d_{113} = d_{223}$. The resulting tensor has the form:

$$\begin{bmatrix} 0 & 0 & d_{113} \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & d_{223} \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} d_{311} & 0 & 0 \\ 0 & d_{322} & 0 \\ 0 & 0 & d_{333} \end{bmatrix} \tag{B.13}$$

which when returned to the reduced form gives:

$$\begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix} \tag{B.14}$$

B.2 Orientation Effects of Crystal Properties

The reduced form of a crystal's tensor gives the materials direct and shear components of a response to an applied stimulus. The process can be taken one step further. By choosing a reference orientation (here we will pick the $\hat{z}$ or d_{33} direction), the response of a crystal can be calculated and mapped out for every possible orientation of applied stimulus. To map out the piezoresponse of a 4mm crystal, the angles between each of the non-zero piezoresponse coefficients and the applied electric field can be calculated in polar coordinates [103]. By summing these five terms together

we obtain the equation:

$$d_{33}^{*} = (d_{31} + d_{15})cos\theta sin^2\theta + d_{33}cos^3\theta \tag{B.15}$$

This is plotted for barium titanate in Figure B.1.

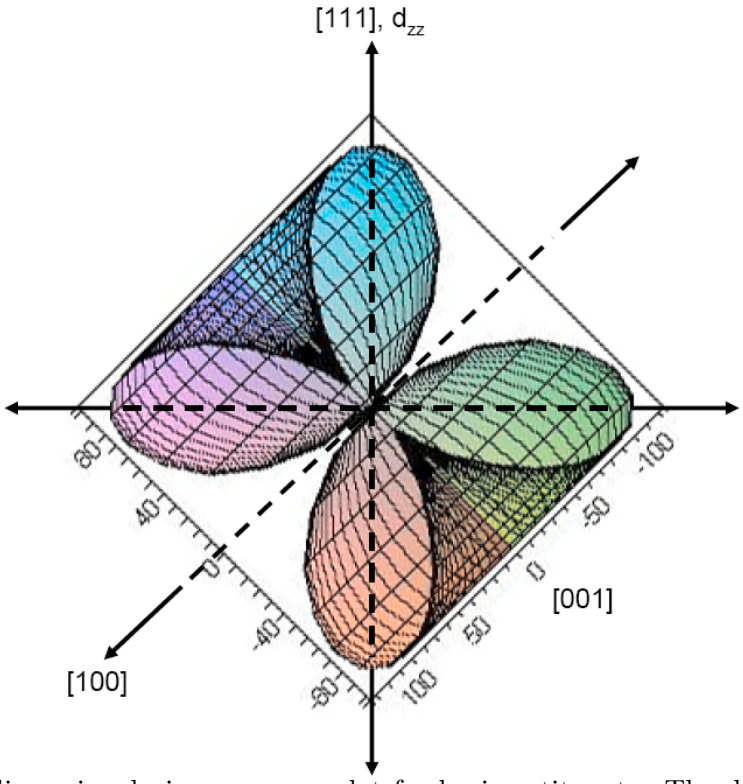

Figure B.1. Three-dimensional piezoresponse plot for barium titanate. The different orientations are labeled on their respective axes, and intensity of piezoresponse is represented as distance from the origin. The scale on the axes is pm/V.