Calculating of crystalline size, strain and Degree of crystallinity of the compound \((\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\sigma})\) by different method

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ABSTRACT: In this study the compound \(\text{Hg Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\sigma}\) was fabricated by RF-sputtering technique on the quartz substrate with a temperature of \(100^\circ\text{C}\). The study of the diffraction of X-ray on The nature of the crystallizing of \(\text{Hg Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\sigma}\) one Crystal system tetragonal structures. The Full width at half maximum (FWHM) was calculated by the Orange Pro program by using X-RAY data. The crystalline size and stress were calculated by Scherrer Williamson-Hall Halder-Wagner and size-strain plot methods Where the average of crystalline size and stress (54.5 nm 5.8 X \(10^{-3}\)) respectively. and Degree of crystallinity was equal to \((33.6\%)\)

Keywords: \(\text{Hg Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\sigma}\) Williamson-Hall Halder-Wagner size-strain plot.

1. Introduction

\(\text{Hg Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\sigma}\) is a compound of Perovskite which are considered a ceramic material they are characterized by abundance. Depinding on the atoms / molecules used in the structure [1]. Perovskite Can contain an impressive array of exciting features interesting Resistance Amonet giant adopted on the transport spin (spintronics) and catalytic properties. It is an exciting Alberowskaat playground for physicists chemists and materials scientists [2]. Its applications extend to energy production environmental containment and waste contained in radioactive waste containers. Radioactive waste encapsulation communications resonant insulating materials [3]. Perovskite and its molecular formula SrTiO3. Perovskite was first discovered in 1839 in the Ural Mountains in Russia and named this name after the Russian metallurgist Lev Percevsky. It is a substance that has a special crystal structure. The Perovskite composition possesses a general quantitative chemical formula \((\text{ABX}_3)\) where \((A)\) and \((B)\) are positive ions (Cations) and the negative ion (Anion). Positive ions \((A)\) and \((B)\) may be It possesses a variety of charges and the original mineral Perovskite composition is \((\text{CaTiO}_3)\) and it has a positive ion \((A)\) represented by calcium (Ca) and has two valence while the positive ion \((B)\) represented by titanium (Ti) has a trivalent valence. The traditional Perovskite network view includes the small positive ion \((B)\) within the octahedral reticular structure of oxygen while the large positive ion \((A)\) is surrounded by symmetry number (12) oxygen atoms [4]. \(\text{HgBa}_{2n+1}\text{Ca}_n\text{Cu}_{2n+2+\delta}\) \((n = 1 2 3 \ldots)\) and the number of \(\text{CuO}_2\) layers per cell unit is an interesting subject for study. The ceramic system \((\text{HBCO})\) consists of (mercury oxide barium oxide calcium oxide and copper oxide) where there are three important systems for materials based on mercury where the first member of this system family is when \((n = 1)\) and the compound is \((1201 \text{Hg})\). but the second member of this family is when \((n = 2)\) and the compound is \((1212 \text{Hg})\) - and the third member in this system is \((1223 \text{Hg})\) in which \((n = 3)\). All phases of the super compound also have a tetragonal crystalline system and perovskite layers. [5] Complex mercury-based copper oxides (cuprates) have
multiple crystalline structures Layers where there are four different types of layers including (CuO2) which differ in their number (from 1 to n per unit cell). These layers (CuO2) can be separated from one another by means of layers (Ca) and it is clear (n-1) that the layers represent each unit cell in general. According to current physical theory the (CuO2) layers are responsible for the superconductivity of these compounds. The (CuO2 and (Ca) layers together form the conductive mass or active block [6]. It is worth noting that there are two other phases in the HBCCO system which are the two phases (1234) and (1245) which consist of four layers and five layers of copper oxide respectively and these two phases have the advantage that their critical temperature is lower than the critical temperature of the phase (2223) and these two phases are often used in thin films by the method of thermal evaporation where they can be prepared as developing laminar crystalline structures and the thickness of the cell unit [7].

2. Experimental technique:

The synthesis of Hg Ba$_2$Ca$_2$Cu$_3$O$_{8+\sigma}$ compounds have been prepared by Thin film method. We have used appropriate weights of pure powders materials 99% of HgO CaO BaO and CuO as starting materials. As the mixing and grinding operations took place in two stages:

The first stage: was carried out using a manual mortar where the process of grinding and mixing took place for a period of an hour.

The second stage: It was by a whirlpool electric mixer using that steel balls for a period of (2 hr) the aim of this mechanism was to obtain accurate powders as well as to obtain the best uniformity.

The mixture was dried in an oven at 150˚C. In the second step the mixture was pressed into disc shaped pellets (50 mm) in diameter and (6-7 mm) thick using hydraulic press under pressure of (7.5 ton/cm$^2$) . The disk was then used to prepare the sample by RF-sputtering technique on the quartz substrate with a temperature of 100˚C Where the power was 100 watts and a deposition time of 3 hours. Then it is put in farness for calcinations at 800˚C during 24hr. With a heating rate of (10 C / min) and under normal atmospheric pressure in order to obtain coherent samples in order to ensure an optimal spread process between the atoms then the samples were cooled to room temperature and at a cooling rate (10 C / min). The structure of the prepared sample was obtained by using x-ray diffract meter. By using the Shimadzu X-ray Inspector with specifications (Cu ka Voltage: 40Kv Current: 30mA Wave Length: 1.5406Å) and within the range (10 o-80o) with a step size of 0.02 o and at room temperature. Then the results of X-ray for the sample are compared by using the match program to ensure that the required compound has been obtained.

3. discussion

(XRD) of the compound Hg Ba$_2$Ca$_2$Cu$_3$O$_{8+\sigma}$ in the range of 10$^\circ$ < 2θ < 80$^\circ$ shows peaks at (22.81° 25.72° 28.74° 32.45° 33.45° 34.26° 34.97° 35.66° 44.078° 49.08° and 55.25°). Corresponding to the planes (100) (012) (013) (014) (111) (006) (112) (116) (202) and (212) respectively. Figure 1 drawing by using the Match! Program showing two phases:

The first phase (Hg Ba$_2$Ca$_2$Cu$_3$O$_{8+\sigma}$) source COD (Crystallography Open Database) Link to orig. entry 1008863. Where the proportion of congruence with this phase was equal to (98.5 %) and Crystal system tetragonal.

The second phase (Hg$_{0.87}$Ba$_2$CaCu$_2$:O$_{6.64}$) source COD (Crystallography Open Database) Link to orig. entry 9009224. Where the proportion of congruence with this phase was equal to (1.5 %) and Crystal system tetragonal.
In order for the Scherrer method to be applied in a healthy way it is very important to calculate the exact value of $\beta_{hkl}$ accurately [8]. This instrumental broadening can be corrected using the following relation

$$\beta_{hkl} = [(\beta_{hkl})^2_m - (\beta_{hkl})^2_i]^{1/2}$$  \hspace{1cm} (1)

Where $\beta_{hkl}$ is the corrected broadening, $(\beta_{hkl})_m$ measured broadening and $(\beta_{hkl})_i$ is the instrumental broadening. The average crystalline size was calculated using Debye-Scherer's formula:

$$D = \frac{k\lambda}{\beta_{hkl} \cos \theta}$$  \hspace{1cm} (2)

Where $D$ is a crystal size, $k$ is a coefficient = 0.9; $\lambda$ X-ray wavelength = 1.540598 Å; $\theta$ is the Bragg angle. Rearranging the above equation we can write

$$\cos \theta = \frac{k\lambda}{D \cdot \beta_{hkl}}$$  \hspace{1cm} (3)

The Fig.2 shown a graph of $1/\beta_{hkl}$ vs $\cos \theta$ for compound HgBa$_2$Ca$_2$Cu$_3$O$_{6+\sigma}$. the Scherrer crystalline size can be calculated from the slope which is found as 54.3 nm. [9]
Williamson–Hall method to find crystalline size and stress. Physical line broadening of the peak of XRD occurs due to the size. So the total broadening due to strain and size in a particular peak having the hkl value can be expressed as

$$\beta_{hkl} = (\beta_{hkl})_{\text{size}} + (\beta_{hkl})_{\text{strain}}$$

(4)

The strain induced peak broadening can be expressed as

$$\beta_{hkl}_{\text{strain}} = 4\varepsilon \tan \theta$$

(5)

The $\beta_{hkl}$ is (FWHM) and the $\varepsilon$ represents the strain. [11, 10]

$$\beta_{hkl} = \frac{k\lambda}{D \cos \theta} + 4 \varepsilon \tan(\theta)$$

(6)

When rearranging equation (6) we get

$$\beta_{hkl}\cos(\theta) = \frac{k\lambda}{D} + 4 \varepsilon \sin(\theta)$$

(7)

The equation above is a straight line equation now plotting a graph of $4 \sin(\theta)$ vs $\beta_{hkl}\cos(\theta)$ for compound Hg Ba$_2$Ca$_2$Cu$_3$O$_{8+\sigma}$ as shown in Fig.3 where $4 \sin(\theta)$ Represents the X axis and $\beta_{hkl}\cos(\theta)$ Represents the Y axis. The slope of this straight line gives the value of the intrinsic strain which is found as 0.0059. The intercept gives the average crystalline size of the compound HgBa$_2$Ca$_2$Cu$_3$O$_{8+\sigma}$ which is found as 53.3 nm. [12]

![Graph](image)

**Fig. 3.** Williamson–Hall (W–H) plot for compound Hg Ba$_2$Ca$_2$Cu$_3$O$_{8+\sigma}$. The SSP method measurement is carried out using the equation [13]. As following

$$[d_{hkl} \cdot \beta_{hkl} \cdot \cos(\theta)]^2 = \frac{k\lambda}{D} \cdot [d_{hkl}^2 \cdot \beta_{hkl} \cdot \cos(\theta)] + \frac{\varepsilon^2}{4}$$

(8)

Plotting a graph of $[d_{hkl}^2 \cdot \beta_{hkl} \cdot \cos(\theta)]$ vs $[d_{hkl} \cdot \beta_{hkl} \cdot \cos(\theta)]^2$ from the above equation is a straight line equation as shown in Fig.4. The slope of this straight line provides the value of average crystalline size which is found as 55.4 nm while the intercept is give the strain of the compound HgBa$_2$Ca$_2$Cu$_3$O$_{8+\sigma}$ which is found as 0.0056. [15, 14]
This method has the advantage that the peaks at low and mid angle ranges are given more weight where the overlap of the diffracting peaks is much less. Now according to the Halder-Wagner process the relation between the crystalline size and the lattice strain is given by [16]

\[
\left( \frac{\beta_{hkl}}{d_{hkl}} \right)^2 = \frac{1}{D} \left( \frac{\beta_{hkl}}{d_{hkl}} \right)^2 + (\varepsilon/2)^2
\]  

(9)

The equation above is a straight line equation now plotting a graph of \( \left( \frac{\beta_{hkl}}{d_{hkl}} \right)^2 \) vs \( \left( \frac{\beta_{hkl}}{d_{hkl}} \right)^2 \) as shown in Fig. 5 where \( \left( \frac{\beta_{hkl}}{d_{hkl}} \right)^2 \) represents the X axis and \( \left( \frac{\beta_{hkl}}{d_{hkl}} \right)^2 \) represents the Y axis. The value of average crystalline size which is found as 54.9 nm was given from the slope. The intercept is give the strain of the compound HgBa\(_2\)Ca\(_2\)Cu\(_3\)O\(_{6+\sigma}\) which are found as 0.006. [18, 17]

**Fig. 5.** Halder-Wagner plot for compound Hg Ba\(_2\)Ca\(_2\)Cu\(_3\)O\(_{6+\sigma}\).

Degree of crystallinity can be evaluated that used x-ray crystallography and many materials such as glass ceramics and some polymers can be prepared so that a mixture of crystalline and amorphous regions can be produced. In such cases crystallinity is generally noted as a percentage of crystalline material volume. Nevertheless the degree of structural perfection can differ even within materials which are fully crystalline. Crystallinity can be measured using x-ray crystallography based on the following equation:

\[
\text{Degree of crystallinity (DOC)} = \frac{\text{Diffraction peaks}}{\text{Diffraction peaks + Amorphous phases}} \times 100\%
\]  

(10)
Table 1 shows. That all the results of the crystalline volume calculation were almost too close to various methods. Table 2 also shows that the degree of crystallization of the compound was in relation to 30.66%.

### Table 1 Geometrical parameters of compound Hg Ba$_2$Ca$_2$Cu$_3$O$_{8+\sigma}$ using different Models.

| Method                        | D (nm) | Strain $\varepsilon$ |
|-------------------------------|--------|----------------------|
| Scherrer Method              | 54.5   |                      |
| Williamson-Hall Method       | 53.3   | 0.0059               |
| Size-Strain Plot Method      | 55.4   | 0.0056               |
| Halder Wagner Method         | 54.9   | 0.006                |

Table 2 Represents a calculation the Degree of crystallinity.

| Profile area                  | Counts |
|-------------------------------|--------|
| Total area                    | 83818  |
| Diffraction peaks             | 25695  |
| Background                    | 58123  |
| Amorphous phases              | 58123  |
| **Degree of crystallinity (DOC)** | **30.66%** |

### 4. Conclusions

We have successfully prepared the compound of Perovskite Hg Ba$_2$Ca$_2$Cu$_3$O$_{8+\sigma}$ was prepared by the pulsed laser deposition method (PLD) on the quartz substrate. Scherrer's method considers only the effect of crystal size on peak broadening of the XRD. However it does not say anything about the microstructures of the lattice Williamson-Hall system simply considering peak broadening as a function of diffraction angle (2θ) that is expected to being a combination of size induced broadening and strain induced broadening. While (SSP) method deals with it the peak profiles analysis. The (H-W) method is built on assuming peak broadening is a symmetrical Voigt function [20].

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