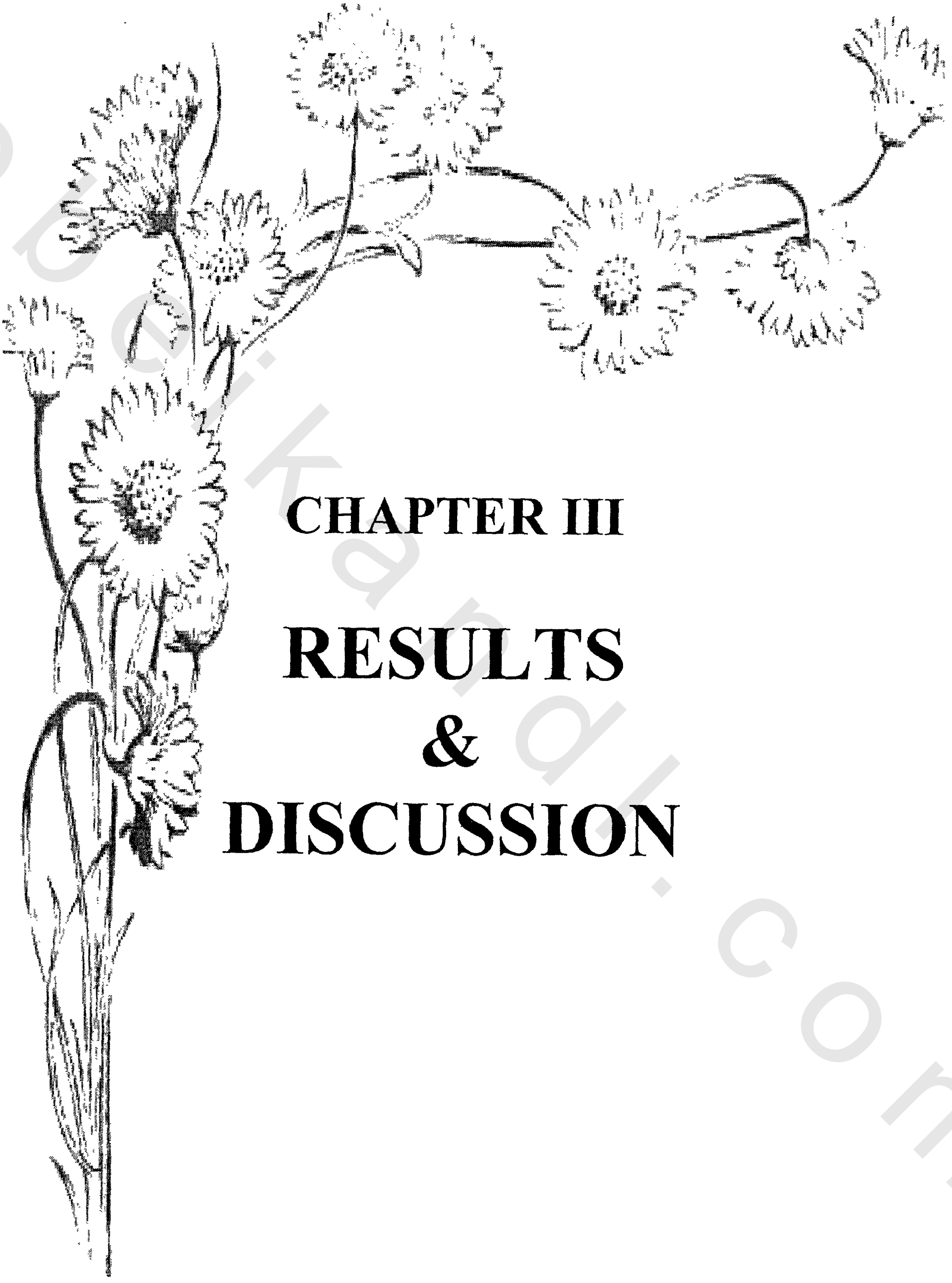

CHAPTER III

RESULTS & DISCUSSION

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III.1. PREPARATION OF BARIUM TITANATE (BT)

Barium titanate $BaTiO_3$ nanopowders were prepared using two methods, organic carboxylic acid precursor and hydrothermal methods. The factors affecting the conversion, % (phase formation, %) of single BT nanopowders phase, crystallite size, microstructure and dielectric properties were systematically studied and the optimum conditions were determined. These factors for organic acid precursor method were organic acid types, organic acid mole ratio, calcination temperature and calcination time. On the other hand, the conditions studied for hydrothermal technique were hydrothermal time, hydrothermal temperature and pH.

III.1.1. Organic Acid Precursor Method

Barium titanate nanopowders were prepared using different organic carboxylic acids (oxalic, citric, tartaric, acetic, and benzoic acids). Factors studied to attain conditions of the process, include calcination temperature, calcination time and organic acid mole ratios related to reacted Ba^{2+} and Ti^{4+} ions. The produced BT particles were characterized using XRD, SEM, TEM, and FT-IR. Moreover, the dielectric properties of the formed powders were measured.

III.1.1.1. Effect of Organic Carboxylic Acid Type

Different types of organic carboxylic acids namely; oxalic, citric, tartaric, acetic and benzoic acids have been used under the following conditions

- Barium / Titanium mole ratio : 1
- Organic acid mole ratio : 1
- Calcination temperature , ° C : 1000
- Calcination time , h : 2

Fig.15 showed that the XRD patterns of samples with different organic carboxylic acids. The results showed that the tetragonal barium titanate $BaTiO_3$ phase was obtained using oxalic, citric and tartaric acids. In contrast, XRD patterns of the powders synthesized by benzoic and acetic acid showed the formation of other phases of $Ba_4Ti_{13}O_{30}$, BaO, and TiO_2. Moreover, the benzoic and acetic acids mole ratios are increase phases of $Ba_4Ti_{13}O_{30}$, TiO_2, and Ti_4O_7 were formed. This is explained on the basis that enough water and acetic acid with short C-C chains would react with TiO_2 to yield –Ti-OH (intermediate species). Finally, almost all TiO_2 and Ti-OR or –O-Ba-OR' (R'= CH_3CO or C_6H_5O), and the final polymerization molecules become the stable network of metal –organic groups linked by oxygen bridge –O–.The stable compounds with O-M-O (M=Ba ,Ti) bonds and C=C bonds led to the increase of calcination temperature to obtain BT. Comparing by oxalic , citric and tartaric acids , long chains were present which led to formation of barium titanate phase (**Wang et al, 2007**). Fig. 16 showed XRD patterns using oxalic, citric and tartaric acids as sources of organic acids. From Fig. 16, the results showed a well crystalline single phase of barium titanate nanopowders was formed at using oxalic acid as a source of carboxylic acid. In contrast, $Ba_4Ti_{13}O_{30}$ phase was also formed with $BaTiO_3$ phase when using citric and tartaric acids as carboxylic acids at the studied conditions.

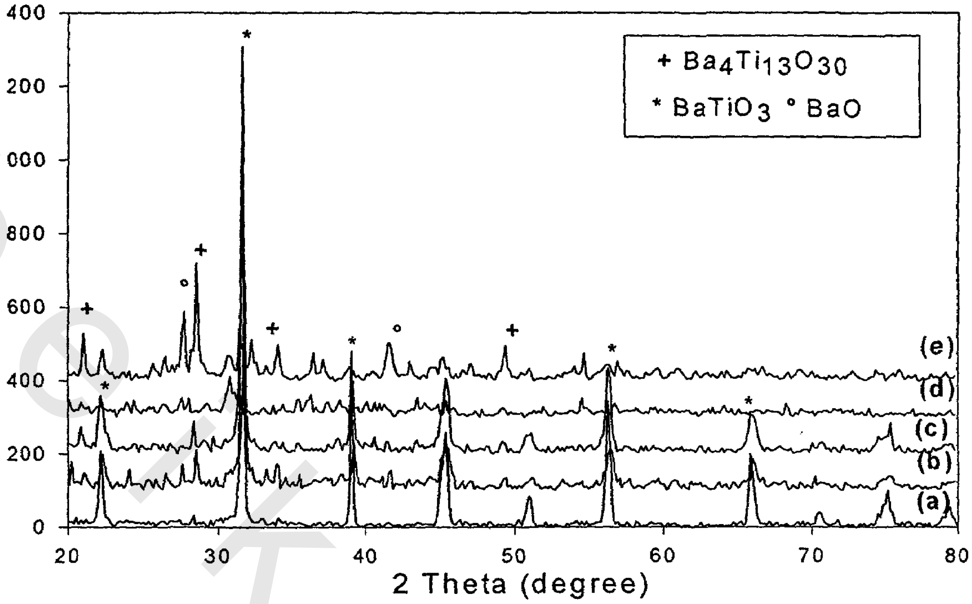


Fig. 15: XRD patterns of produced barium titanate powders with different types of organic carboxylic acid [(**a**): using oxalic acid, (**b**): citric acid, (**c**): tartaric acid, (**d**): acetic acid, and (**e**): benzoic acid]

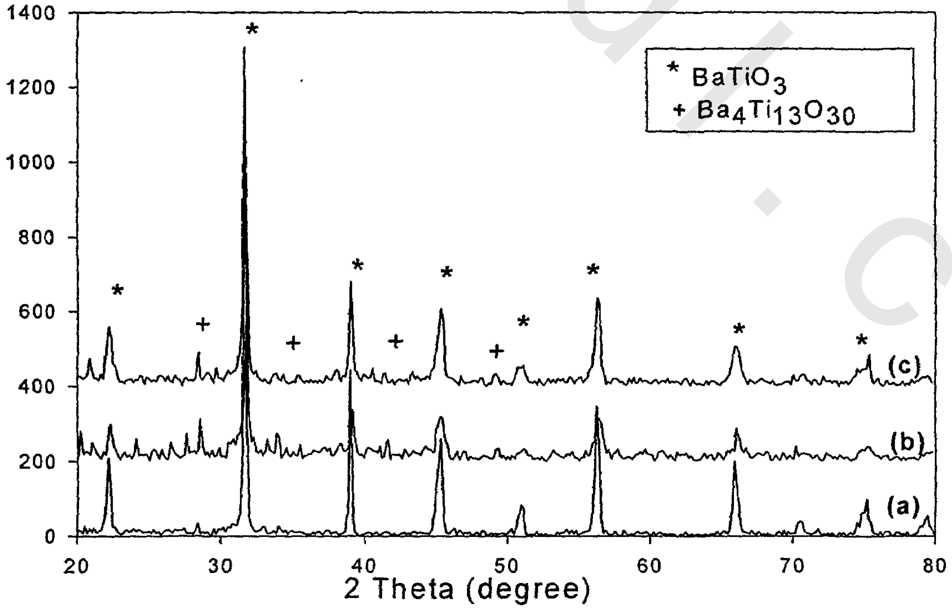


Fig. 16: XRD patterns of produced barium titanate with different organic acid types [(**a**): using oxalic acid, (**b**): citric acid, (**c**): tartaric acid]

III.1.1.2. Preparation of Barium Titanate by Oxalic Acid

The procedure for synthesis of barium titanate using oxalic acid as organic carboxylic acid source is called oxalate precursor method. Different experiments were carried out using different conditions of calcination temperature, calcination time, and oxalic acid mole ratios. The statistical design (Box- Behnken design) was used to estimate the optimum conditions. In oxalate precursor, the barium titanate powders were formed by transformation of barium chloride and titanium dioxide in the presence of oxalic acid into barium titanyl oxalate (BaC_2O_4. $TiOC_2O_4$) precursor. The formed precursors were converted to barium titanate by thermally treated at high temperature according to the following equations:

$$Ba^{2+} + C_2O_4^{2-} \longrightarrow BaC_2O_4 \quad (18)$$

$$TiO_2 + H_2C_2O_4 \longrightarrow TiOC_2O_4 + H_2O \quad (19)$$

$$BaC_2O_4 + TiOC_2O_4 \longrightarrow BaCO_3 + TiO_2^{*} + 2CO + CO_2 \quad (20)$$

$$BaCO_3 + TiO_2^{*} \longrightarrow BaTiO_3 + CO_2 \quad (21)$$

$$\therefore \mathbf{BaC_2O_4 + TiOC_2O_4 \longrightarrow BaTiO_3 + 2CO_2 + 2CO} \quad (22)$$

* Means TiO_2 is product

Response data for all 15 experiments design runs of Box-Behnken experimental design perform the effect of three different variables on the crystal structure, crystallite size and morphology of BT nanopowders. The factors studied were calcination temperature (800-1200°C), calcination time (0.5-4 h), and oxalic acid mole ratio related to added ratios of barium and titanium (0.5-1.5). The barium titanate phase formation, % and its crystallite size at different temperature were listed in Table 12.

Table 12: Conversion and crystallite size of $BaTiO_3$ according to experimental statistical design conditions

Run No.	Factors			Crystallite size, nm	$BaTiO_3$ Conversion, %
	A:Temp. °C	B:Time, h	C: Oxalic acid mole ratio		
1	800	0.5	1	63	15.8
2	1200	0.5	1	82.7	95.1
3	800	4	1	55.5	80
4	1200	4	1	87.6	100
5	800	2.25	0.5	68.4	100
6	1200	2.25	0.5	92.7	100
7	800	2.25	1.5	41.6	73.2
8	1200	2.25	1.5	96	95.7
9	1000	0.5	0.5	70	95.45
10	1000	4	0.5	73.7	90.32
11	1000	0.5	1.5	44.8	52.5
12	1000	4	1.5	56.8	77
13	1000	2.25	1	69	100
14	1000	2.25	1	73.2	100
15	1000	2.25	1	70.1	100

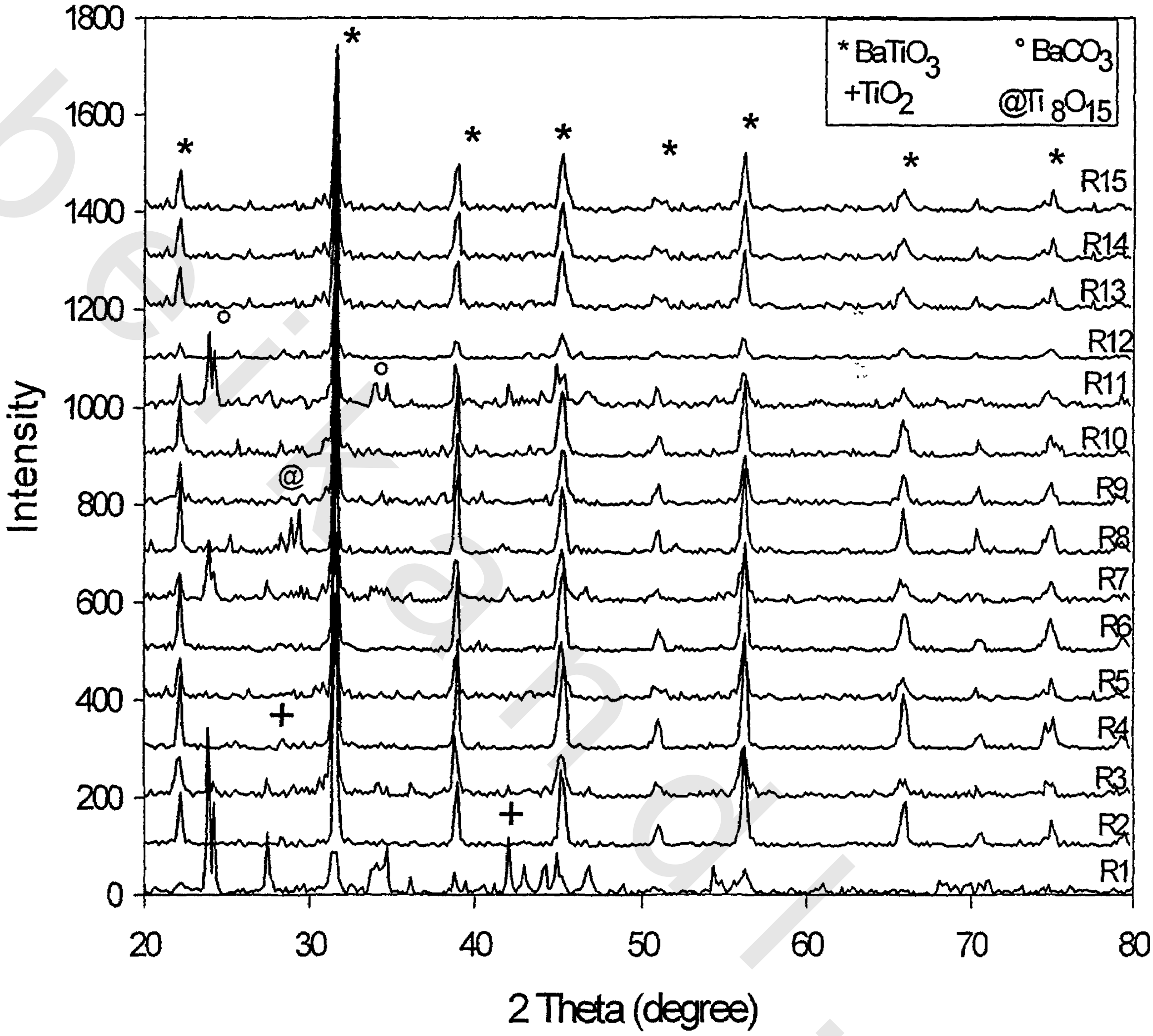


Fig. 17: XRD patterns of produced powders at different experiments statistical design conditions

From Table 12 and XRD data, the results showed that at oxalic acid mole ratio 0.5, a pure well crystalline single phase of tetragonal barium titanate phase (JCPDS #79-2264) was obtained at different temperatures from 800 to 1200°C (Run 5 and 6).

At low temperature, the conversion of oxalate precursors into barium titanate phase was decreased. Mixture of tetragonal barium titanate and barium carbonate $BaCO_3$ phase (JCPDS #71-2394), were formed. The conversion, % of barium titanate was increased from 15.8 to 80 % by increasing the calcination time from 0.5 to 4 h at 800°C (Run 1, 2). Increasing the calcination temperature 1200°C at low calcination time 0.5 h, the conversion of barium titanate phase was 95.1 % (Run 3). With increasing the oxalic acid mole ratio to 1.5 at low time not formed single phase barium titanate but formed $BaTiO_3$ with $BaCO_3$ phases due to increased oxalic acid mole ratios leading to increase excess of barium carbonate $BaCO_3$ which react with titanium dioxide TiO_2 to form barium titanate (BT) and barium carbonate. Increasing the temperature up to 1200°C tend to the formation of single phase barium titanate $BaTiO_3$ powders at high oxalic acid mole ratio. The formation of barium titanate phase nanopowders was in the range from 52.5 to 95.7 % (Run 7, 8, 11, and 12). The average crystallite size was increased by increasing the temperature. It increased from 68.4 nm at low calcination temperature 800°C to 96 nm at high calcination temperature 1200°C.

Fig.18 showed the effect of calcination temperature and calcination time on conversion % of produced BT at different oxalic acid mole ratios (0.5, 1, and 1.5). It is observed that at oxalic acid mole ratio 0.5, low calcination time and temperature, the formation of barium titanate phase was decreased but increased the calcination time and temperature, the formation of barium titanate phase increased. Moreover, the formation of barium titanate phase was decreased with high oxalic acid mole ratio 1, 1.5 at low calcination time and temperature. In contrast, comparing the oxalic acid mole ratios at the similar time and temperature, the conversion of barium titanate phase increased at low oxalic acid mole ratio 0.5.

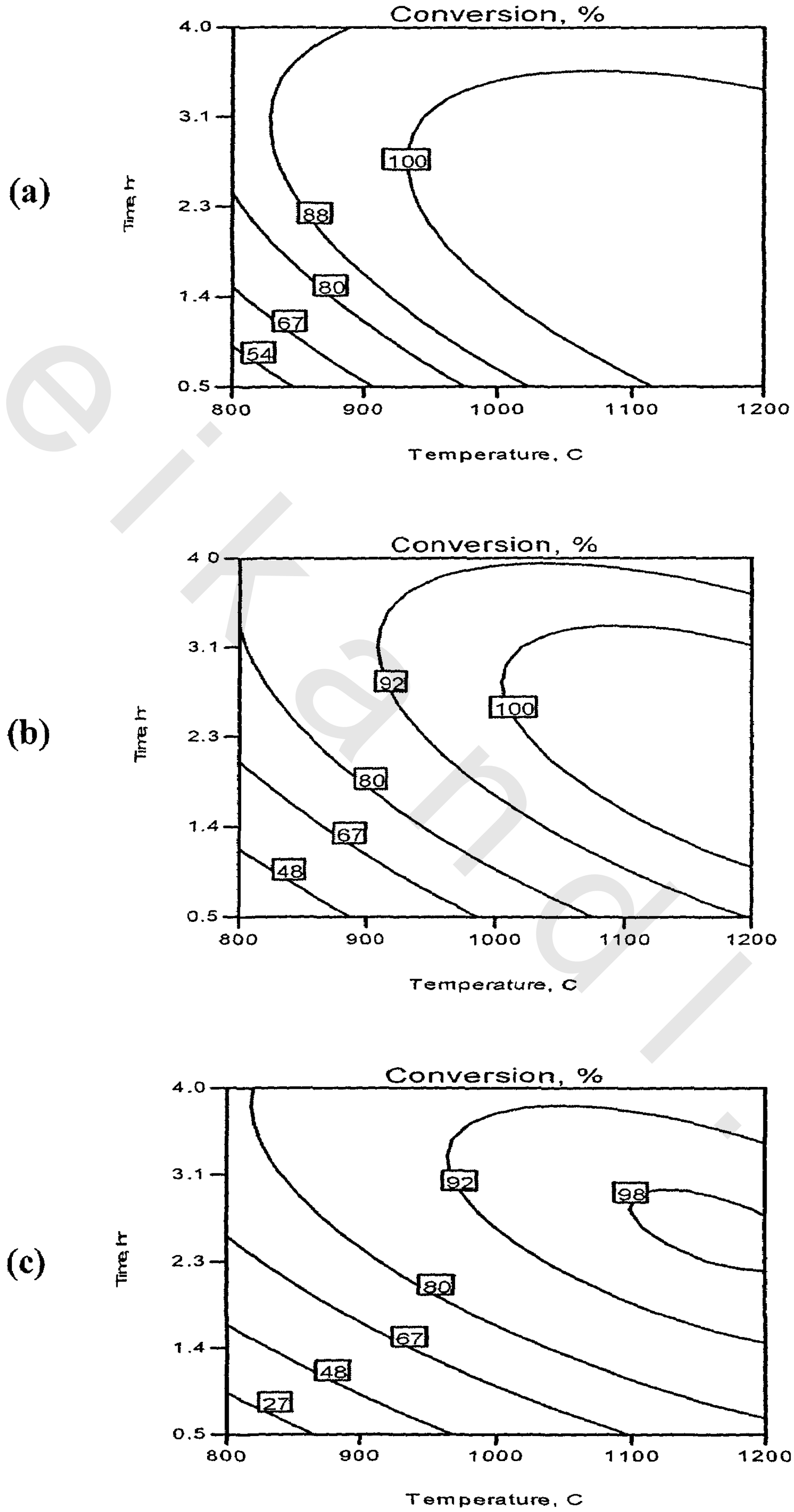


Fig.18: Contour plots for the effects of calcination temperature and time on conversion % of $BaTiO_3$ phase at different oxalic acid mole ratios [(**a**): 0.5, (**b**): 1 and (**c**): 1.5]

III.1.1.2.1.Effect of Calcination Temperature

From statistical design results, the effect of calcination temperature on the conversion, % of barium titanate phase was determined at constant oxalic acid mole ratio and different calcination time. Fig.19 showed the effect of calcination temperature on conversion of BT at different times for constant oxalic acid mole ratio 0.5, 1, and 1.5. The results showed that increasing the temperature the formation of barium titanate phase is increased. Moreover, when the calcination time is increased at high temperature, the formation of barium titanate phase is increased. At high temperature, the energy and velocity of the reactant of particles increases, thus the collision between them become more violent and the kinetic energy of particles is high and the product formation increases without increasing the time. While at lower temperature, the number of collisions between reactant is lower because the particles are moving more slowly. In conclusion, the calcination temperature is one of the most significant factors on the BT phase formation by oxalate precursor method. For instance at low oxalic acid mole ratio 0.5 and constant reaction time, the conversion was increased gradually with increasing the reaction temperature from 800 to1050°C.

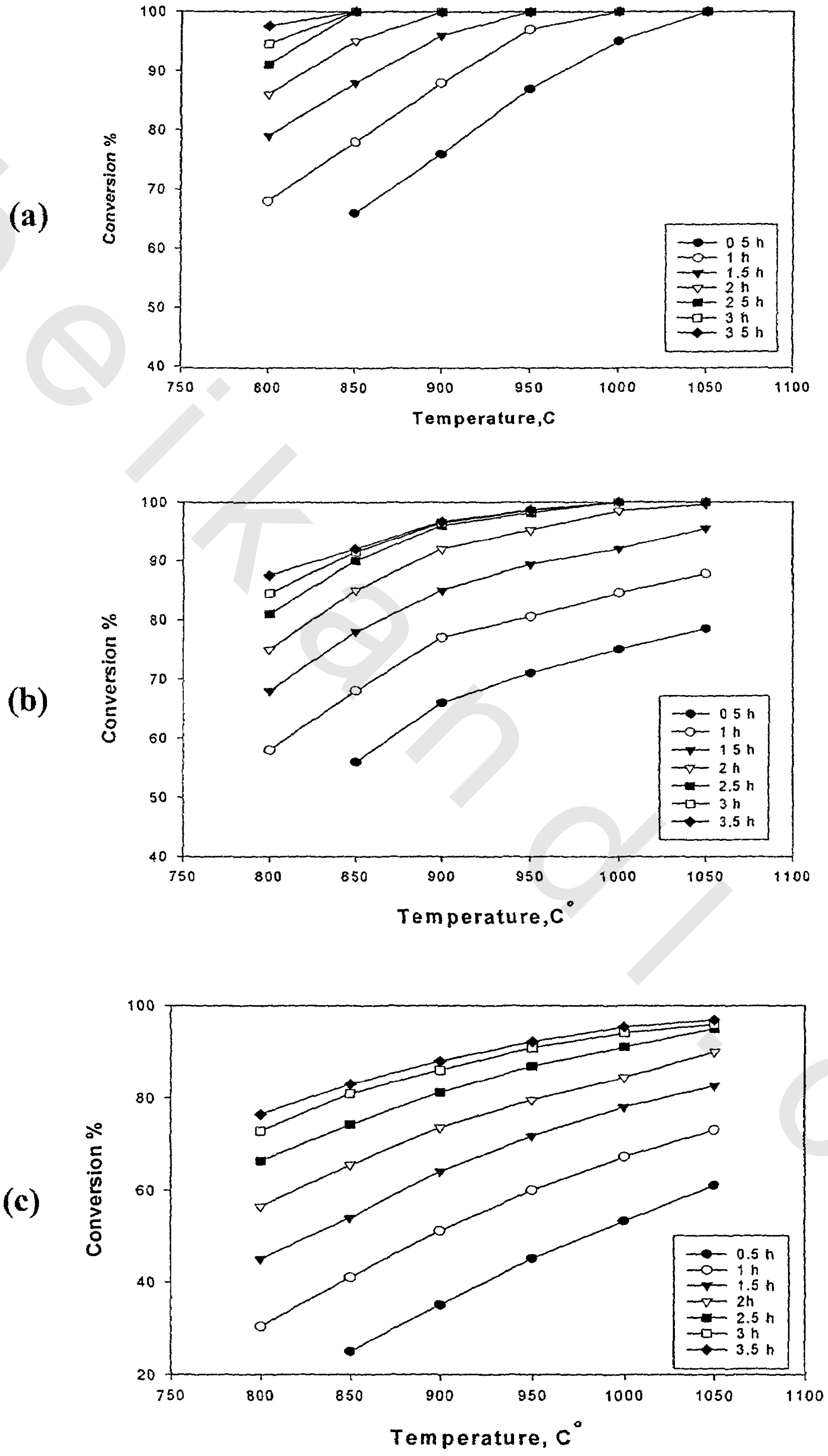


Fig. 19: Effect of calcination temperature on the conversion of BT at different time and oxalic acid mole ratios [(**a**) 0.5, (**b**) 1 and (**c**) 1.5]

III.1.1.2.2.Effect of Calcination Time

The calcination time and calcination temperature are the most important factors that affect the phase formation of barium titanate. Increasing the calcination time leads to an increased collision probability between reactants to product formation and the vice versa.The effect of calcination time from 0.5 to 4 h on the barium titanate phase formation at different calcination temperature from 800 to 1050°C and constant oxalic acid mole ratio was given in Fig. 20. The results show an increase in calcination time at low calcination temperature led to an increase in the barium titanate phase formation. Increasing calcination time with increasing calcination temperature led to increased the conversion, % to barium titanate phase. Moreover , At low calcination time with different calcination temperature , the conversion, % of BT was decreased. Increasing of calcination temperature and calcination time at high oxalic acid mole ratio led to increase in the formation of BT phase. At low oxalic acid mole ratio 0.5, we need only calcination time ranging from 1 to 2.5 h at calcination temperature 950 and 1050 °C to achieve a pure well crystalline barium titanate phase .

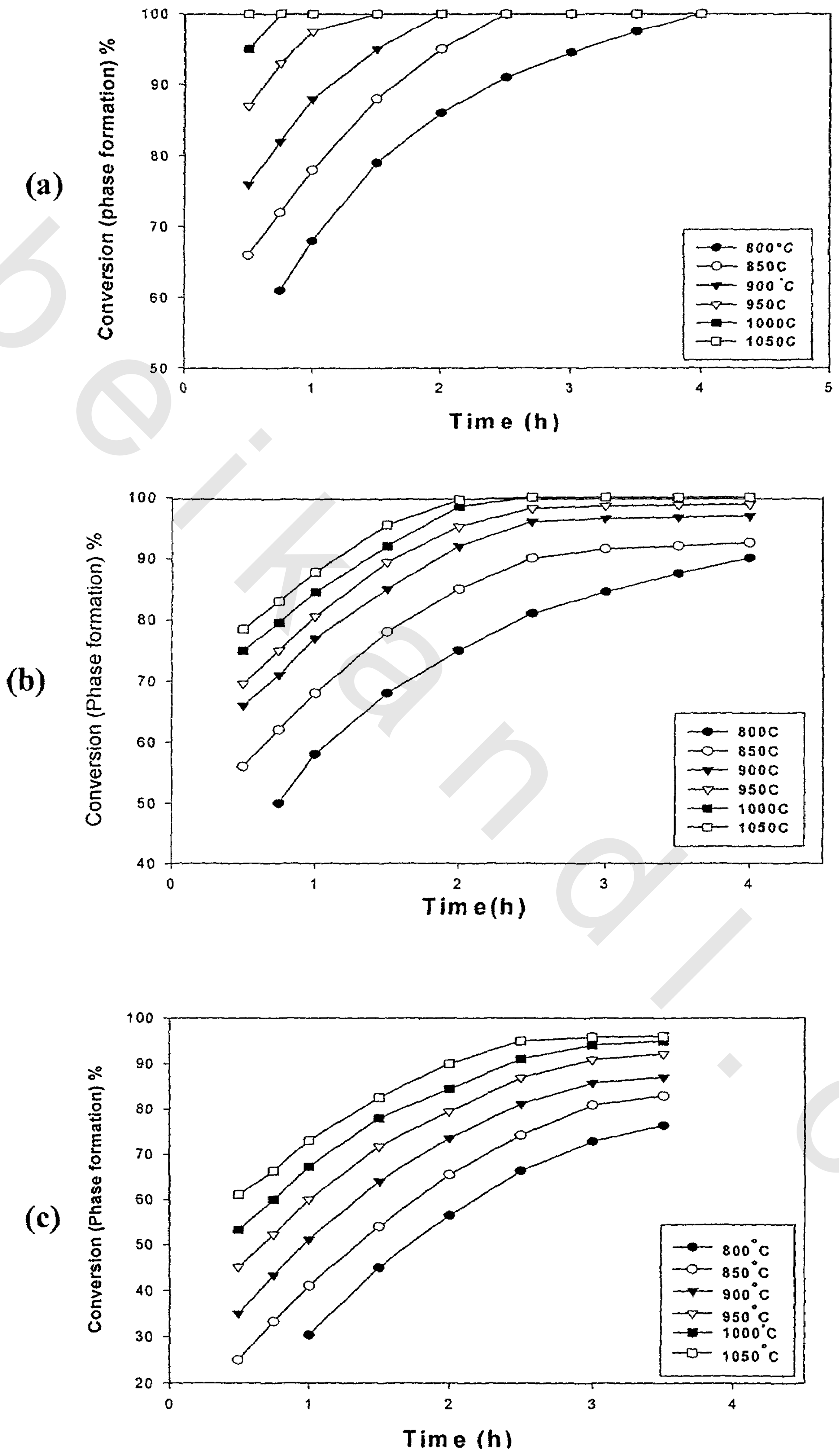


Fig.20: Effect of time on conversion of BT at different temperature and oxalic acid mole ratio **(a)** 0.5, **(b)** 1 and **(c)** 1.5]

III.1.1.2.3.Effect of Oxalic Acid Mole Ratios

Different experiments were carried out to study the effect of oxalic acid mole ratio on the conversion, % of tetragonal barium titanate nanopowders as the following conditions :

Calcination temperature , °C	: 800
Calcination time, h	: 2.25

The results obtained were given by XRD patterns in Fig.21. The results showed that at oxalic acid mole ratio 0.5, a single phase of tetragonal $BaTiO_3$ was obtained (JCPDS #79-2264). Increasing the oxalic acid mole ratios to 1 and 1.5, a mixture of tetragonal $BaTiO_3$ and barium carbonate $BaCO_3$ (JCPDS #71-2394) was formed due to an increased oxalic acid mole ratio which leads to increase in excess of barium carbonate $BaCO_3$. The increased oxalic acid mole ratio need to increase the calcination temperature and calcination time until the precursor is converted to $BaTiO_3$ while decreasing the oxalic acid mole ratio decreases the temperature and then increases the conversion of the precursor to $BaTiO_3$ nanopowders.

All the experimental results, collected in the 3-D cubic plots diagram as shown in Fig.22. The results revealed that conversion of barium titanate, which ranged from 11 to 100 %, were produced. The smallest conversion of BT phase can be obtained at low levels of calcination temperature, calcination time and high level of oxalic acid mole ratios. The formation of $BaTiO_3$ with a conversion percentage of 11.75 can be obtained at low calcination temperature and low calcination time. On the other hand, the formation of pure $BaTiO_3$ 100%, can be achieved at high level of calcination temperature and low levels of both calcination reaction and oxalic acid mole ratio.

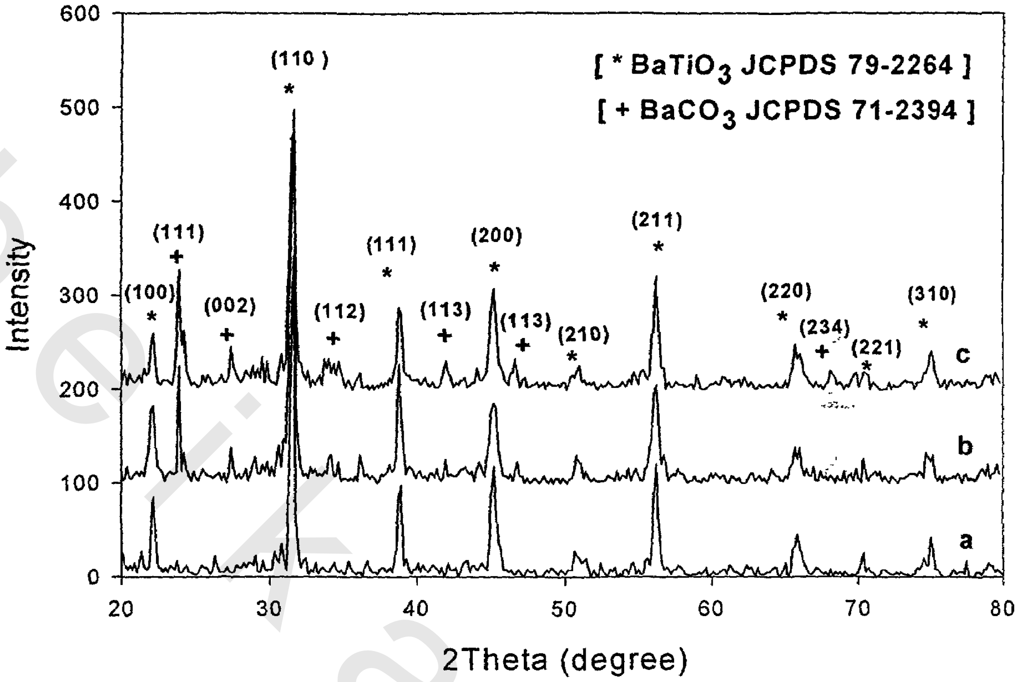


Fig.21: XRD analysis of the product barium titanate using oxalic acid at calcination temperature 800 °C and calcination time 2.25 h [(**a**) mole ratio 0.5, (**b**) mole ratio 1, (**c**) mole ratio 1.5]

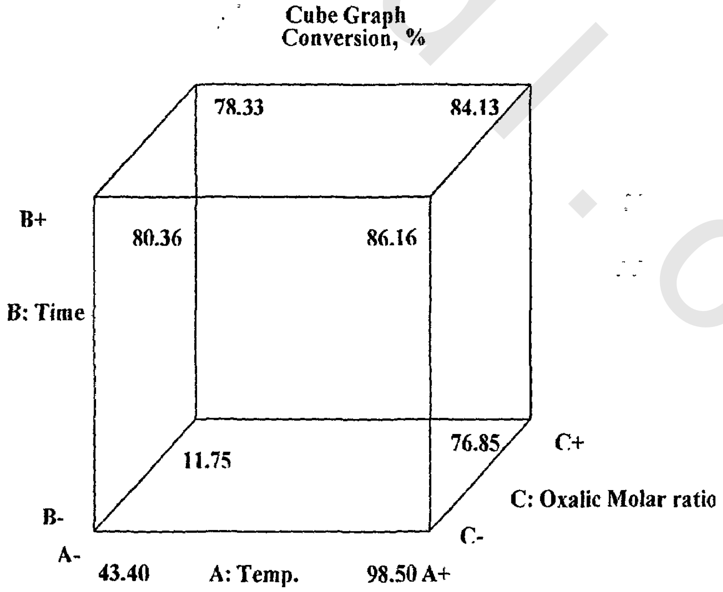


Fig.22: 3-D Plot Graph for all experimental data for conversion of BT (Standard Deviation: 12.01; R^2: 0.8662)

III.1.1.2.4. Crystallite Size of Barium Titanate powders using Oxalic Acid

The crysrallite size of tetragonal barium titanate nanopowders as calculated from XRD analyses using Debye -Scherer formula was obtained for all experiments studied at different conditions of the variables. The results from Statestical design studied showed that average crystallite size of BT phase with standared deviation is (6.08). Moreover, the determination coefficient R-square (0.9481) indicated the agreement of the generated model and the experimental results. Fig.23 show the effect of calcination temperature and calcination time on crystallite size of obtained powders. The results showed that increased calcination time with calcination temperature at the same oxalic acid mole ratio increases the average crystallite size of the produced barium titanate nanopowders. In contrast decreasing the calcination temperature with decreasing the calcination temperature at the same oxalic acid mole ratio decreases the crystallite size. The average crystallite size of conversion BT produced range from 68.4 to 96 nm from statistical design calculation and average crystallite size of the single phase BT was in the range between 69-87 nm from the experimental data.

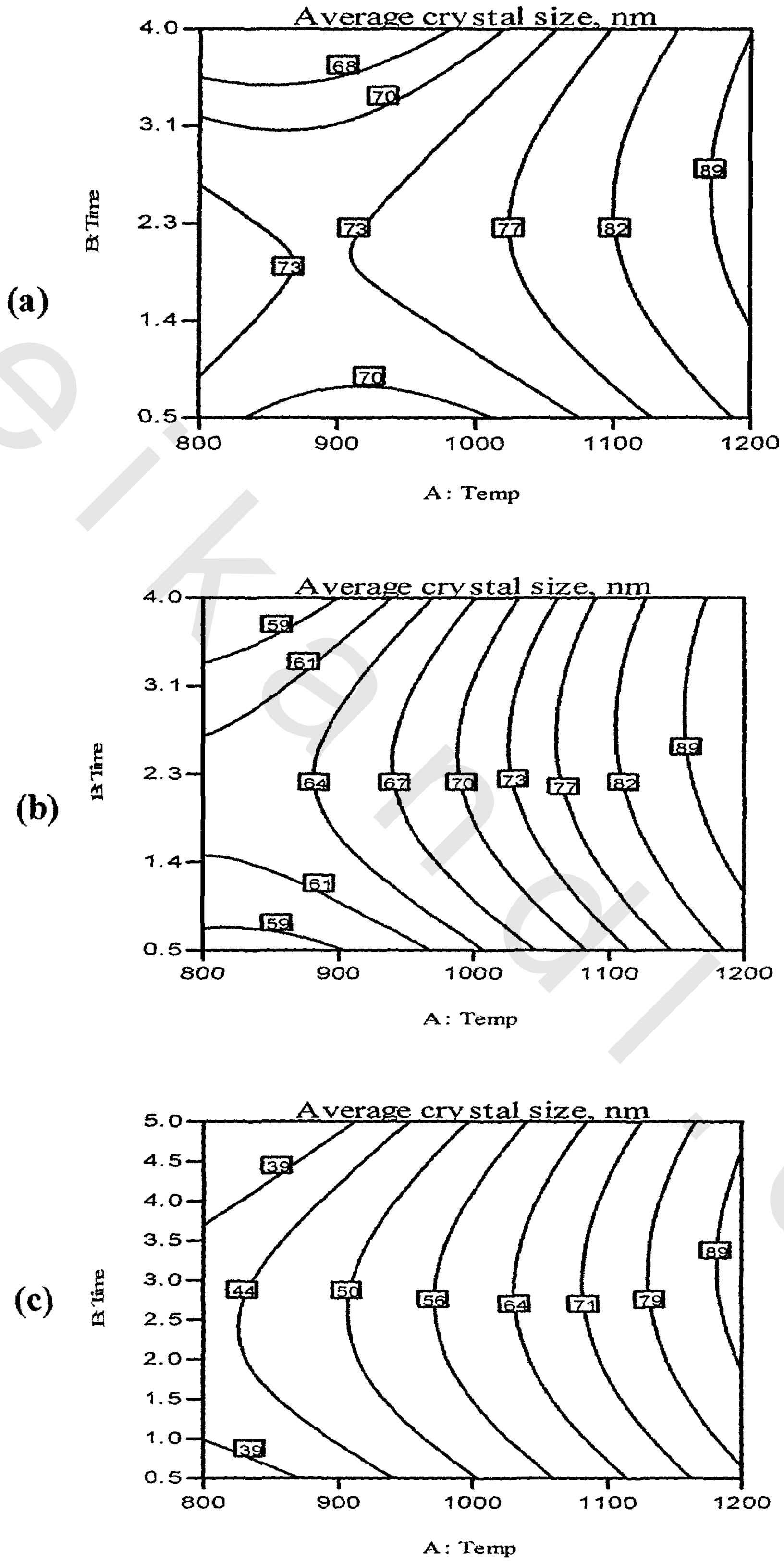


Fig.23: Contour plots for the effects of calcination temperature and time on crystallite size in the conversion $BaTiO_3$ at different oxalic acid mole ratios [(**a**): 0.5, (**b**): 1 and (**c**): 1.5]

All the experimental data, collected at the 3-D cubic graph as shown in Fig. 24 revealed that the lowest crystallite size can be obtained at low levels of calcination temperature and calcination time and high level of oxalic acid mole ratio. In contrast, the highest crystallite size can be obtained at high levels of calcination time, calcination temperature and low level of oxalic acid mole ratios.

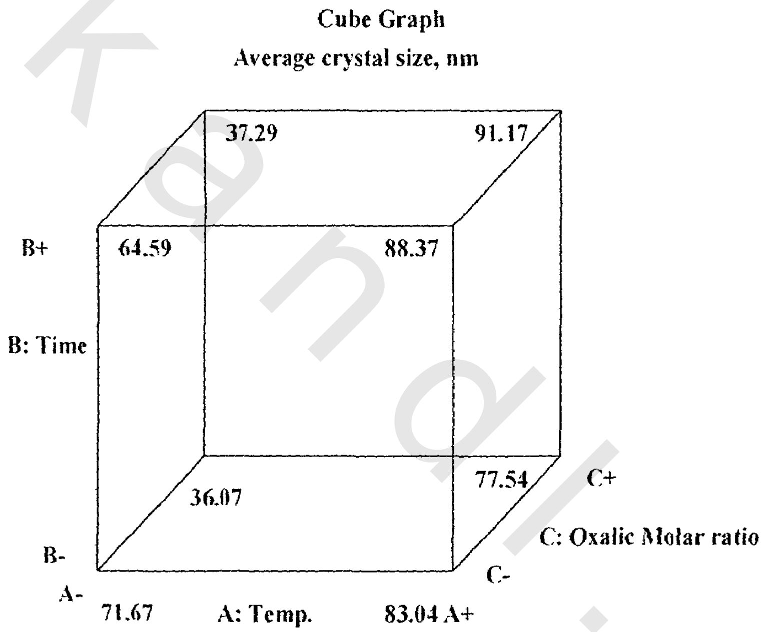


Fig. 24: 3-D plot graph for all experimental data for average crystallite size of conversion BT

III.1.1.2.5. Morphology of Barium Titanate Powders using Oxalic Acid

SEM micrographs of the formed $BaTiO_3$ nanopowders at different oxalic acid mole ratios at calcination temperature 800°C for calcination time 2 h are shown in Fig. 25. It is observed that a pure single tetragonal structure shape can be obtained at low oxalic acid mole ratio. The formed BT particles were homogenous, very fine and uniform size. The tetragonal structure shape obtained, $BaTiO_3$ produced without any agglomeration of small crystal size. Increasing the oxalic acid mole ratio up to 1, a mixture of two shapes (tetragonal and orthorhombic shapes) with random particle size distribution was obtained.

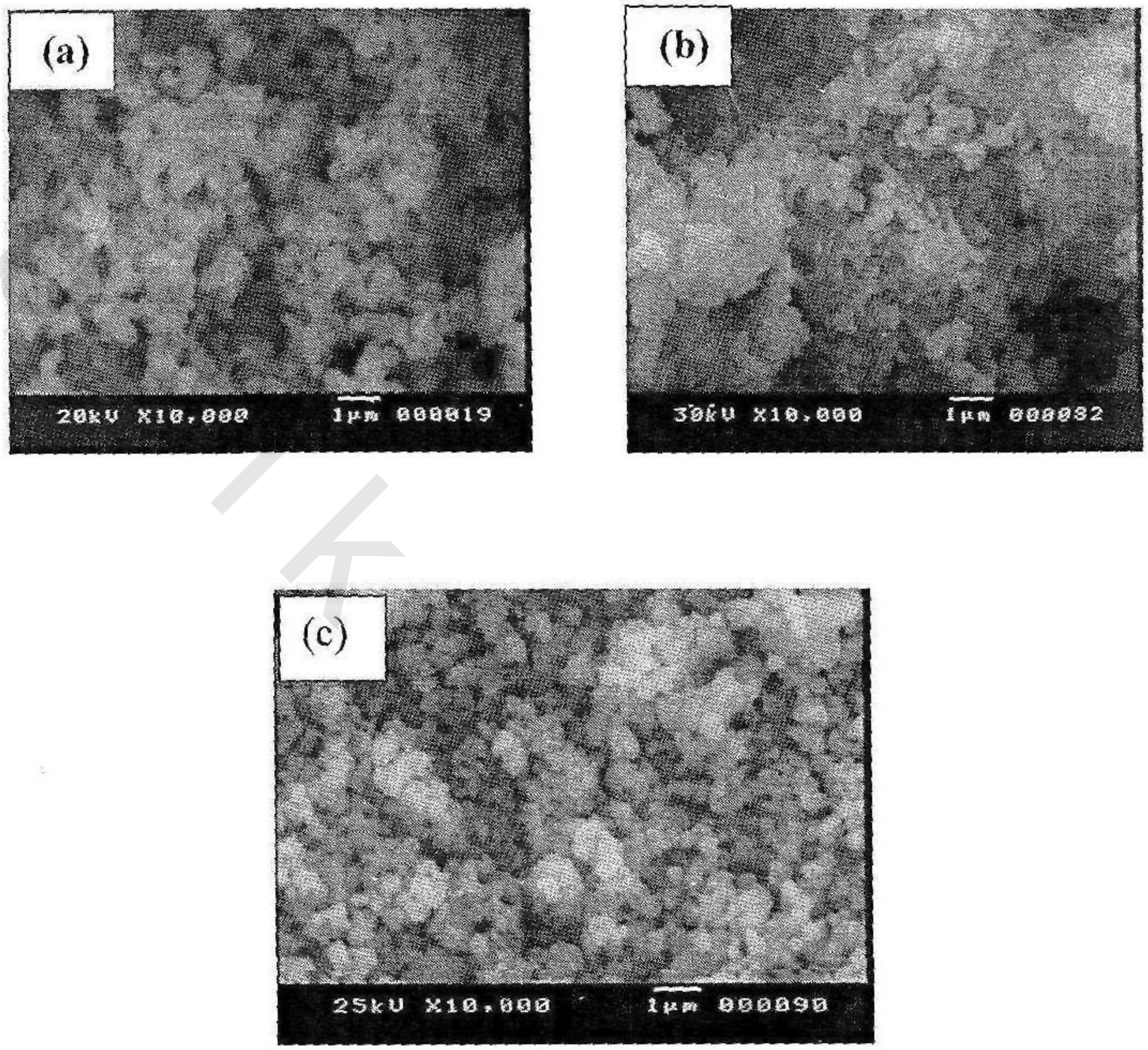


Fig.25: SEM micrographs of barium titanate nanopowders obtained at calcination temperature 800°C, calcination time 2.25 h and different oxalic acid mole ratios [(**a**) 0.5, (**b**) 1, (**c**) 1.5]

III.1.1.2.6. Infrared Spectra using Oxalic Acid

The FT-IR spectra for barium titanyl oxalate precursors at different oxalic acid mole ratios were shown in Fig. 26. It is observed that the characteristic absorption bands at 716, 1263, 1426.1 and 1690 cm^{-1} corresponding to the different modes of vibration oxalate group. The broad band centered around 3390.24 cm^{-1} may be assigned to symmetric stretching vibration of OH group and 1613 cm^{-1} due to H-O-H bending of coordinated water. Furthermore, the sharp peaks at 2520.5 cm^{-1} related to the CO_3^{-2} groups. Moreover two broad absorption peaks at 474.4 and 554cm^{-1} the Ti-O vibration.

The FT-IR spectrum after calcination of the precursor at constant temperature 800°C and calcination time 2.25 h is shown in Fig. 27. The results obtained show that for pure BT at mole ratio 0.5, two broad absorption peaks one of them at 540 due to Ti-O vibration and another at 568.8 cm^{-1} correspond to $BaTiO_3$. The intensities of peaks at 1602 and 3452 cm^{-1}, respectively are assigned to the OH group. At mole ratio 1 and 1.5, other absorption peaks were observed at 750, 858, 1116 and 1433.8 cm^{-1} which can be attributed to barium carbonate and the two broad absorption peaks at 432.9 and 568.8 cm^{-1} are related to Ti-O vibration.

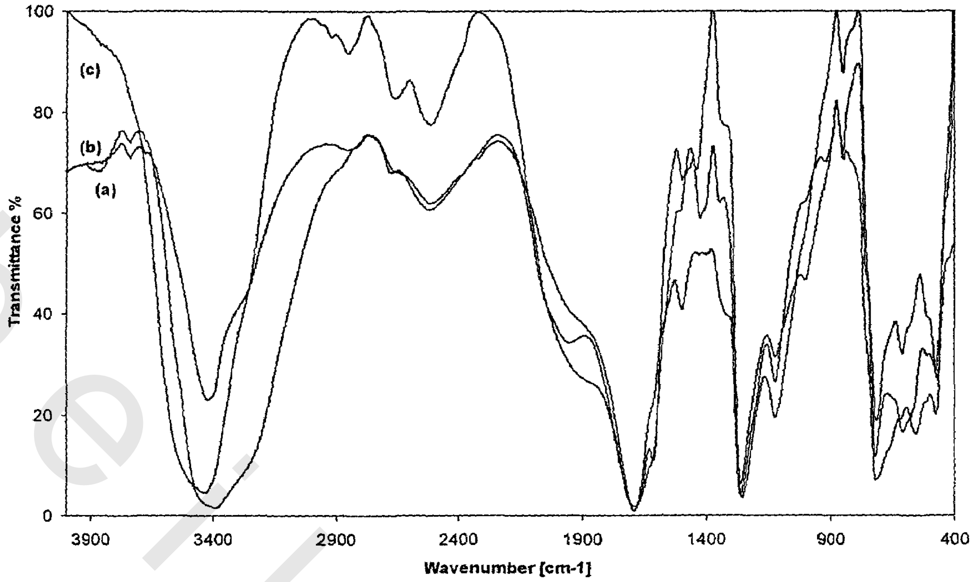


Fig. 26: IR spectra of precursor at different oxalic acid mole ratios [(**a**) oxalic acid mole ratio 0.5, (**b**) oxalic acid mole ratio 1 and (**c**) oxalic acid mole ratio 1.5]

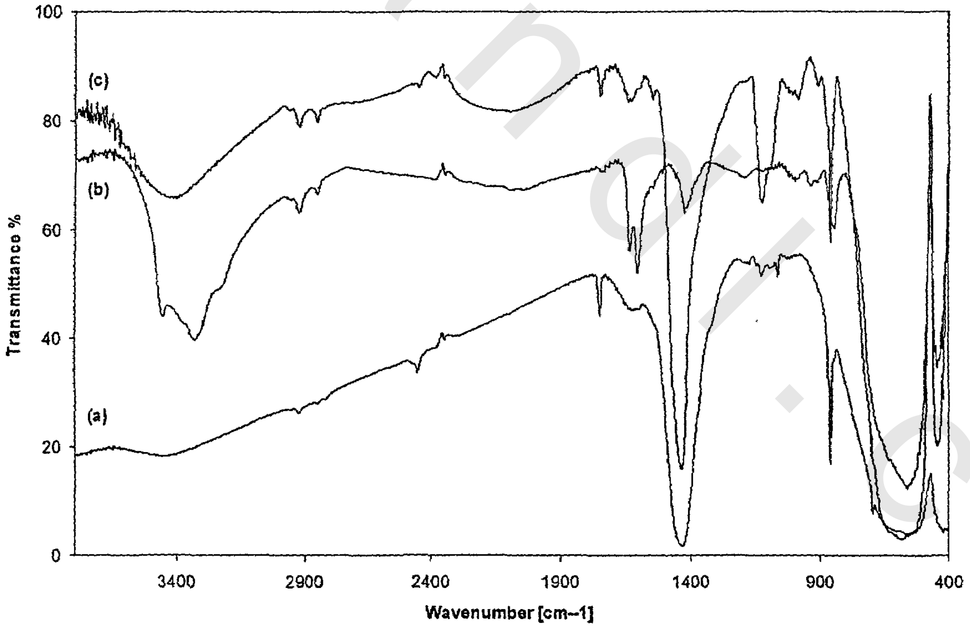


Fig.27: IR spectra of spectra after calcination at different oxalic acid mole ratios [(**a**) oxalic acid mole ratio 0.5, (**b**) oxalic acid mole ratio 1 and (**c**) oxalic acid mole ratio 1.5]

III.1.1.2.7. Dielectric Properties of Barium Titanate using Oxalic Acid

The dielectric constant of barium titanate was strongly dependence on temperature , Fig. 28 show the variation of the dielectric constant as a function of frequency with various temperature at oxalic acid mole ratio 0.5 , calcination time 2.25h and different calcination temperatures (800 , 1000 and 1200°C). The results show that the dielectric constant of barium titanate which was formed at different calcination temperatures first increases with decreasing the frequency and with increasing frequency rapidly decrease. The low frequency rise in dielectric constant is attributable to the interfacial effects. These take place at the contacts or in the bulk of the material at the grain boundaries. Charges are able to accumulate at these interfacial sites and thereby able to contribute to the total capacity or dielectric permittivity or dielectric constant as the frequency is raised.

The dielectric constant of BT single phase formed at calcination temperature 800°C in room temperature was 7.5E+06 and increased at 100°C to 1.86E+07 then rapidly decreases to 7894 at 130°C. Moreover, the dielectric constant of BT formed using calcination temperature 1000°C in room temperature was 4.07E+05 and increases at 100°C to 1.58E+06 then rapidly decreases at 120°C to 255.8. Furthermore, the dielectric constant of BT formed at calcination temperature 1200°C in room temperature was 2607 and increases at 100°C to 1. 47E+05 then rapidly decreases to 43 at 120°C.

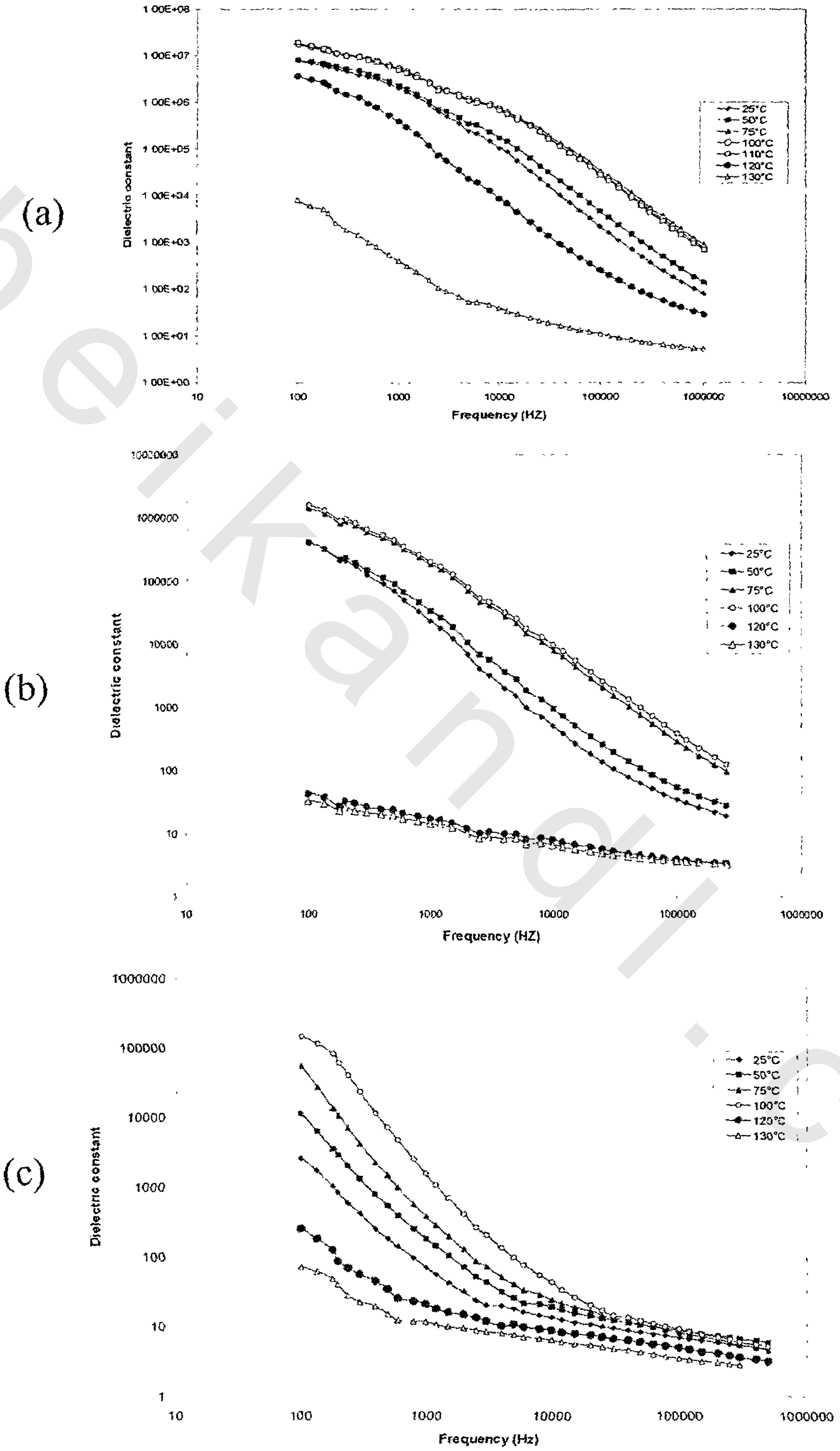


Fig.28: Temperature dependence of di electric constant of BT with different frequency at calcination time 2h, oxalic acid mole ratio 0.5, calcination temperature [(**a**): 800°C, (**b**): 1000°C and (**C**)1200°C]

III.1.1.2.8. Effect Zr^{4+} ions on Barium Titanate using Oxalic Acid

Recently, barium titanate is commonly used with several additions. One of these additions zirconium ions which are used in commercial formulations such as container crucibles for reactions, melting and sintering with other oxides, sensor for H_2S in ambient conditions. The addition of Zr^{4+} ions substitution of Ti^{4+} leads to lower Curie temperature, increased dielectric constant, decreased dielectric losses and increased aging rate of BT as capacitors.

The effect of Ti / Zr mole ratio during preparation of BT at the optimum synthesis condition using oxalic acid and effects on phase formation morphology and dielectric properties were systematically studied on phase formation. .

A series of experimental was carried out with different Ti / Zr moles [0.9/0.1, 0.7/0.1 and 0.5/ 0.5] under the following conditions:

Barium / Titanium mole ratio	: 1
Oxalic acid mole ratio	: 0.5
Calcination temperature	: 1000°C
Calcination time	: 2h

Fig. 29 showed the XRD patterns of samples without addition of zirconium ions and by using different Ti/Zr mole ratios from 0.9/0.1 to 0.5/0.5. The results show that without added zirconium ions only single phase of tetragonal $BaTiO_3$ was formed (JCPDS # 79-2264). Addition of different Ti/Zr mole ratios led to formation of $BaTiO_3$ and cubic barium zirconate $BaZrO_3$ (JCPDS# 74-1299) phase. Increasing the Ti/Zr mole ratios decreased the percentage of barium titanate phase and increasing the percentage of barium zirconate phase. At Ti/Zr mole ratios 0.9/0.1, the conversion or phase formation, % of tetragonal barium titanate ≈ 90 and ≈10 barium zirconate, Ti/Zr mole ratios 0.7/0.3, the conversion or phase formation, % of tetragonal barium titanate ≈ 69 and ≈31 barium zirconate. Furthermore, Ti/Zr at mole ratios 0.5/0.5, the conversion or phase formation, % of tetragonal barium titanate was 47, barium zirconate 45 and zirconium oxide ZrO_2 8.

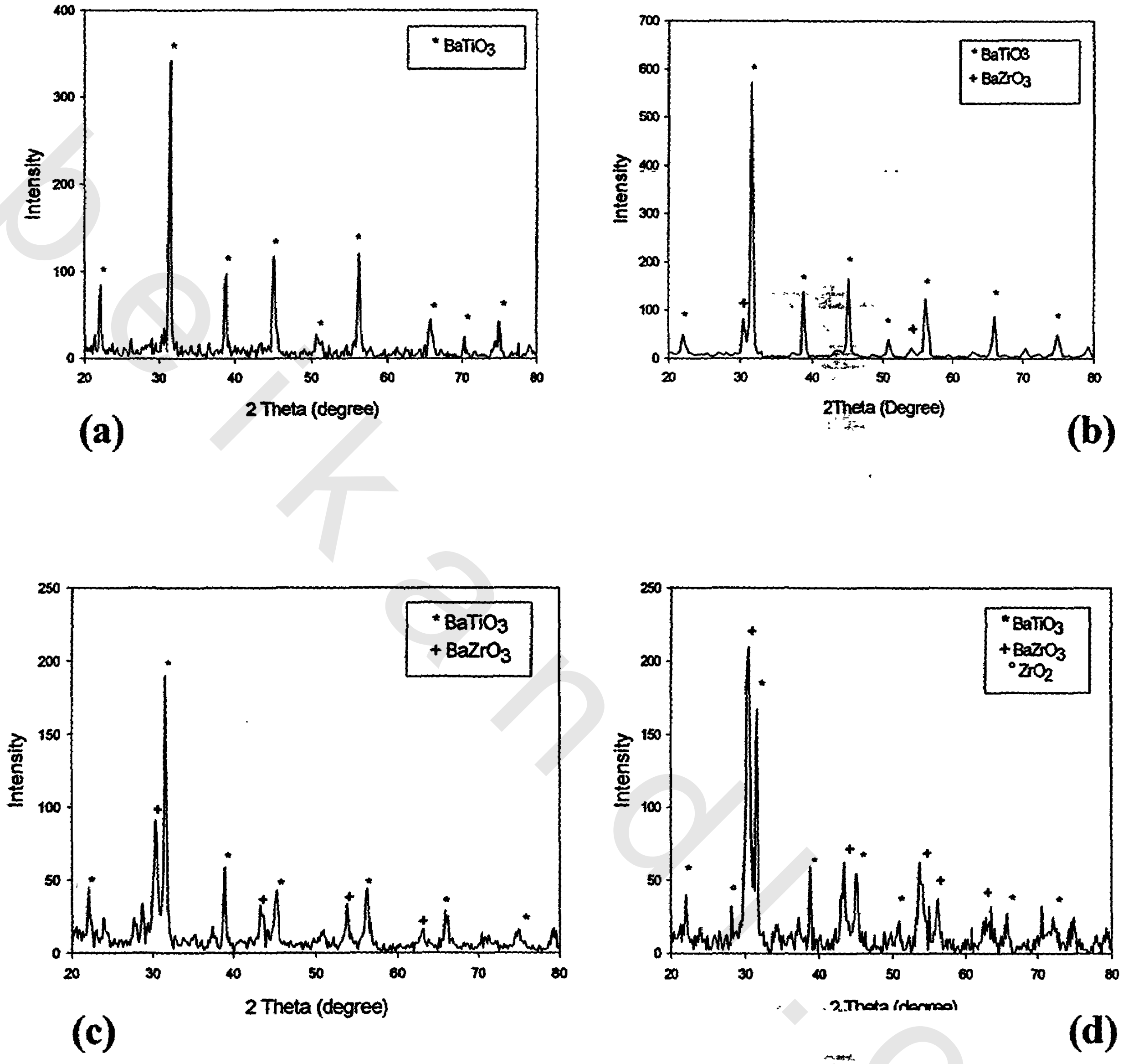


Fig.29: Effect of Ti/ Zr mole ratio on phase formation, where; [(**a**) without added zirconium ions, (**b**) Ti / Zr mole ratio 0.9/0.1, (**c**) Ti / Zr mole ratio 0.7/0.3, (**d**) Ti / Zr mole ratio 0.5/0.5]

Fig. 30 show the SEM micrographs of samples produced without addition of zirconium ions and by using different mole ratios of Ti/Zr from 0.9/0.1 to 0.5/0.5 at barium: titanium mole ratio equal 1, oxalic acid mole ratio 0.5, calcination temperature1000°C and calcination time 2h. The result show that without addition of zirconium ions pure tetragonal structure shape with homogenous, without any agglomeration of small crystal size of very fine , uniform size is obtained. By addition of different Ti/ Zr mole ratios a mixture shape (tetragonal structure of BT and cubic structure of $BaZrO_3$ powders) with nano-sized homogenous grain is obtained. However, some of agglomerated particles were obtained. Characterization of the powders produced with added of Ti/ Zr mole ratios by TEM are shown in Fig.31. The results show a narrow- distribution of spherical nanoparticles that contain part of light color and dark color with homogeneity distribution which indicates those barium zirconate and barium titanate phases were formed.

The average crystallite size of the two phases was 31 nm from TEM micrograph. The data is in good agreement with average crystallite size calculated using Scherrer equations.

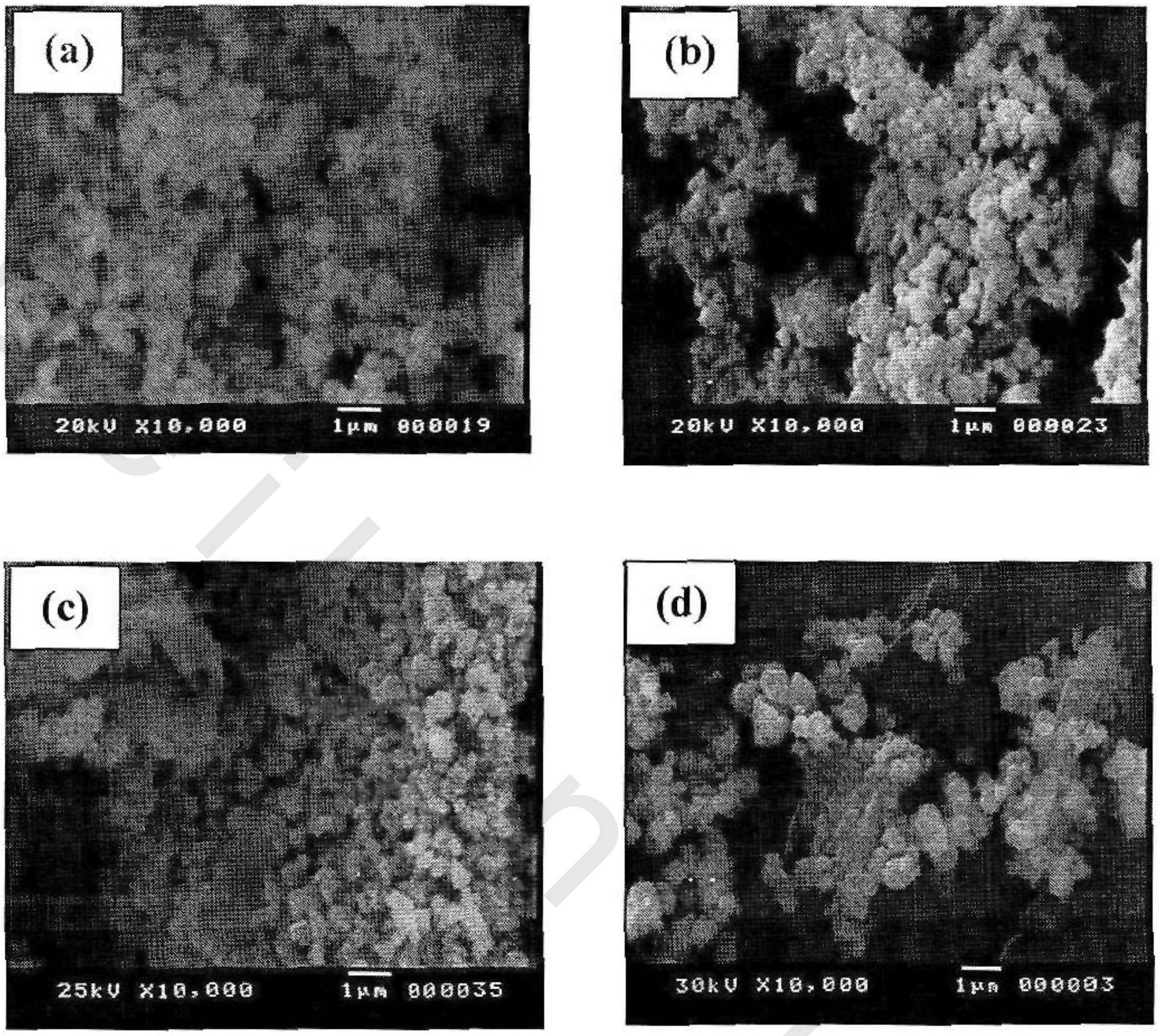


Fig.30: SEM micrographs of produced samples using different Ti/ Zr mole ratios, where; [(**a**) without added zirconium ions, (**b**) Ti/ Zr mole ratio 0.9/0.1 , (**c**) Ti/ Zr mole ratio 0.7/0.3 and (**d**) Ti/ Zr mole ratio 0.5/0.5]

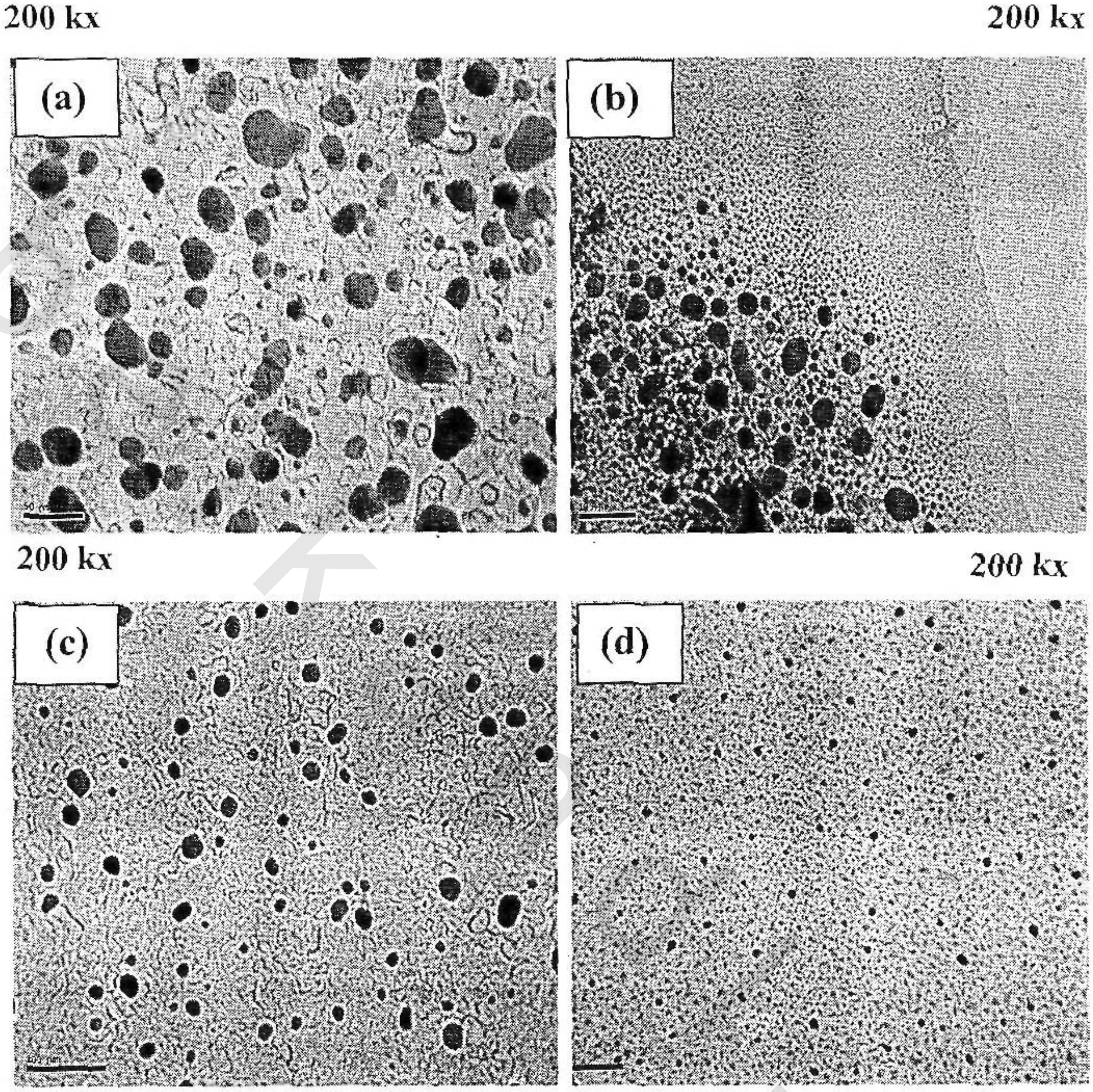


Fig.31: *TEM images of produced samples using different* Ti/ Zr mole ratios [(**a**) without added zirconium ions, (**b**) Ti/ Zr mole ratio 0.9/0.1, (**c**) Ti/ Zr mole ratio 0.7/0.3 and (**d**) Ti/ Zr mole ratio 0.5/0.5]

The EDX analysis of barium titanate phase powders formation without addition of zirconium ions using different mole ratios of Ti/Zr from 0.9/0.1 to 0.5/0.5, oxalic acid mole ratio 0.5, calcination temperature1000°C and calcination time 2h were shown in Fig.32. The result show EDX analysis of barium titanate powders without addition of zirconium ions formed Ti-rich or Ba-rich are difficult to confirm which the dominating species element due to the overlap of Ba and Ti energy lines. By increasing the Ti/Zr mole ratio a strong Zr peak and the increase of Ti/Zr mole ratio increase the percent of Zr element. Fig.33 show the variation of the dielectric constant as a function of frequency at various temperatures at oxalic acid mole ratio 0.5 , calcination time 2.25 h and different of Ti/Zr mole ratios from 0.9/0.1 to 0.5/0.5. The result showed that the dielectric constant depend on temperature , the temperature corresponding to the maximum value of the dielectric constant decrease with increasing Zr content, implying that the Zr substitution in $BaTiO_3$ influence the transition temperature. The dielectric constant of samples produced at Ti/Zr mole ratio 0.9/0.1, the maximum dielectric constant at 130°C was 1.14E+05, dielectric constant of samples produced at Ti/Zr mole ratio 0.7/0.3, the maximum dielectric constant was 5.7 E+04 at 75 °C and rapidly decrease to 5476 at 100 °C and the dielectric constant of samples produced at Ti/Zr mole ratio 0.5/0.5, the maximum dielectric constant was 22604 at 75 °C and rapidly decreases to 1250 at 100°C.

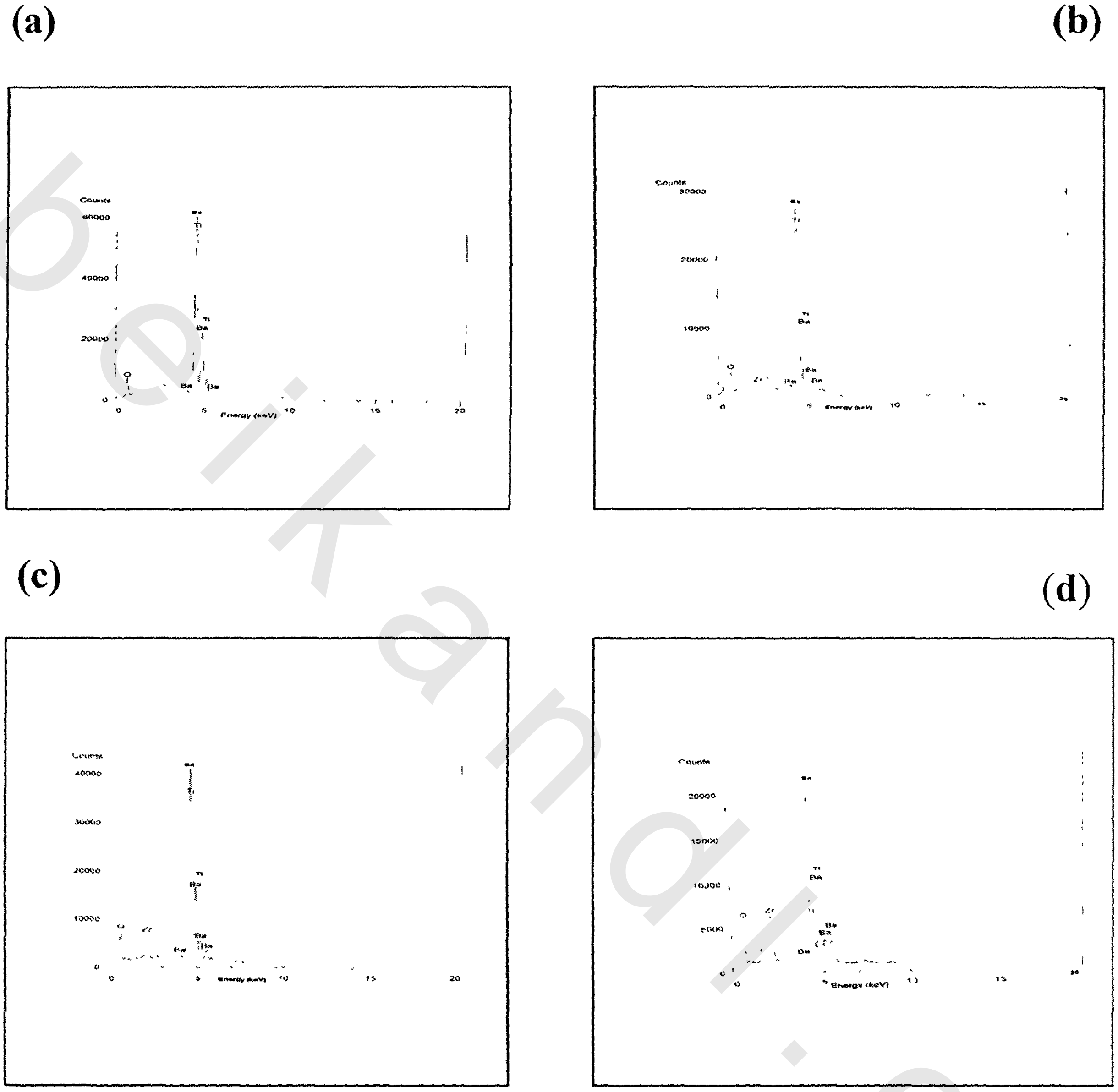


Fig.32: EDX analysis of produced samples using different Ti/ Zr mole ratios, where; [(**a**) without added zirconium ions, (**b**) Ti/ Zr mole ratio 0.9/0.1, (**c**) Ti/ Zr mole ratio 0.7/0.3 and (**d**) Ti/ Zr mole ratio 0.5/0.5]

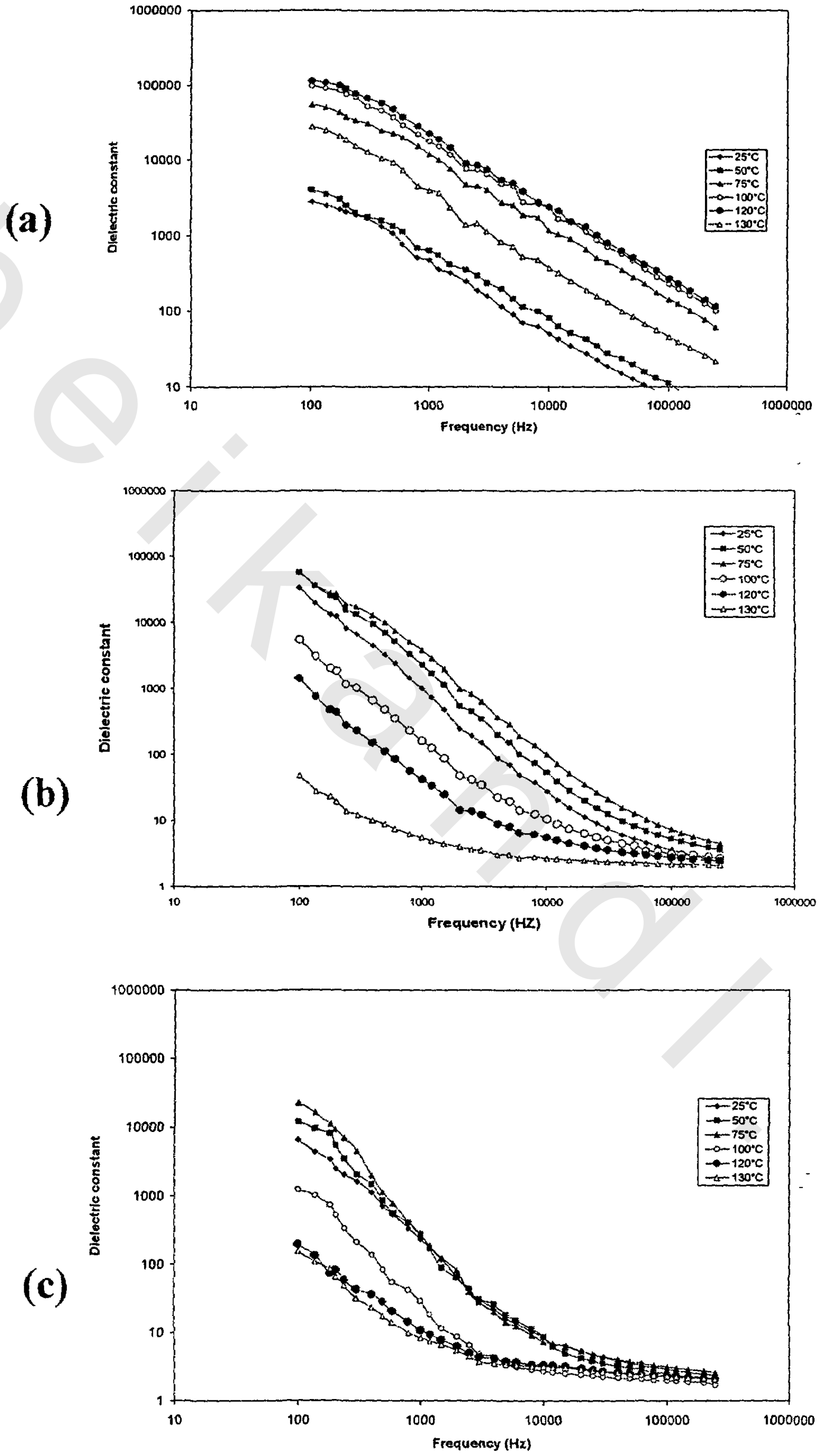


Fig. 33: Dielectric properties of produced samples using different Ti/ Zr mole ratios, where [(**a**) Ti/ Zr mole ratio 0.9/0.1, (**b**) Ti/ Zr mole ratio 0.7/0.3 and (**c**) Ti/ Zr mole ratio 0.5/0.5]

III.1.1.3. Preparation of Barium Titanate using Citric and Tartaric Acid

Different experiments were carried out for the preparation of barium titanate powders using citric and tartaric acids as a source of organic carboxylic acid at different conditions of calcination temperature, calcination time, citric and tartaric acid mole ratios. The main reaction occurring with increasing temperature in the formation of $BaTiO_3$ from (Ba, Ti)-citrate and (Ba, Ti)-tartarate complex precursors are defined as:

(a) Dehydration of the citrate or tartarate polymeric complex precursors

(b) Decomposition / oxidation of the dehydrated citrate or tartaric polymeric complex precursor with the formation of the intermediate phases (BaTi) compounds

(c) Formation of barium titanate as a consequence of the reaction between the previously formed intermediate by products **(Vinothini, et al 2005, Ghosh, et al 2007)**.

When the optimum conditions resulting from statistical design experiments in Table12 using citric and tartaric acids as a source of organic acid at calcination temperature 1000°C, calcination time 2 h, citric and tartaric acid mole ratio 0.5 we applied. The results show that the formed barium titanate ($BaTiO_3$) phase is included with other phases of $Ba_4Ti_{13}O_{30}$, BaO, and TiO_2. Therefore, the effect of citric and tartaric acids mole ratio, calcination temperature, calcination time on $BaTiO_3$ phase formation and morphology were systematically studied.

III.1.1.3.1. Effect of Citric and Tartaric Acid Mole Ratios

To study the effect of citric and tartaric acids mole ratio on the barium titanate phase formation, experiments were carried out at different citric and tartaric acids mole ratios from 0.5 to 1.5 under the following conditions:

- Calcination temperature, °C : 1000
- Calcination time, h : 2

The XRD patterns of the formed BT phase are given in Fig.34-35. The results show that decrease in the citric and tartaric acids mole ratios lead to a decrease in the phase formation of barium titanate (BT). Moreover, at (citric, tartaric) acid moles ratio 1.2 and 1.5, a pure crystalline of tetragonal barium titanate (BT) phase was obtained. In the other hand, at citric acid 0.5 and 1, mixtures of tetragonal $BaTiO_3$ and ($Ba_4Ti_{13}O_{30}$) phases were formed. This is attributed to an increase in the citric and tartaric acids mole ratio enough to oxidize the precursors which result in the formation of CO_2, $BaCO_3$, and TiO_2 leading to the formation of $BaTiO_3$ phase. The crystallite size of tetragonal phase barium titanate as calculated from XRD analysis using Debye-Scherrer formula was obtained by studying the effect of citric and tartaric acid mole ratios. The crystallite size of pure barium titanate powders were 75.4 and 97.4 nm at citric acid mole ratios 1.2 and 1.5. Moreover, the crystallite size of pure barium titanate at tartaric acid mole ratio 1.2 and 1.5 were 83.4 and 100.7 nm. From the results it is concluded that the crystallite size decreases with decreasing citric and tartaric mole ratios to 1.2.

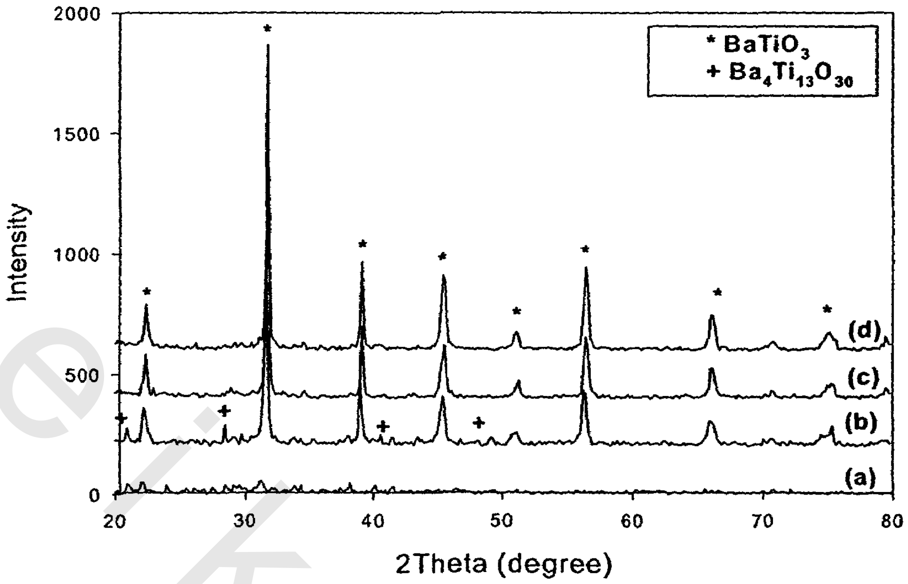


Fig.34: XRD analysis of the produced BT samples using citric acid [(**a**) mole ratio 0.5, (**b**) mole ratio 1, (**c**) mole ratio 1.2 and (**d**) mole ratio1.5]

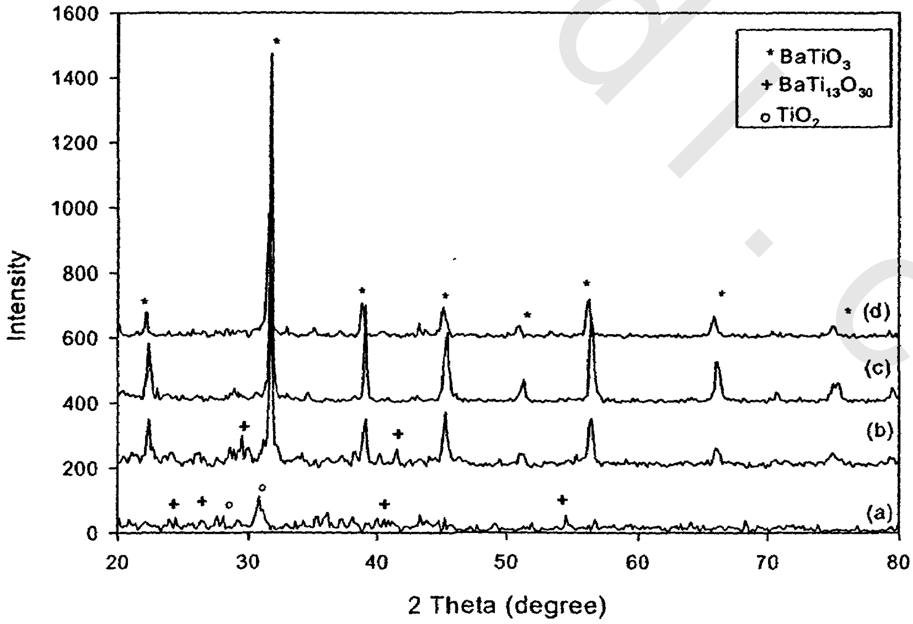


Fig.35: XRD analysis of the produced samples using tartaric acid [(**a**) mole ratio 0.5, (**b**) mole ratio 1, (**c**) mole ratio 1.2 and (**d**) mole ratio1.5]

III.1.1.3.2. Effect of Calcination Temperature using Citric and Tartaric Acid

A series of experiments was carried out by changing the calcination temperature from 800 to 1000°C, under the following conditions:

- Citric and Tartaric acid mole ratio : 1.2
- Calcination time, h : 2

Fig. 36-37 show XRD patterns of produced BT samples using citric and tartaric acids at different calcination temperature from 800 -1000°C. Increasing the calcination temperature up to 1000°C led to an increase in the phase formation of BT while decreasing the calcination temperature below 1000°C a mixture of $BaTiO_3$ and $Ba_4Ti_{13}O_{30}$ phases using citric acid were formed. Moreover, a well crystalline barium titanate phase was obtained using tartaric acid with increasing the calcination temperature up to 900°C while at calcination temperature 800 °C, the formed barium titanate phase contained other phases namely $Ba_4Ti_{13}O_{30}$ and TiO_2. In comparison, barium titanate phase using citric and tartaric acids as a source of organic acid need high temperature to form barium titanate compared with using oxalic acid due to presence of O-H group and carboxylic group that need high temperature conversion of the formed complex into barium carbonate and titanium dioxide and carbon dioxide. Also, formations of barium titanate using citric acid need high calcination temperature than which formed using tartaric acid because increasing carboxylic acid in citric acid (3- carboxylic acid) than present in tartaric acid (2- carboxylic acid).

The crystallite size of tetragonal phase increased with increasing the temperature. The crystallite size of tetragonal barium titanate phase was obtained at different calcination temperatures 800, 900 and 1000°C; citric acid mole ratio 1.2 and calcination time 2h were 56.7, 64.9 and 75.4 nm. Moreover, the crystallite size of barium titanate phase using tartaric acid mole ratio 1.2 at different calcination temperatures 800, 900 and 1000°C were 43, 66 and 83.4 nm.

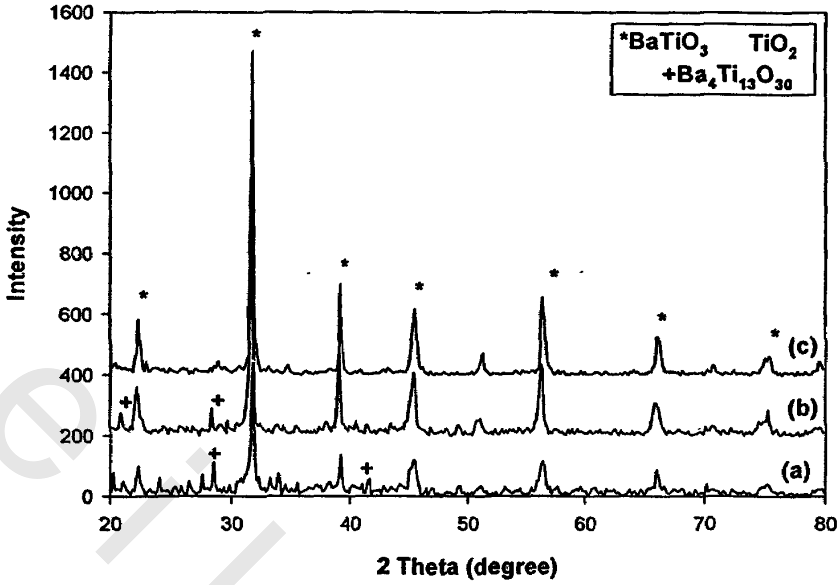


Fig.36: XRD patterns of the produced samples using citric acid mole ratio 1.2, calcination time 2h and different calcination temperatures [(a) 800°C, (b) 900°C, (c) 1000°C]

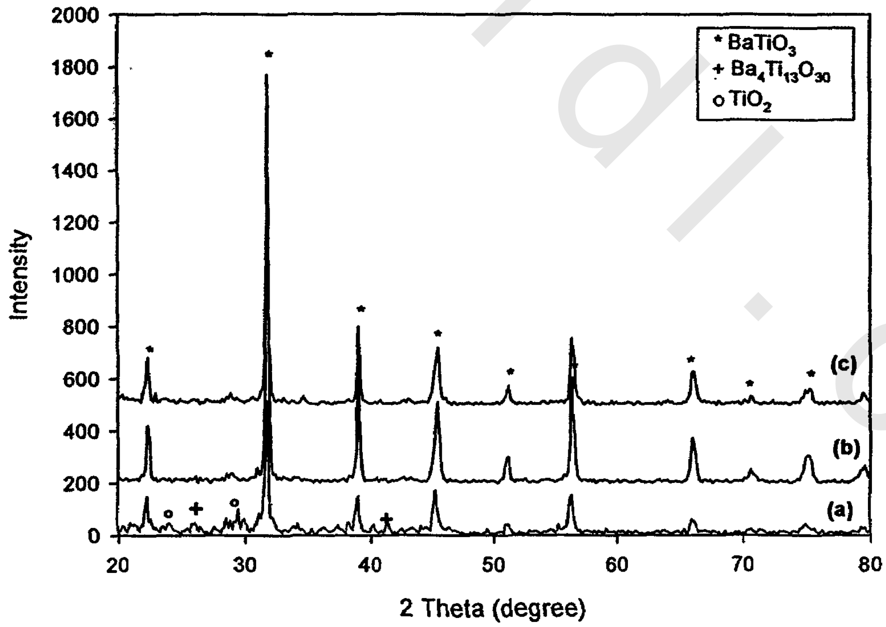


Fig.37: XRD patterns of the produced samples using tartaric acid mole ratio 1.2, calcination time 2h and different calcination temperatures [(a) 800°C, (b) 900°C, (c) 1000°C]

III.1.1.3.3. Effect of Calcination Time using Citric and Tartaric Acids

Different experiments were carried out by changing the calcination time from 1 to 2 h, under the following conditions:

Citric and tartaric acid mole ratio	: 1.2
Calcination temperature, °C using citric acid	: 1000
Calcination temperature, °C using tartaric acid	: 900

Fig. 38-39 show XRD patterns of produced samples at different calcination time. The results indicate that increasing the calcination time led to an increase in the formation of pure single phase crystalline of tetragonal phase $BaTiO_3$. The well crystalline BT phase was attained at 2 h. At lower calcination time than 2 h; a mixture of barium titanate and barium carbonate phases was obtained. Therefore, it can be concluded that the optimum conditions for formation of single barium titanate phase using citric acid as organic acid sources were citric acid mole ratio1.2, calcination temperature 1000°C and calcination time 2 h. Moreover, the optimum conditions of formation single phase of $BaTiO_3$ using tartaric acid at mole ratio 1.2, calcination temperature 900°C and calcination time 1.5 h.

The crystallite size of the obtained barium titanate powders were increased by increasing the calcination time. The crystallite size of barium titanate $BaTiO_3$ formed at different calcination times (1, 1.5 and 2h), citric acid mole ratio 1.2 and calcination temperature 1000 °C were 28.5, 58.3 and 75.4 nm. Also, the crystalline size of BT using tartaric acid as a source of organic acid at mole ratio 1.2 , calcination temperature 900°C and different calcination times (1,1.5 and 2h) were 43.2, 52 and 66.6 nm. In comparison, the crystalline size of pure single phase of BT at optimum conditions using citric acid 75.4 nm was higher than the crystalline size of BT using tartaric acid 66.6 nm.

III.1.1.3.4. Morphology of Barium Titanate Powders using Citric and Tartaric Acids

SEM micrographs of the barium titanate powders using citric acid mole ratio 1.2, calcination temperature 1000°C and calcination time 2 h are given in Fig.40. The results indicate that a pure single phase of tetragonal structure shape was obtained and the particles were homogenous with nearly spherical like structure, uniform distribution and very fine powders. The crystallite size of barium titanate using citric and tartaric acids were nearly similar to the crystallite size obtained from XRD analysis calculation data using Debye- Scherer formula.

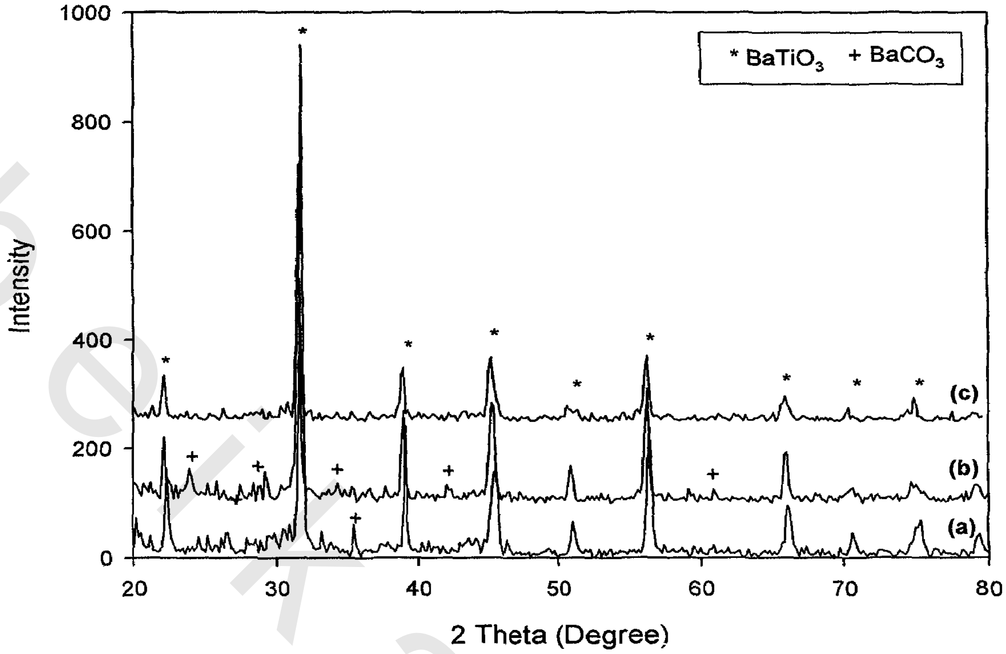


Fig.38: XRD patterns of produced samples using citric acid mole ratio 1.2, calcination temperature 1000°C at different calcination time[(**a**) 1 h, (**b**) 1.5h and (**c**) 2 h]

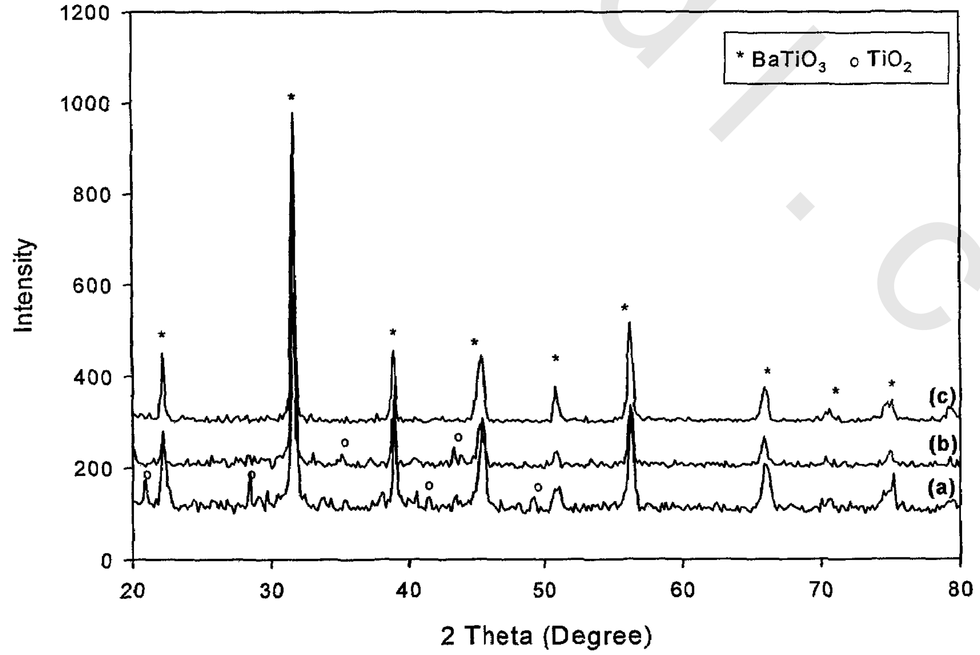


Fig.39: XRD patterns of produced samples using tartaric acid mole ratio 1.2, calcination temperature 900°C at different calcination time [(**a**) 1 h, (**b**) 1.5h and (**c**) 2 h]

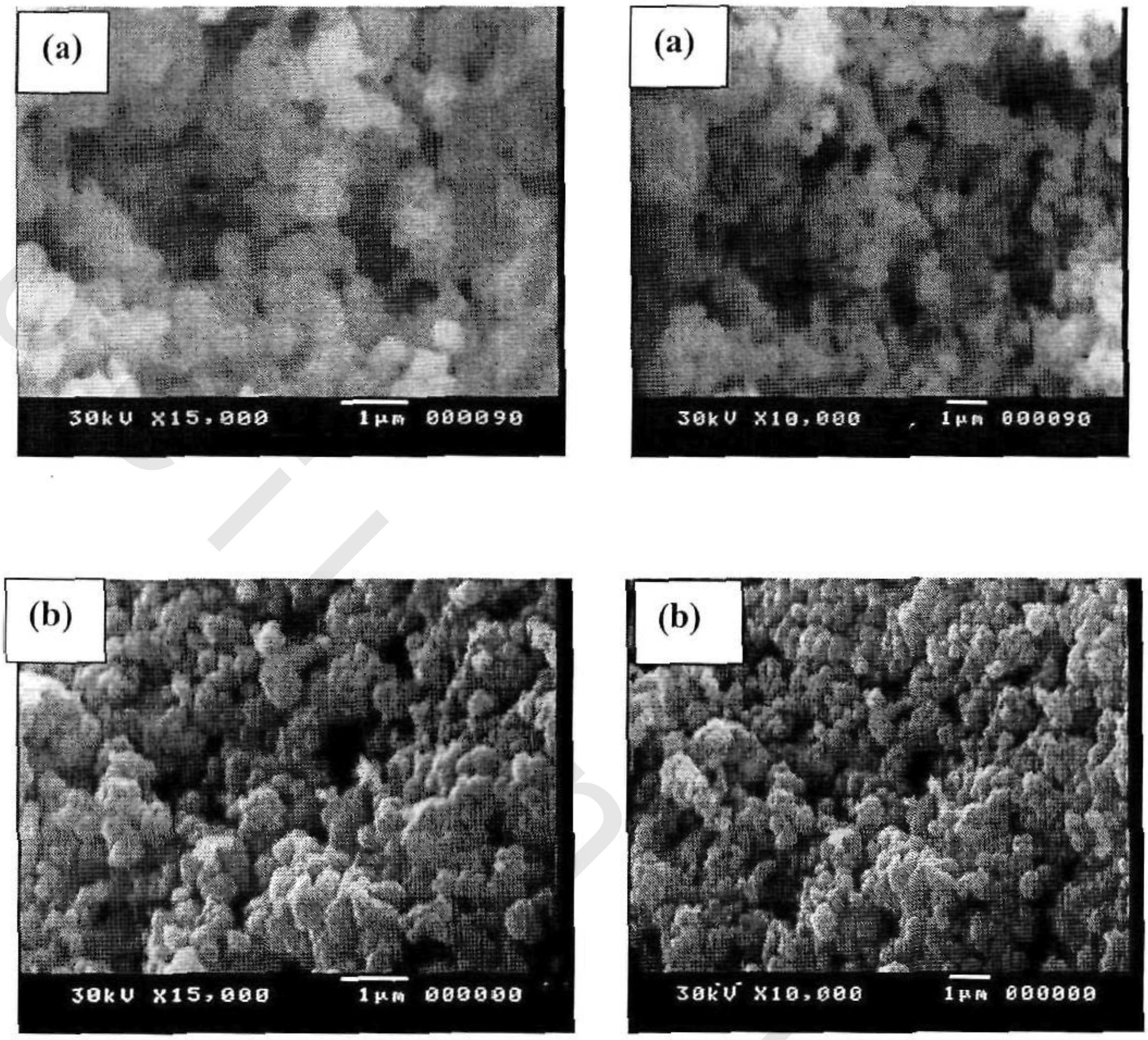


Fig.40: SEM micrographs of barium titanate nanopowders obtained at calcination temperature 1000°C, calcination time 2h using [(**a**) using citric acid mole ratio 1.2 and (**b**) tartaric acid mole ratio 1.2]

III.1.1.3.5. Infrared Spectra using Citric and Tartaric Acid

The FT-IR spectra for precursor using citric and tartaric acid mole ratio 1.2 are shown in Fig.41. FT-IR spectra of barium titanyl citrate precursor formed using citric acid as a source of organic acid shows the absorption bands peaks at 3425.9 cm^{-1} related to O-H stretching modes in crystallization water. In addition, the peaks at 1234, 1407 and 1762 cm^{-1} correspond to carboxylate group stretching modes. The peak at 656 cm^{-1} is related to Ti-O vibration mode.

Moreover, FT-IR spectra of barium titanyl tartarate precursor formed using tartaric acid shows absorption bands at 881, 1262 , 1399, 1738 and 2627cm^{-1} corresponding to the different modes of carboxylate group. Also, the broad band centered around 3380.6 cm^{-1} may be assigned to antisymmetric and symmetric stretching vibration of OH group and that of 1624 cm^{-1} due to H-OH bending of coordinated water. In addition, three broad absorption peaks at 529, 680 and 881 cm^{-1} for Ti-O observed in precursor sample. The characteristic absorbion band at 2977 cm^{-1} related to O-H is present in tartaric acid spectra.

The FT-IR spectra of barium titanate BT nanopowders produced after calcination at 1000°C for calcination time 2 h using citric and tartaric acids as shown in Fig.42. It is observed that the characteristic absorption bands at 1609 and 3380 cm^{-1} are assigned to O-H stretching and bending vibration, respectively. Also, the absorption bands at 426 and 582 cm^{-1} were characteristic of Ti-O.

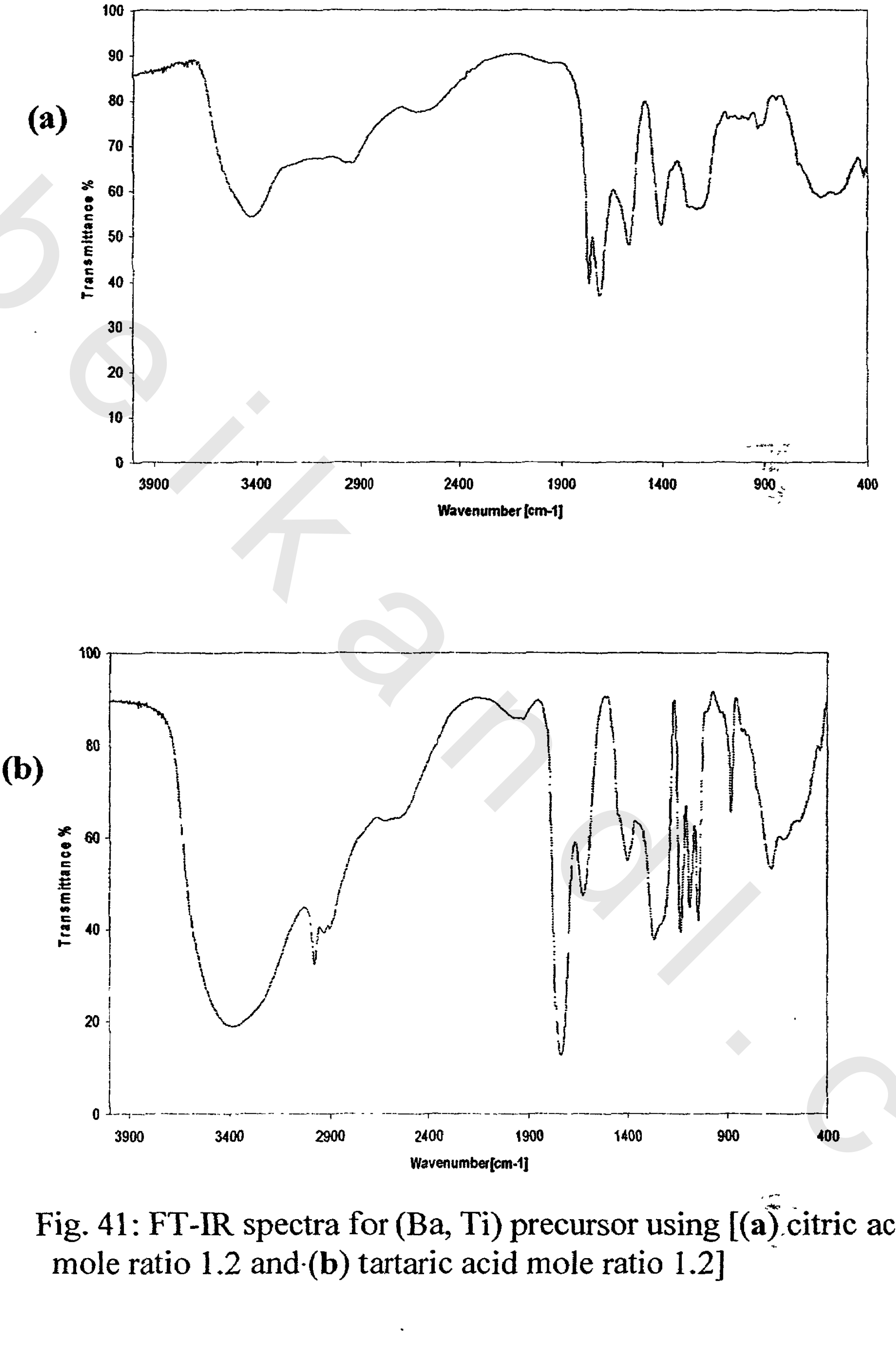


Fig. 41: FT-IR spectra for (Ba, Ti) precursor using [(a) citric acid mole ratio 1.2 and (b) tartaric acid mole ratio 1.2]

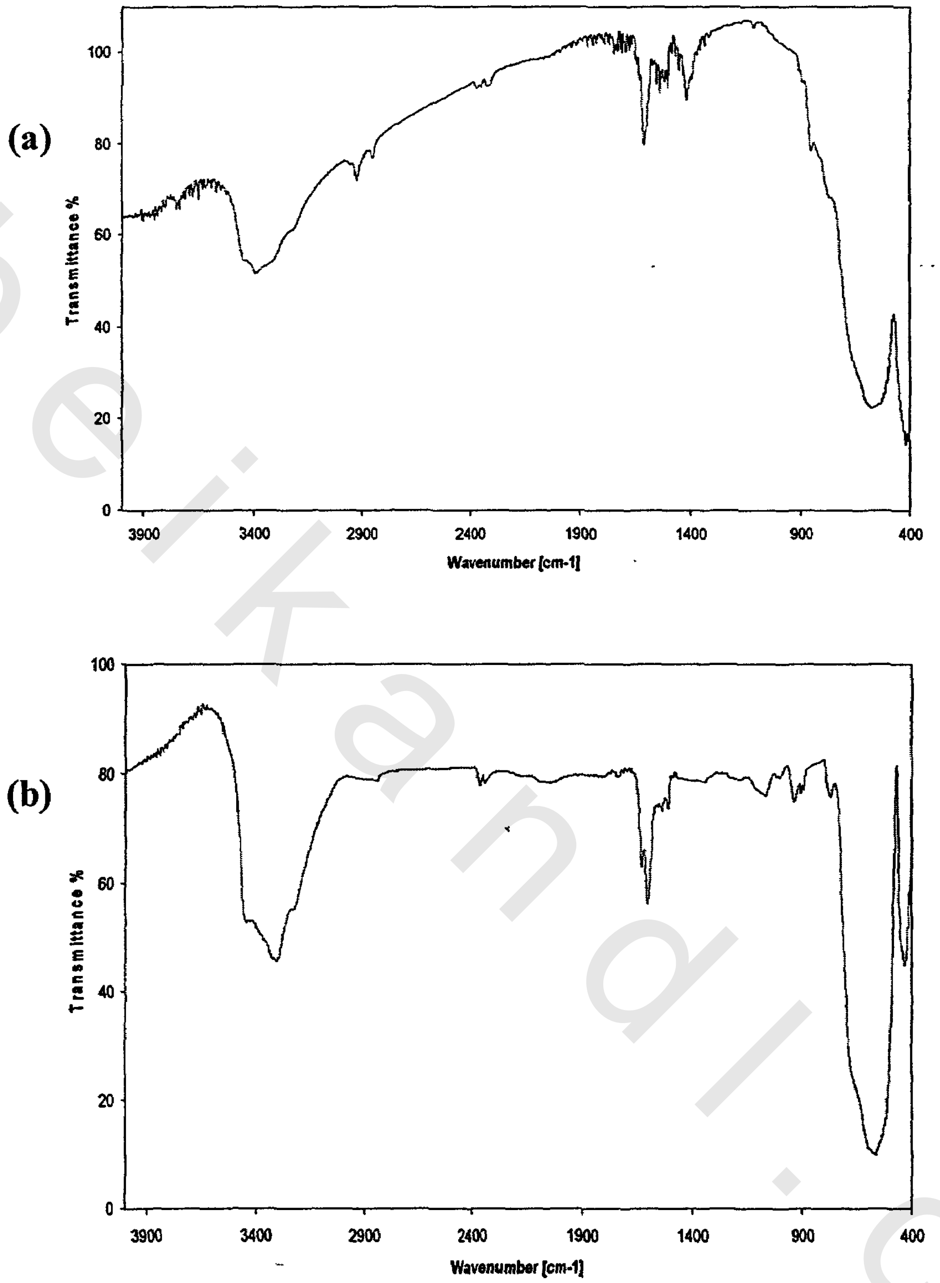


Fig.42: FT-IR spectra of barium titanate powders at calcination temperature1000°C, calcination time 2 h at [(**a**) citric acid mole ratio 1.2 and (**b**) tartaric acid mole ratio 1.2]

III.1.1.3.6. Dielectric Properties of Barium Titanate using Citric and Tartaric Acids

The dielectric constant as a function of frequency at various temperatures with calcination time 2h, calcination temperature 1000°C, citric and tartaric acids mole ratio 1.2 is shown in Fig. 43. The result showed that the dielectric constant of barium titanate using citric acid as a source of organic acid increased with decreasing the frequency due to a decrease in the dipolar polarization of matrix and the accumulation of charges at the interface between ceramic particles. At low frequency the dielectric constant increases with increasing the temperature until 75°C after this temperature, rapidly decreasing dielectric constant. The maximum dielectric constant of BT using citric acid is 4295.668 at low frequency 100 Hz and room temperature. The dielectric constant decreased after 75°C due to the defects in the crystal or the residual stress. Moreover, the dielectric constant of barium titanate using tartaric acid at constant frequency 100 Hz and room temperature is 4576.659. Moreover increasing the temperature to 100°C increased the dielectric constant to 5.6+E 04.

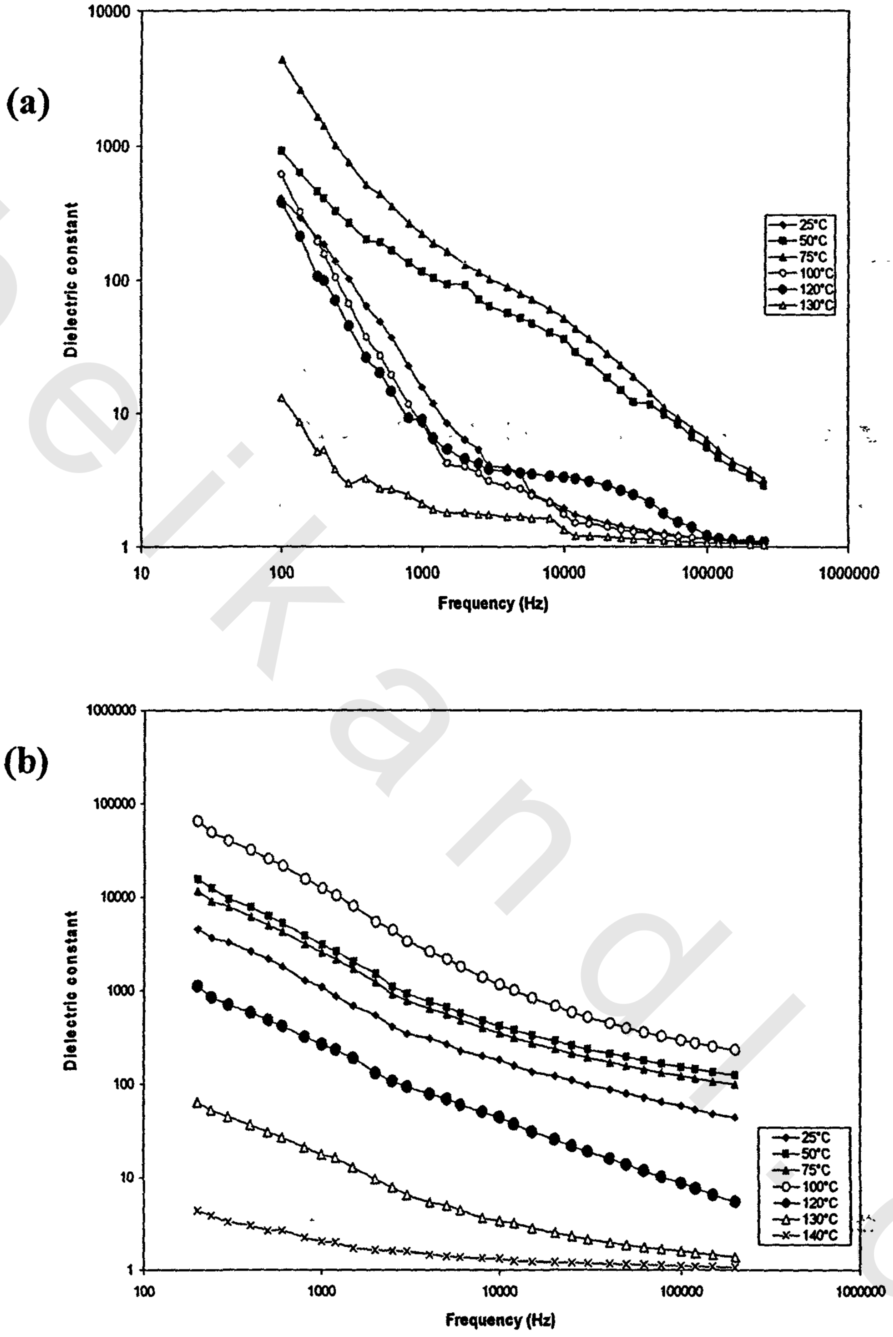


Fig. 43: Dielectric properties of barium titanate nanopowders at calcination temperature 1000 °C, calcination time 2h using [(**a**) citric acid mole ratio 1.2 and (**b**) tartaric acid 1.2

III.1.2. Preparation of Barium Titanate by Hydrothermal Method

The optimum conditions for the synthesis of barium titanate nanopowders via hydrothermal method were determined on the basis of Box-Behnken statistical design. The conditions studied were hydrothermal time (12-24h), hydrothermal temperature (150-200 °C) and pH (12-14). The response data (phase formation and crystallite size) were performed for 15 experiments done by changing the conditions. The results obtained are given in Table (13).

In the hydrothermal method, the barium titanate powders are formed by the reaction between barium hydroxide aqueous solution and liquid titanium isopropoxide which can be described by two steps process:

1. Precipitation of a Ti-rich amorphous phase
2. Crystallization of barium titanate by reaction between the Ti-amorphous phase and Ba^{2+} ions left in solution.

The reactions in hydrothermal process can be described as below:

$$Ba(OH)_2 \longrightarrow Ba^{2+} + 2OH^- \qquad (23)$$

$$Ti\,(isopropoxide) + 2\,OH^- \longrightarrow Ti(OH)_6^{-2} \qquad (24)$$

$$Ba^{2+} + Ti(OH)_6^{2-} \longrightarrow BaTiO_3 + 3H_2O \qquad (25)$$

Increasing $[OH^-]$ concentration and reaction temperature can facilitate the formation of $BaTiO_3$ **(Vivianiet al, 2003 & Qi et al, 2004)**.

From Table (13), it can be observed that a pure well crystalline barium titanate phase can be obtained at pH 13, hydrothermal temperature 200°C and hydrothermal time 24h. Increasing the pH from 12 to 13 and 14 promotes the formation of barium titanate phase. For example the percentage of barium titanate phase formation increases from 52.9 % at pH 12 to 96.3 % at pH 14 for constant hydrothermal temperature 200°C and hydrothermal time 18h. Moreover, increasing the temperature led to an increase the formation of barium titanate phase. The barium titanate phase conversion, % increased from 94.8 (R11) at hydrothermal temperature 150°C to 100 (R12) at hydrothermal temperature 200°C for pH 13 and hydrothermal time 24 h. Also, the hydrothermal time slightly increases the formation of barium titanate phase, for instance, the barium titanate conversion, % was increased from 88.2 (R6) at hydrothermal time 12 to 91 (R8) at hydrothermal time 24h for hydrothermal temperature 175°C and pH14. On the other hand, the crystallite size decreases by increasing the pH, hydrothermal temperature and hydrothermal time.

Table 13: Barium titanate phase conversion and crystallite size according to experimental statistical Design conditions

Run	Factors			Conversion, %	Av.Crystal Size .nm
	pH	Temp. (°C)	Time (h)		
1	12	150	18	40	91.9
2	14	150	18	84.3	47.4
3	12	200	18	52.9	57.2
4	14	200	18	96.3	62.8
5	12	175	12	52.3	75.0
6	14	175	12	88.2	71.1
7	12	175	24	62.8	108.9
8	14	175	24	91.0	71.2
9	13	150	12	85.5	88.6
10	13	200	12	95.5	72.0
11	13	150	24	94.8	76.0
12	13	200	24	100	78.3
13	13	175	18	94.6	68.3
14	13	175	18	96.6	80.8
15	13	175	18	96.7	75.0

III.1.2.1. XRD Data of Barium Titante by Hydrothermal Method

Fig.44 showed XRD patterns of the produced barium titanate samples at different variables of hydrothermal temperature, hydrothermal time, and pH value of solution.

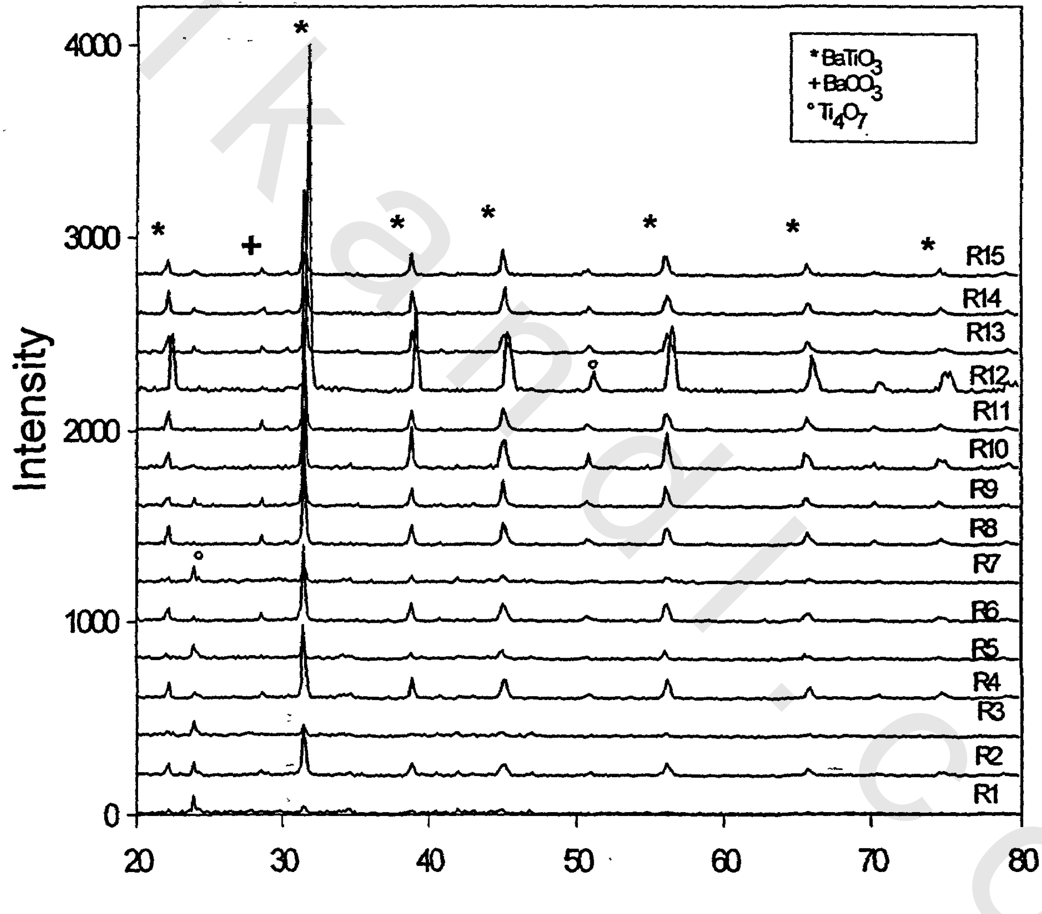


Fig. 44: XRD patterns of produced BT powders samples by experimental statistical design at different hydrothermal conditions.

From statistical design program, the barium titanate phase conversion % and the crystallite size (nm) are determined and the standard deviation for the result from the program was 4.11 and the determination coefficient R-squared was 0.9845 which indicates the agreement of the generated model and the experimental results. From XRD patterns in Fig. 44 the results show that at low hydrothermal temperature, the barium titanate phase formation decreases and appeared as tetragonal structure (JCPDS #81-2202). Moreover, barium carbonates $BaCO_3$ (JCPDS #44-1487), and titanium dioxide Ti_6O_{11} phases (JCPDS #50-0788) are also appear at (Run 10, 9, 13). The conversion, % of barium titanate increases from 40 to 62.8 % by increasing the hydrothermal time from 12 h to 24 h at pH 12 and hydrothermal temperature from 150-200 °C (Run 5, 3, 7). Increasing the hydrothermal temperature up to 200°C with increasing the pH to 13 led to increases the barium titanate conversion, % from 85.5 to 100. At low hydrothermal time 12 h and the similar conditions of hydrothermal temperature and pH, the conversion, % to barium titanate phase was 95.5. A pure well crystalline tetragonal barium titanate phase can be achieved by increasing the pH to 13, hydrothermal temperature 200°C and hydrothermal time 24h (R12). The average crystallite size was decreased by increasing the pH at constant hydrothermal temperature and hydrothermal time. The average crystallite size of BT at hydrothermal temperature 150°C and hydrothermal time 18 h were decreased from 109 at pH 12 to 47 nm at pH 14.

The effect of hydrothermal temperature and pH on the barium titanate phase conversion, % was given in Fig. 45 from the results, it can be showed that increasing hydrothermal temperature and the pH at constant hydrothermal time increased the barium titanate phase conversion, %. At low hydrothermal time 12 h, a well crystalline barium titanate with 100% conversion can be achieved at pH 13.5 and hydrothermal temperature 180°C. Increasing the hydrothermal time up to 18 h, the hydrothermal temperature will be decreased to 175°C to get pure barium titanate phase. Moreover, at hydrothermal time 24h the pure BT phase will form at hydrothermal temperature 200°C for pH 13.25.

Fig.46 showed the effect of hydrothermal temperature and hydrothermal time on barium titanate phase formation, at constant pH from 12 to 14. The results showed that the pH is the most significant factor for the formation of BT phase by hydrothermal method at the conditions studied. At low pH 12, it is very difficult to attain single phase of barium titanate. The maximum conversion, % was 60. Increasing the pH up to 13-14, the conversion, % of barium titanate phase increased and the availability for formation of pure barium titanate increased.

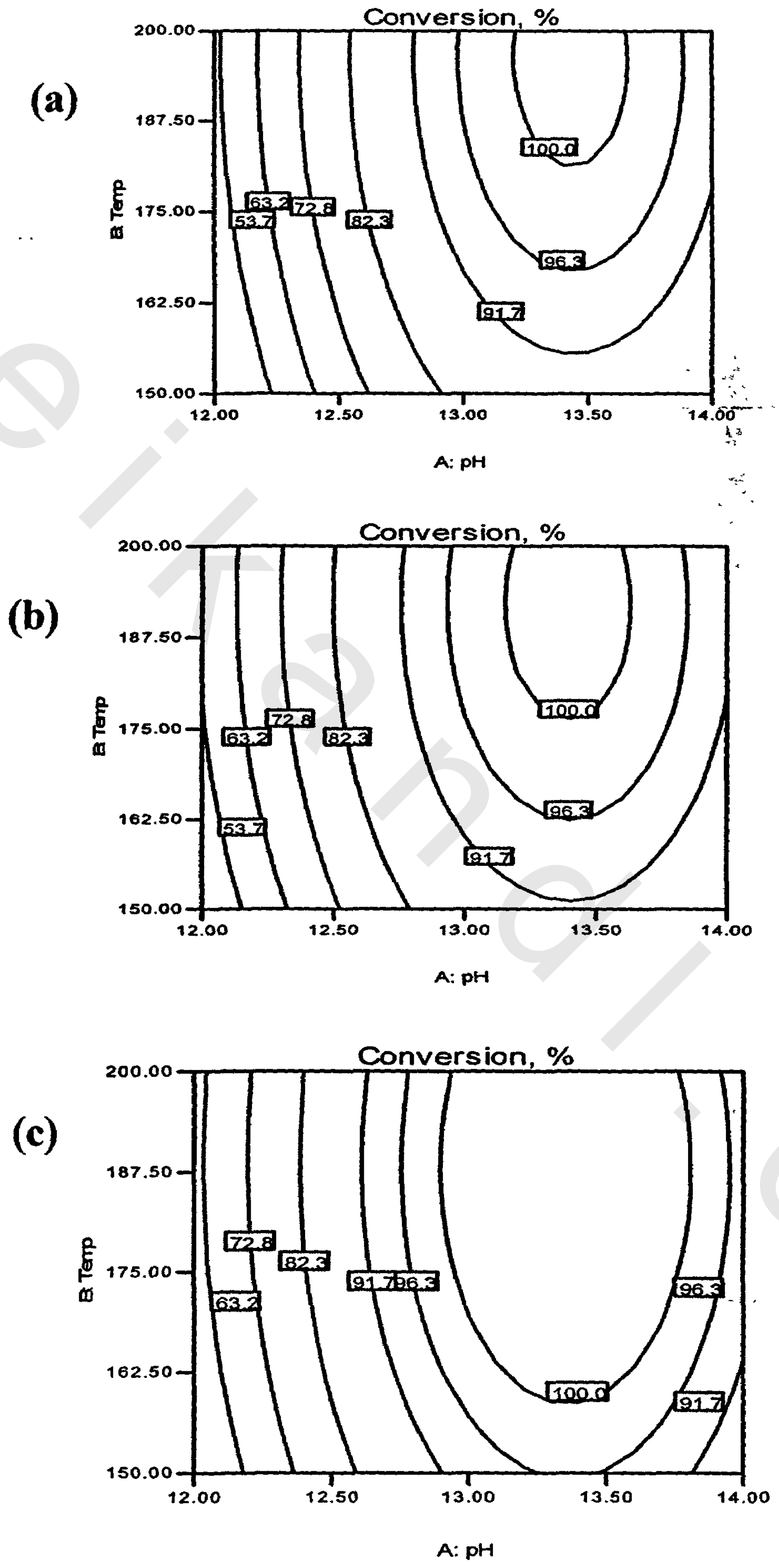


Fig 45: .Contour plots for the effects of hydrothermal temperature and pH on conversion of BT [(**a**): hydrothermal time =12 h; (**b**): 18 h; (**c**): 24 h]

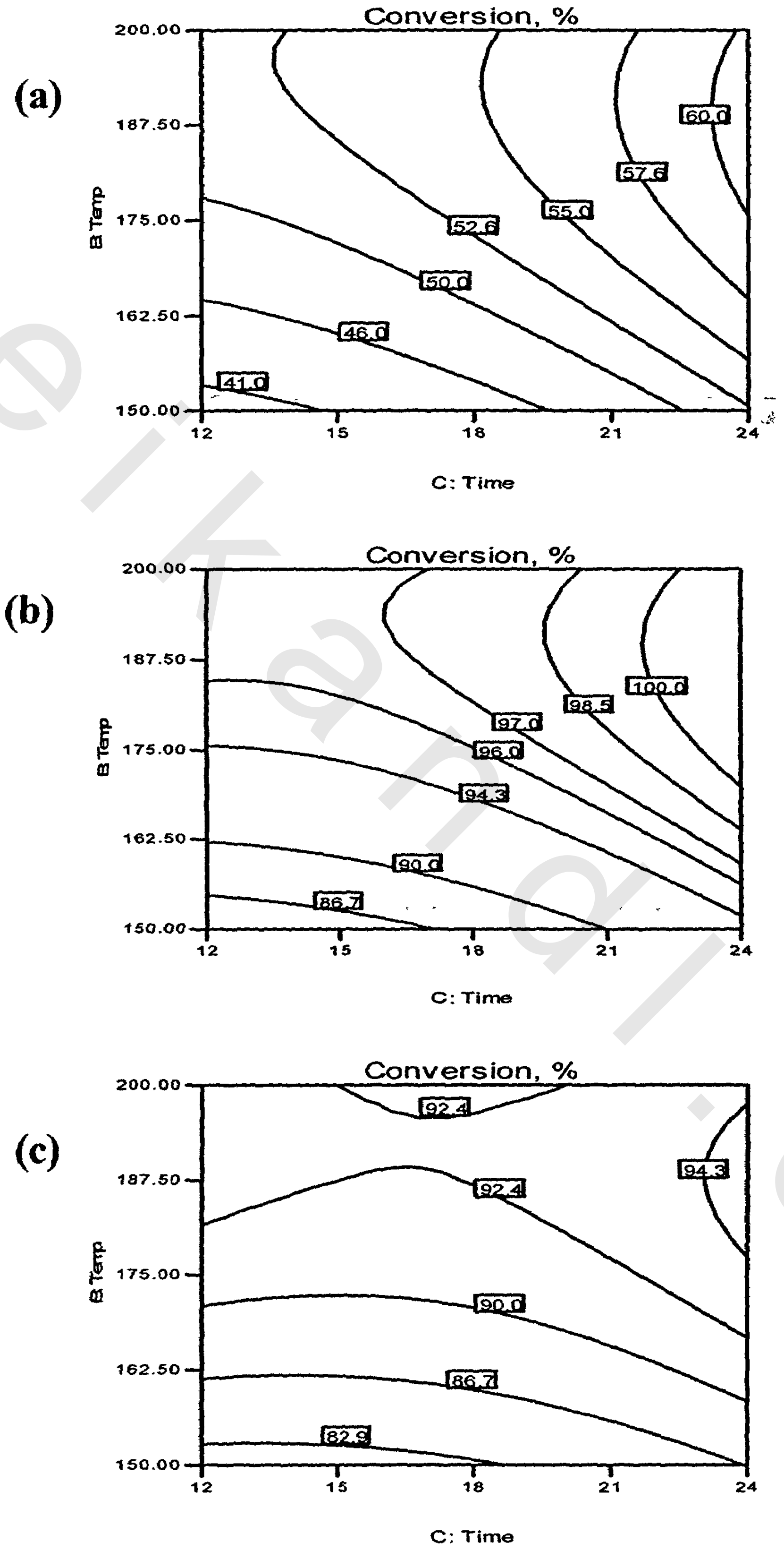


Fig. 46: Contour plots for the effects of hydrothermal temperature and hydrothermal time on conversion of BT [(**a**): pH =12; (**b**): 13; (**c**): 14]

III.1.2.2.Effect of Hydrothermal Temperature

The effect of hydrothermal temperature on barium titanate phase formation at different pH values at constant hydrothermal times 12, 18, and 24 h, respectively were shown in Fig 47. The results show that increased hydrothermal temperature with increasing the pH led to an increase of the conversion of tetragonal barium titanate phase. For instance, at low hydrothermal time (12h), the formation of well crystalline tetragonal barium titanate phase can be achieved at pH 13.25-13.5 and hydrothermal temperature (190-210°C). Furthermore, increasing the hydrothermal time up to 18 h), the 100% conversion of tetragonal barium titanate phase can be attained at hydrothermal temperature (175-210°C) at pH (13.25-13.5). Moreover, increasing the hydrothermal time up to 24 h decreased the hydrothermal temperature to (155-210°C) at the pH (13-13.5) led to formation of tetragonal barium titanate phase.

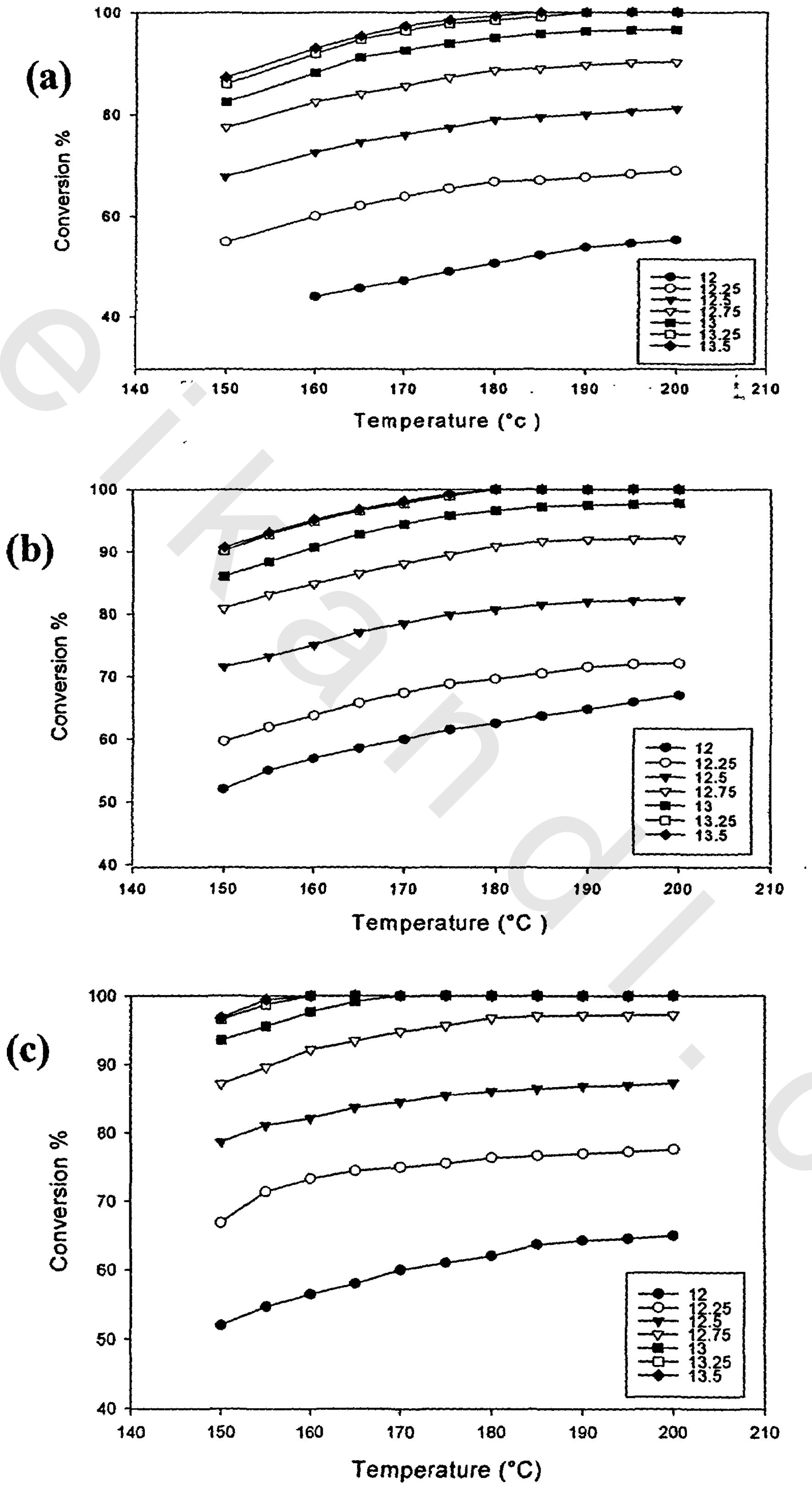


Fig.47: Effect of hydrothermal temperature on the conversion of BT at different pH and different hydrothermal time [(**a**) 12, (**b**) 18 and (**c**) 24 h].

III.1.2.3.Effect of Hydrothermal Time

The effects of hydrothermal time on the barium titanate phase formation at different hydrothermal temperature from 150-200°C at constant pH 12 and 13 , respectively were studied. The data obtained from the statestical design program were given in Fig.48. The results showed that barium titanate phase percentage was gradually increased with increasing the hydrothermal time. For example, the tetragonal barium titanate phase percentage increased from 95 to 100% when the hydrothermal time increased from 12 to 22 h at pH 13. Moreover, the results showed that pH 12 was insufficient to attain well crystalline tetragonal barium titanate phase, the BT conversion percentage was the range between 36-60 % at different hydrothermal temperature from 150-190°C. In conclusion, at pH 13, well crystalline barium titanate phase formation (100%) can be attained at hydrothermal temperature 180-190 °C and hydrothermal time 22-24 h .

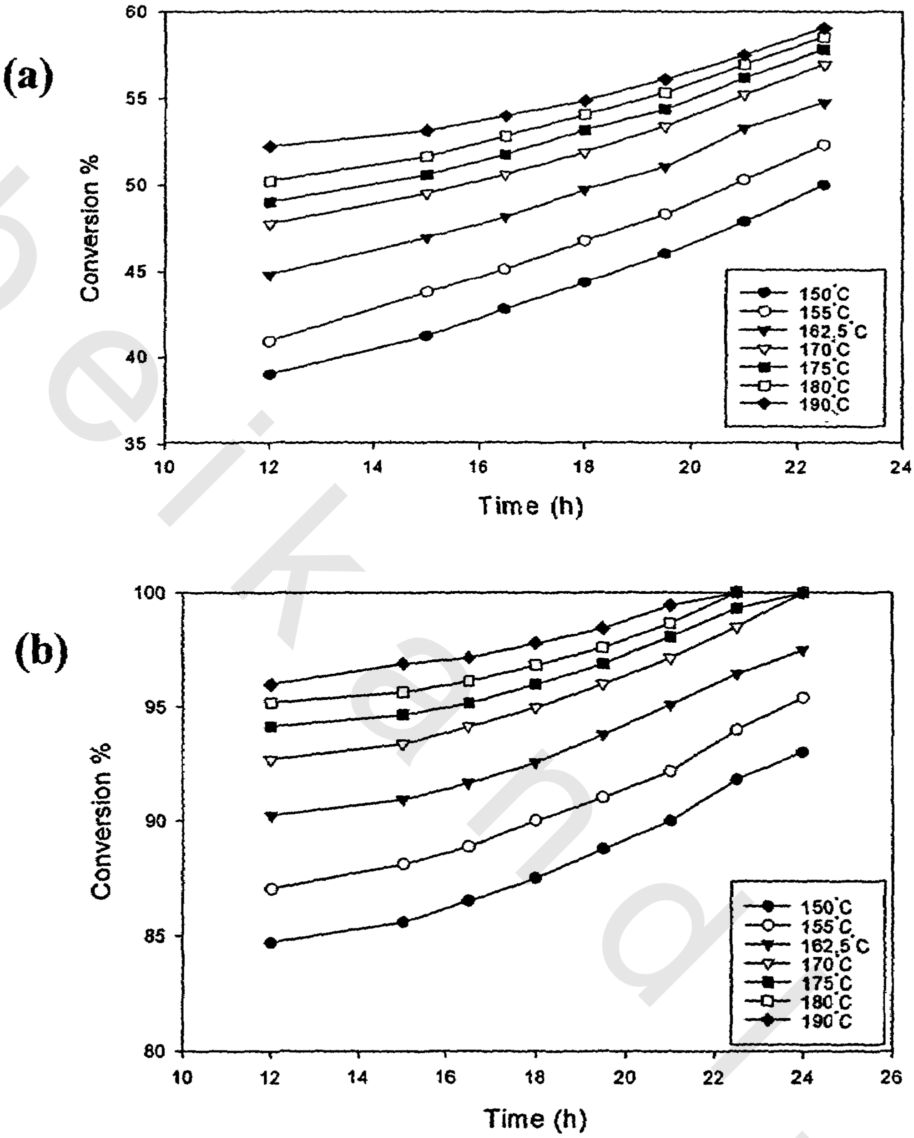


Fig. 48: Effect of time on conversion of BT at different hydrothermal temperature with different pH [(a): 12 and (b):13]

III.1.2.4. Effect of pH

The pH values play an important role in the nucleation and crystallization of barium titanate crystal under hydrothermal conditions thermodynamically. The OH – ions seemed to act as catalysts by accelerating the transition of Ba-OH bonds to form $BaTiO_3$ crystals. Where, the pH values of the starting suspension and consequently the aqueous suspension of already formed barium titanate nuclei after the hydrothermal synthesis were very important for preparation of $BaTiO_3$ grains after the formation of $BaTiO_3$ nuclei from supersaturating solution. At high pH the aqueous suspension of barium titanate nuclei is stable after synthesis and a greater super saturation by the increased solubility of reactants leading to greater nucleation rate than growth rate.

Fig 49 show the effect of pH phase formation at different hydrothermal temperatures and constant hydrothermal time (12-24). The results show that increasing the pH from 12 to 13.5 increases the formation of barium titanate at constant time and temperature. For instance, the barium titanate phase formation increased from 55 to 100% when the pH increased from 12 to 13.25 at hydrothermal temperature 190°C. Furthermore, increasing the pH with hydrothermal time increased the formation of barium titanate phase at low hydrothermal temperature. The well crystalline barium titanate phase can be achieved at hydrothermal temperature 175°C, hydrothermal time 18 h and 13.25. Moreover, increasing the hydrothermal time up to 24 h, the single phase of barium titanate phase can be obtained at 155 -175°C and pH 13-13.5

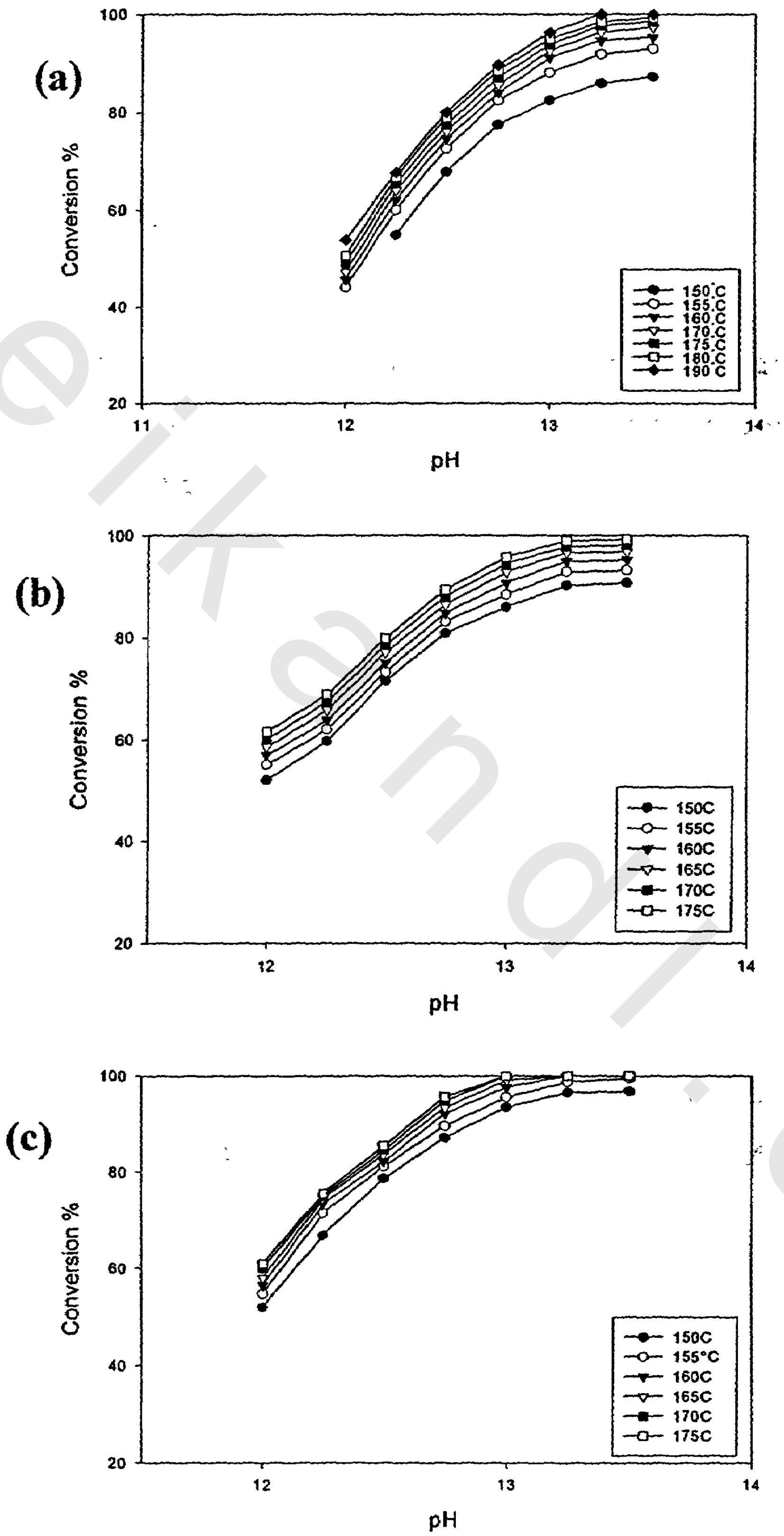


Fig 49: Effect of pH value on phase formation at different hydrothermal temperatures with different hydrothermal time [(**a**): 12h, (**b**): 18h and (**c**): 24 h]

All the experimental results, collected in the 3-D cubic as shown in Fig. 50, revealed the conversion of barium titanate, which ranged from 40 to 100 %,. The smallest conversion of BT can be obtained at high levels of hydrothermal temperature, high hydrothermal time and high level of pH of solution. The formation of BT with conversion 40 % can be obtained at low pH of solution, low hydrothermal temperature and hydrothermal time. On the other hand, the conversion of BT (100%) can be achieved at high level of pH, high hydrothermal temperature and hydrothermal time.

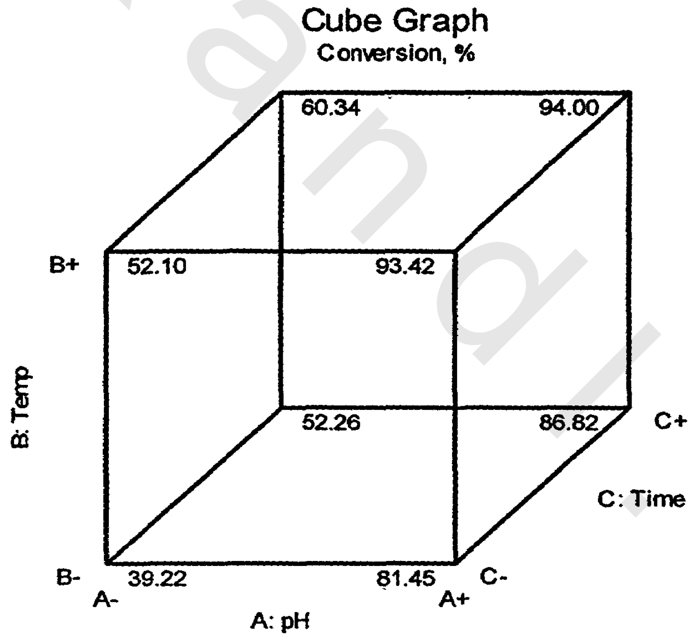


Fig.50: 3-D plot graph for all experimental data for conversion of BT (Standard Deviation: 14.11; R^2: 0.984)

III.1.2. 5. Crystallite Size of Barium Titanate by Hydrothermal Method

The crysrallite size of barium titanate powders were calculated from XRD analyses using Debye -Scherer formula. Statestical design showed that average crystallite size of BT at the studied different variables. Fig 51 show the effect of hydrothermal temperature and pH at different hydrothermal time on crystallite size of obtained BT powders. The results show that the average crystallite size of barium titanate produced range from 47.5 to 100 nm. Increasing the pH or high OH^- concentration with decreased hydrothermal temperature and time leads to a decrease in the average crystallite size because of the high degree of critical supersaturation , the solvent can dissolve most of the Ba^{2+} and $Ti(OH)_6^{-2}$ ions before the barium titanate $BaTiO_3$ particles are heterogeneously nucleated after the ions concentration in the solution exceeds the critical supersaturating concentration "burst " nucleation occurs, and numerous small nuclei are produced , leaving a small quantity of Ba^{2+} and $Ti(OH)_6^{2-}$ ions; growth of the barium titanate particles then is hindered and crystalline $BaTiO_3$ powder is produced (**Xu et al 2003 & Wang et al 2006**).

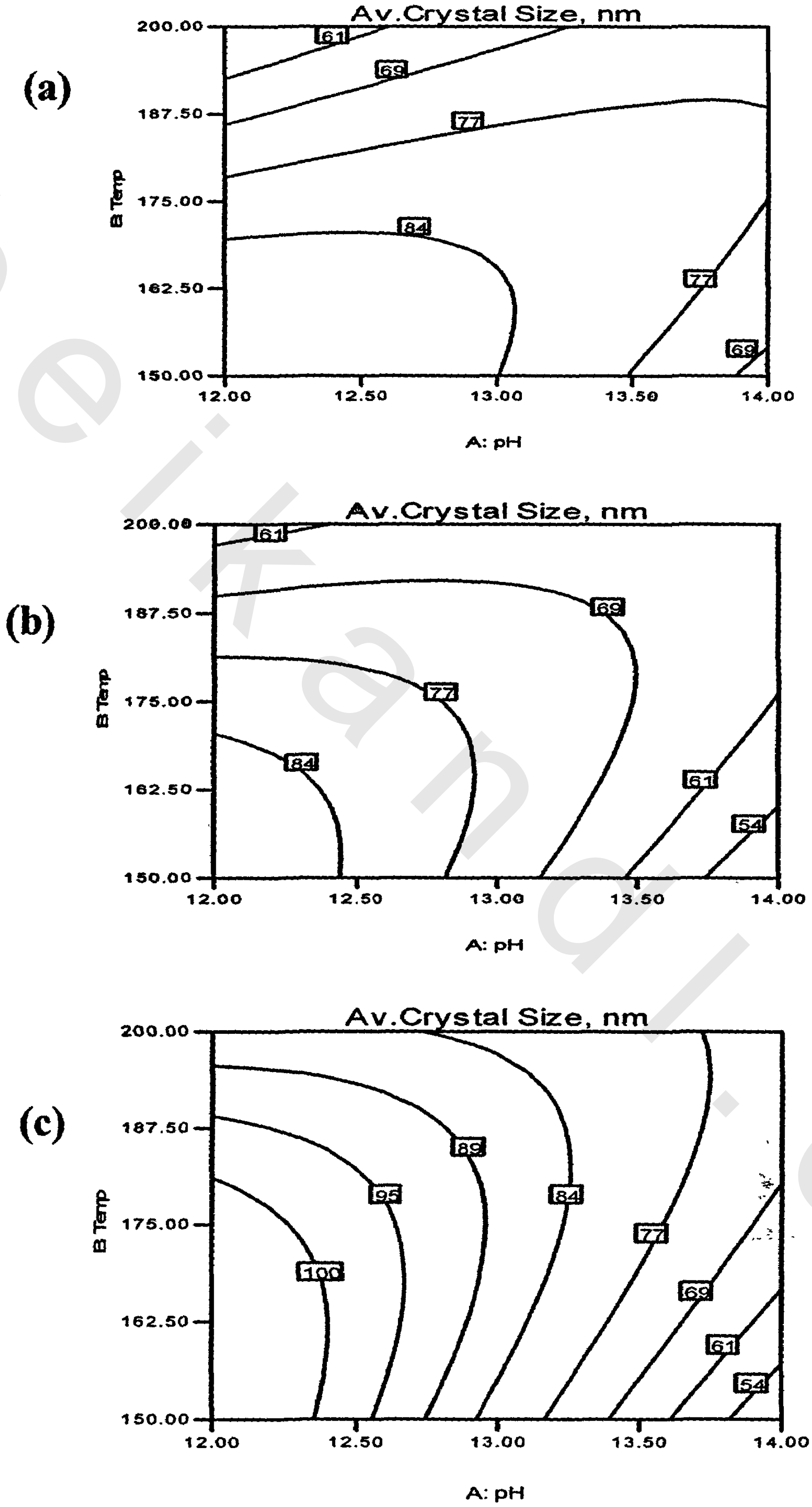


Fig.51: Contour plots for the effects of hydrothermal temperature and pH on crystallite size of conversion $BaTiO_3$ at different hydrothermal time [(**a**): 12, (**b**): 18 and (**c**): 24h]

All the experimental data, collected at the 3-D cubic graphs as shown in Fig.52 revealed that the lowest crystallite size can be obtained at low levels of hydrothermal temperature and hydrothermal time and high level of pH. In contrast, the highest crystallite size can be obtained at high levels of hydrothermal time, hydrothermal temperature and high pH.

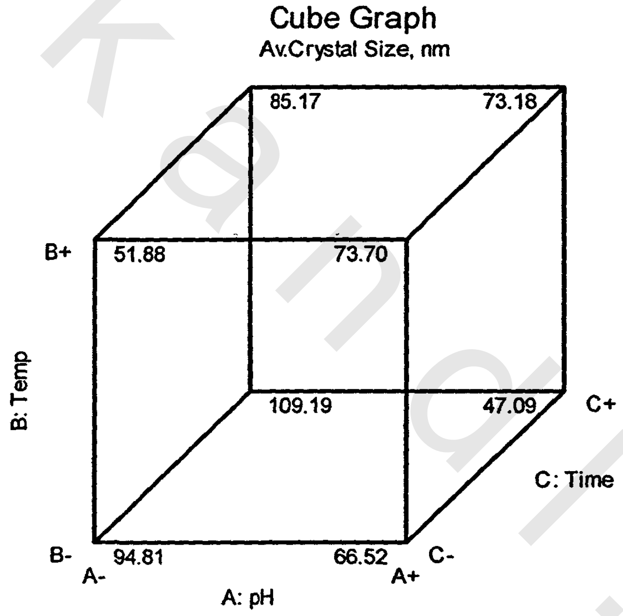


Fig. 52: 3-D plot graph for all experimental data for average crystallite size of conversion BT by hydrothermal method

III.1.2. 6. Morphology of Barium Titanate by Hydrothermal Method

SEM micrographs of the formed $BaTiO_3$ nanopowders at different hydrothermal times 12 and 24 h and hydrothermal temperature 200°C were shown in Fig. 53. It is observed that barium titanate with spherical shape can be obtained. The formed BT particles were homogenous, very fine and the crystallite size was identical to the data obtained from XRD patterns. The tetragonal structure obtained, $BaTiO_3$ without any agglomeration of small crystal size. The basic forces responsible for agglomeration process are Vander Waals forces. To reduce surface energy, the primary particles have a basic tendency to form agglomerate. By forming nearly spherical or equi-axed agglomerates, maximum packing density, minimum ratio of surface to volume and hence minimum surface free energy can be achieved (**Guo ,et al 2006**).

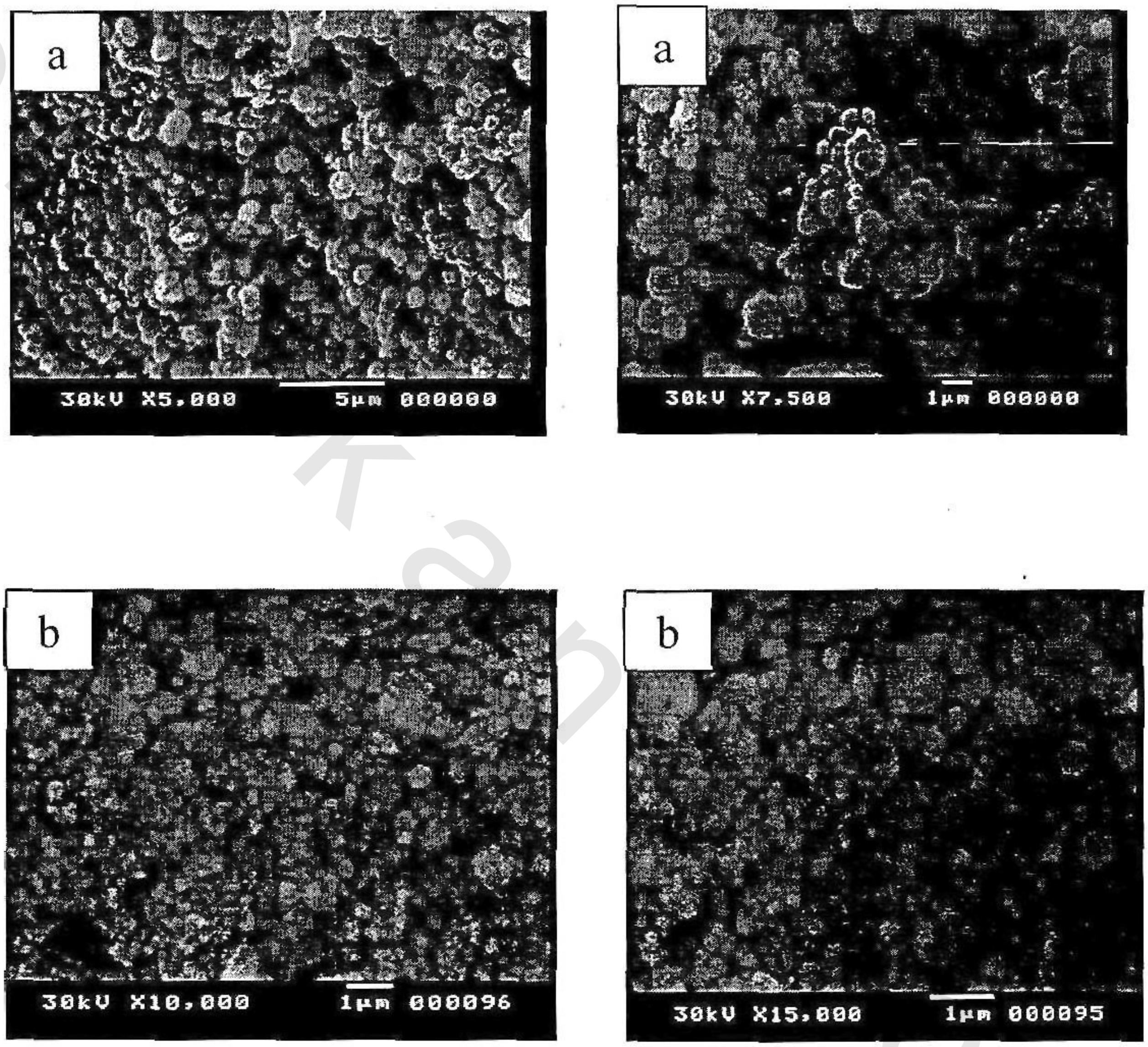


Fig.53 : SEM micrographs of barium titanate nanopowders by hydrothermal method obtained at hydrothermal temperature 200°C and pH 13 [(**a**) hydrothermal time 24 h, (**b**) hydrothermal time 12 h]

III.1.2. 7. Infrared Spectra by Hydrothermal Method

FT-IR spectra of barium titanate nanopowders at hydrothermal temperature 170°C, hydrothermal time 24 h and pH 13 was shown in Fig 54. From results noticed that two broad absorption peaks; one of them at 404 cm^{-1} characteristic of tetragonal barium titanate and the other at 543.8 cm^{-1} due to the Ti-O vibration of tetragonal barium titanate. Other absorption peak are observed at 3461.6 cm^{-1} and 162.8 cm^{-1} assigned to antisymmetric and symmetric stretching vibration of OH group due to H-O-H bending of coordinated water.

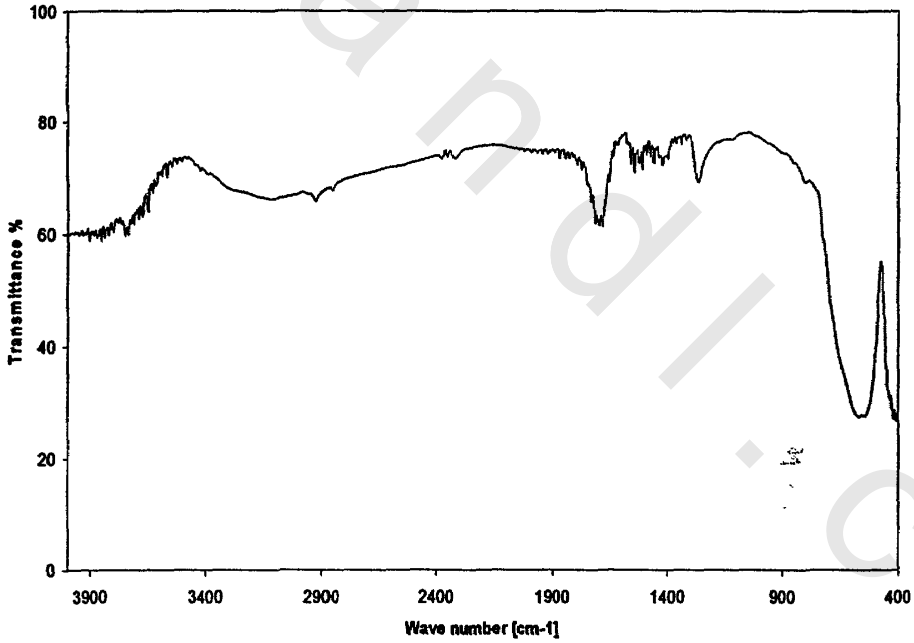
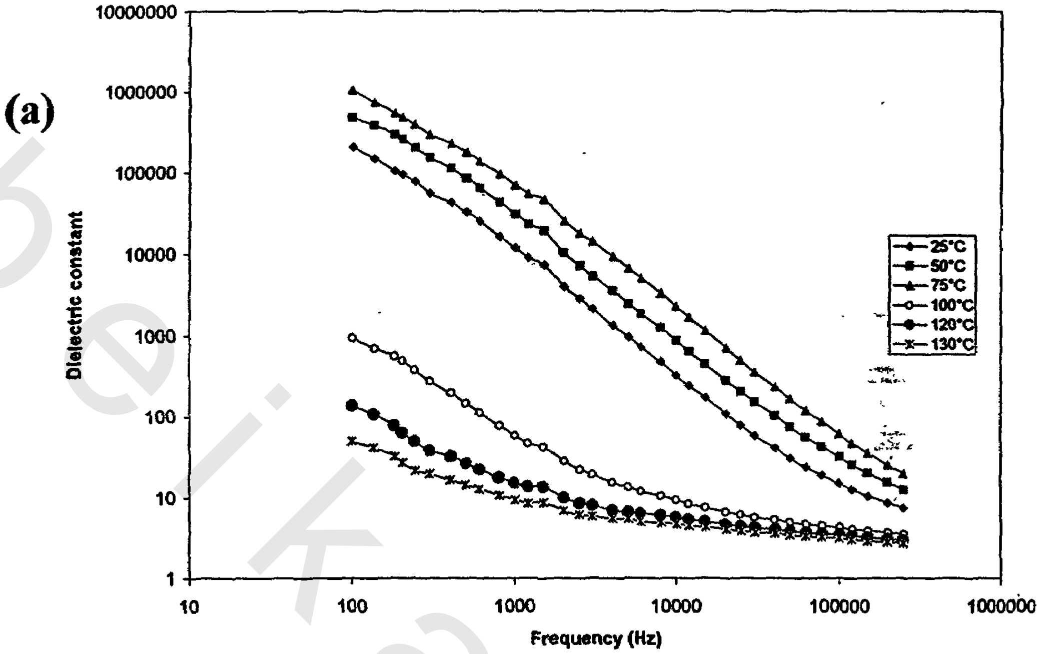


Fig.54: FT-IR spectra of barium titanate powders using hydrothermal method at hydrothermal temperature170°C, hydrothermal time 24 h and pH 13

III.1.2. 8. Dielectric properties of Hydrothermal produced BT

The temperature dependences of dielectric constant of barium titanate powders using hydrothermal method at hydrothermal temperature 170°C and hydrothermal time 12 and 24 h at pH 13 are shown in Fig 55. The result showed that the dielectric constant increase until 110°C and then rapidly decrease due to a transition from the tetragonal to cubic structure or material converted from ferroelectric material to paraelectric material. The dielectric constant of BT formed at hydrothermal time 12h at room temperature and 100 Hz was 2E+05 and increases at 75°C to 1.01E+06 then rapidly decreases at 100°C to 923. Moreover the dielectric constant of BT formed at hydrothermal time 24 h at 100 Hz with room temperature was 1.3E+05 and increasing at 100°C to 1.37E+06 then rapidly decreases at 120°C to 141. In comparison the dielectric constant of barium titanate formed at hydrothermal time 12, 14 and pH 13 show an increase in the dielectric constant of barium titanate which is formed at hydrothermal time 24 h than 12 h due to decrease the crystallite size.



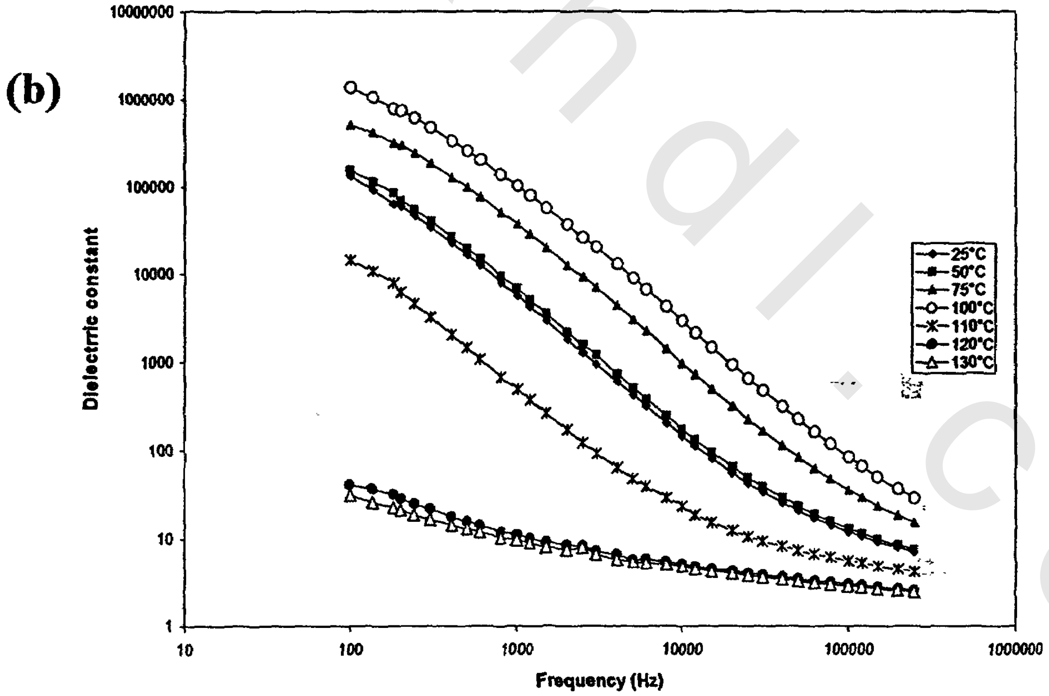


Fig. 55: Dielectric constant of BT using hydrothermal temperature at hydrothermal temperature 170°C, pH value 13 and hydrothermal time [(**a**): 12 h , (**b**): 24h]

III.2. PREPARATION OF LEAD TITANATE (PT)

Lead titanate $PbTiO_3$ nanopowders have been prepared using two different methods, organic carboxylic acid precursor and hydrothermal methods. The factors affecting the phase formation, crystallite size, microstructure and dielectric properties were systematically studied and the optimum conditions were determined. These factors studied for organic acid precursor method were organic acid types, calcination temperature and calcination time. On the other hand, the conditions studied for hydrothermal technique were hydrothermal time, hydrothermal temperature and pH.

III.2.1. Preparation of Lead Titanate by Organic Acid Precursor Method

Lead titanate nanopowders were prepared by organic acid precursors using the different variables mentioned before in the production of barium titanate. The organic carboxylic acid studied were (oxalic, citric and tartaric acids).

In organic acid precursor method, the lead titanate powders were formed by transformation of lead acetate and titanium dioxide in the presence of organic acids into lead titanyl (oxalate, citrate, tartarate) precursor. The formed precursors were oxidized to lead oxide PbO, titanium dioxide TiO_2 and CO_2 then lead oxide and titanium dioxide combined with each other at high calcination temperature in the formation of lead titanate $PbTiO_3$ phase.

III.2.1. 1. Effect of Calcination Temperature

To study the effect of calcination temperature on the lead titanate phase formation, a series of experiments were carried out at different organic carboxylic acids (oxalic, citric and tartaric) under the following conditions:-

Calcination time, h	: 2
Pb: Ti mole ratio	: 1
Ratio of acid to Pb^{2+} and Ti^{2+} ions	: 1

Fig. 56 show the effect of calcination temperature on formation of single phase of PT for constant time 2h and organic acids mole ratio 1. The results indicate that increasing calcination temperature increased the formation of lead titanate phase. In conclusion, the calcination temperature is one of the most significant factors on the PT phase formation by organic precursor method. Increases the calcination temperature up to 600°C, increases the single $PbTiO_3$ phase formation while decreasing the calcination temperature to 500°C, a mixture of $PbTiO_3$, PbO and TiO_2 phases were formed. The diffraction peaks are corresponding to diffraction planes (200), (100), (101), (110) and (001) planes at 2θ values of 21.76, 22.64, 31.705, 32.28 and 39.317 which ascribed to tetragonal $PbTiO_3$ (JCPDS # 75-438) were obtained.

The conversion phase formation 100 % of PT phase using oxalic, citric and tartaric acids can be obtained at calcination temperature 600-1000°C, respectively. Conversion, % of PT phase at calcination temperature 500°C were 53.3, 80 and 81 using tartaric , citric and oxalic acids , respectively .

The crystallite size of tetragonal lead titanate $PbTiO_3$ was obtained at different calcination temperature from 600 to 1000°C; calcination time 2 h using (oxalic, citric and tartaric acids) as a source of organic acids. The results are shown in Table 14. The results indicate that a decrease in the calcination temperature, a decrease in the crystallite size take place and vice versa using oxalic, citric and tartaric acids. This is due to the increase calcination temperature lead to the agglomeration of the particles with each others.

Table 14: Crystallite size of lead titanate PT using different of organic acids at calcination time 2h

Temperature ,°C	**Crystallite size (nm)**		
	Using oxalic acid	**Using citric acid**	**Using tartaric acid**
600	32	28.3	32.6
700	34.4	32	33.6
900	85.5	56	59.8
1000	103.5	90.9	91.4

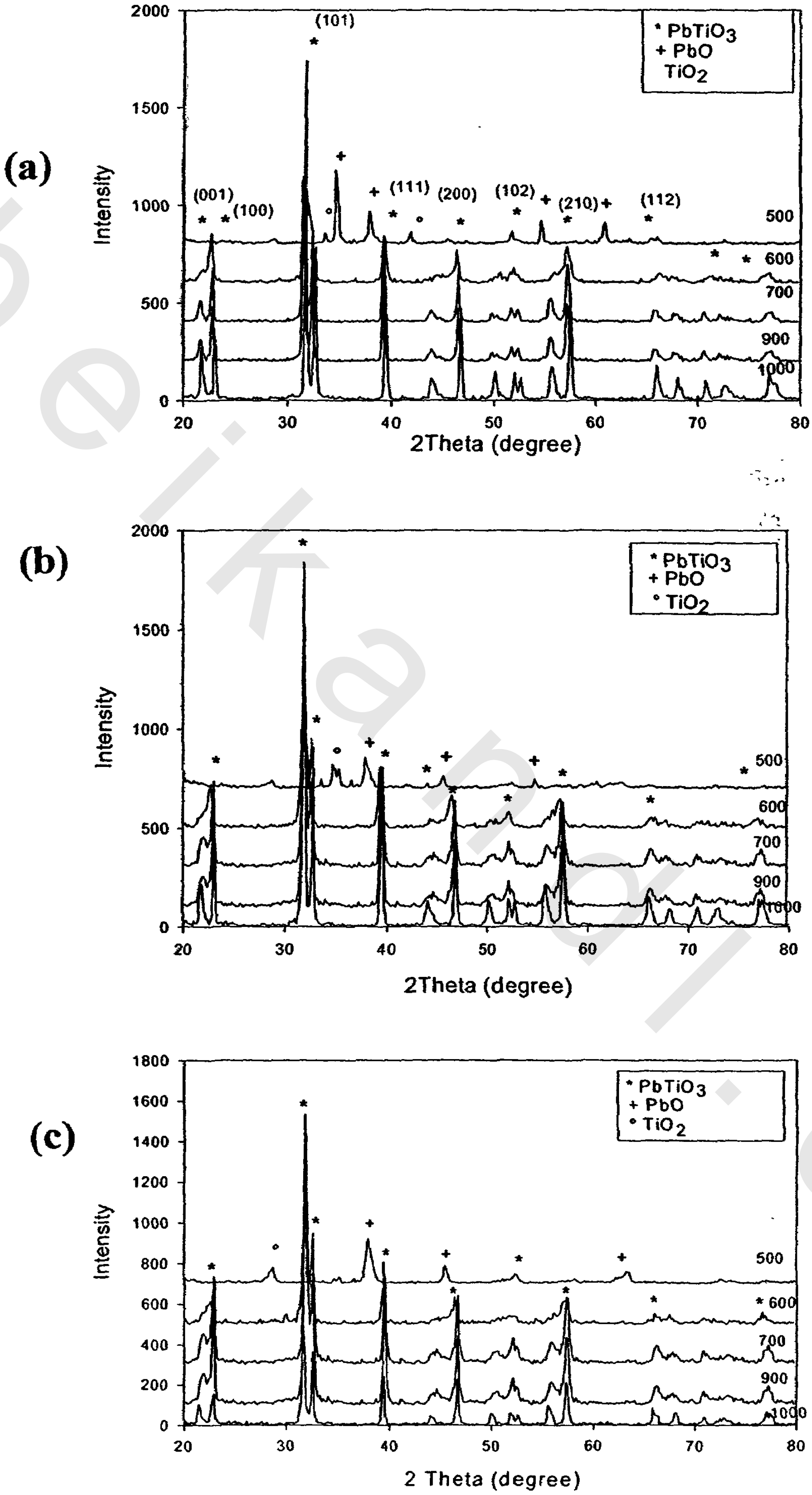


Fig.56: XRD patterns of lead titanate powders at different calcination temperature 500-1000 °C, calcination time 2h using [(**a**) oxalic acid, (**b**)citric acid and (**c**) tartaric acid]

III.2.1. 2. Effect of Calcination Time

Different experiments was carried out to study the effect of calcination time from 1 to 2 h on the lead titanate phase formation % at calcination temperature 600 °C using (oxalic , citric , tartaric) acids and the results obtained were given in Fig. 57

The results showed that an increase in the calcination time led to an increase in the formation on pure single tetragonal lead titanate phase. The well crystalline PT phase was attained at 1.5 h. At lower calcination time than1.5 h; a mixture of lead titanate and lead oxide phases were obtained. The phase formation, % of the precursor transformation to PT phase using oxalic acid was 64.03 and 100 at calcination time 1 and 1.5, respectively. Moreover, the conversion of phase formation, % PT using citric acid was 90.2, 92.1 and 100 at calcination time 1, 1.5 and 2 h, respectively. Furthermore, the percentage of PT conversion using tartaric acid was 88.2, 93.1 and 100 at calcination time 1, 1.5 and 2 h, respectively.

In comparison, the optimum conditions for synthesis of single phase lead titanate at calcination temperature 600°C, calcination time 2 h using citric and tartaric acid as organic acid precursor. On the other hand, the well crystalline PT phase can be attained at 1.5 h and the similar temperature.

The crystallite size of PT was 28, 32 and 32.6 nm using citric oxalic and tartaric acids, respectively at calcination time 2h. Moreover, the crystallite size of pure PT phase using oxalic acid at calcination time 1.5 h was 29.4 nm.

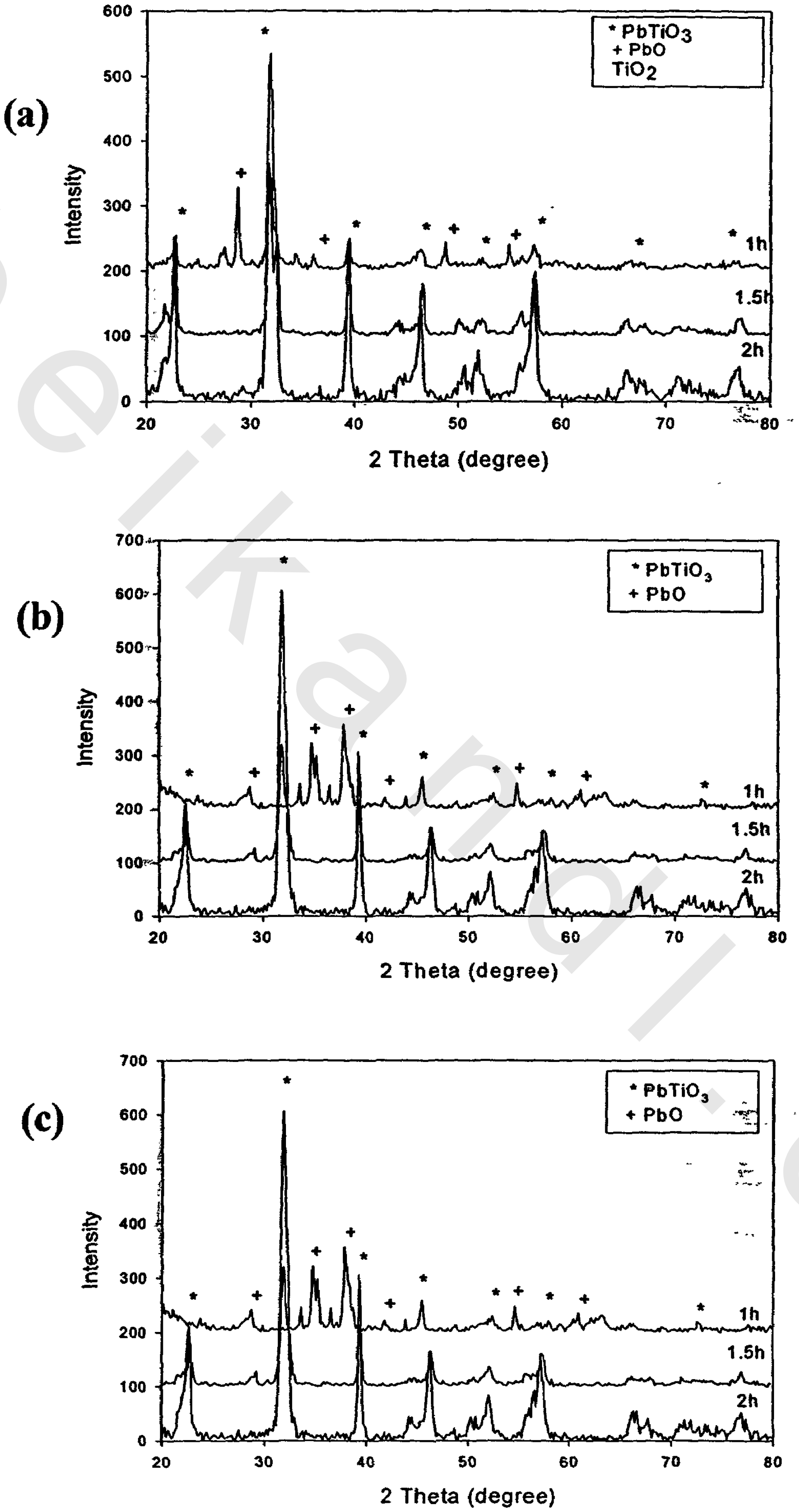


Fig.57: XRD patterns of lead titanate at different calcination time 1-2 h calcination temperature 600 °C using [(**a**) oxalic acid, (**b**) citric acid and (**c**) tartaric acid]

III.2.1. 3. Morphology of Lead Titanate

SEM micrographs of $PbTiO_3$ nanopowders at calcination temperature 700- 1000°C for calcination time 2 h using oxalic, citric and tartaric acids as a source of organic acid showed in Fig.58 It is observed that a pure single tetragonal structure shape is obtained when the formed PT particles are homogenous, very fine, uniform size and $PbTiO_3$ produced without any agglomeration of small crystal size.

From SEM micrograph, the results obtained showed that the morphology of PT is calcination temperature independent. The PT powders are homogeneous spherical shape at 700°C. Increasing the calcination temperature to 1000°C increases the crystallinity of the produced powders.

TEM micrographs of the $PbTiO_3$ nanopowders formed at calcination temperature 600°C, calcination time 2 h using oxalic, citric and tartaric acids are show in Fig.59. It is observed that the $PbTiO_3$ nanospheres had a uniform morphology. The crystallite size obtained from TEM was 31nm using oxalic acid and 12 nm using citric and tartaric acids.

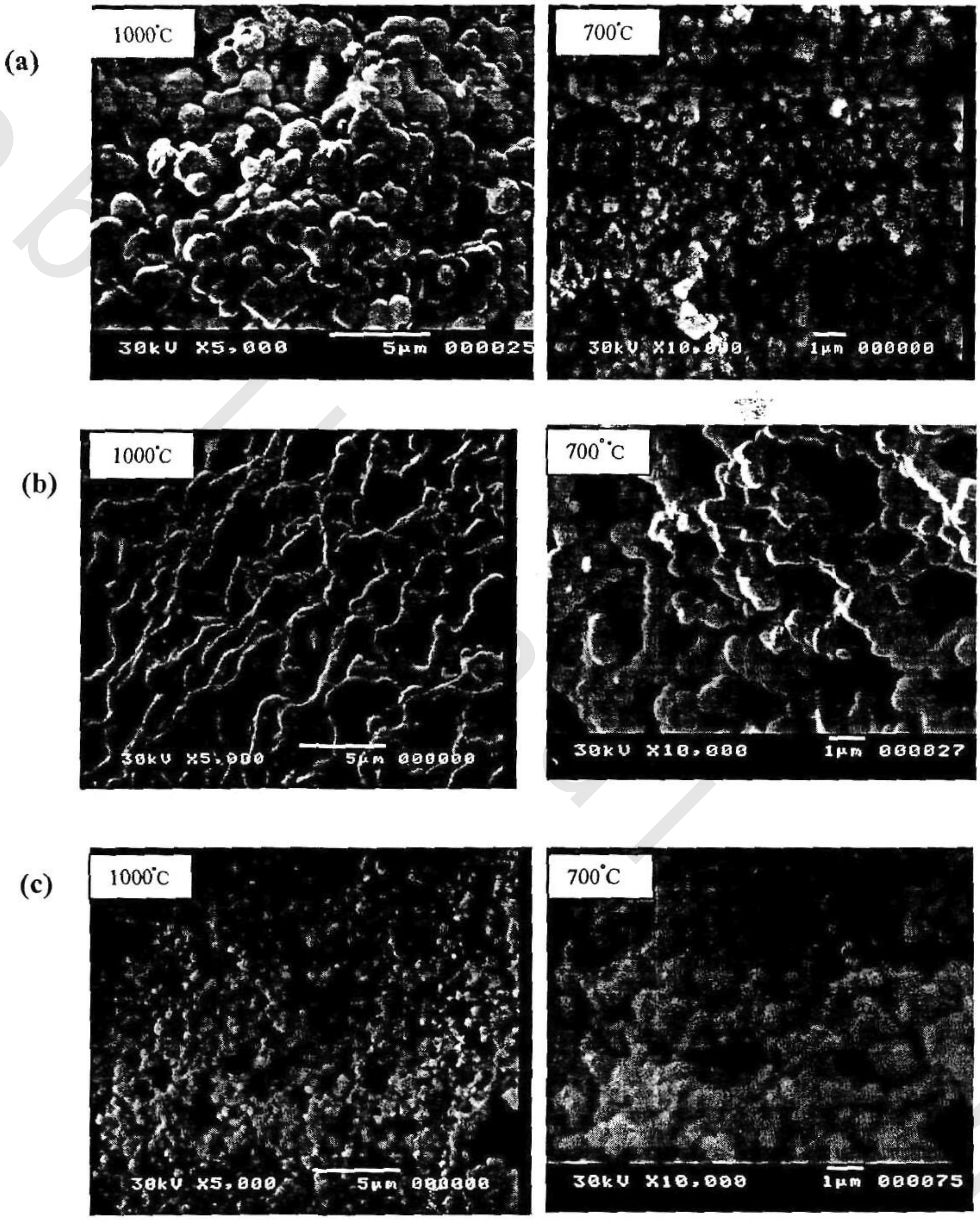


Fig. 58: SEM micrographs of lead titanate powders at calcination temperature (700&1000°C), calcination time 2 h using [(**a**) oxalic acid, (**b**) citric acid and (**c**) tartaric acid]

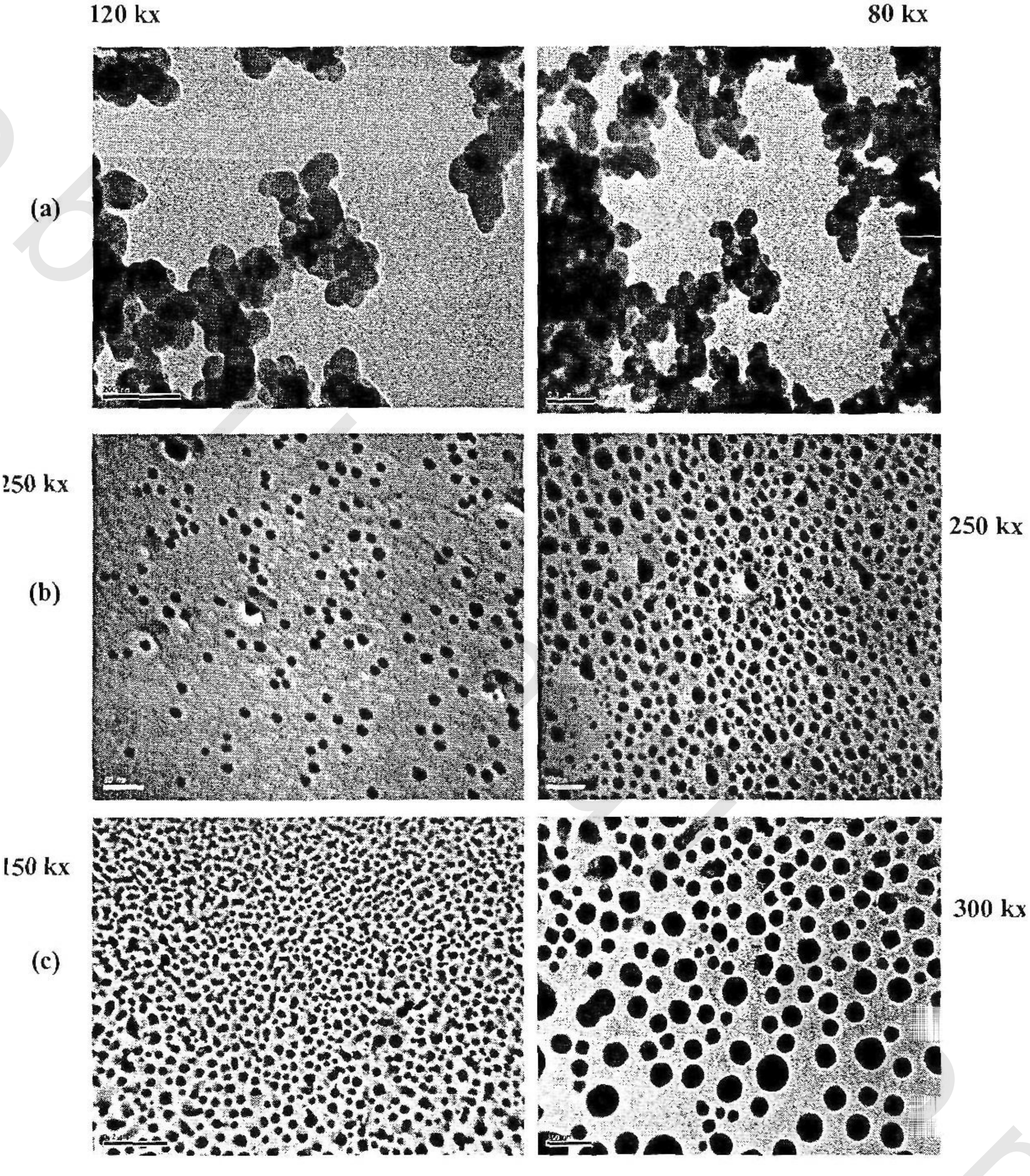


Fig.59: TEM micrographs of lead titanate powders at calcination temperature 600 °C, Calcination time 2 h using [**(a)** oxalic acid, **(b)** citric acid and **(c)** tartaric acid]

III. 2.1. 4. Infrared Spectra of Lead Titanate

The FT-IR spectra for organic precursors using oxalic, citric and tartaric acids as a source of organic acids were shown in Fig.60. FT-IR spectra for the lead titanyl oxalate precursor formed using oxalic acid is observed that the characteristics absorption bands at 783.9, 1260, 1477 and 2680 cm^{-1} were corresponding to the different modes of vibration oxalate group. The broad band centered around 3413 cm^{-1} may be assigned to antisymmetric and symmetric stretching vibration of OH group and that of 1690 cm^{-1} due to H-O-H bending of coordinated water. The peaks at 477, 607 and 783.9 cm^{-1} due to Ti-O vibration also, the peak at 421 cm^{-1} characteristic to strong absorption band of PbO.

Moreover , FT-IR spectra for lead titanyl citrate using citric acid as organic precursor was observed that the absorption bands peaks at 3461.6 cm^{-1} was related to O-H stretching modes in crystallization water and at 1718 cm^{-1} due to H-OH-bending of coordination water. Moreover, the peaks at 1077, 1225 and 1571cm^{-1} are corresponded to carboxylate group stretching modes. In addition, the peaks at 563 and 626 cm^{-1} was related to Ti-O vibration mode and peak at 1759 cm^{-1} due to C=O stretching modes in COO-Pb and the peak at 420 cm^{-1} characteristic to strong absorption band of PbO.

Furthermore, FT-IR spectra for lead titanyl tartarate precursor using tartaric acid was observed the absorption bands at 1399, 1407.7, 1730, 2698 cm^{-1} were corresponding to the different modes of carboxylate group also, the broad band centered around 3317 cm^{-1} may be assigned to antisymmetric and symmetric stretching vibration of OH group and that of 1574 cm^{-1} due to H-OH bending of coordinated water. In addition, two broad absorption peaks at 522 and 683.4 cm^{-1} for Ti-O observed in precursor sample. The characteristics absorbed band at 2978.5 cm^{-1} related to O-H present in tartaric acid and 485 cm^{-1} characteristic to strong absorption band of PbO.

The FT-IR spectrum for the organic precursor using (oxalic, citric and tartaric acids) was calcinated at 600°C for 2 h in Fig. 61. The result showed that the characteristics peaks observed bands 1602 and 3775.9 cm^{-1} which are assigned to O-H stretching and bending vibration, respectively. The absorption bands were 426, 582 and 602 cm^{-1} due to Ti-O vibration corresponding to $PbTiO_3$.

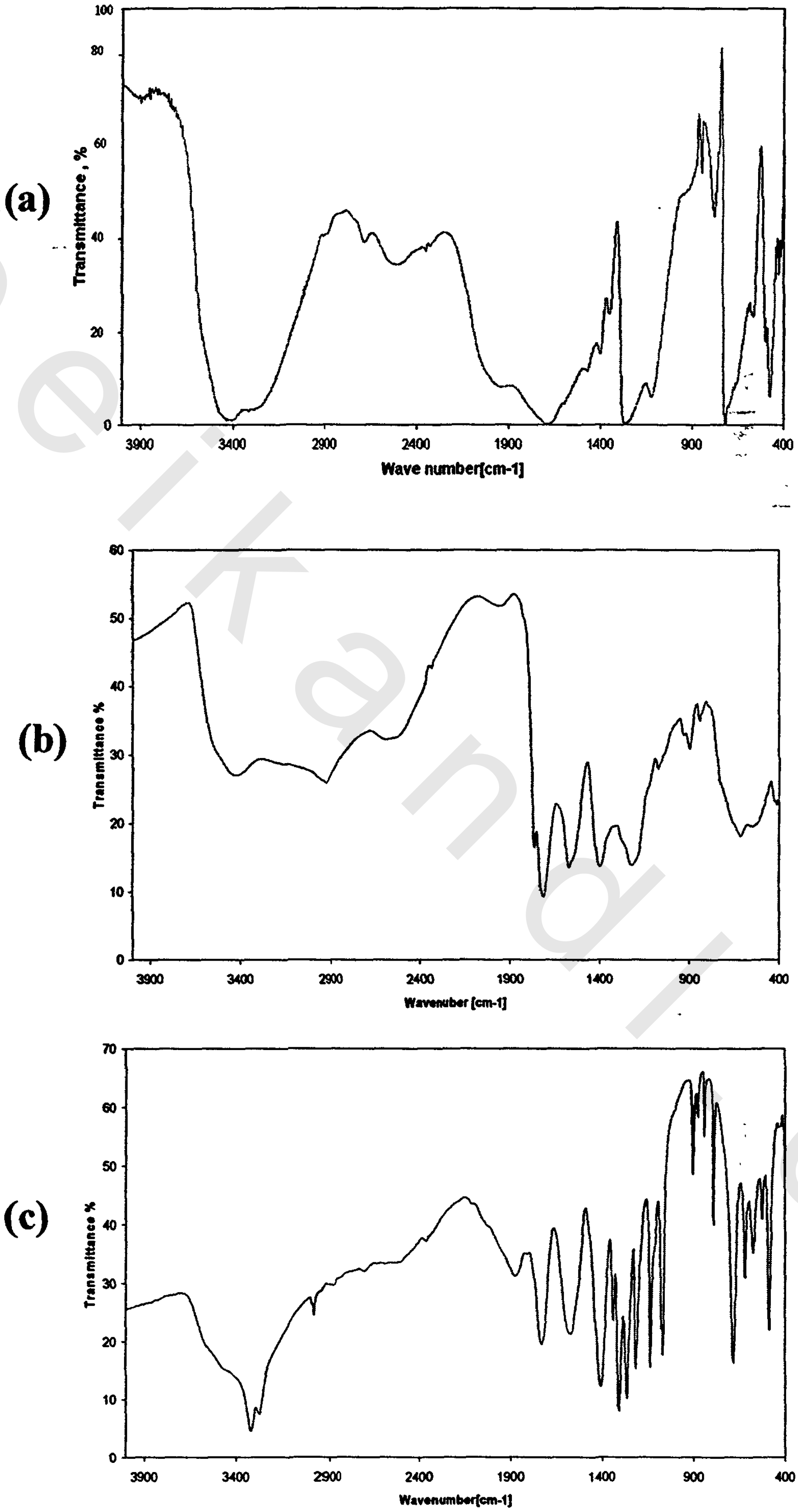


Fig. 60: IR spectra of precursors using [(**a**) oxalic acid, (**b**) citric acid and (**c**) tartaric acid]

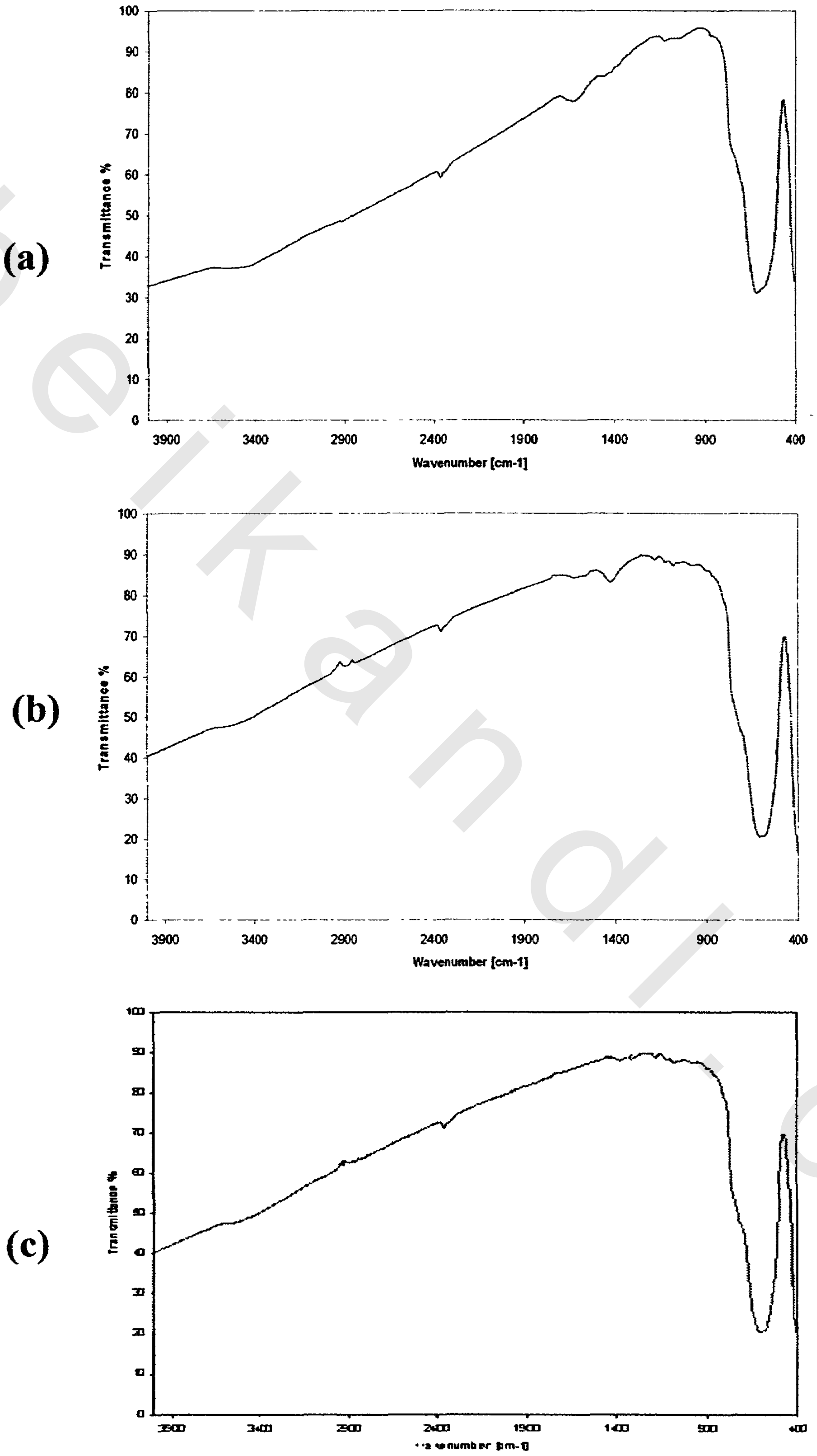


Fig.61: FT-IR spectra of spectra after calcination of the precursor at calcination temperature 600°C and calcination time 2 h using [(**a**) oxalic acid, (**b**) citric acid and (**c**) tartaric acid]

III. 2.1.5. Dielectric properties of Lead Titanate

Fig. 62 showed the dielectric constant as a function of frequency for lead titanate at room temperature which formed at constant calcination temperature 600°C and calcination time 2h using oxalic, citric and tartaric acids.

It can be observed that the values of dielectric constant decreased with increasing frequency due to decrease the dipolar polarization of the matrix and the accumulation of charges at the interface between particles. The dielectric constant of lead titanate using oxalic acid as source of carboxylic acid at room temperature was 2420, 2506 and 8801 at 100 KHz, 1 kHz and 100 Hz, respectively. Moreover, the dielectric constant of lead titanate using citric acid was 15, 1255 and 5836 at 100 KHz, 1 kHz and 100 Hz. Furthermore, the dielectric constant of lead titanate using tartaric acid as a source of organic acid at room temperature was13.4 , 3840 and 12702 at 100 KHz, 1 kHz and 100 Hz.

In comparison , the dielectric constant of lead titanate using oxalic , citric and tartaric acids were found to fall rapidly with increasing frequency and using oxalic acid increased than using citric and tartaric acids due to decreased the crystallite size .

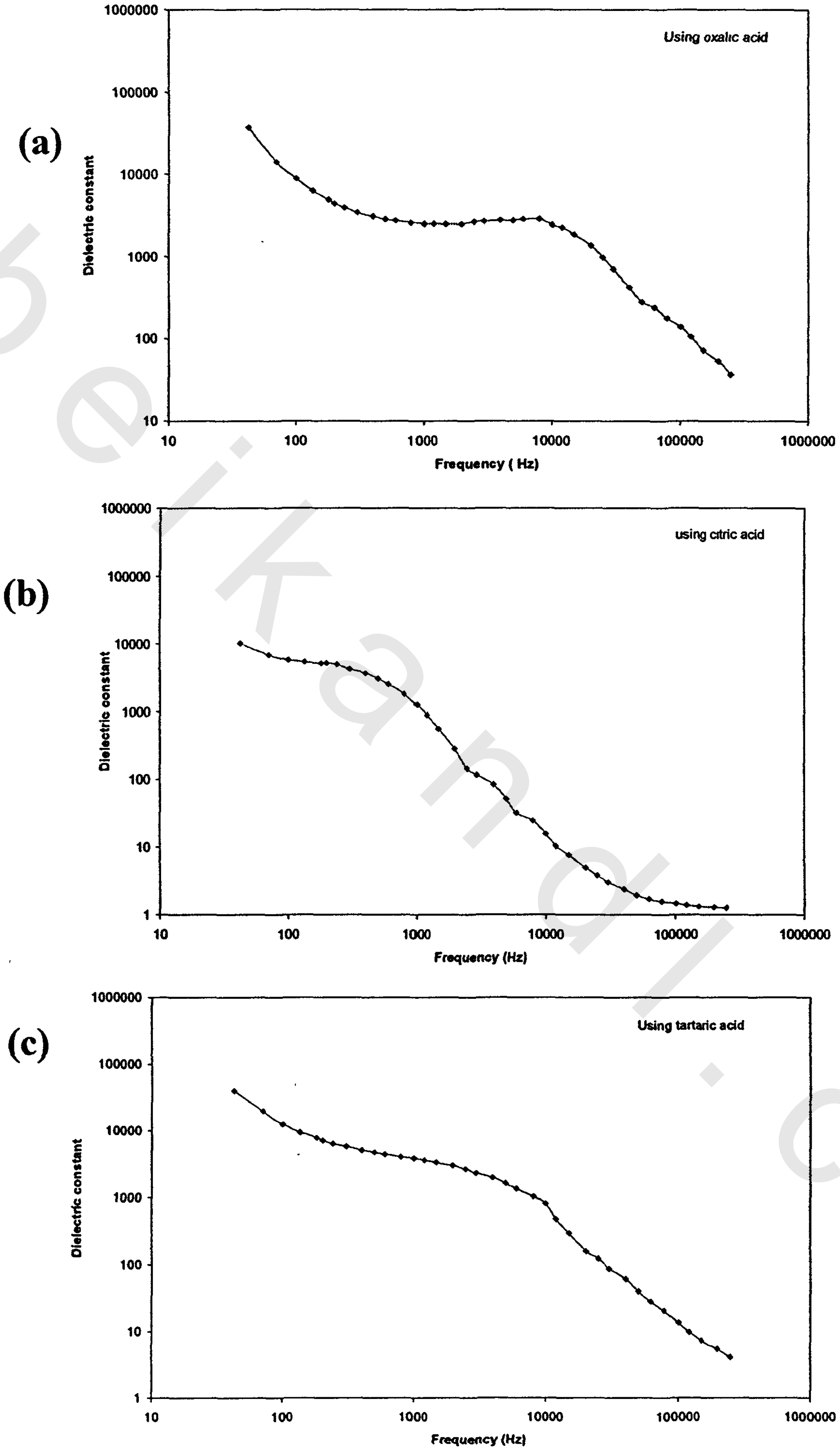


Fig.62: Dielectric properties of lead titanate powders at calcination temperature 600 °C, calcination time 2 h using [(**a**) oxalic acid, (**b**) citric acid and (**c**) tartaric acid]

III. 2.1.6. Effect of Zr^{4+} ions on Crystal Structure of Lead Titanate

A series of experimental was carried out with different Ti / Zr moles [0.9/0.1, 0.7 /0.1 and 0.5/ 0.5] under the following conditions:-

Lead / titanium mole ratio : 1
Oxalic acid mole ratio : 1
Calcination temperature, °C : 600
Calcination time, h : 1.5

Fig.63 showed that the XRD patterns of samples without addition of zirconium ions and with addition different Zr^{4+} ions mole ratios from 0.1 to 0.5. The results indicated that without addition of zirconium ions at studied conditions. The formation of single phase tetragonal $PbTiO_3$ (JCPDS # 75-0438) was obtained. The addition of different Zr^{4+} ions mole ratios, two phases of lead titanate and lead zirconate $PbZrO_3$ orthorhombic phases (JCPDS# 81-2042) were obtained. Increasing Zr^{4+} ions mole ratios were decreased the percentage of lead titanate phase and the percentage of lead zirconate phase was increased. At Zr^{4+} ions mole ratios 0.1, the phase formation, % was tetragonal lead titanate 93.6 and lead zirconate 6.4. Moreover, at Zr^{4+} ions mole ratios 0.3, the phase formation, % was tetragonal lead titanate 89 and lead zirconate 11. At high Zr^{4+} ions mole ratios 0.5/0.5, the phase formation, % of tetragonal lead titanate was 88 and lead zirconate 22.

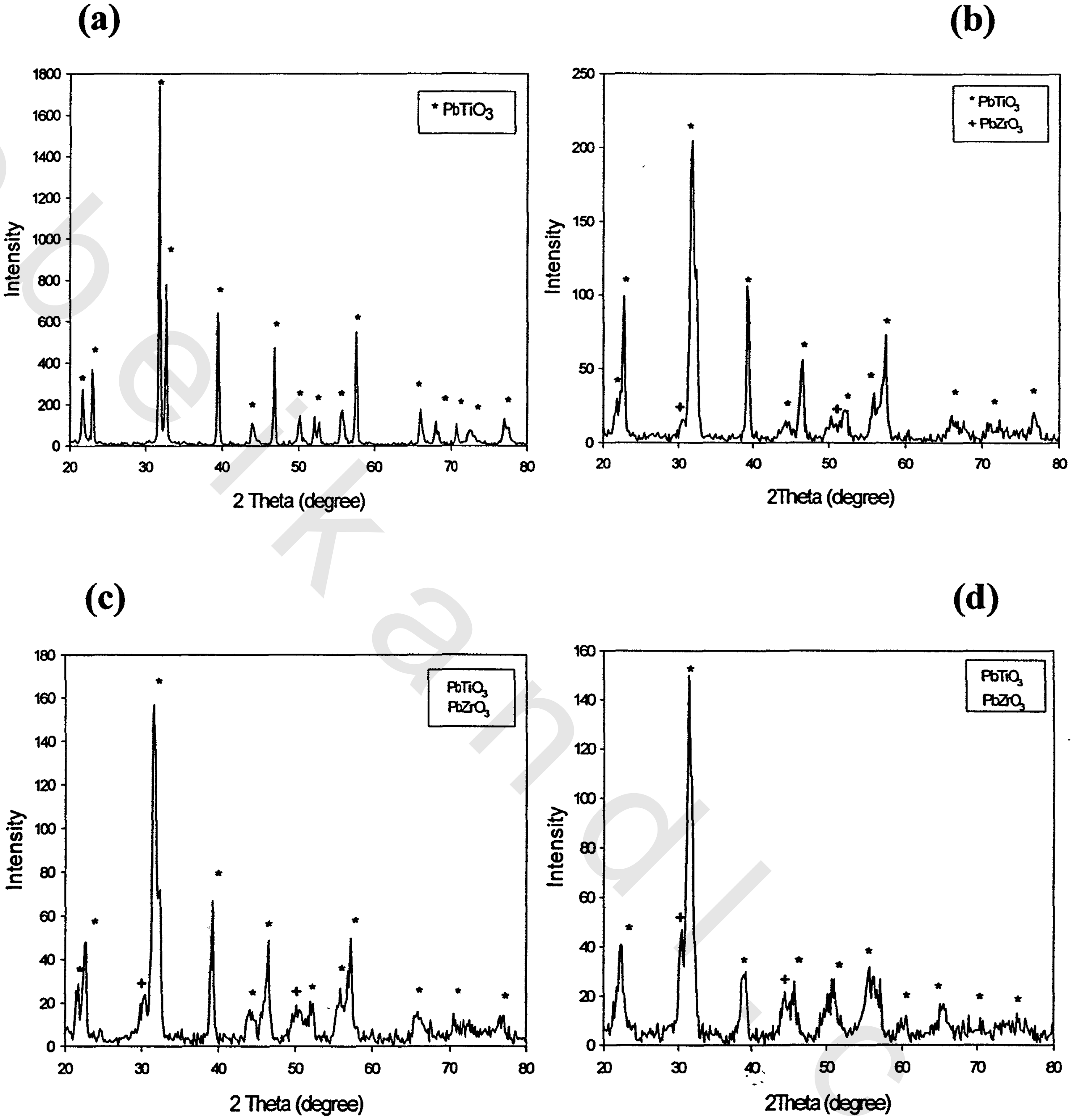


Fig.63: Effect of Ti/ Zr mole ratio on phase formation of lead titanate, where; [(**a**)without Zr^{4+}ions, (**b**)Ti / Zr mole ratio 0.9/0.1, (**c**) Ti / Zr mole ratio 0.7/0.3, (**d**) Ti / Zr mole ratio 0.5/0.5]

Fig. 64 showed TEM micrographs of samples product using different mole ratios of Zr^{4+} ions from 0.1 to 0.5 at lead: titanium mole ratio equal 1, oxalic acid mole ratio 1, calcination temperature 600°C and calcination time 1.5 h. The micrographs showed spherical nanoparticles for each of these particles contain two colors (light and dark) with homogeneity distribution which indicates that formed two phases with added of Zr^{4+} ions without any agglomeration of small crystal size. Moreover, the crystallite size was 9.5, 8 and 15 nm after addition of different mole ratios of Zr^{4+} ions 0.1, 0.3 and 0.5, respectively.

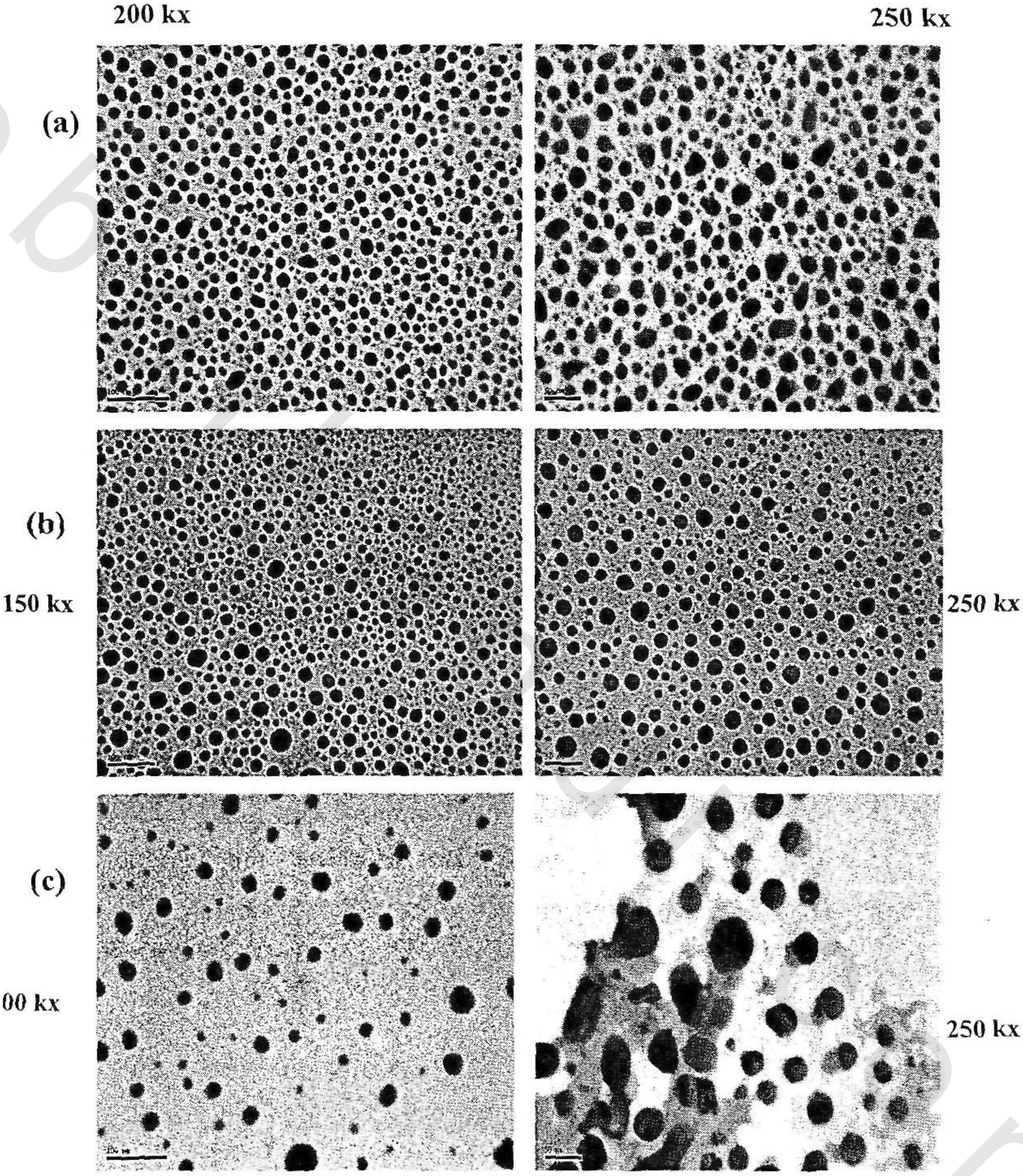


Fig.64: TEM images of produced samples using different of Zr^{4+} ions mole ratios [(**a**) Zr^{4+} ions mole ratio 0.1, (**b**) Zr^{4+} ions mole ratio 0.3 and (**c**) Zr^{4+} ions mole ratio 0.5]

The EDX analyses of different phases with and without addition of Zr^{4+} ions were showed in Fig.65. The EDX analysis of product powder confirmed the above finding and agrees with the theoretical aspects. The percentage of Pb and Ti without added Zr^{4+} ions was observed 69.5 and 30. At Zr^{4+} ions mole ratio 0.1, the percentage of Pb, Ti and Zr were 62.9, 22 and 13.9. Increasing the Zr^{4+} ions mole ratio to 0.3, the percentage of Pb, Ti and Zr were 59.9, 21.9 and 16.6. Moreover at high Zr^{4+} ions mole ratio 0.5, the percentage of Pb, Ti and Zr were 58.8, 18.4 and 20.5, respectively.

Fig.66 showed the dielectric constant of lead titanate at different Zr^{4+} ions mole ratio. The results indicated that the values of dielectric constant decreased with increasing the frequency and the dielectric constant decreased with increasing Zr^{4+} ions mole ratio. The dielectric constant of produced powders at Zr^{4+} ions mole ratio 0.1 were 8801, 2506 and 2420 at 100Hz, 1 kHz and 10 kHz . At Zr^{4+} ions mole ratio 0.3, the dielectric constant were 9162, 915.94 and 7.6 at 100Hz, 1 kHz and 10 kHz; Moreover , the dielectric constant at Zr^{4+} ions mole ratio 0.5 were 10856, 2570 and 40.09 at 100Hz, 1 kHz and 10 kHz.

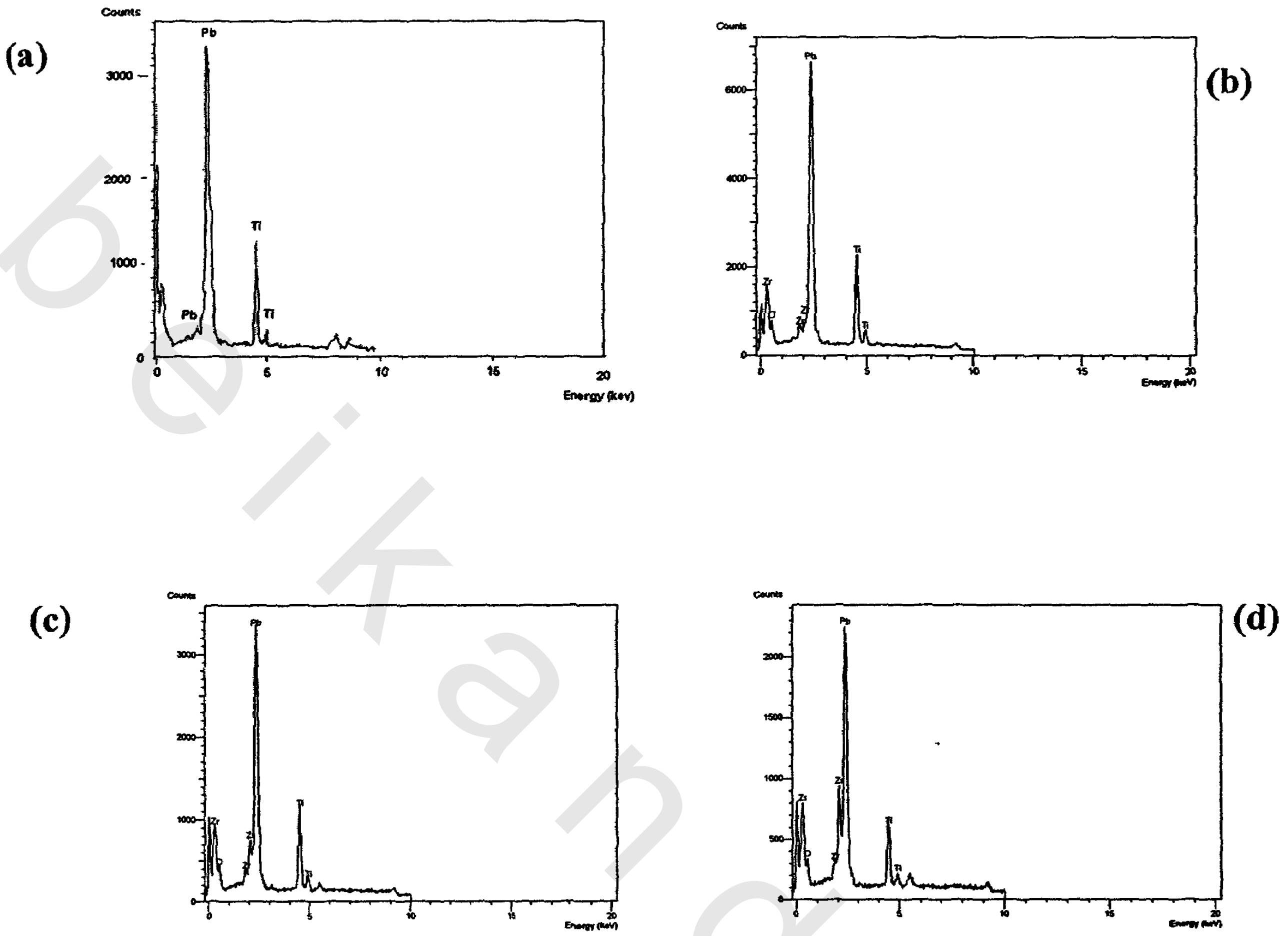


Fig.65: EDX analysis of produced samples using different of Ti/Zr mole ratios, where; [(**a**) without added zirconium ions, (**b**) Zr^{4+} ions mole 0.1,(**c**) Zr^{4+} ions mole 0.3 and (**d**) Zr^{4+} ions mole 0.5]

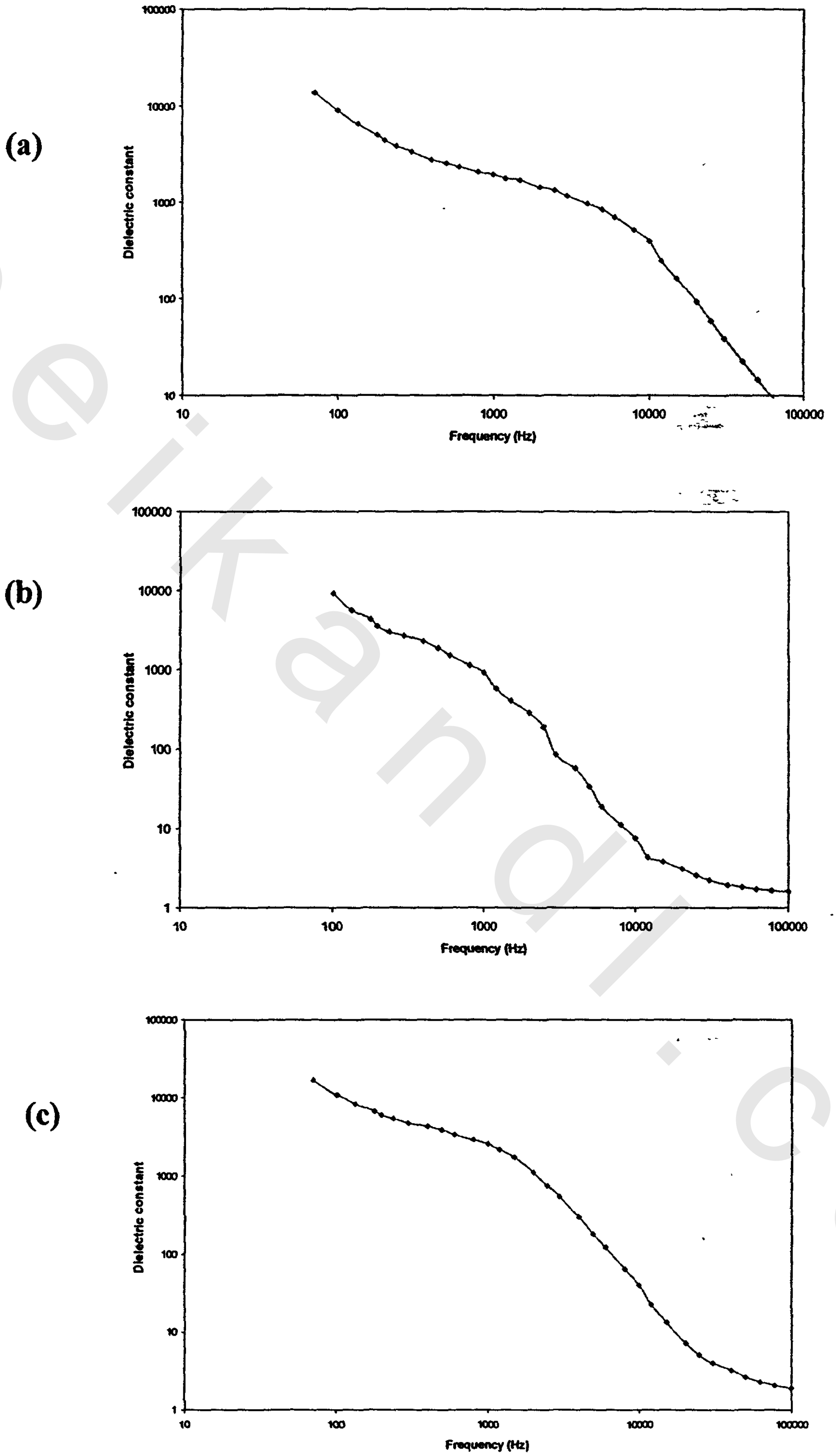


Fig. 66: Dielectric properties of produced samples using different of Zr^{4+} ions mole ratios, [(**a**) Zr^{4+} ions mole ratio 0.1, (**b**) Zr^{4+} ions mole ratio 0.3 and (**c**) Zr^{4+} ions mole ratio 0.5]

III.2.2.Preparation of Lead Titanate by Hydrothermal Method

In hydrothermal method, the lead titanate powders were formed by the reaction between the lead acetate aqueous solution and liquid titanium isopropoxide can be described by the two- steps mechanism.

1- Precipitation of a Ti-rich amorphous phase

2-Crystallization of lead titanate by the reaction between the Ti-amorphous phase and Pb^{2+} ions left in solution.

The reactions in hydrothermal process can be described as below:

$$Pb^{2+} + Ti(OH)_6^{2-} \longrightarrow PbTiO_3 + 3H_2O \qquad (26)$$

Increasing $[OH^-]$ concentration and reaction temperature can facilitate the formation of $PbTiO_3$ **(Chen et al, 2005 & Rujiwatra et al, 2006)**.

The optimum conditions for the formation of lead titanate nanopowders were:

Hydrothermal time, h : 24-36
Hydrothermal temperature, °C : 150-230
pH : 12-14

III.2.2.1.Effect of Hydrothermal Temperature

Different series of experiments were carried out by changing the hydrothermal temperature from 150 to 230 °C and the results obtained were given in Fig.67 to study the effect of hydrothermal temperature on lead titanate phase formation at the following conditions:

- Hydrothermal time ,h : 24
- pH : 13.5
- Lead / titanium mole ratio : 1

The result showed that an increase in the hydrothermal temperature from (150 to 230) °C enhanced the phase formation of tetragonal lead titanate $PbTiO_3$ (JCPDS # 75-1605) at pH 13.5, hydrothermal temperature 200°C and hydrothermal time 24h. On the other hand, a decrease in the hydrothermal temperature than 200°C at the same studied conditions, mixture phases of lead titanate $PbTiO_3$, PbO and $Pb_2Ti_2O_6$ were obtained. The percentage of lead titanate $PbTiO_3$ phase formation at hydrothermal temperature 150, 180 and 200°C at hydrothermal time 24 h and pH 13.5 were 38.4, 75 and 100, respectively.

The crystallite size of tetragonal lead titanate single phase $PbTiO_3$ obtained at hydrothermal temperature 200 and 230°C were 14.1 and 9.6 nm, respectively.

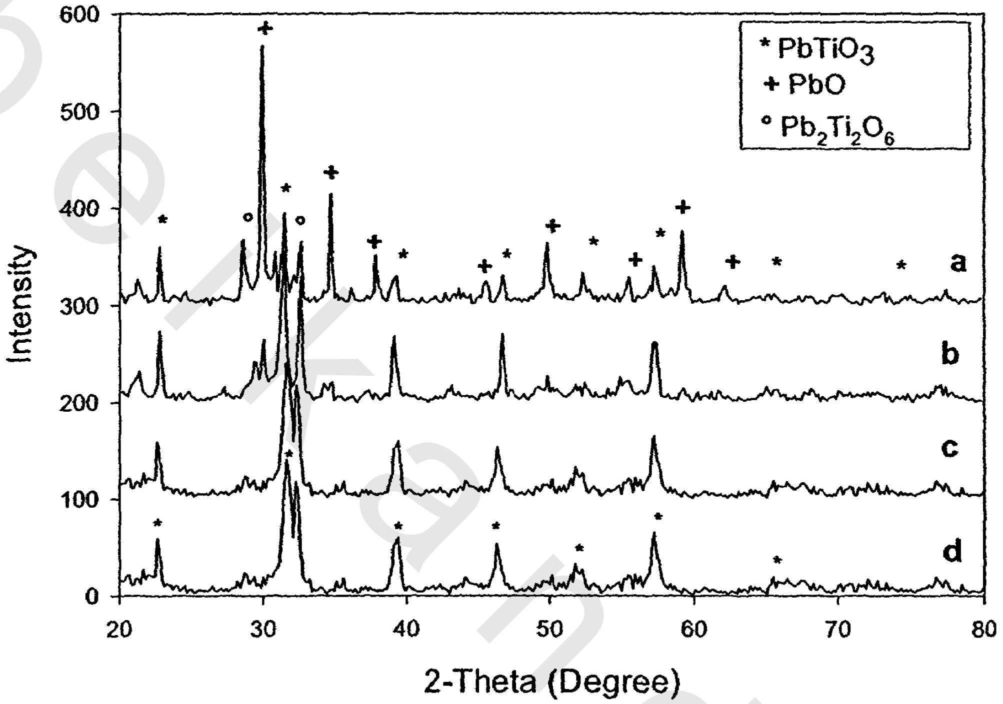


Fig.67: XRD patterns of lead titanate synthesized by hydrothermal method at different hydrothermal temperature, hydrothermal time 24h and pH 13.5 [**(a)** 150°C, **(b)** 180°C, **(c)** 200°C , **(d)** 230 °C]

III.2.2.2.Effect of Hydrothermal Time

Different series of experiments were carried out by changing the hydrothermal time from 24 to 36 h to study the effect of hydrothermal time on the phase formation % of tetragonal lead titanate nanopowders under the following condition

- Hydrothermal temperature , °C : 200
- pH : 13
- Lead / titanium mole ratio : 1

Fig.68 showed the effect of hydrothermal time on phase formation of PT at constant hydrothermal temperature 200°C and pH 13. The results from XRD patterns showed that increasing the hydrothermal time from 12-14 hrs gradually increased the phase formation of tetragonal lead titanate $PbTiO_3$ at pH 13 and hydrothermal temperature 200°C. A hydrothermal time decrease than 30 h at the same condition a mixture of phases of lead titanate $PbTiO_3$ and PbO were formed. The conversion, % of phase formation lead titanate $PbTiO_3$ at hydrothermal time 24, 30 and 36 h at hydrothermal temperature 200°C and pH 13 were 75, 100 and 100 %, respectively.

The Crystallite size of tetragonal lead titanate single phase $PbTiO_3$ was obtained at hydrothermal time 30 & 36 h; hydrothermal temperature 200 °C and pH 13 were 24.9 and 36.1 nm, respectively. It is observed that a decrease in the hydrothermal time leads to decrease the crystallite size.

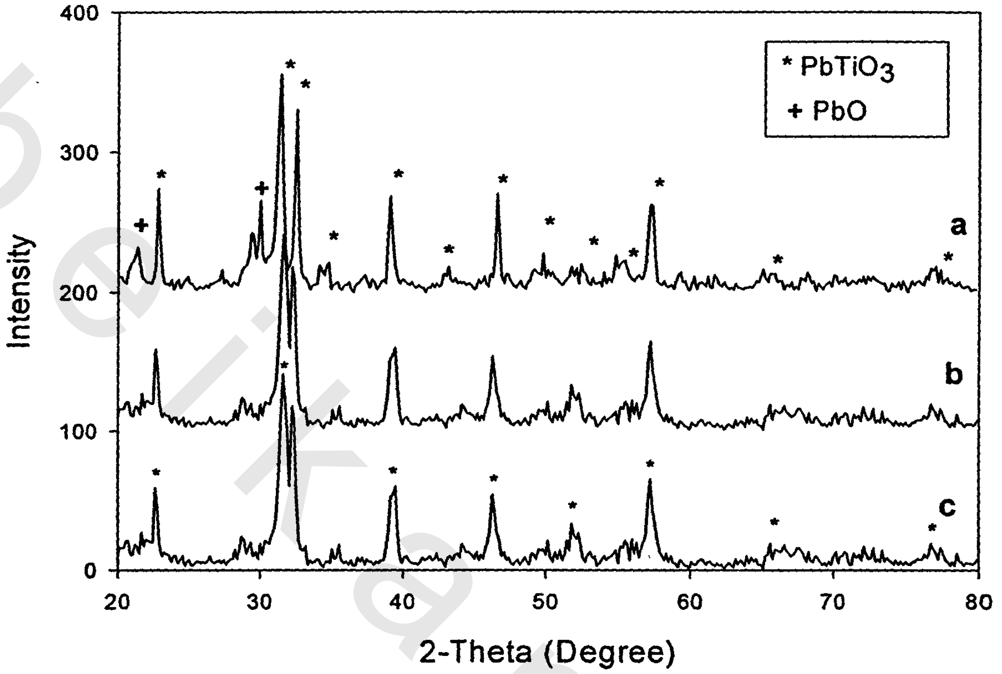


Fig.68: XRD patterns of lead titanate samples at different hydrothermal time at constant hydrothermal temperature 200°C & pH 13 [(**a**) 24h, (**b**) 30 h and (**c**) 36 h]

III.2.2.3.Effect of pH

To study the effect of pH, different experiments were carried out by changing the pH from 13 to 14 on the phase formation % of tetragonal lead titanate nanopowders under the following conditions:-

- Hydrothermal temperature , °C	: 200
- Hydrothermal time , h	: 24
- Lead /titanium mole ratio	: 1

Fig.69 show the effect of pH on phase formation at constant hydrothermal temperature and hydrothermal time. The results from XRD patterns showed that increasing the different pH from 13 to 14 increases the phase formation of tetragonal lead titanate $PbTiO_3$. In contrast a decrease pH than 13.5 at the same conditions led to the formation of a mixture of $PbTiO_3$ and PbO phases. The percentage of phase formation of lead titanate $PbTiO_3$ at hydrothermal time 24h, hydrothermal temperature 200 °C and pH (13, 13.5 and 14) were 82,100 and 100, respectively.

The crystallite size of tetragonal pure crystalline phase of lead titanate $PbTiO_3$ at pH 13.5 and 14 were 14.1 and 11 nm, respectively. In conclusion, the increasing pH led to a decrease the crystallite size of $PbTiO_3$ powders.

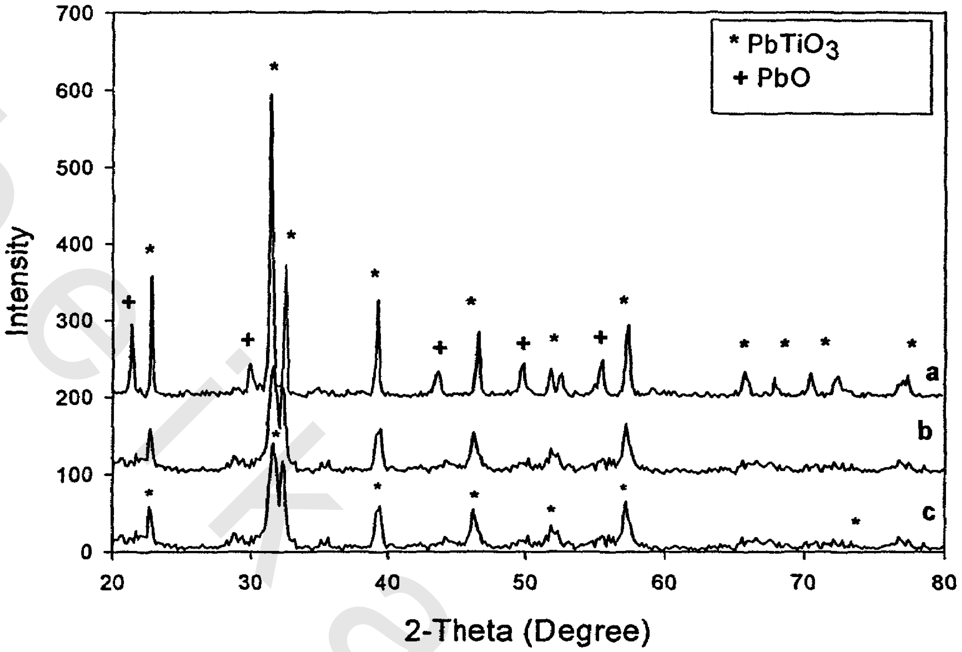


Fig. 69: XRD patterns of lead titanate samples at different pH at constant hydrothermal temperature 200°C & hydrothermal time 24 h [(**a**) pH 13, (**b**) 13.5 and (**c**) 14]

III.2.2.4. Morphology of Lead Titanate by Hydrothermal Method

TEM micrographs of the formed $PbTiO_3$ nanopowders at hydrothermal temperature 200°C, hydrothermal time 30h and pH 13 were given in Fig.70. It is observed that spherical nanoparticals of $PbTiO_3$, uniform morphology, homogenous, very fine, uniform size, narrow size distribution and the average crystallite size of lead titanate was 11.5 nm. Moreover , an increase in the pH up to 14 (pH ≥14) at the same conditions the morphology of lead titanate change from nanosphere to nanowires with straight and uniform cylindrical structures and diameters in the range of 7.6-11 nm as shown in Fig. 71.

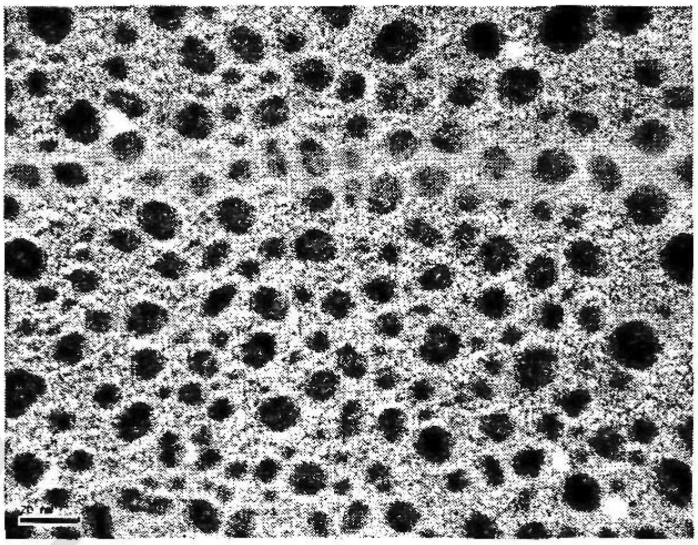


Fig.70 : TEM micrographs of lead titanate at hydrothermal temperature 200°C, hydrothermal time 30 h and pH 13

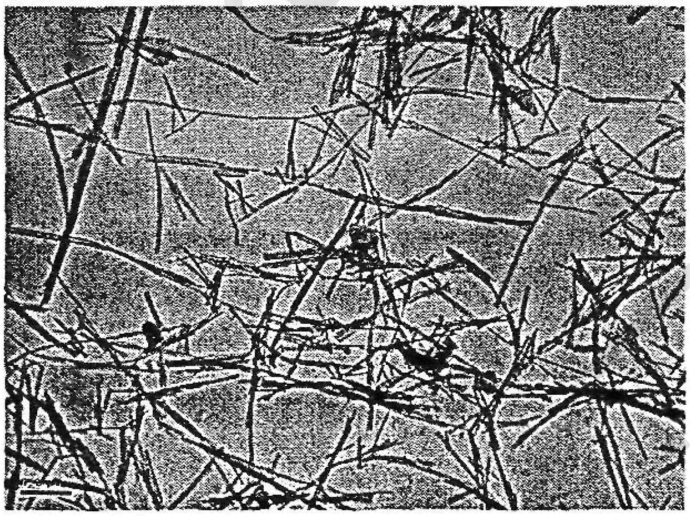


Fig.71 : TEM micrographs of lead titanate at hydrothermal temperature 200°C, hydrothermal time 30 h and pH 14

III.2.2.5. Infrared Spectra of lead titanate by Hydrothermal Method

FT-IR spectra of nanopowders of lead titanate at hydrothermal temperature 200°C, hydrothermal time 30 h and pH 13 is shown in Fig 72. It is observed that pure lead titanate $PbTiO_3$ has absorption peaks at 600 cm^{-1} due to the Ti-O vibration and another absorption peak at 3778 cm^{-1} and 1580 cm^{-1} assigned to as symmetric and symmetric stretching vibration of OH group due to H-O-H bending of coordinated water.

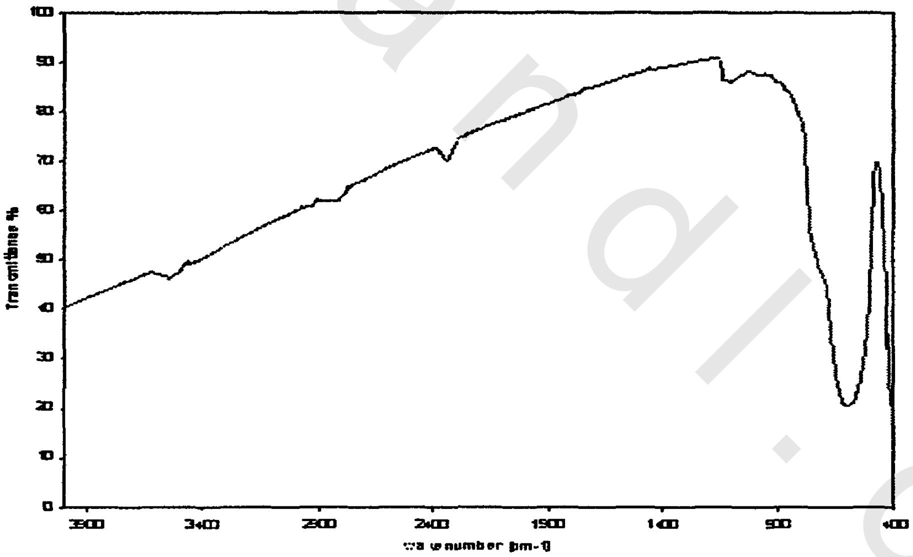


Fig.72: IR spectra of lead titanate nanopowders at hydrothermal temperature 200°C, hydrothermal time 30h and pH 13

III.2.2.6. Dielectric Properties of Lead Titanate by Hydrothermal Method

Fig.73 showed the dielectric constant of lead titanate at room temperature as a function of frequency which formed at hydrothermal temperature 200°C, hydrothermal time 30 h and pH 13.5. It can be observed that the values of dielectric constant decreased with increasing the frequency. The dielectric constant of lead titanate at room temperature were 955, 2153, 257 at 100Hz, 1 kHz, 10 kHz which found to fall rapidly with increasing frequency.

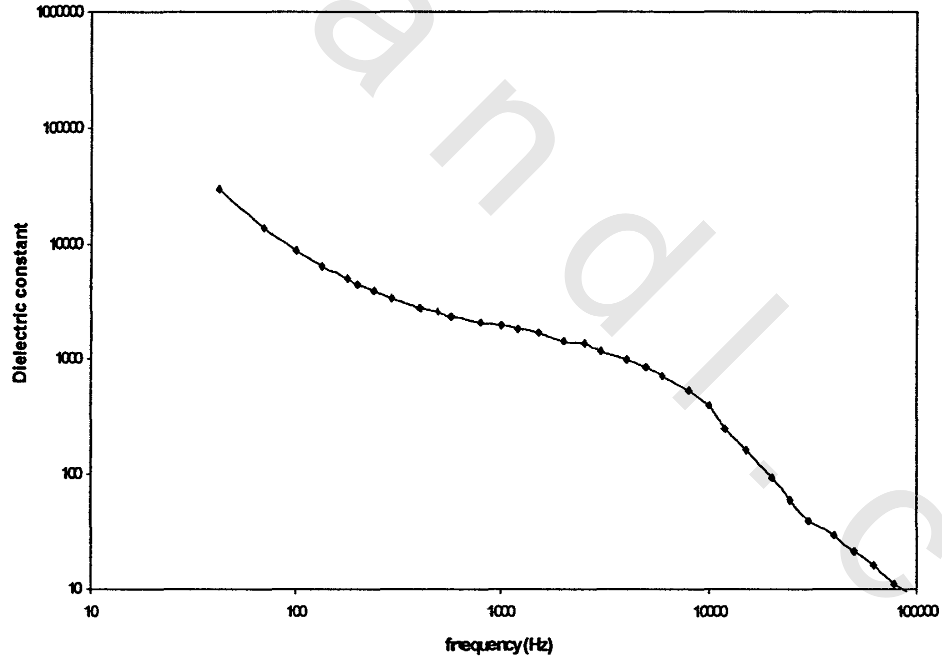


Fig.73: Dielectric constant of lead titanate nanopowders at hydrothermal temperature 200 °C, hydrothermal time 30 h and pH 13 .