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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°C and 1400°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°C) and have a spontaneous random polarization. In this temperature range, (120°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°C) which is stable between ($-90^\circ\text{C} < T < 5^\circ\text{C}$). Rhombohedra phase, this phase occurs at a temperature below (-90°C). As shown in Figure 2 [7].

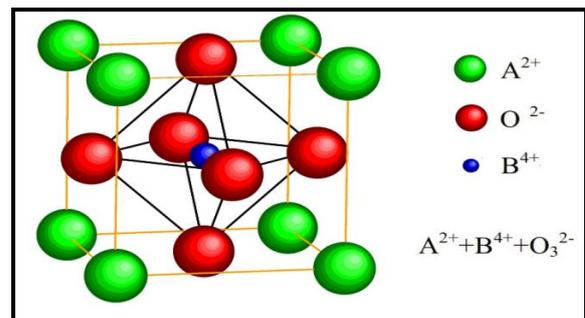


Figure 1: Barium Titanate Structure [5]

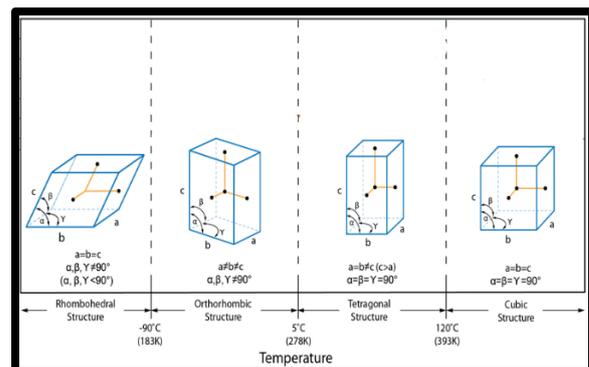


Figure 2: Phase transformations of pure $BaTiO_3$ vs. temperature [7].

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 BaCO₃ and TiO₂ and additive of (5%, 10%) of zirconium oxide ZrO₂ to prepare (BZT) (BaTi_{1-x}Zr_xO₃) by substitution of

Ti⁴⁺ ion instead Zr⁴⁺ 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.

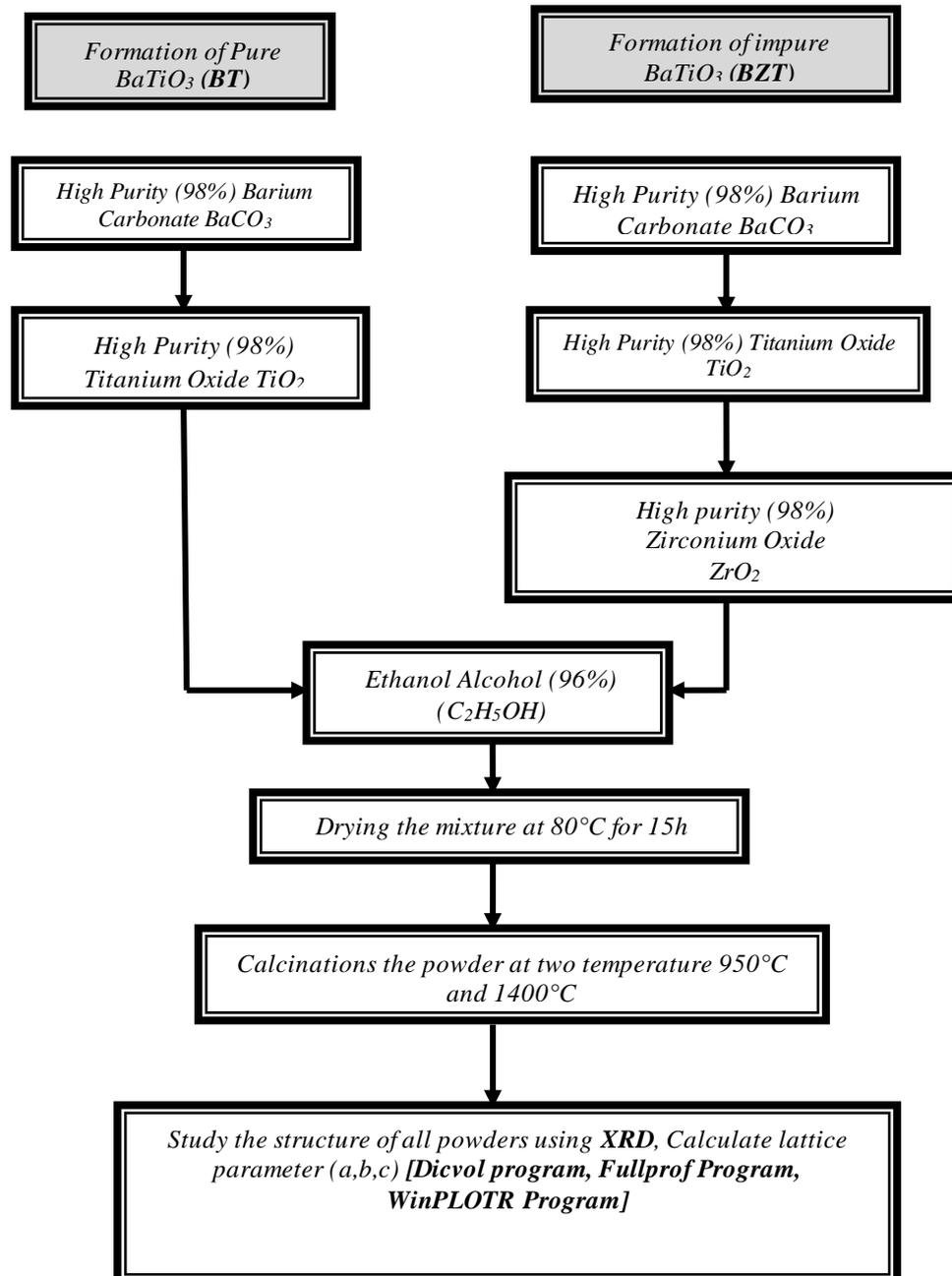


Figure 3: Flow Chart of synthesized pure (BT) and impure (BZT).

4. Result and Discussion

I. X-ray diffraction of raw material

Fig. 4 refers to the XRD pattern of raw materials BaCO₃ and TiO₂ before calcinations this pattern matched with the standard pattern of barium

carbonate no. (00-005-0378) and standard of titanium dioxide TiO₂ no. (00-021-1272).

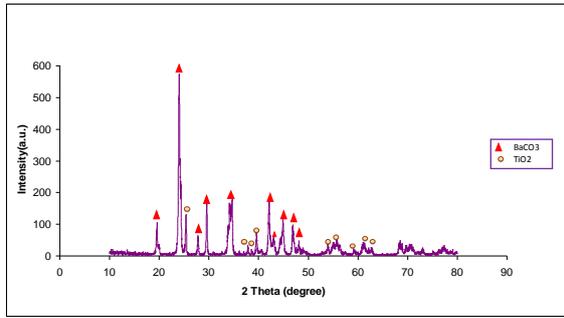


Figure 4: XRD patterns for Barium Carbonate BaCO₃ and Titanium oxide TiO₂ before calcinations

II X-ray diffraction of pure BaTiO₃ (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°C temperature, there was a low intensity of TiO₂ (Titanium Dioxide) but there was no BaCO₃ (Barium Carbonate). The symbol * show the peaks for the (TiO₂) titanium dioxide this means not the complete reaction of formation of barium titanate because of the present of another peak belong to TiO₂ [8].

At (1400°C) temperature there was no residual material detected by XRD technique indicated to complete reaction, this reaction appears high resolution in 2θ position for peaks indicated to a good crystallinity and formation of pure barium titanate (BaTiO₃). So it can be seen diffraction peaks at 2θ=44.950°, 45.379°, 50.704°, 50.998°, 51.096°, 56.018°, 56.293°, are widened gradually and lastly split during an increase in the calcinations temperature. This phenomenon refers to the (tetragonal structure) of barium titanate (BaTiO₃) 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 ZrO₂ to the barium titanate with two molar ratios (5%, 10%) calcinations at two temperature (950°C and 1400°C) then study the structure of barium titanate using x-ray diffraction after this additive, the additives of ZrO₂ to barium titanate lead to change from tetragonal phase to cubic phase at 1400°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 (Zr⁴⁺) substitution in barium titanate, the (2θ) peaks shifted towards lower angle side refers to the increase in lattice parameter, as shown in Figures 6-9 This indicates

to substitute (Zr⁴⁺) ions instead of (Ti⁴⁺) ions on the (A) sites of the BaTiO₃ lattice. This is because of the ionic radius of zirconium ion (Zr⁴⁺) (0.72 Å) is Larger as compared to titanium ion (Ti⁴⁺) (0.60 Å) [12].

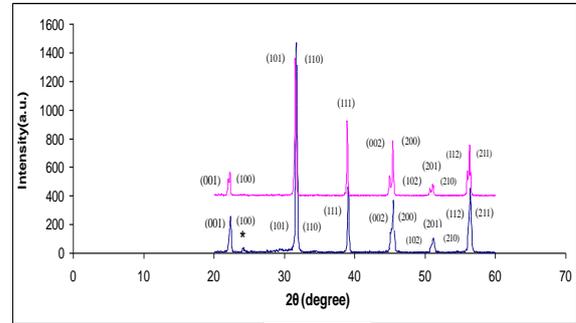


Figure 5: XRD patterns for pure barium titanate (a) at 950°C and (b) at 1400°C

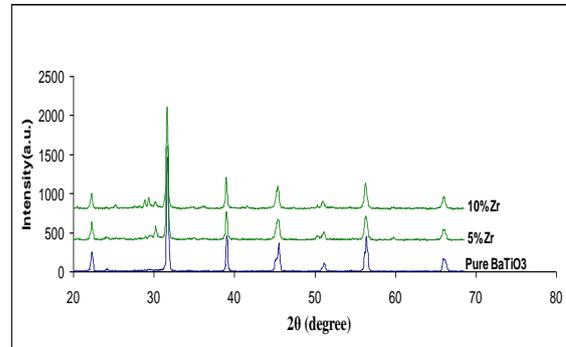


Figure 6: XRD for BaTiO₃ with additives ZrO₂ (5%, 10%) at 950°C.

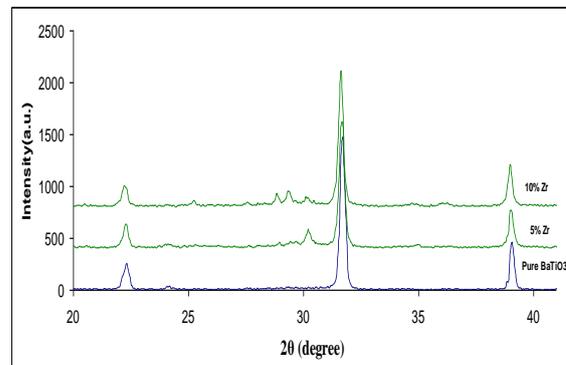


Figure 7: The shifted of the first three peaks of (BZT) at 950°C.

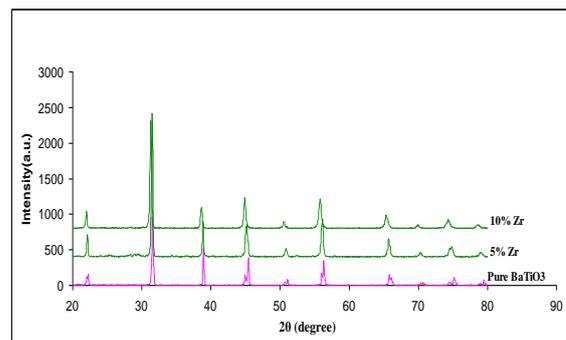


Figure 8: XRD for BaTiO₃ with additives ZrO₂ (5%, 10%) at 1400°C

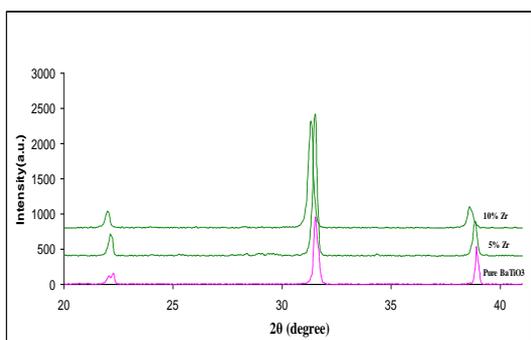


Figure 9: The shifted of the first three peaks of (BZT) at 1400°C

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 BaTiO₃ 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 BaTiO₃ (BT)

Calcinations Temp.	a=b(Å)	c(Å)
950°C	3.9912	4.0167
1400°C	3.9939	4.0300

VI. Lattice parameter of impure BaTiO₃ (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 BaTiO₃ (BZT)

Calcinations Temp.	a=b(Å)		c(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 ZrO₂ 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 (Zr⁴⁺) ion (0.72 Å) which is smaller than (Ti⁴⁺) ion (0.60 Å) in the (A) sites of BaTiO₃ and this refers to increase in lattice parameters, calculation of lattice parameter appears matched with X-ray diffraction.

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