Analysis of Phase Change of BaTiO$_3$ Ferroelectric Material from a Tetragonal Crystal Structure (BaTiO$_3$) to Orthorhombic (Ba$_4$Ti$_{13}$O$_{30}$) to Monoclinic (Ba$_6$Ti$_{17}$O$_{40}$)

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Abstract. BaTiO$_3$ ferroelectric material is very interesting to study, because BaTiO$_3$ ferroelectric material has spontaneous polarization properties when given an electric field from outside the system. This spontaneous polarization property of BaTiO$_3$ ferroelectric material can be applied as a light sensor (ferroelectric properties), temperature sensors (pyroelectric properties), pressure sensors (piezoelectric properties). Has successfully analyzed the phase change of BaTiO$_3$ ferroelectric material from a tetragonal crystal structure (BaTiO$_3$) to orthorhombic (Ba$_4$Ti$_{13}$O$_{30}$) to monoclinic (Ba$_6$Ti$_{17}$O$_{40}$) using the Cramer-Cohen method. This shows that the Cramer-Cohen method is very accurate in calculating the lattice constants of the crystal structure of ferroelectric materials and other materials.

1. Introduction

BaTiO$_3$ ferroelectric material is very interesting to study, because BaTiO$_3$ ferroelectric material has spontaneous polarization properties when given an electric field from outside the system. This spontaneous polarization property of BaTiO$_3$ ferroelectric material can be applied as a light sensor (ferroelectric properties), temperature sensors (pyroelectric properties), pressure sensors (piezoelectric properties)[1 - 6].

Previous researchers have succeeded in developing analysis of lattice parameters and phase change in crystal structures using the Cohen method, including: Cohen's method revisited [7], Determination of lattice parameters with the aid of a computer [8], Crystallographically engineered BaTiO$_3$ single crystals for high-performance piezoelectrics [9], Confirmation of MB-type monoclinic phase in PMNTO: A powder neutron diffraction study [10], Precision Lattice Constant Determination [11], The Crystal Structure of the Monoclinic Form of n-Hexadecanol [12], A simple method for the determination of lattice parameters from powder X-ray diffraction data [13], A Modification of the Cohen Procedure for Computing Precision Lattice Constants from Powder Data [14], Android based XRD data analysis software design for cube crystal structure with analytic and cohen methods [15].

The purpose of this study was to Analysis of Phase Change of BaTiO$_3$ Ferroelectric Material from a Tetragonal Crystal Structure (BaTiO$_3$) to Orthorhombic (Ba$_4$Ti$_{13}$O$_{30}$) to Monoclinic (Ba$_6$Ti$_{17}$O$_{40}$) using Cramer-Cohen Method.

2. Method

There are two steps in this program, including: (i) the first step is to implement the Cramer-Cohen method as an algorithm in the excel program, (ii) The second step is to test the performance of the excel program in performing calculations by comparing the results with the actual lattice parameter.
data. The International Center for Diffraction Data (ICDD) was referred to obtain sample lattice parameter data.

The algorithm used in this excel program is the Cramer-Cohen method. When the program runs, the program will ask the user to type in the code of crystal structure. After that, the program will ask the user to type in the number of rows of x-ray diffraction data they have along with the diffraction angles and Miller indexes one by one.

The “MDETERM” command from the Excel program facility can solve the value of the Determinant of the Cramer-Cohen Method of any matrix of order n x n and its application to obtain the lattice parameter values of the crystal structure: (i) Tetragonal (order 3 x 3) for BaTiO$_3$, (ii) Orthorhombic (order 4 x 4) for Ba$_4$Ti$_{13}$O$_{30}$, (iii) Monoclinic (order 5 x 5) for Ba$_6$Ti$_{17}$O$_{40}$.

3. Result and Discussions

3.1. Bragg’s law

Bragg's law is the main principle used in the x-ray diffraction method. Two x-rays hitting some parallel lattice planes must interfere each other. Constructive interference happens when the difference path length of two rays is equal to multiple of positive integers of the x-ray wavelength used. Bragg's law is mathematically formulated in equation (1)(1),

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

where $d$ is the distance between the parallel lattice planes [16]. For analysing two rays in two neighboured parallel planes, substitute $m = 1$, so the equation (2)(2) is obtained.

$$\frac{1}{d} = \frac{2\sin \theta}{\lambda}$$

3.2. XRD data analysis for tetragonal crystal structure

A tetragonal crystal structure is a crystal structure with the unit cell dimensions are equal on two axis only, but all the axis of the unit cell remain perpendicular to each other. Therefore, a tetragonal crystal has 2 output lattice parameter which is usually denoted as '$a$' and '$b$'. The distance between the lattice planes in the tetragonal crystal is shown in equation (3) kesalahan! Sumber referensi tidak ditemukan.,

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2 + c^2}$$

with $h$, $k$, and $l$ are unit cell dimensions on x, y and z axis, respectively [17]. Equation kesalahan! Sumber referensi tidak ditemukan. is then compared with equation (2), so equation (4) kesalahan! Sumber referensi tidak ditemukan., (5) are obtained.

$$\frac{h^2 + k^2 + l^2}{a^2 + c^2} = \frac{4\sin^2 \theta}{\lambda^2}$$

$$\sin^2 \theta - \frac{\lambda^2}{4}(\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}) = 0$$

By replacing zero in the equation above with error during measurement that is expressed as $F \sin^2 2\theta$, equation (6), (7), (8) are obtained.

$$\sin^2 \theta - \frac{\lambda^2}{4a^2}(h^2 + k^2) - \frac{\lambda^2}{4c^2}(l^2) = F \sin^2 2\theta$$

$$\sin^2 \theta = \frac{\lambda^2}{4a^2}(h^2 + k^2) + \frac{\lambda^2}{4c^2}(l^2) + F \sin^2 2\theta$$

$$\sin^2 \theta = C\alpha + B\gamma + A\delta$$
with $C = \frac{\lambda^2}{4a^2}, B = \frac{\lambda^2}{4c^2}, A = \frac{F}{10}, \alpha = h^2 + k^2, \gamma = l^2$, and $\delta = 10\sin^2 2\theta$. Transform equation (6), (7), (8) into a linear matrix equation (order 3 x 3) shown in equation (9).

Solution of the equation (9) can be found using the Cramer method for tetragonal crystal structure.

### 3.3. XRD data analysis for orthorhombic and monoclinic crystal structure

The same steps as the Transform equation (6), (7), (8) into a linear matrix equation (order 4 x 4) for orthorhombic shown in equation (10):

$$
\begin{align*}
\Sigma \tau \sin^2 \theta \\
\Sigma \phi \sin^2 \theta \\
\Sigma \chi \sin^2 \theta \\
\Sigma \psi \sin^2 \theta \\
\end{align*}
\begin{bmatrix}
\Sigma \alpha \sin^2 \theta \\
\Sigma \gamma \sin^2 \theta \\
\Sigma \delta \sin^2 \theta \\
\Sigma \epsilon \sin^2 \theta \\
\end{bmatrix} =
\begin{bmatrix}
\Sigma \alpha^2 \\
\Sigma \gamma^2 \\
\Sigma \delta^2 \\
\end{bmatrix}
\begin{bmatrix}
\Sigma \alpha \gamma \\
\Sigma \alpha \delta \\
\Sigma \gamma \delta \\
\end{bmatrix}
\begin{bmatrix}
C \\
B \\
A \\
\end{bmatrix}
$$

(9)

and into a linear matrix equation (order 5 x 5) for monoclinic shown in equation (11).

Solution of the equation (10) can be found using the Cramer method for orthorhombic crystal structure, and solution of the equation (11) can be found using the Cramer method for monoclinic crystal structure.

### 3.4. Algorithm of the excel program

The algorithm used in this excel program is the Cramer-Cohen method. When the program runs, the program will ask the user to type in the code of crystal structure. After that, the program will ask the user to type in the number of rows of x-ray diffraction data they have along with the diffraction angles and miller indexes one by one.

The “MDETERM” command from the Excel program facility can solve the value of the Determinant of the Cramer-Cohan Method of any matrix of order n x n and its application to obtain the lattice parameter values of the crystal structure: (i) Tetragonal (order 3 x 3) for BaTiO$_3$, (ii) Orthorhombic (order 4 x 4) for Ba$_4$Ti$_{13}$O$_{30}$, (iii) Monoclinic (order 5 x 5) for Ba$_6$Ti$_{17}$O$_{40}$.

### 3.5. Evaluation of the program’s performance

The program is tested by analysing the diffraction angle and the miller index to determine the lattice parameter of the sample. The literature data of lattice parameter of these samples were obtained from the International Center of Diffraction Data (ICDD) [18, 19, 20].
Table 1. Results of lattice parameter measured by Cramer Cohen methods.

| Molecule   | Structure       | Lattice constants (Å) | Cramer-Cohen Analyze | Lietrature (ICDD) |
|------------|-----------------|-----------------------|----------------------|-------------------|
| BaTiO$_3$  | Tetragonal      | a: 3.994, b: 3.994, c: 4.038 | a: 3.986, b: 3.986, c: 4.029 | Lietrature (ICDD) [18] |
| Ba$_4$Ti$_{13}$O$_{30}$ | Orthorhombic | 14.059, 17.065, 9.867 | 13.939, 16.913, 9.782 | Lietrature (ICDD) [19] |
| Ba$_6$Ti$_{17}$O$_{40}$ | Monoclinic     | 16.930, 17.103, 9.891 | 19.245, 17.385, 10.065 | Lietrature (ICDD) [20] |

Based on table 1 shows that the result of calculating the lattice constants using the Cramer-Cohen method is close to the literature data, this means that the Cramer-Cohen method is very accurate in calculating the lattice constants of the crystal structure of ferroelectric materials and other materials.

4. Conclusion
Has successfully analyzed the phase change of BaTiO$_3$ ferroelectric material from a tetragonal crystal structure (BaTiO$_3$) to orthorhombic (Ba$_4$Ti$_{13}$O$_{30}$) to monoclinic (Ba$_6$Ti$_{17}$O$_{40}$) using the Cramer-Cohen method. This shows that the Cramer-Cohen method is very accurate in calculating the lattice constants of the crystal structure of ferroelectric materials and other materials.

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