3.014 Materials Laboratory
Nov. 16th – Nov. 22st, 2005

**Lab Week 3 – Module $\alpha_3$**

# Crystal Polymorphs

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**MATERIALS:**
Lead Titanate

**METHOD:**
Temperature Resolved X-ray Diffraction

## OBJECTIVES

- ✓ Understand diffraction and diffractometers
- ✓ Understand thermal expansion coefficients
- ✓ Understand the structure of perovskites
- ✓ Review why perovskites structures can lead to piezo-electric behavior

## OPEN QUESTIONS

1) Why does a diffraction pattern change with temperature?

2) Why the diffraction pattern contains information about the materials volume?

2) What is the difference between a 002 and a 200 peak in a tetragonal cell?

**BACKGROUND**

**X-ray Diffraction from Crystalline Materials**

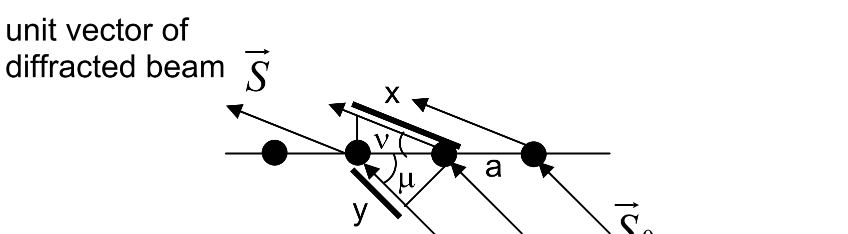
As discussed in 3.012, a periodic arrangement of atoms will give rise to constructive interference of scattered radiation having a wavelength $\lambda$ comparable to the periodicity *d* when Bragg's law is satisfied:

$$n\lambda = 2d\sin\theta$$

where n is an integer and $\theta$ is the angle of incidence.

Bragg's law tells us necessary conditions for diffraction, but provides no information regarding **peak intensities**. To use x-ray diffraction as a tool for materials identification, we must understand the relationship between structure/chemistry and the intensity of diffracted x-rays.

Recall from 3.012 class that for a 1d array of atoms, the condition for constructive interference can be determined as follows:




$$x = a\cos\nu$$
$$y = a\cos\mu$$

The total path difference: $x - y = a\cos\nu - a\cos\mu = h\lambda$

$$\left(\vec{S} - \vec{S_0}\right)\cdot\vec{a} = h\lambda$$

Defining $\vec{s} = \dfrac{\left(\vec{S} - \vec{S_0}\right)}{\lambda}$, the condition for 1d constructive interference becomes:

$$\vec{s}\cdot\vec{a} = h$$

For 3 dimensions, we have: $\vec{s}\cdot\vec{a}=h$

$$\vec{s}\cdot\vec{b}=k$$

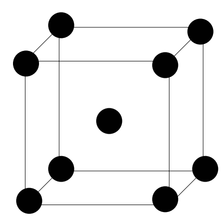
$$\vec{s}\cdot\vec{c}=l$$

where h, k and l are the Miller indices of the scattering plane.

For a single unit cell having M atoms, the scattered amplitude is proportional to the **structure factor**, defined as:

$$F(s)=\sum_{n=1}^{M} f_n \exp\left[2\pi i\vec{s}\cdot\vec{r_n}\right]$$

where $\vec{r_n}$ is the atomic position vector for the nth atom in the unit cell:

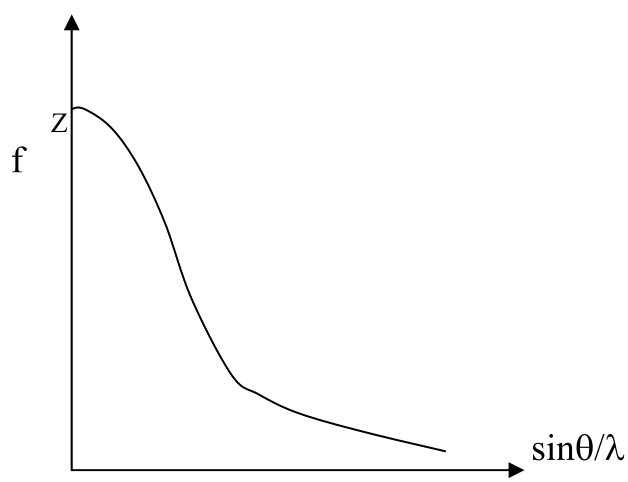


$$\vec{r}_n = x_n\vec{a}+y_n\vec{b}+z_n\vec{c}$$

where ($x_n$, $y_n$, $z_n$) are the atomic position coordinates.

Example: for a BCC structure, there are 2 atoms/cell at (0,0,0) and (1/2,1/2,1/2).

The parmater $f_n$ is the **atomic scattering factor**, proportional to the atomic number *Z* of the nth atom. Hence, atoms of high *Z* scatter more strongly than light elements. The atomic scattering factor is a function of θ and λ.



Substituting $\vec{r}_n$ into the structure factor:

$$F(s) = \sum_{n=1}^{M} f_n \exp\left[2\pi i\vec{s}\cdot(x_n\vec{a} + y_n\vec{b} + z_n\vec{c})\right]$$

$$F_{hkl} = \sum_{n=1}^{M} f_n \exp\left[2\pi i(hx_n + ky_n + lz_n)\right]$$

For a BCC crystal:

$$F_{hkl} = f\exp\left[2\pi i(0)\right] + f\exp\left[2\pi i\left(\frac{h}{2}+\frac{k}{2}+\frac{l}{2}\right)\right] = f + f\exp\left[\pi i(h+k+l)\right]$$

$F_{hkl} = 2f$ h+k+l even

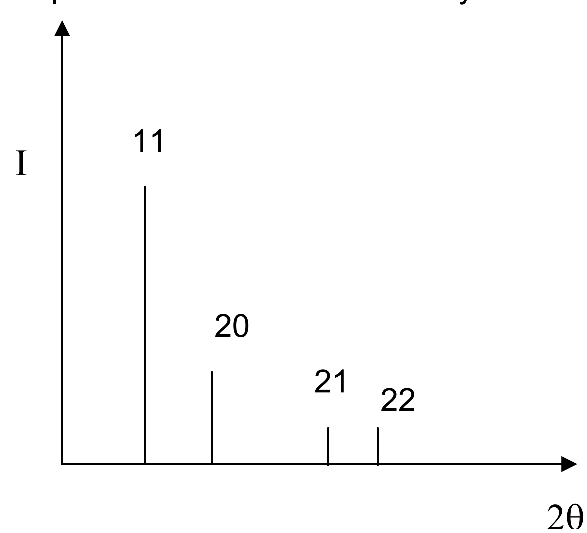
$F_{hkl} = 0$ h+k+l odd

The scattered intensity is related to the structure factor:

$I_{coh} \propto FF^* = \left|F_{hkl}\right|^2 = 4f^2$ h+k+l even

$I_{coh} = 0$ h+k+l odd

Note that the total coherent intensity will be a sum of the contributions of all unit cells in the crystal. For a BCC crystal, reflections from planes with Miller indices where h+k+l is an odd integer will be absent from the diffraction pattern, while reflections from (110), (200), (211), etc. will be present with reduced intensity as h+k+l increases.



In our hypothetical case above, constructive interference occurs only at the exact Bragg angle and the I vs. 2θ curve exhibits sharp lines of intensity. In reality, diffraction peaks exhibit finite breadth, due both to instrumental and material effects. An important source of line broadening in polycrystalline materials is finite crystal size. In crystals of finite dimensions, there is incomplete destructive interference of waves scattered from angles slightly deviating from the Bragg angle. If we define the angular width of a peak as:

$$B = \frac{1}{2}\left(2\theta_1 - 2\theta_2\right)$$

then the average crystal size can be estimated from the Scherrer formula as:

$$t = \frac{0.9\lambda}{B\cos\theta_B}$$

Interplanar spacings can be calculated for different *hkl* planes from geometric relationships for a given crystal system:

Cubic: $d^2 = \dfrac{h^2 + k^2 + l^2}{a^2}$

Orthorhombic: $d^2 = \dfrac{h^2}{a^2} + \dfrac{k^2}{b^2} + \dfrac{l^2}{c^2}$

Tetragonal: $d^2 = \dfrac{h^2 + k^2}{a^2} + \dfrac{l^2}{c^2}$

Hexagonal: $d^2 = \dfrac{4}{3}\left(\dfrac{h^2 + hk + k^2}{a^2}\right) + \dfrac{l^2}{c^2}$

Monoclinic: $d^2 = \dfrac{1}{\sin^2\beta}\left(\dfrac{h^2}{a^2} + \dfrac{k^2\sin^2\beta}{b^2} + \dfrac{l^2}{c^2} - \dfrac{2hl\cos\beta}{ac}\right)$

**Lead Titanate:**

Lead Titanate ($PbTiO_3$) is a ceramic material of the family of perorvskites. [1] These are ternary compounds of the general formula $ABO_3$ where the two cations (A and B) differ considerably in size. The unit cell of perovskites is illustrated in figure 1 for the case of $BaTiO_3$. It should be noticed that no sub-lattice (e.g. the lattice formed by Ti atoms) is closed packed, but the sub-lattice formed by the Barium and the Oxygen atoms (fig. 1a) is an FCC lattice. In the center of the unit cell there is a Ti atom. One of the driving forces that leads to the formation of this unique arrangement is the formation of 6 octaheadral bonds between the Ti atom and 6 oxygen atoms surrounding it. These bonds are not purely ionic, in fact they have been known to be partially covalent.[2] The

A B

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**Figure 1** Schematic drawing of $BaTiO_3$ unit cell (A) and crystallographic arrangement (B). This is a good example of a perovskite. Lead titanate is also a perovskite.
Note how every Ba and Ti atom. (Picture taken from reference [1])

Perovskites are among the many crystals that can exist in different crystalline forms. Two crystals of identical composition but of different crystallographic nature are called polymorphs.[3] There are two general families of transformations that can drive the transformation between one polymorph to another.

The first type of transformation is the **displacive** one, in which no element changes its first coordination shell. These transformations are the least structurally demanding. The second type of transformation is called **reconstructive**, it requires a change in the coordination (i.e. the bonding) of at least one component of the crystal. (See fig.2)

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**Figure 2** Schematic representation of possible transformations between polymorphic forms of a generic crystal. The transformations between (a) and (b) or (c) are displacive, while the transformation between (a) and (d) is reconstructive. (Picture taken from reference [3])

Lead Titanate, like many other perovskites, has two main polymorphic forms. The first, stable at lower temperatures, is a tetragonal cell in which the titanium atom is not in the exact center of the cubic cell defined by the oxygen and lead atoms (see figure 3). The second, stable at higher temperatures, has a cubic cell in which the Titanium atom is exactly in the center of the cubic cell.

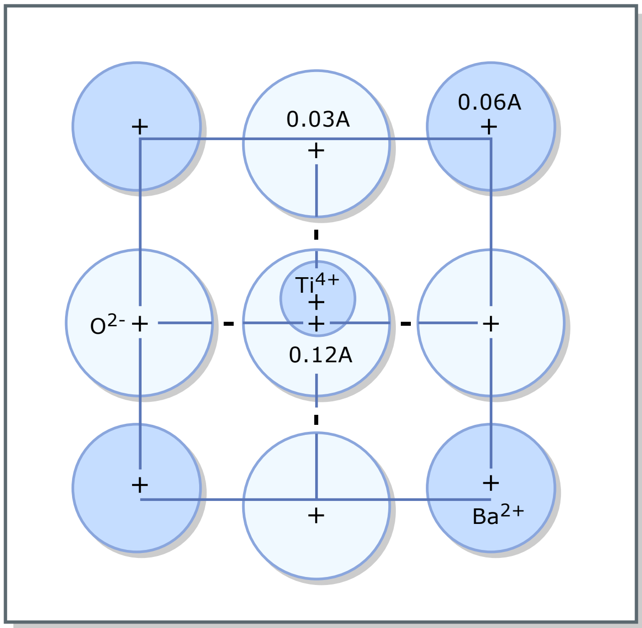


Figure by MIT OCW.

**Figure 3.** Schematic representation of the ion position in a tetragonal $BaTiO_3$ cell. The Ti ion is elevated 0.12 Å respect to the center of the cell.

In the case of perovskites polymorphic transformation are responsible for changes in a large number of properties. First of all, while the cubic cell is centrosymmetric the tetragonal is not. The cubic unit cell has no net dipole; on the other end (as illustrated in figure 3) in the tetragonal cell the center of gravity for the negative ions is in the center of the cubic cell while the center of gravity for the positive is close to the titanium atom. Hence, the tetragonal cell has a finite dipole. The presence of this dipole is responsible for the ferroelectric and piezoelectric properties of lead titanate. The transition temperature where piezoelectricity is lost (that is the temperature where the tetragonal polymorph converts into the cubic one) is called the Curie temperature. In the case of lead titanate that temperature is $490^0$C.[4]

Lead titanate has another very interesting and unique property, it posses a negative thermal expansion coefficient. That is, it contract as temperature increases from $0^0$C to $490^0$C. Typically materials expand as temperature increases. This is due to the anharmonicity of the bond energy as illustrated in figure 4. This leads to a positive expansion coefficient.

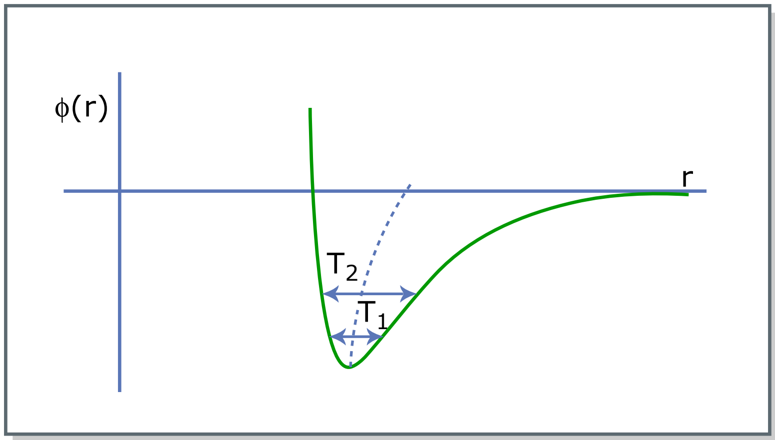


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**Figure 4** Leonard-Jones energy plot for a typical bond. Due to the anharmonic of shape of the curve as the temperature increase the equilibrium distance for the bond increases as indicated by the dotted line. Figure adapter from reference [5]

In the case of lead titanate the cell contracts with temperature (figure 5). This probably happens because as temperature raises there is more space for the central titanium atom to find a more central position.

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**Figure 5** Temperature dependence of lattice parameters for $PbTiO_3$ derived from temperature X-ray diffraction studies in reference [4].

## Conclusions

In this laboratory we will use diffraction to determine the Curie temperature and the expansion coefficient of Lead Titanate.

## References

[1] Perovskite Structure extract for Y.-M. Chang, D. P. Birnie, W. D. Kingery, *Physical Ceramics*, John Wiley & Sons: New York, 1997, pp. 38, 41
[2] D. Vanderbilt, "First-principles based modelling of ferroelectrics", Current Opinion In Solid State & Materials Science 2,701-705, 1997
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[4] J. Chen, X. Xing, R. Yu, and G. Liu "Thermal Expansion Properties of Lanthanum-Substituted Lead Titanate Ceramics", J. Am. Ceram. Soc., 88, 1356–1358, 2005.
[5] G D. Barrera, J. A.O. Bruno, T. H. K. Barron, and N L Allan "Negative thermal expansion" J. Phys.: Condens. Matter, 17, R217–R252, 2005

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