

Preparaion Of Lead Free Nanosized Barium Titanate And Barium Calcium Titanate-Zirconate Powders By Using Urea Formaldehyde Resin

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Abstract:

Barium titanate, BaTiO₃ [BT] and Barium calcium titanate-zirconate BaCa(Ti Zr)O₃ [BCTZ] powders were prepared utilizing sol gel polymeric method using urea formaldehyde resin, as a template. The obtained gel dried at 80°C/48h, then calcined at different temperature 800, 1000 and 1100°C/3h. FT-IR analysis, thermal analysis in terms of DTA-TG were carried to the polymer gel, and gel hosting cations at 80°C. Phase composition using X-ray diffraction (XRD) was investigated to the calcined powder at the previous temperatures, Microstructure using scanning electron microscopy (SEM) was studied at 1100°C/3h. It was found that the pure perovskite of (Tetragonal-orthorhombic-monoclinic) barium titanate [BT] and (Tetragonal-orthorhombic-monoclinic) [BCTZ] powder was obtained at a calcination condition of 1100 °C for 3h. The average crystal size 24.14 nm for BT powder while BCTZ powder recorded 22.83 nm. Uniform grain microstructure powders contain nearly spherical pores was obtained

Key worde: Nanosized, Barium titanate (Ba TiO₃), sol gel, powder, urea formaldehyde, resin.

الملخص

تم تحضير بودرة فى حجم النانومتر من تيتانات الباريوم والباريوم كالسيوم تيتانات زيرونات باستخدام راتنج اليوريا فورمالدهيد كحامل. تم تجفيف الجيل المحضر عند درجة حرارة ٨٠ درجة سيليزية لمدة ٤٨ ساعة ثم بعد ذلك تم الحريق عند درجات حرارة ٨٠٠، ١٠٠٠، ١١٠٠ درجة سيليزية. تم توصيف الجيل المحضر بمفرده وايضا المرتبط بالكاتيونات المجفف ٨٠ درجة سيليزية لمدة ٤٨ ساعة بتحليل الاشعة تحت الحمراء والتحليل الحرارى. تم دراسة التركيب البلورى للبودرة الناتجة باستخدام تحليل الاشعة السينية ومنه تم حساب الجم البلورى للبودرة الناتجة بالنانومتر. تم استخدام الماسح الضوئى (الميكروسكوب) لدراسة التركيب النسجى للبودرة التى تم حرقها عند ١١٠٠ درجة سيليزية لمدة ٣ ساعات. تم تحضير بودرة تيتانات الباريوم و الباريوم كالسيوم تيتانات زيرونات ذات حجم كريستالات يساوى ٢٤,١٤ و ٢٢,٨٣ نانومتر على الترتيب، عند الحريق على ١١٠٠ درجة سيليزية لمدة ٣ ساعات

كلمات دالة: حجم النانو- تيتانات الباريوم-بودرة- راتنج اليوريا فورمالدهيد- محلول غروى بوليمرى

INTRODUCTION

Due to the high toxicity of lead based materials such as Lead titanate (PbTiO_3) that used in a wide range of electronic devices [Pontes et al., 2004]. The displacement of this compound by barium titanate compounds is an environmental goal. BT and BCTZ ceramics have a wide range of applications [Ertuğ, 2013], e.g. electronic, electro-optical, and electromechanical. Barium titanate, with a perovskite structure is a ferroelectric material with a common high dielectric constant widely utilized in the manufacturing of electronic components such as multilayer capacitors (MLCs), Positive temperature coefficient thermistors, piezoelectric transducers, and a variety of electro-optic devices. On the other hand, low dielectric constant barium titanate compounds which have been used in the microwave devices [Guo et al., 2012]. The most recently synthesis methods used for the preparation of BT powders; are solid- state reaction, mechano-chemical and wet chemical methods such as; co-precipitation, hydrothermal, sol-gel, as well as via polymeric precursor. BT can be synthesized as powder [Harizanov, 1998; Cheung et al., 1999; Jiang et al., 2000; Beck et al., 2001 & Lee and Zhang 2001].

The electrical properties of BT perovskite structure can be changed through the partial or complete substitution of barium and titanium sites by other cations, such as Ca^{2+} , Sr^{2+} , Zr^{4+} etc. [Herbert, 1985 & Yi and Kalkur, 2001].

Polymers are used as templates to guide the different inorganic species to homogeneously distribute in a network to form nano particles after burning out the organic part, as described by Ibrahim et al., [1991, 1999], The author prepared single oxide zirconium, (1991) as well as compounds namely, aluminum titanate (1999). The inorganic salts are added to the diluted solution of the prepared polymer or resin; namely urea formaldehyde. The conditions of preparation, pH, temperature, and time of reaction are optimized for each reaction. Ethylene glycol was found to be the appropriate alcohol to terminate the reaction.

The aim of the present work to prepare BT as well as $\text{Ba}_{0.95} - \text{Ca}_{0.05} (\text{Ti}_{0.85} - \text{Zr}_{0.15}) \text{O}_3$ (BCTZ) utilizing polymeric Sol-gel route; urea-formaldehyde resin innovated as a template.

MATERIAL AND METHODS

a-Starting Materials:

The following chemical reagents were used for the preparation of BT as well as BCTZ powders via sol-gel polymeric route using urea-formaldehyde resin as a template, Barium chloride dihydrate, Calcium carbonate and Zirconium oxychloride were acquired from Oxford, (India), titanium trichloride (Sigma, Aldrich), Formaldehyde (Loba Chemie Co., India), Ethylene glycol (Nice Chemicals Co., India), Urea (Sigma Chemicals Co.). Ammonia solution and Hydrochloric acid were bought from (Adwic Co.). The reactants were used as received from the suppliers without further purification except calcium chloride that prepared as the following:

One mole of Calcium carbonate reacts with two moles of Hydrochloric acid as the following equation:



The product, CaCl_2 were dried in an oven at 80°C for 48 h, then preserved from moisture to be used.

b- Procedure

Resins were prepared using the proportion (1:2:2) of urea : formaldehyde : ethylene glycol. The reaction proceeded in two pH ranges. The starting pH was between 8 - 9 and the reaction was terminated in a neutral media for resin free of cations. Also, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, TiCl_3 and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, CaCl_2 , TiCl_3 , $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ were added in the stoichiometric ratio to get molar concentration of Ba^{2+} , Ti^{4+} and $(\text{Ba}^{2+}, \text{Ca}^{2+})$, $(\text{Ti}^{4+}, \text{Zr}^{4+})$; (1:1) and (0.95:0.05), (0.85:0.15) as displayed in Table 1. A batch to yield about 20 g of oxide powder was prepared for each composition. Resins hosting the respective cations, Ba^{2+} , Ti^{4+} and $(\text{Ba}^{2+}, \text{Ca}^{2+})$, $(\text{Ti}^{4+}, \text{Zr}^{4+})$ were synthesized by adding salt solutions of Barium, titanium chloride and Barium, calcium, titanium chloride beside zirconium oxychloride simultaneously with ethylene glycol in the final stage of reaction. The duration time of all step of the reaction including preparation of resin and resin hosting salts is three hours and the pH in the final stage were found to be in acidic media. The resin observed transparent clear in neutral media and transparent clear violet during hosting cations in acidic media. The different components and compounds prepared are shown in Table (1). Reagents were left to digest under reflux, while stirring for three hours comprising half an hour for the resin formation from urea and formaldehyde alone, while the other two hours and half after the addition of salt solution and alcohol. Water and other by-products were pumped out using a vacuum pump. The resins were first slowly dried in an oven at $80^\circ\text{C}/48\text{h}$. Then calcined to yield the respective ceramic oxide powders.

Table (1) Composition of resin hosting cations prepared by the polymeric sol-gel route using urea-formaldehyde resin.

Batch name	Resin Concentration (Urea:Formaldehyde :Ethylene glycol)	Total Mole of BaTiO_3 or $\text{Ba}_{0.95} - \text{Ca}_{0.05} (\text{Ti}_{0.85} - \text{Zr}_{0.15})\text{O}_3$	Concentration of Cation (Ba:Ca:Ti:Zr)
URBT	1:1:2	1	1.0 : 0.0 : 1.0 : 0.0
URBCTZ	1:1:2	1	0.95 : 0.05 : 0.85 : 0.15

The proportions of urea and formaldehyde were added in a three neck round bottom flask of a volume 500 C.C, Fig.1. The reagents comprised two thirds of the volume. A reflux condenser was inserted in the middle neck. A thermometer and a separating funnel were placed each on either side. The whole apparatus was immersed in a water bath heated up to the respective temperature. The prepared resin hosting salts were treated under vacuum distillation as well as aged overnight, dried for 48 h at 80°C and the blank experiment BT were calcined at different temperature 600, 800, 1000 and $1100^\circ\text{C}/3\text{h}$. Thermal analysis in terms of (DTA/TG) was performed from 25 to 1000°C at a heating rate of $20^\circ\text{C}/\text{min}$ in (Netzsch STA 449 F3 Jupiter TG/DTA system, Selb, Germany) as well as Fourier-transform infra-red spectrum (FT-IR, Spectrum 400, PerkinElmer, USA) were carried to the dried gel of urea formaldehyde resin which dried at $80^\circ\text{C}/48\text{h}$ without cations, hosting two cations (BT) and hosting four cations (BCTZ). X-ray powder diffraction patterns of all samples obtained during the experiments were measured using a diffractometer with a Cu anode and a Ni filter for $\text{CuK}\beta 1$ radiation, $\text{IK}\alpha 2:\text{IK}\alpha 1 = 2:1$ (Philips PW1830, PanAnalytical, Almelo, the Netherlands). X-ray diffraction (XRD) used to examine phase composition. Microstructures were investigated to the selected

samples by high-resolution scanning electron microscopy (HR-SEM, 0.5-2.0 keV, Zeiss 1550, Zeiss, Sliedrecht, Netherlands).

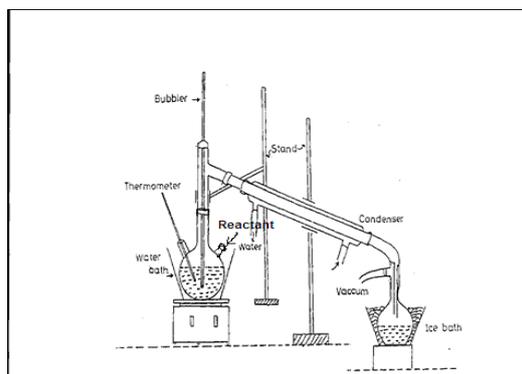
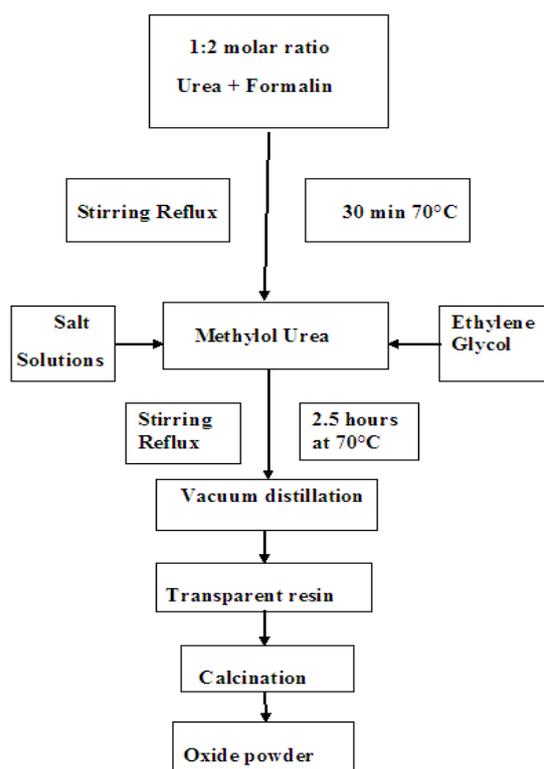


Fig.1. The apparatus used for the preparation of the precursor resins Urea – formaldehyde.



.2. The flow chart sol – gel polymeric route using urea formaldehyde.

RESULTS AND DISCUSSION

a- Characterization of dried gel and prepared powder

The FTIR- spectral analysis of urea-formaldehyde modified with ethylene glycol is displayed in Fig. 3 and Table 2, The spectrum is clearly differentiated to show the vibration bands characteristic of NH and OH stretching at 3388 cm^{-1} , CH stretching vibration represented by three bands occurring; at 3106.76 , 2992.01 and 2772.17 cm^{-1} . As well as NH_2 in plane bending and C=O stretching vibrations at 1621.84 cm^{-1} . Sharp (C-O, CO-NH-R) stretching band taking place at 1400.06 cm^{-1} followed by two small bands at 1019.19 and 861.06 cm^{-1} corresponding to broad NH wagging vibration. The spectra of resins containing Ba^{2+} and Ti^{4+} cations are shown in Fig. 3. A broad band corresponding to the NH stretching, OH stretching and CH stretching occur between $3400 - 2400\text{ cm}^{-1}$. The splitting at 3121.22 and 3010 cm^{-1} refer to (NH, OH) and CH stretching bands, respectively. Another vibration band related to CH occurs at 2794.34 cm^{-1} , the carbonyl band C=O shows stretching bands at 1631.48 and 1539.8 cm^{-1} . Metal coordinated to oxygen causes a shift in the position of this band. The sharp band at 1400 cm^{-1} is characteristic of mono-substituted amide to C-O to give CO-NH-R. While small bands occurring at 1068.38 cm^{-1} are characteristic of C-O and CN

stretching vibration bands. Finally, absorption bands at wave numbers smaller than 800 cm^{-1} are related to M-O bands e.g., at 638.32 and 537.07 cm^{-1} .

The spectrum of the resin hosting barium, calcium, titanium and zirconium cations is shown also in Fig. 3, it resembles to a great extent the latter ones. The vibration bands related to the different bands; mainly the NH stretching, OH and CH occur between 3400 to 2400 cm^{-1} . The variation recorded is in the band at 1620.87 cm^{-1} corresponding to C=O. The same shift occurs in the position of the bands of metal CO-ordinated to oxygen. There is a sharp band at 1400 cm^{-1} corresponding to mono-substituted amide CO-NH-R. The band characteristic of C-O is still present at 1072 cm^{-1} . Ba-O stretching mode, occurs at 1620.76 cm^{-1} . N-H bending mode occurs at 855.27 cm^{-1} . Absorption bands at wave numbers smaller than 800 cm^{-1} namely, bands occurring at 632.32 and 536.47 cm^{-1} are related to M-O bonds.

The co-ordination of Metal with O^{2-} results in a shift of the bands in the region of $1600-1700\text{ cm}^{-1}$. The complexity of the spectrum indicates the complex chain structure present. The interaction of the different polymers with the hosted cations namely: Ba^{2+} , or Ba^{2+} , Ti^{4+} and or Ba^{2+} , Ca^{2+} - Ti^{4+} and Zr^{4+} cations, show the absorption bands at wave numbers smaller than 800 cm^{-1} attributed to M-O bonds, as given by **Harizanov et al., (2004)**. The coordinated bonds of; NH out of plane, C=O stretching vibration, NH bending and CH out of plane in the range $700 - 1800\text{ cm}^{-1}$ caused a shift and splitting of the bands. The complexity of the spectrum indicates the complex chain structure present. Ba-O stretching mode reported by **Bazeera and Amrin, (2017)** and C=O stretching vibration taking place at 1610.27 cm^{-1} evidence the substitution. Also, a new band appears at 564.07 cm^{-1} corresponding to Ba-O stretching mode as demonstrated by **Akbarzadeh and Amiri, (2015)**. Whereas, chlorine did not participate in the structure of the resin as indicated by the absence of any specific FTIR-band in the region $230-380\text{ cm}^{-1}$. The resin hosting either two cations namely Ba^{2+} and Ti^{4+} or four cations Ca^{2+} -and Zr^{4+} beside Ba^{2+} and Ti^{4+} cations show nearly the same spectra with slight difference. In the latter case, the band in NH, the sharp bands presenting the C-O and C=O groups in the former (Ba^{2+} , Ti^{4+}) broadens shifts and splits with the introduction of the two other cations. The NH wagging, CH out of plane is shifted from 780.06 to 855.27 cm^{-1} . The bands characteristic of M-O bonding for all cation substitution occur between $800-400\text{ cm}^{-1}$. The substitution of Ba-O, Ca-O show bands at higher wave length than 800 cm^{-1} indicating the chelation with C=O stretching vibration occurs at 1631.48 and 1620.87 cm^{-1} , respectively, as given by **Bazeera and Amrin, (2017)**. Titanium chelation in the resin structure, as reported by **Abd-EL-Mounem,**

(1997). caused a shift in the bands at 1400 and 1078 cm^{-1} presenting C=O, CH₂ groups. While the bands related to Ti-O and Zr-O occur at 1068.38 and 1400 cm^{-1} . Chelation of Ti-O-Ti occurs at 780.06 , 855.27 and 638.32 632.32 cm^{-1} , respectively. while the bands related to Ti-O and Zr-O occur at 1068.38 and 1400 cm^{-1} . Chelation of Ti-O-Ti occurs at 780.06 , 855.27 and 638.32 632.32 cm^{-1} , respectively.

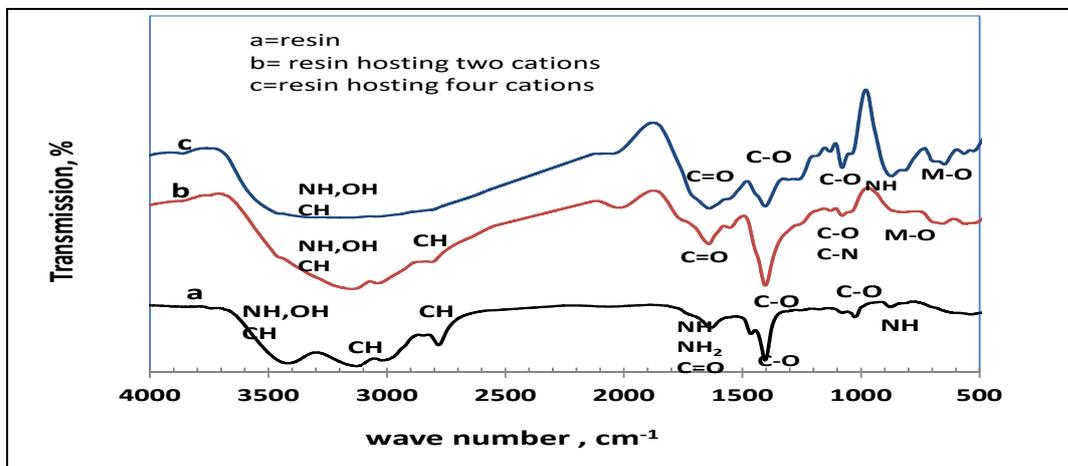


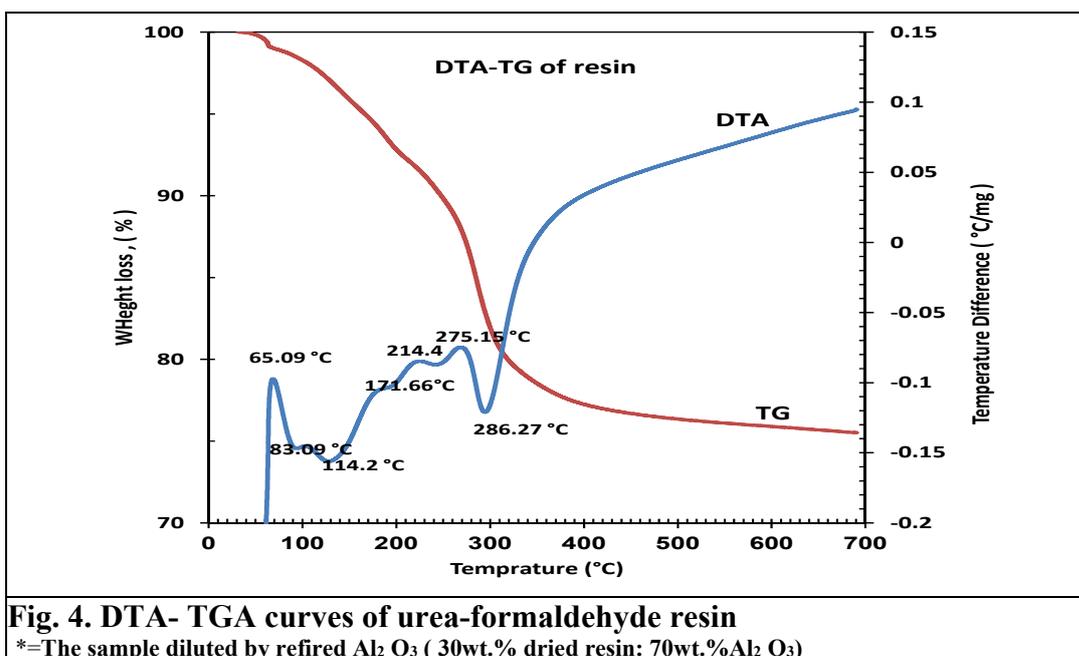
Fig. 3 . FTIR spectra of resin : a- free b-hosting two cations c-hosting four cations

Table 2. FTIR spectra of resin free and hosting different number of cations

Polymers Types of bands	Urea formaldehyde resin	Urea formaldehyde resin hosting hosting Ba ²⁺ , Ti ⁴⁺ cations	Urea formaldehyde resin hosting Ba ²⁺ , Ca ²⁺ , Ti ⁴⁺ and Zr ⁴⁺ cations
	Wave number, cm ⁻¹	Wave number, cm ⁻¹	Wave number, cm ⁻¹
NH stretching vibration	3388	3121.22	2780.84,3438.45
OH stretching vibration	3388	3121.22	2780.84,3438.45
CH stretching vibration	3106.76, 2992.01, 2772.17	3010	2780.84,3438.45
NH out of plane	1621.84	1539.88	1535
NH ₂ in plane bend	1621.84	--	--
C=O stretching vibration	1621.84	1631.48	1620.8
C-O (CO-NH-R) stretching	1400.06, 1019.19	1400, 1068.38	1400, 1072
NH wagging, CH out of plane	861.06	780.06	855.27
C-N stretching vibration	--	1068.38	855.27

N-H Bending mode	861.06	780.06	855.27
Ba-O stretching mode or M-O	--	1631.48,1539.80,1068.38,638.32,537.07	1620.87, 1072632.32, 536.47

TGA of urea-formaldehyde resin modified with ethylene glycol is shown in Fig. 4 and Table (3) and DTA is shown in Fig. 4 and Table (4). depicting a dissociation reaction of the organic resin occurring in three steps in the TGA curve evidenced by endothermic or exothermic peaks explain the effect of heat during these three main steps; The first step starts from 40 and ends at 220°C, with a loss in weight equivalent to about 31.75%, This is attributed to the loss of reaction by-products as ammonium chloride, indicative of dehydration of the precursor preceded at 75.06°C, 89.11 °C as well as melting of urea formaldehyde resin started at as indicated by small shoulder at 171.66°C, 214.4°C showed by DTA curve. The second step takes place between 220 and 325°C with a loss in weight of 51.43%, which corresponds to the combustion of the carbonaceous residue left of resin evidenced by small exothermic peaks at 235.34 and endothermic 286.27°C. The loss in weight in the third step is gradual until it ends at 690°C with another 14.99%, the compustion reaction completed at about 700°C, the end of DTA line, the previous study nearly agreed with **Abd-EL-Mounem, (1997)**. The DTA curve of both urea-formaldehyde resin hosting either two cations; Ba²⁺, Ti⁴⁺ or hosting four cation; Ba²⁺, Ca²⁺,Ti⁴⁺, Zr⁴⁺ are shown in Figs. (5-b,c) and Table (4). The effect of heat on the resin hosting cation nearly the as same as without cations. The peaks between 65°C to about 700 due to complete destruction of resin, table (4). A different pattern from the free resin spotted in both patterns of resin hosting cations, is the presence of a small exothermic peak at 916.04°C, it may be caused by crystallization of (BT).



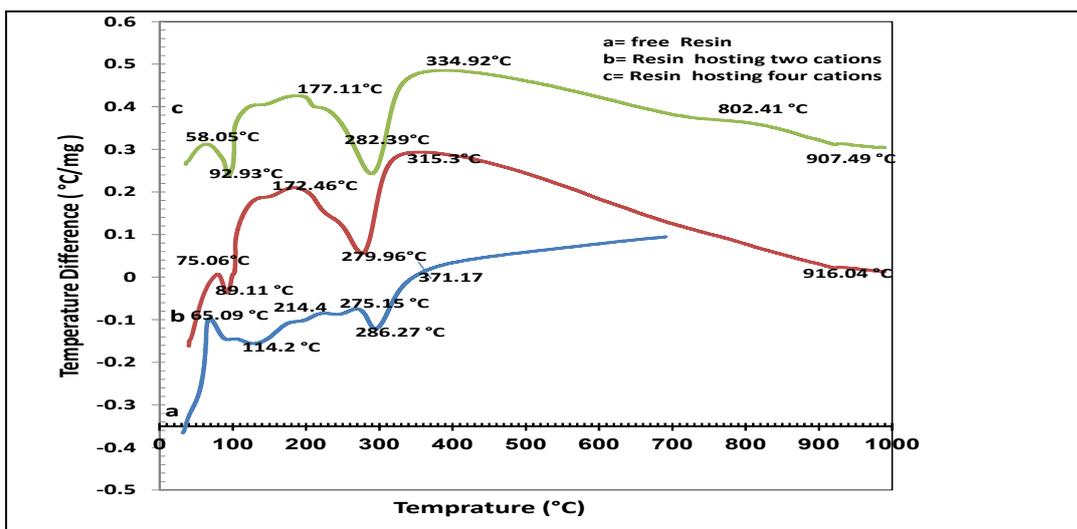


Fig.5. DTA curves of: a) resin b) resin hosting two cations(Ba^{2+}, Ti^{4+}) c) resin hosting four cations ($Ba^{2+}, Ca^{2+}, Ti^{4+}, Zr^{4+}$)

Table[3]: Temperatures of the main weight loss in Urea-formaldehyde resin detected in the TGA pattern

Urea-formaldehyde resin	Main steps					
	Step I		Step II		Step III	
	Temp. range, °C	Wt. loss, %	Temp. range, °C	Wt. loss, %	Temp. range, °C	Wt. loss, %
	40-220	31.75	220-325	51.43	325-690	14.99

Table (4): Main DTA peaks detected in the patterns of the three polymers. free and hosting either two cations; Ba^{2+}, Ti^{4+} or four cations; $Ba^{2+}, Ca^{2+}, Ti^{4+}, Zr^{4+}$

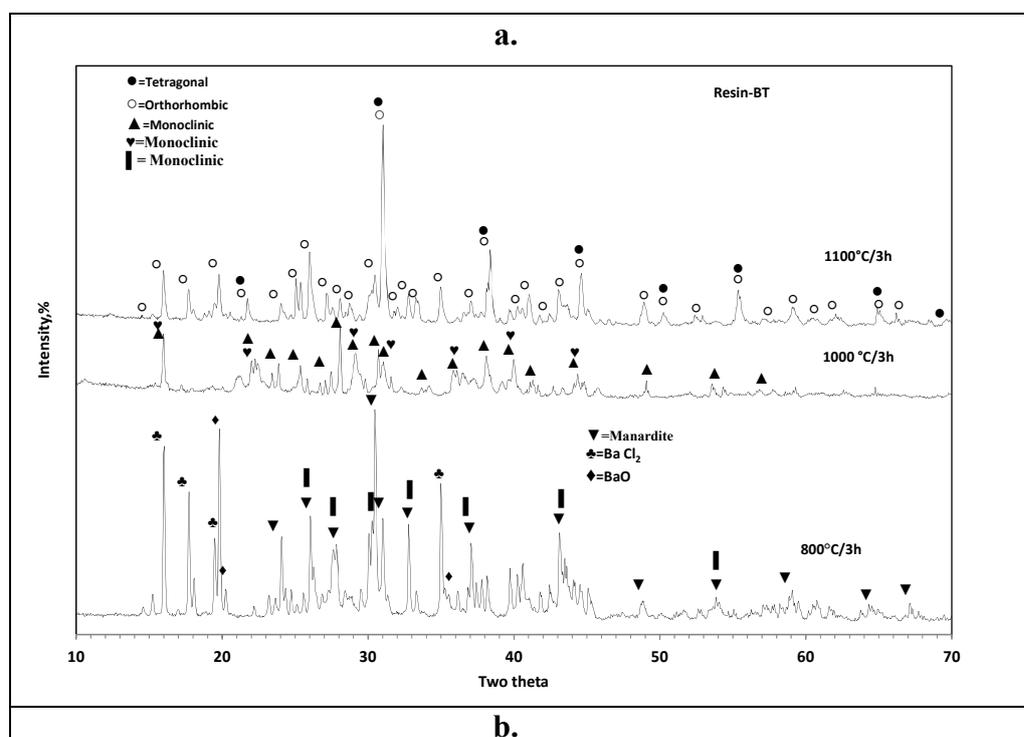
Material	Endothermic peaks temperature, °C					Exothermic peaks temperature, °C.				
	1 st	2 nd	3 rd	4 th	5 th	1 st	2 nd	3 rd	4 th	5 th
Urea-formaldehyde resin	83.09	114.2	191.34	235.34	286.27	214.4	275.15	371.17	--	--
Urea-formaldehyde resin hosting, Ba^{2+}, Ti^{4+} cations	89.11	279.96	916.04	--	--	75.06	172.46	315.3	--	--
Urea-formaldehyde resin hosting, $Ba^{2+}, Ca^{2+}, Ti^{4+}, Zr^{4+}$ cations	92.93	282.39	907.49	--	--	58.05	177.11	334.92	802.41	--

The X-ray diffraction (XRD) patterns of powder samples fired at 1000°C prepared using resin hosting both two as well as four cations were similar, as demonstrated in Table (5) and Fig. 6, Tetragonal Manardite phase ($Ba_{1.15}Ti_8O_{16}$), with crystallite size 16.5 nm, was only detected in the undoped sample fired at 800°C, beside remnants of the precursor barium chloride ($BaCl_2$). The unit cell dimensions recorded shows that grains will attain a platy shape as evident from the c/a ratio, Table 5. The estimated semiquantitative percent recorded was 15.7%. Monoclinic ($BaTi_5O_{11}$), with crystallite size 12.77, 15.57 & 21.4 nm. at 800, 1000 & 1100°C, respectively, in the undoped powder and following the percent recorded; were 50.5, 67.9 and 39%, respectively. This indicates that, it gave path for another phase to manifest itself. Whereas, the recorded crystallite sizes for the doped powders were; 21.4 & 19.03nm, at 1000 & 1100°C, respectively. It was detected as major phase reaching about 66% at 1000°C, but reached 5% at 1100°C, of the total crystalline phases. The expected shape for the phase is a prism as predicted from the lattice parameters determined. Monoclinic (Ba_2TiO_4), with crystallite size 12.7 nm at 800°C, that changed to the orthorhombic phase with size 15.57 nm at 1000°C and disappeared at 1100°C. The recorded percent were 17.6 and 32.1%, respectively. While the doped phase showed the orthorhombic phase at 1000°C with a slight coarser size of 17.3 nm. It forms about 33.8%, of the total crystalline phases. The change in the crystal form is accompanied by a change in the lattice parameters; axes and angles. Tetragonal ($BaTiO_3$), phase was not detected at 800°C, but appeared at 1000 and 1100°C; with crystallite size; 18.93 and 23.54 nm. While the doped samples the calculated sizes were; 23.54 and 26.93 nm, respectively. The semi-quantitative percents recorded were 30 and 20%, respectively. Orthorhombic ($Ba_2Ti_{13}O_{22}$), was detected at 1100°C, in both undoped and doped phases, with crystallite size; 24.47 and 22.54 nm, while the recorded semi-quantitative percents were, 638.9 and 58.5%, respectively. The phase equilibria in the BaO-TiO₂ system show the presence of seven stable phases: Ba_2TiO_4 , $BaTiO_3$, $BaTi_3O_5$, $Ba_4Ti_{13}O_{30}$, $BaTi_4O_9$, and $Ba_2Ti_9O_{20}$, as reported by Lee et al., (2007) $BaTiO_3$ is the most important of these compositions for its dielectric properties. It is directly formed from the respective oxides by solid state reaction at relatively high temperatures of 1350°C. There are often problems obtaining a pure phase because of the intermediate formation of other compounds as Ba_2TiO_4

Table 5. The crystalline size, specific surface area, X-Ray density and lattice parameters of the resulted phases for powders prepared by using urea formaldehyde resin, calcined at different temperature, 800, 1000 and 1100 °C/3h:

BT powder prepared by using urea formaldehyde resin											
Calcination temperature	Phase detected	Semiquantitative, %	X-Ray Density g/cm ³	Space group	Volume (Å ³)	a (Å)	b (Å)	c (Å)	c/a	Crystalline size(nm)	Specific surface area m ² /g
800 °C/3h	Tetragonal-(Manardite) ($Ba_{1.12}Ti_8O_{16}$)-(77-0883)	15.7	4.38	I4 (79)	300.42	10.07	10.07	2.96	0.293	16.51	60.56
	Monoclinic ($BaTi_5O_{11}$) (35-0805)	50.5	4.57	P21/n (14)	800.12	7.67	14.02	7.52	0.980	12.77	78.30
	Monoclinic (Ba_2TiO_4) (35-0813)	17.6	4.57	P21/n (14)	494.24	10.54	7.67	6.11	0.579	14.27	70.07
	Ba Cl ₂ 01-0948	16.2	-	-	-	-	-	-	-	-	-
	Monoclinic ($BaTi_5O_{11}$) (74-0538)	67.9	4.589	P21/n (14)	800.12	7.67	14.02	7.52	0.980	15.57	64.22

1000 °C/3h	Orthorhombic (Ba ₂ Ti O ₄) (38-1481)	32.1	5.208	Pnam/n (62)	492.97	7.65	10.55	6.10	0.797	17.12	58.41
1100 °C/3h	Tetragonal (BaTiO ₃)- (80-6372)	21.2	5.05	P4mm (99)	76.55	4.31	4.31	4.10	0.951	26.56	46.38
	Orthorhombic (Ba ₂ Ti ₁₃ O ₂₂)- (82-1430)	38.9	5.02	Cmca (64)	1652.87	11.65	14.10	10.05	0.862	24.47	40.86
	Monoclinic (Ba Ti ₅ O ₁₁) (74-0538)	39.0	4.589	P21/n (14)	802.64	7.66	14.04	7.53	0.983	21.41	64.72
BCTZ- prepared by using urea formaldehyde resin											
Calcination temperature	system	Semiquantitative %	X-Ray Density g/cm ³	Space group	Volume (Å ³)	a(Å)	b(Å)	c(Å)	c/a	Crystalline Size (nm)	Specific surface area m ² /g
1000 °C/3h	Monoclinic (Ba Ti ₅ O ₁₁) (74-0538)	66.2	4.589	P21/n (14)	800.12	7.67	14.02	7.52	0.980	21.41	46.72
	Orthorhombic (Ba ₂ Ti O ₄) (38-1481)	33.8	5.208	Pnam/n (62)	492.97	7.65	10.55	6.10	0.797	17.3	57.80
1100 °C/3h	Tetragonal (BaTiO ₃)- (80-6372)	36.5	5.05	P4mm (99)	76.55	4.31	4.31	4.10	0.951	26.93	37.13
	Orthorhombic (Ba ₂ Ti ₁₃ O ₂₂)- (82-1430)	58.5	5.02	Cmca (64)	1652.87	11.65	14.10	10.05	0.862	22.54	44.36
	Monoclinic (Ba Ti ₅ O ₁₁) (74-0538)	5.0	4.589	P21/n (14)	802.64	7.66	14.04	7.53	0.983	19.03	52.54



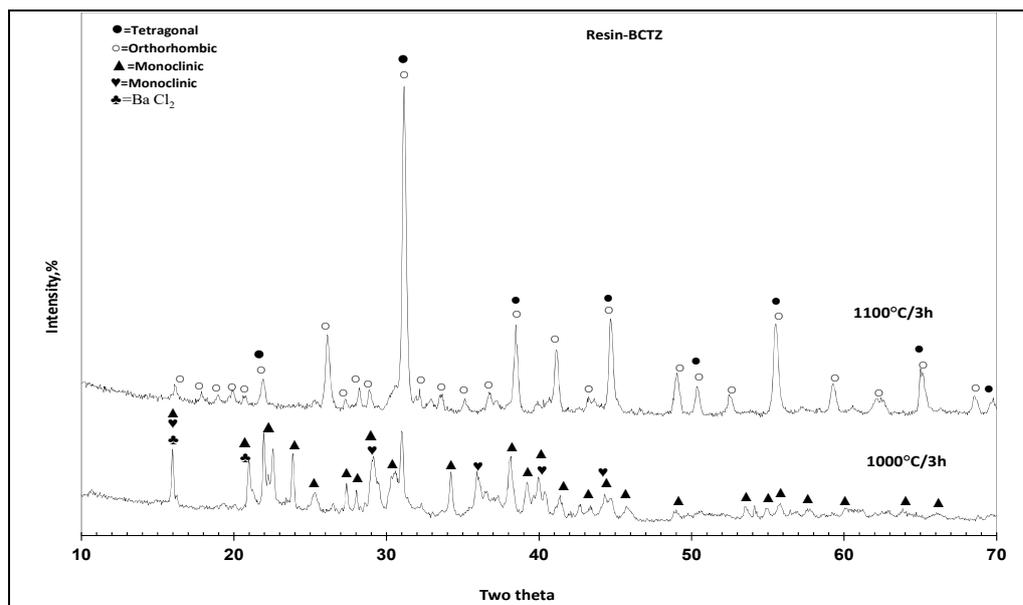


Fig. 6 . XRD of powders prepared using Resin; a) Ba TiO₃ (1:1) calcined 800, 1000 and 1100°C b) Ba Ca(Ti Zr)O₃ (1:1) calcined 1000 and 1100°C.

- =Tetragonal BaTiO₃ card number (80-6372)
- =Orthorhombic Ba₂ Ti₁₃O₂₂ card number(82-1430)
- ▼= Orthorhombic Ba₂ Ti O₄ card number (38-1481)
- = Monoclinic Ba₂ Ti O₄ card number (35-0813)
- ▲=Monoclinic Ba Ti₅ O₁₁ card number (35-0813,74-0538)
- ▼ = Manardite Ba_{1.15} Ti₈ O₁₆ card number (77-0884)
- ◆= Barium oxide Ba O card number(73-2220)
- ♣= Barium chloride Ba Cl₂ card number(11-0137)

still the chemical synthesis route, as sol-gel process, results in the presence of such phases as: Ba₂TiO₄, BaTi₂O₅ and BaTi₄O₉. It is governed by the availability of the respective cations to participate in the reaction. The appearance of the other titanate as major phases; Ba₂TiO₄, BaTi₅O₁₁ as well as Ba₄Ti₁₃O₃₀, indicates that the needed ratios for their formation of the reactants were available. This is expected, as a conspicuous portion of the BaCl₂ did not participate in the polymer structure and left it enriched in TiO₂, giving path to their

BaCO₃ and TiO₂ and firing at temperatures between 700 and 1150°C. According to **Hsu et al., (2013)**, Monoclinic BaTi₅O₁₁ readily forms between 700 to 800°C, and sintered at 1100°C/4h. While, Ba₄Ti₁₃O₃₀ as a single phase was difficult to prepare. It was obtained as film through CVD by laser **Guo et al., (2012)** and as nano crystals by a hydrothermal method utilizing barium acetate **Li et al., (2019)**.

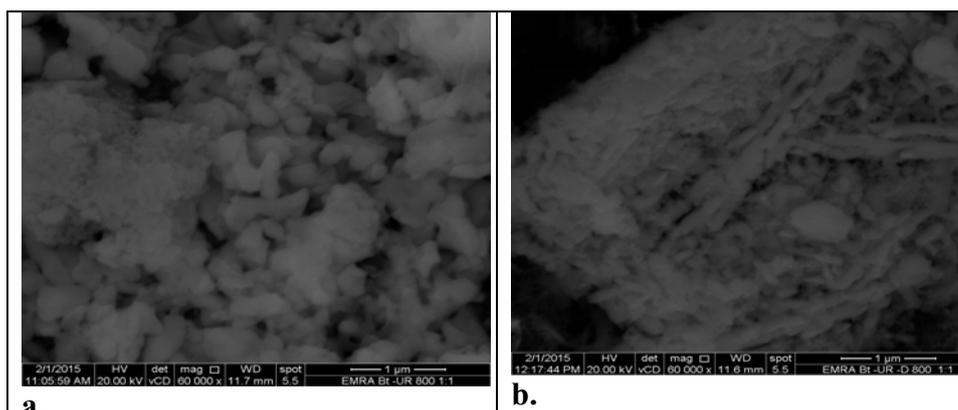


Fig. 7. SEM of powders a) BaTiO₃ (1:1) powder fired at 800 °C/ 3h. b) Ba Ca(Ti Zr)O₃ (1:1) powder fired at 800 °C/ 3h.

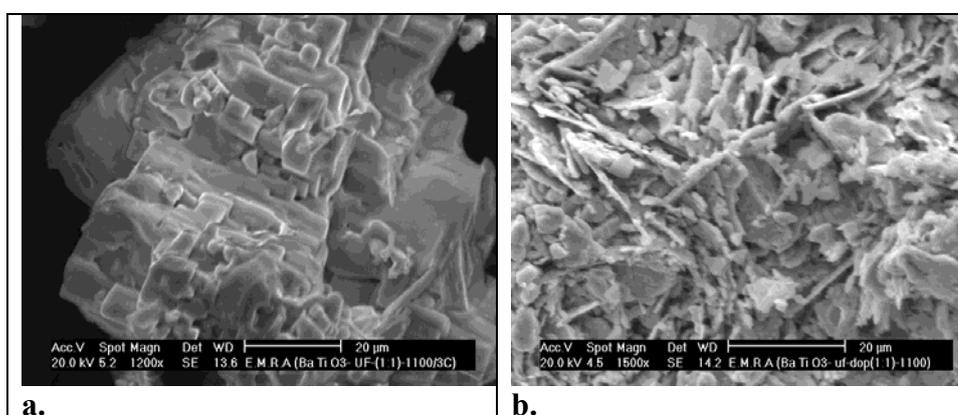


Fig. 8. SEM of powders; a) BaTiO₃ (1:1) powder fired at 1100 °C/ 3h. b) Ba Ca(Ti Zr)O₃ (1:1) powder fired at 1100 °C/ 3h.

The SEM micrographs of the powder calcined at 800 as well as 1100 °C showing morphology and particle size of products are illustrated in Fig. 7 and 8, respectively. All of these were well crystallized and crystallite growth occurs at this temperature showing the former structure of the resin net work lace like very uniform distribution of pores between the particles, shows the structure of the resin with pores very uniform in size and its shape nearly spherical, resulting from the volatilization of the organic matter of the resin. The oxide grains are fused together having flaky shape agglomeration of particle. As the same as for the received powder at 1100°C, the particles nearly discrete. The crystal size, grin growth increase with increasing calcination temperature between 800-1100°C. This result agreed with another authors [Bongkarn et al., 2008 & Ghayour and Abdellahi, 2016], The obtained SEM micrographs show the flaky shape phenomena of the particle with bimodal distribution. Micrograph analyses demonstrate that with increasing the temperature, larger grains are formed either from single grains or as a result of the agglomeration of smaller grains [Mesquita et al., 2012]. used for Doping by Ca²⁺, Zr⁴⁺ on Ba TiO₃ enhance the microstructure, grain growth of the prepared powder [Zhang et al., 2009 and Hsieh et al., 2012].

CONCLUSION

Pure perovskite (Tetragonal-orthorhombic-monoclinic) barium polytitanate (BT) and (Tetragonal-orthorhombic-monoclinic) (BCTZ) powder was obtained at a calcination temperature of 1100 °C/3h, utilizing sol gel polymeric method using urea formaldehyde resin.

The starting material as barium chloride has an effect of on the resulted microstructure. The urea formaldehyde resin affect the microstructure of the prepared powder.

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