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## Preparation and Study the Structure of Pure and Impure Barium Titanate with $Zr^{4+}$ Ion

**Abstract:** In this research, pure and impure barium titanate with  $Zr^{4+}$  ion with two molar ratios  $x = (5, 10) \%$  have been synthesized by solid-state reaction technique. The powders calculations at two temperatures ( $950^\circ\text{C}$  and  $1400^\circ\text{C}$ ). An XRD technique was used in order to study the crystal structure of pure and impure barium titanate, which confirmed the formation of the tetragonal phase of  $BaTiO_3$ , then calculate the lattice parameters of pure and impure barium titanate, the addition of zirconium ion  $Zr^{4+}$  lead to increases lattice parameters.

**Keywords:** Barium titanate, Ferroelectric, Piezoelectric, X-ray diffraction.

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### 1. Introduction

Barium titanate has been used in wide application such as capacitors and multilayer capacitors (MICS) [1,2], PTC thermistors, piezoelectric transducers, variety of electro-optic devices and integral capacitors in printed circuit boards (PCB).  $BaTiO_3$  is also a semiconducting and non-linear optical material when doped with other elements, and therefore can be used for resistors with a positive temperature coefficient of resistivity [3].

### 2. Barium titanate Phase transformations

Barium titanate  $BaTiO_3$  has a perovskite structure with formula  $A^{2+}B^{4+}O_3$ , where A is the large cation which is located at eight corners, B is the small cation located in the body center and oxygen atoms in the face center [4] as shown in Figure 1.

It has a wide application because of its ferroelectric and piezoelectric properties. Barium titanate has four-phase transition depend in temperature (cubic, tetragonal, orthorhombic and rhombohedra) [6]. Cubic phase, this phase occur above Curie temperature ( $120^\circ\text{C}$ ) and have a spontaneous random polarization. In this temperature range, ( $120^\circ\text{C}$ )  $Ti^{4+}$  ion lies in the center of the structure. Tetragonal phase, its ferroelectric and stable phase between ( $5^\circ\text{C} < T < 120^\circ\text{C}$ ). Orthorhombic phase, this phase occurs at temperature ( $5^\circ\text{C}$ ) which is stable between ( $-90^\circ\text{C} < T < 5^\circ\text{C}$ ). Rhombohedra phase, this phase occurs at temperature below ( $-90^\circ\text{C}$ ). As shown in Figure 2 [7].

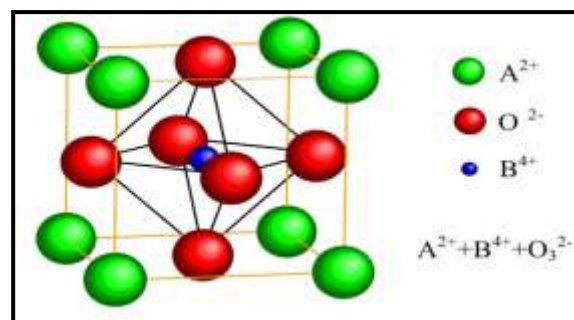


Figure 1: Barium Titanate Structure [5]

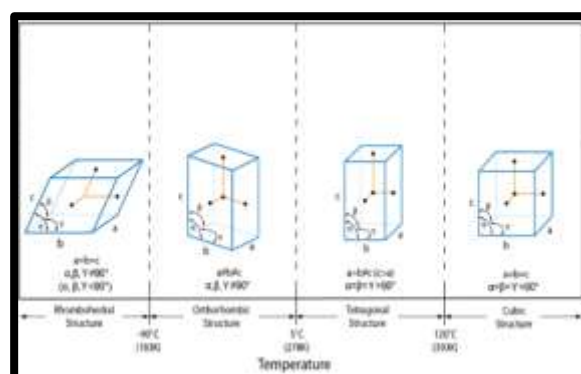


Figure 2: Phase transformations of pure  $BaTiO_3$  vs. temperature [7].

### 3. Experimental

Pure and impure barium titanate was synthesized via solid-state reaction, pure barium titanate ( $BaTiO_3$ )(BT) was synthesized by mixing raw materials barium carbonate  $BaCO_3$  with purity (98%) and titanium dioxide  $TiO_2$  with purity (98%) of molar ratio [1:1], add ethanol alcohol with purity (98%) in order to obtain good

homogeneous, all mixture were mixed in ball milling and grinding for 24h, drying the mixture at 80°C for 15h to get rid of alcohol, calcinations the powder at two temperature (950°C and 1400°C) for four hours.

Impure barium titanate (BZT) as the same steps as above, impure barium titanate synthesized by mixing raw materials BaCO<sub>3</sub> and TiO<sub>2</sub> and additive of (5%, 10%) of zirconium oxide ZrO<sub>2</sub> to prepare (BZT) (BaTi<sub>1-x</sub>Zr<sub>x</sub>O<sub>3</sub>) by substitution of

Ti<sup>4+</sup> ion instead Zr<sup>4+</sup> ion. The crystal structure was studied to all powders were synthesized (BT) and (BZT) using X-ray diffraction with Cu target and wavelength 1.54 Å, operating at (40Kv), (30mA) and the samples were scanned from (20-60°2θ) with scan speed (8deg/min). Figure 3 shows the flow chart of synthesized pure and impure barium titanate.

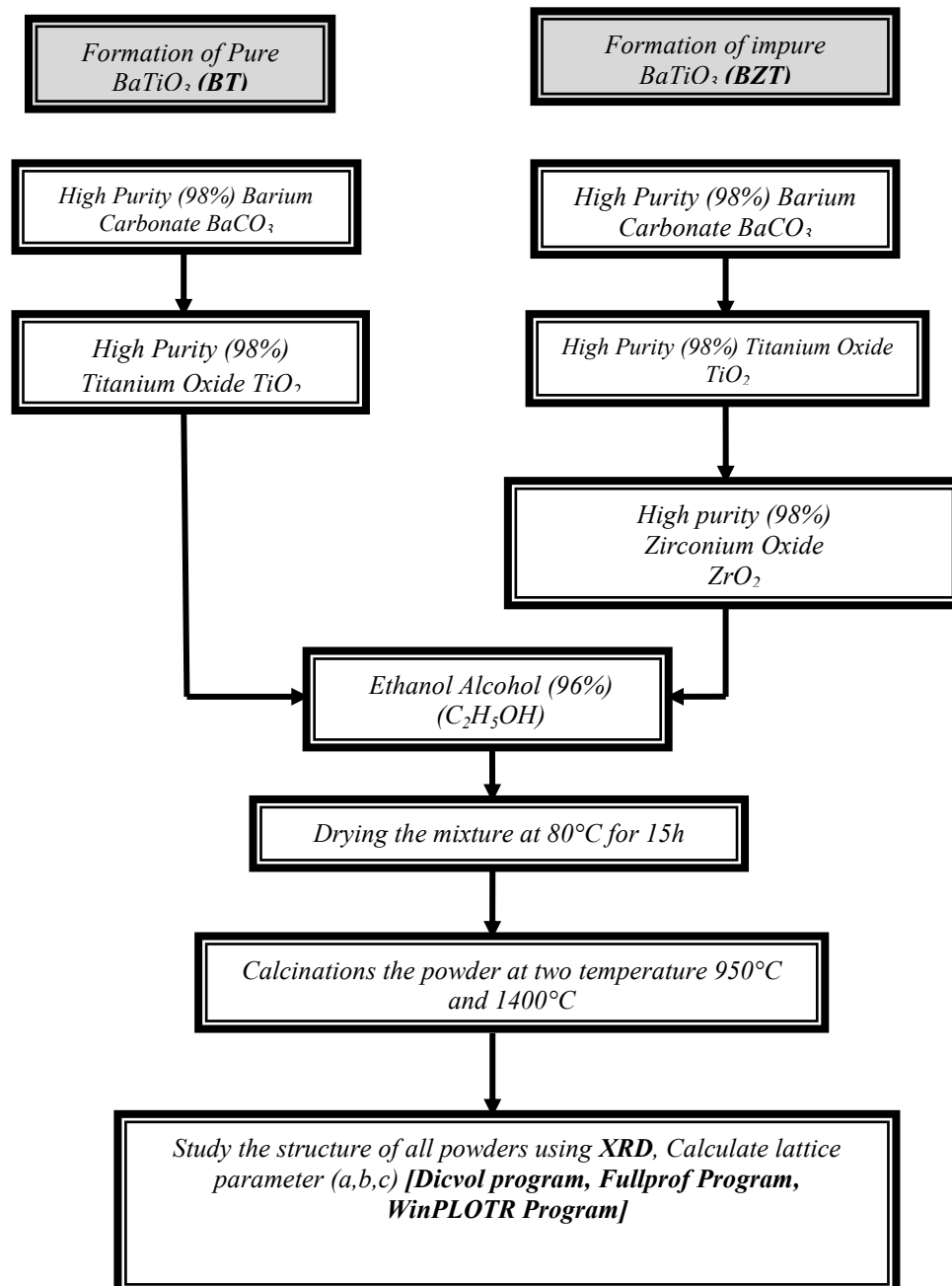


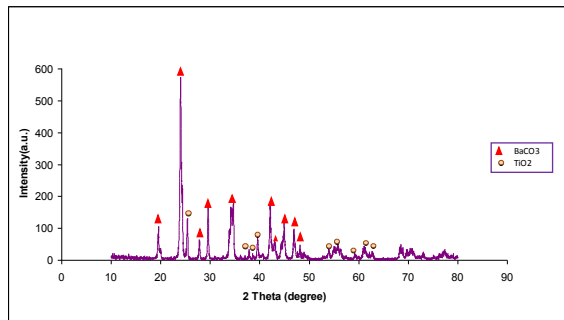
Figure 3: Flow Chart of synthesized pure (BT) and impure (BZT).

#### 4. Result and Discussion

##### I. X-ray diffraction of raw material

Fig. 4 refers to the XRD pattern of raw materials BaCO<sub>3</sub> and TiO<sub>2</sub> before calcinations this pattern

matched with the standard pattern of barium carbonate no. (00-005-0378) and standard of titanium dioxide TiO<sub>2</sub> no. (00-021-1272).



**Figure 4: XRD patterns for Barium Carbonate  $\text{BaCO}_3$  and Titanium oxide  $\text{TiO}_2$  before calcinations**

### II X-ray diffraction of pure $\text{BaTiO}_3$ (BT).

Figure 5 X-ray diffraction pattern confirmed the existence of the barium titanate with tetragonal phase (the pattern matched with the standard pattern JCPDS no 05-0626). At  $950^\circ\text{C}$  temperature, there was a low intensity of  $\text{TiO}_2$  (Titanium Dioxide) but there was no  $\text{BaCO}_3$  (Barium Carbonate). The symbol \* show the peaks for the ( $\text{TiO}_2$ ) titanium dioxide this means not the complete reaction of formation of barium titanate because of the present of another peak belong to  $\text{TiO}_2$  [8].

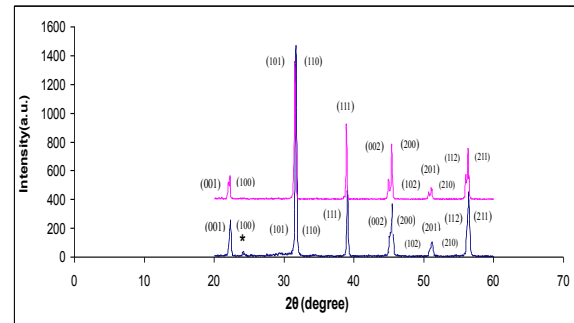
At ( $1400^\circ\text{C}$ ) temperature there was no residual material detected by XRD technique indicated to complete reaction, this reaction appears high resolution in  $2\theta$  position for peaks indicated to a good crystallinity and formation of pure barium titanate ( $\text{BaTiO}_3$ ). So it can be seen diffraction peaks at  $2\theta=44.950^\circ$ ,  $45.379^\circ$ ,  $50.704^\circ$ ,  $50.998^\circ$ ,  $51.096^\circ$ ,  $56.018^\circ$ ,  $56.293^\circ$ , are widened gradually and lastly split during an increase in the calcinations temperature. This phenomenon refers to the (tetragonal structure) of barium titanate ( $\text{BaTiO}_3$ ) phase was formed well with increases in calcinations temperature [9].

### III X-ray diffraction of impure barium titanate (BZT)

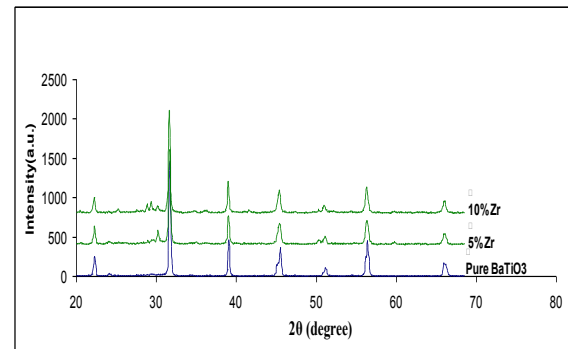
In this part additive zirconium oxide  $\text{ZrO}_2$  to the barium titanate with two molar ratios (5%, 10%) calcinations at two temperature ( $950^\circ\text{C}$  and  $1400^\circ\text{C}$ ) then study the structure of barium titanate using x-ray diffraction after this additive, the additives of  $\text{ZrO}_2$  to barium titanate lead to change from tetragonal phase to cubic phase at  $1400^\circ\text{C}$  and an increase in lattice parameters [10], this is a clear refers to the addition of Zr lead to disorder in the barium titanate structure[11].

X-ray technique show change in peak position as compared to pure barium titanate. So it can be seen that with ( $\text{Zr}^{4+}$ ) substitution in barium titanate, the ( $2\theta$ ) peaks shifted towards lower angle side refers to the increase in lattice parameter, as shown in Figures 6-9 This indicates

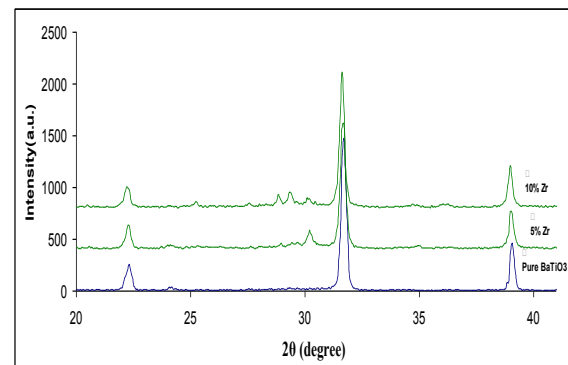
to substitute ( $\text{Zr}^{4+}$ ) ions instead of ( $\text{Ti}^{4+}$ ) ions on the (A) sites of the  $\text{BaTiO}_3$  lattice. This is because of the ionic radius of zirconium ion ( $\text{Zr}^{4+}$ ) ( $0.72 \text{ \AA}$ ) is Larger as compared to titanium ion ( $\text{Ti}^{4+}$ ) ( $0.60 \text{ \AA}$ ) [12].



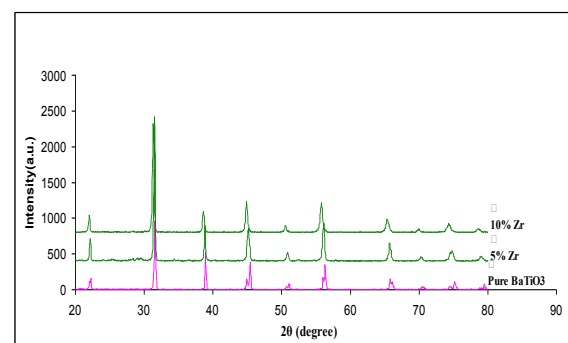
**Figure 5: XRD patterns for pure barium titanate (a) at  $950^\circ\text{C}$  and (b) at  $1400^\circ\text{C}$**



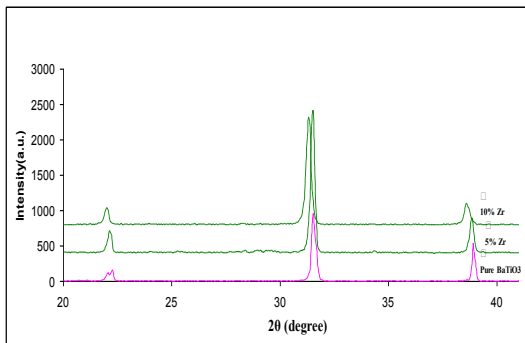
**Figure 6: XRD for  $\text{BaTiO}_3$  with additives  $\text{ZrO}_2$  (5%, 10%) at  $950^\circ\text{C}$ .**



**Figure 7: The shifted of the first three peaks of (BZT) at  $950^\circ\text{C}$ .**



**Figure 8: XRD for  $\text{BaTiO}_3$  with additives  $\text{ZrO}_2$  (5%, 10%) at  $1400^\circ\text{C}$**



**Figure 9: The shifted of the first three peaks of (BZT) at 1400°C**

#### IV. Lattice parameters

Calculation the lattice parameters using (Dicvol Program, Fullprof Program, WinPLOTR Program) for pure and impure barium titanate with two molar ratio  $x = (5, 10) \%$ , at two temperature 950°C and 1400°C. Table 1 and 2 show the lattice parameters of pure and impure barium titanate.

#### V. Lattice parameter of pure BaTiO<sub>3</sub> at 950°C and 1400°C.

Table 1 show lattice parameter of the tetragonal phase of pure (BT) calcinations at 950°C and 1400°C respectively.

**Table 1: Lattice parameter of Pure BaTiO<sub>3</sub> (BT)**

Calcinations Temp.	$a=b(\text{Å})$	$c(\text{Å})$
950°C	3.9912	4.0167
1400°C	3.9939	4.0300

#### VI. Lattice parameter of impure BaTiO<sub>3</sub> (BZT) at 950°C and 1400°C.

At 950°C for both ratios (5%, 10%) mol of additives of zirconium ion in barium titanate, x-ray analysis Figure 6 show the tetragonal phase of barium titanate, at 1400°C Zr ion lead to disorder in the barium titanate structure and lead to change from tetragonal phase to cubic phase and an increase in lattice parameters. As shown in Table 2.

**Table 2: Lattice parameter of impure BaTiO<sub>3</sub> (BZT)**

Calcinations Temp.	$a=b(\text{Å})$		$c(\text{Å})$	
	5%	10%	5%	10%
1400°C	4.0122	4.0304	4.0122	4.0304

#### Conclusion

In this study we observed pure barium titanate with tetragonal phase has been found at (1400°C) that means it formed at high temperature, the additives of ZrO<sub>2</sub> to barium titanate lead to change from tetragonal phase to cubic phase and increase in lattice parameters. Diffraction peaks

undergo shifted toward lower angle because of the doped of (Zr<sup>4+</sup>) ion (0.72 Å) which is smaller than (Ti<sup>4+</sup>) ion (0.60 Å) in the (A) sites of BaTiO<sub>3</sub> and this refers to increase in lattice parameters, calculation of lattice parameter appears matched with X-ray diffraction.

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