

Dielectric Properties Of Nanosized Barium Titanate Ceramics Sintered At Low Temperature

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Abstract:

Barium titanate, BaTiO₃ (BT) and Barium calcium titanate zirconate BaCa(Ti Zr)O₃ (BCTZ) ceramics were prepared by dry pressing. The prepared ceramic bodies were sintered at different temperatures, 1100, 1150 and 1200°C/4h., physical properties in terms of bulk density as well as relative density and average grain size were studied. Phase composition using X-ray diffraction (XRD) was investigated to these ceramic bodies at the previous temperatures, Microstructure using scanning electron microscopy (SEM) was studied to the selected samples at 1200°C/3h. It was found that the pure perovskite of (Tetragonal-orthorhombic) (BT) and (Cubic-orthorhombic) (BCTZ) ceramics was obtained at 1200 °C/4h. Prepared bodies BT and BCTZ, sintered at 1200 °C/4h have uniform very fine grain size porous microstructure, with average grain size 604, 804 nm as well as relative density recorded 83.26, 92.39%, respectively. Dielectric constant (ϵ) enhanced and recorded, 2802.25 for BCTZ and 27.59 for BT ceramics

Keywords: Dielectric properties, Barium titanate ceramics, Nanosized, Low temperature

الملخص

تم تحضير أجسام سيراميكية في حجم النانومتر من تيتانات الباريوم والباريوم كالسيوم تيتانات زيروونات بطريقة الكبس الجاف. تم حريق الاجسام المحضرة عند 1100، 1150، 1200 درجة سيليزية لمدة 4 ساعات. تم دراسة الخواص الفيزيائية من حيث الكثافة الظاهرية والكثافة النسبية و متوسط الحجم الحبيبي لهذه الاجسام المحضرة. تم دراسة التركيب البللوري للاجسام السيراميكية الناتجة عند درجات الحرارة السالفة الذكر باستخدام تحليل الاشعة السينية. تم استخدام الماسح الضوئي (الميكروسكوب) لدراسة التركيب النسجي للاجسام السيراميكية الناتجة وكذلك الخواص الكهربائية مثل ثابت العزل ومعامل فقد الكهري للاجسام التي تم حرقها عند 1200 درجة سيليزية لمدة 4 ساعات. تم تحضير أجسام سيراميكية من تيتانات الباريوم و الباريوم كالسيوم تيتانات زيروونات ذات متوسط حجم حبيبي يساوي 604-804 نانومتر على الترتيب، عند الحريق على 1200 درجة سيليزية لمدة 4 ساعات. وأيضا الكثافة النسبية 83.26 و 92.39 بالإضافة الى ثابت عزل كهري 27.59 و 2802.25 على الترتيب لهذه الاجسام السيراميكية

كلمات دالة: الخواص الكهربائية - سيراميك تيتانات الباريوم - حجم النانو - درجة حرارة منخفضة

INTRODUCTION

Barium titanate (BaTiO₃/BT) is the first discovered ferroelectric compound with general formula ABO₃ characteristic of the mineral perovskite [Geetha et al., 2016]. The binary phase diagram of barium oxide (BaO)–titanium dioxide (TiO₂) shows several phases that have been proven to be useful for a number of electroceramic applications. The most important phase is the perovskite BaTiO₃ used for capacitor and positive temperature coefficient resistors. Ceramics containing Ba₂Ti₉O₂₀ or BaTi₄O₉ have been used as microwave dielectric resonator filters, while BaTi₅O₁₁ is used as a dielectric material, [Masse et al., (1971); O'Bryan et al., (1974) & Ritter

et al., (1986, BaTi₂O₅ compound is prepared as single phase and used as a ferroelectric material with a high phase transition temperature [Akinshige et al., 2004 & Waghmare et al., 2004].

However, the solubility limits of BaO and TiO₂ in BT, were not well defined. It was estimated that the hexagonal and cubic solid solutions could accommodate < 2 mole % excess TiO₂ at about 1600°C, whereas, the cubic phase could dissolve 1 mole % TiO₂ at about 1400°C [Rase and Roy., 1955]. BT material is characterized by a fairly low piezoelectric coefficient. Researchers worked on enhancing its piezoelectricity response, by design means of domain, defects, as well as phase boundary engineering. This is achieved through substitution in the crystal lattice of the perovskite structures. The substituents are divided into two categories, donor and acceptors dopants. The donor dopants are of higher charge than that of the ions they replace, are therefore compensated by cation vacancies. The other dopants, acceptors, i.e. dopants of lower charge than that of the replaced ions, are compensated by oxygen vacancies. Each dopant type tends to suppress the vacancy type that the other promotes. In contrast, in BT, in which the volatility of the constituents during sintering is low, small concentrations (< 1 mol. %) of donors are compensated by electrons in the conduction band with an accompanying change of color from pale yellow to grey or black. However, higher donor concentrations lead to a decrease in crystal size in ceramics sintered to full density, and an increase in resistivity above that for un-doped BT together with a reversion to the pale color [Moulson and Herbert, 2003].

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 Ca²⁺, Sr²⁺, Zr⁴⁺ etc. [Herbert, 1985, Yi and Kalkur, 2001]. These substitutions enhance its possible application, which require specific dielectric, piezoelectric, semiconductive and optical properties. Ba₂TiO₄ and Sr₂TiO₄, crystallize in the β -K₂SO₄ and K₂NiF₄ structures (A₂BO₄ type), respectively, as displayed in Fig.1, Shanker et. al., (2004), claimed that, oxides prefer the β -K₂SO₄ structure when the A-cations are much larger than the B-cations and the K₂NiF₄ structure when the size of the A-cations are smaller. Pure barium titanate has a curie temperature peak value at 130 °C, this is shifted to room temperature by partially substituting Ba²⁺ by Ca²⁺ and Ti⁴⁺ by Zr⁴⁺ in the perovskite structure, to allow its dielectric constant to meet Y5V specifications [Yamamatsu et al., 1996 & Hennings., 2001].

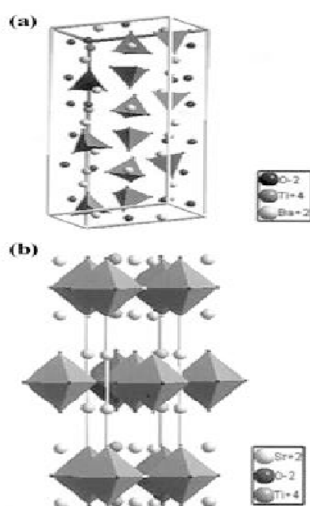


Fig.1. Structure of (a) orthorhombic Ba₂TiO₄ and (b) Sr₂TiO₄ [Shanker et. al., 2004].

Microwave dielectrics of the TiO₂-rich BaO–TiO₂ system; poly-titanates; BaTi₄O₉ and Ba₂Ti₉O₂₀ show a high level of inhomogeneity when prepared by the conventional method. Some alternative methods are applied to minimize the influence of non-equilibrium phases on microwave dielectric properties. The use of precipitation methods lead to a more homogeneous microstructure. Alkoxides, acetates, chlorides, hydroxides, nitrates, citrates, oxalates of barium as well as titanium, and combinations of them are utilized to form high purity sub-micrometer sized powders of BaTiO₃, BaTi₄O₉, and Ba₂Ti₉O₂₀ [Phule and Risbud, 1990]. The application of organic acid salts mainly the citrate routes are preferred over other methods [Choy et al., 1995]. Pure and well-crystallized BaTi₄O₉ particles of 30-50 nm are obtained through the thermal decomposition of citrate gel precursors at 900 °C for 1 h, as confirmed by the results of XRD. Moreover, BaTi₄O₉ sintered at 1250 °C/10h, shows all the characteristics peaks of the orthorhombic symmetry [Lukaszewicz, 1957].

The aim of the present work is investigate the effect of physical properties, phase composition and microstructure on the prepared ceramics.

MATERIAL AND METHODS

a-Starting materials

The powder prepared as in the previous work by sol gel polymeric method utilizing urea formaldehyde resin, Ba TiO₃ and Ba_{0.95} – Ca_{0.05} (Ti_{0.85} – Zr_{0.15}) O₃ with an average crystal size 24.14 nm to (BT) powder while (BCTZ) powder recorded 22.83 nm at 1100°C/3h as well as mole concentration of cations as shown Table (1).

Table (1) Composition of cations, average crystal size of the used powders:

Powder name	Concentration of Cation (Ba:Ca:Ti:Zr)	Average crystal size
BT	1 : 0.00 : 1 : 0.00	24.14
BCTZ	0.95 : 0.05 : 0.85 : 0.15	22.83

b- Processing:

Synthesized powder of Ba TiO₃ and Ba_{0.95}-Ca_{0.05}(Ti_{0.85}-Zr_{0.15})O₃ were mixed by grinding the calcined powder at 1100 °C/3h in an agate mortar for one hour, passed from 45 µm sieve then mixed with 3 %wt. solution of poly vinyl alcohol. The obtained powders were pressed at 20 kN under uniaxial press to form pellets of 1cm in diameter and 2.5 mm thickness as well as were sintered at 1100, 1150 and 1200°C/ 4h. Physical properties in terms of bulk density were determined using ASTM C-373-72. The method depend on calculated Bulk density at 1200°C/ 4h using the following eqn. No. 1, in which (D) refer to dry weight of samples, (S) saturated wt., with water and (I) immersed sample wt., in water using a suspending wire.

$$\text{Bulk density} = \frac{D}{S-I} \quad \text{----- (1)}$$

The relative density was calculated from eqn. 2;

$$\text{Relative density} = \frac{1}{\text{Bulk density}} \times 100 \quad \text{----- (2)}$$

The phases developed were identified by 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 CuKβ1 radiation, I Kα2: I Kα1= 2:1 (Philips PW1830, Pan Analytical, Almelo, the Netherlands). Microstructures were investigated by high-resolution scanning electron (HR-SEM,

0.5–2.0 keV, Zeiss 1550, Zeiss, Sliedrecht, Netherlands) for the selected samples as well as microscopy average grain size were determined using SEM photos by linear intercept methods. The dielectric behaviors in terms of Dielectric constant (ϵ) and Dielectric loss (D) were investigated with Concept Turnkey Dielectric, Conductivity and Impedance Spectrometers with Temperature Control (Broadband Dielectric Spectrometer Concept 40, Novo-Control, Germany).

RESULTS AND DISCUSSION

The results of grain size (nm) as well as Specific surface area are demonstrated in Table (2). The results show the small grain size of the sintered bulk ceramic bodies at 1200°C/4h. Results highlighted the sol–gel polymeric fabrication using resin as template and they effect on the resulted grain size. The average grain size tended to increase as the samples were doped with Ca^{2+} and Zr^{4+} than the un-doped samples. On the other hand, surface area

decreased with doping process. The average grain size of the samples that prepared by using resin increased from 604 to 804 nm combined with decreasing specific surface area from 1.65 to 1.24 m^2/g . The physical properties in terms of bulk density, relative density %, of processed bodies sintered at 1100, 1150, 1200°C/4h displayed in Table (3). The values of relative density of BCTZ samples indicate that the reaction between oxides was well densified than the BT samples. A maximum of 92.39% was obtained for bodies fired at 1200°C for BCTZ compared to 83.26% for BT. All prepared samples on the other hand show better densification with increasing temperature from 1100 to 1200°C/4h. XRD patterns of the fired bodies for BT as well as BCTZ are demonstrated in Table (4) and Fig. 2. At 1100 and 1150 and 1200°C the peaks corresponding to BT ceramics showed the formation of (tetragonal BaTiO_3) and Orthorhombic ($\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$) as major phases were found [Li et al., 2013]. Whereas, with doping by Ca^{2+} and Zr^{4+} cations at 1100 and 1150 and 1200°C, Cubic (BaTiO_3), and Orthorhombic ($\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$) were the dominant phases, [Bijalwan, 2018] discussed that with doping by Ca^{2+} and Zr^{4+} tetragonal phase transform to cubic phase. The accompanied change in the unit cell of the formed phases and their conversion was followed in the measured symmetry axes and the ratio between c/a axes, Table 4. The crystallinity and perovskite phase of BaTiO_3 increase with increasing calcination temperature. Qi et al., (2011) discussed that existence of BaO and annealing temperature lead to secondary phase. Ceramic bodies were prepared by Ying and Hsieh (2007) and sintered between 1100 and 1300°C. The author investigated that XRD patterns of the prepared bodies resulted in Tetragonal, Monoclinic as well as Cubic with increasing temperature and multiple phase were found caused by low sintering temperature.

Table (2): The average grain size and specific surface area of the bodies sintered

Batch name	Firing temperature (°C)	Average grain size (nm)	Specific surface area m^2/g
BT	1200/4h	604	1.65
BCTZ	1200/4h	804	1.24

Table (3): The physical properties in terms of bulk density, relative Density of processed bodies sintered at different temperature

Batch name	Firing temperature (°C)/4h	Bulk density g/cm ³	Relative Density, %
BT	1100	2.91	63.04
	1150	3.45	75.00
	1200	3.83	83.26
BCTZ	1100	3.14	68.26
	1150	3.64	79.13
	1200	4.25	92.39

Figure 3 (a) and (b) are the results of SEM micrographs for the processed ceramic bodies sintered at 1200°C/4h; for BT as well as BCTZ, respectively. They have a general feature indicating the very fine nature of grains less than 1 μm , uniform microstructure with flaky shape and bimodal size distribution of grains. Some of the grains are arranged preserving the ring and branched structure of the former resin. Therefore, there arises patches of these fired grains totally densified giving the appearance of one big grain. While the grains forming the branches are arranged in a more or less curve linear form there around these patches leaving some pores. Pores are very fine within the patch indicating the center of the former rings and they are intra-granular. Also, pores are formed between the patches and branches as a result of the adherence of the some of the grains, Photos No. (a₁, b₁). No intergranular pores were identified. Better densification is achieved in the BCTZ bodies that fired at the same temperature 1200 °C/4h, reflect how the particles combined with each other to form grains and matrices of ceramic bodies

Figure 3.(b₃). poly titanate phases are obvious in all samples specially Photos No. (a₂, a₃, b₂), tetragonal (BaTiO₃) and Orthorhombic (Ba₄ Ti₁₃O₃₀). **Li et al., (2013)** stated that tetragonal distinguished by large grain while orthorhombic has small one. Dielectric measurements in terms of dielectric constant (ϵ) and dielectric loss (D) for BT, BCTZ were carried out at room temperature, 25°C for disks that were sintered at 1200°C/4h., as displayed in In general, Fig. 4 (a,b), respectively shows the decrease of dielectric constant (ϵ) and dielectric loss (D) with increasing frequency, for BT ceramic bodies, dielectric constant (ϵ) decreased from 27.592 to 9.521 and dielectric loss (D) decreased from 0.1685 to 0.0005 with increasing frequency from 0.10 Hz to 3.12 M Hz. As the same as for BCTZ, meanwhile, it recoded higher values than the BT. The dielectric constant (ϵ) decreased from 2802.250 to 23.592 and dielectric loss (D) decreased from 3.4687 to 0.0255 with increasing frequency from 0.10 Hz to 3.12 MHz., [**Tan, et al., 2015 & Ghayour and Abdellahi, 2016**], the dielectric constant of the BaTiO₃ ceramics first increases with decreasing average grain size, reaching a maximum value in the, 0.8–1.1 μm grain size range. Electrical measurement results showed that both the dielectric constant (ϵ) and dielectric loss (D) decrease as frequency increases in all samples.

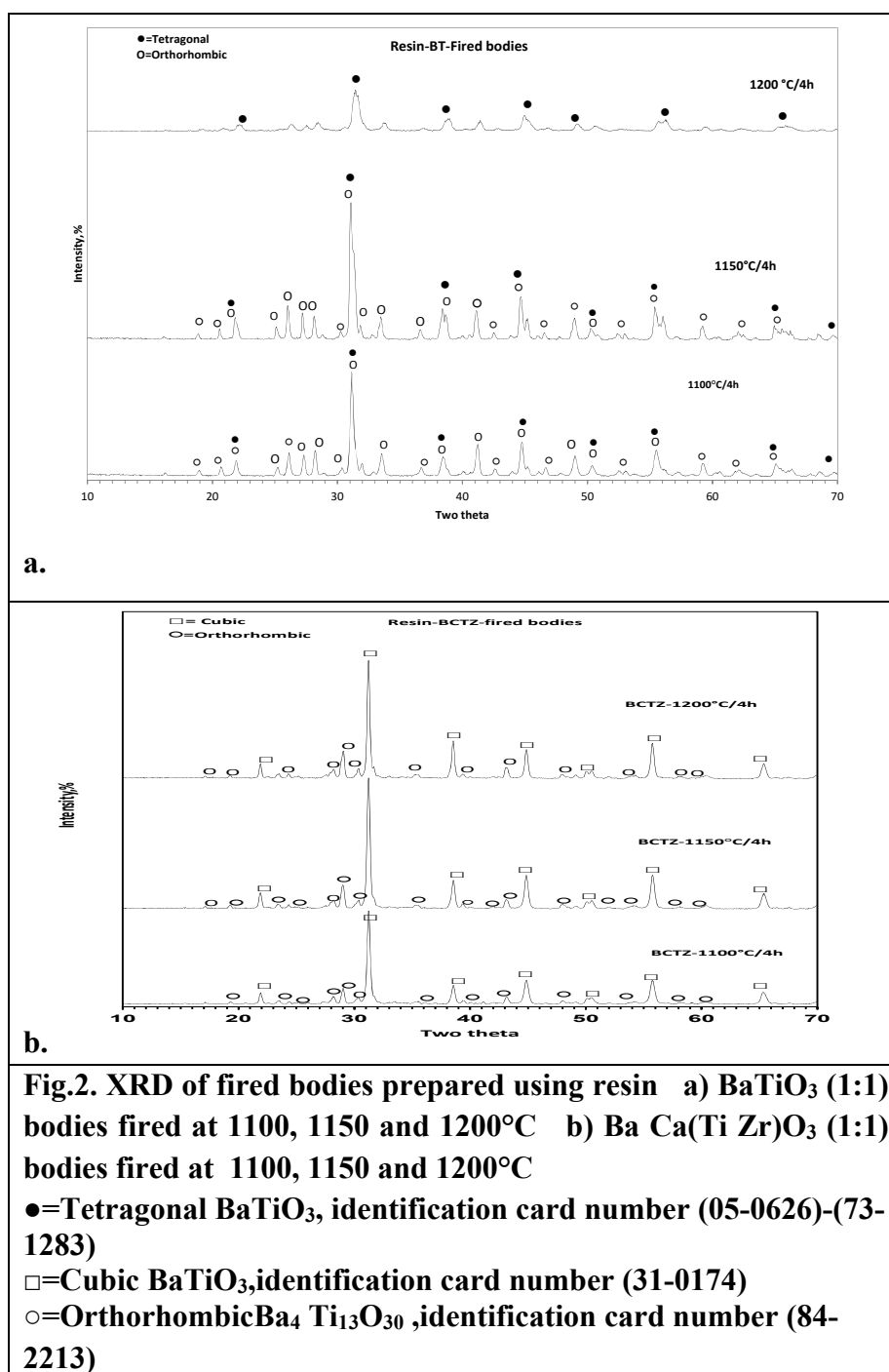


Table (4) The detected phases and lattice parameter of the BT as well as BCTZ ceramics fired at different temperatures.

BT									
Firing temperature	Phase Detected	Semi quantitative %	X-Ray Density g/cm^3	Space group	Volume (\AA^3)	a(\AA)	b(\AA)	c(\AA)	c/a

1100 °C/4h	Tetragonal (BaTiO ₃)- (05-0626)	39	5.92	P4mm (99)	64.31	3.99	3.99	4.02	1.007
	Orthorhom bic (Ba ₄ Ti ₁₃ O ₃₀)- (84-2213)	59	4.64	Cmca (64)	2364.30	17.0 6	9.86	14.05	0.823
1150 °C/4h	Tetragonal (BaTiO ₃)- (05-0626)	48.2	5.92	P4mm (99)	64.31	3.99	3.99	4.02	1.007
	Orthorhom bic (Ba ₄ Ti ₁₃ O ₃₀)- (84-2213)	51.8	4.64	Cmca (64)	2364.30	17.0 6	9.86	14.05	0.823
1200 °C/4h	Tetragonal (BaTiO ₃)- (05-0626)	57	5.92	P4mm (99)	64.31	3.99	3.99	4.02	1.007
	Orthorhom bic (Ba ₄ Ti ₁₃ O ₃₀)- (84-2213)	43	4.64	Cmca (64)	2364.30	17.0 6	9.86	14.05	0.823
BCTZ									
Firing temperat ure	Phase detected	Semi quantitat ive %	X- Ray Densi ty g/cm ³	Space group	Volume (Å ³)	a(Å)	b(Å)	c(Å)	c/a
1100 °C/4h	Cubic- (BaTiO ₃) 31-0174	44	6.01	P m -3 m (221)	65.50	4.03	4.03	4.03	1.00
	Orthorhom bic (Ba ₄ Ti ₁₃ O ₃₀)- (84-2213)	56	4.64	Cmca (64)	2364.30	17.0 6	9.86	14.05	0.823
1150 °C/4h	Cubic- (BaTiO ₃) 31-0174	51	6.01	P m -3 m (221)	65.50	4.03	4.03	4.03	1.00
	Orthorhom bic (Ba ₄ Ti ₁₃ O ₃₀)- (84-2213)	49	4.64	Cmca (64)	2364.30	17.0 6	9.86	14.05	0.823
	Cubic-								

1200 °C/4h	(BaTiO ₃) 31-0174	59	6.01	Pm-3m (221)	65.50	4.03	4.03	4.03	1.00
	Orthorhombic (Ba ₄ Ti ₁₃ O ₃₀)- (84-2213)	41	4.64	Cmca (64)	2364.30	17.06	9.86	14.05	0.823

It has noted that the dielectric constant (ϵ) and dielectric loss (D) at room temperature for all compositions gives a higher value for BT and BCTZ, 27.592,2802 when the frequency recorded lower value 0.1Hz, these result agreed with [Vishnu et al., 2004] and explained by Kashif et al., (2014), the higher values of dielectric constant at low frequency suggest the presence of all types of polarization (interfacial, atomic, dipolar, ionic and electronic) at room temperature. Also, they added that, at very low frequency, high value of dielectric constant obtained because dipoles follow the field, with increasing frequency dipoles begin to lag behind the field and the dielectric constant slightly decreases. Further, at high frequencies dipoles can no longer follow the field and we have low values of dielectric constant (Pontes et al., 2004). There are many factors affecting the electrical properties in terms of low sintering temperature, methods of preparation, effect of secondary phases, effect of dopant, Ca and Zr cations, as showed in Table (5) that highlighted different studies achieved by earlier researchers devoted in the synthesis of barium titanate and barium calcium titanate zirconate by different methods and different condition of

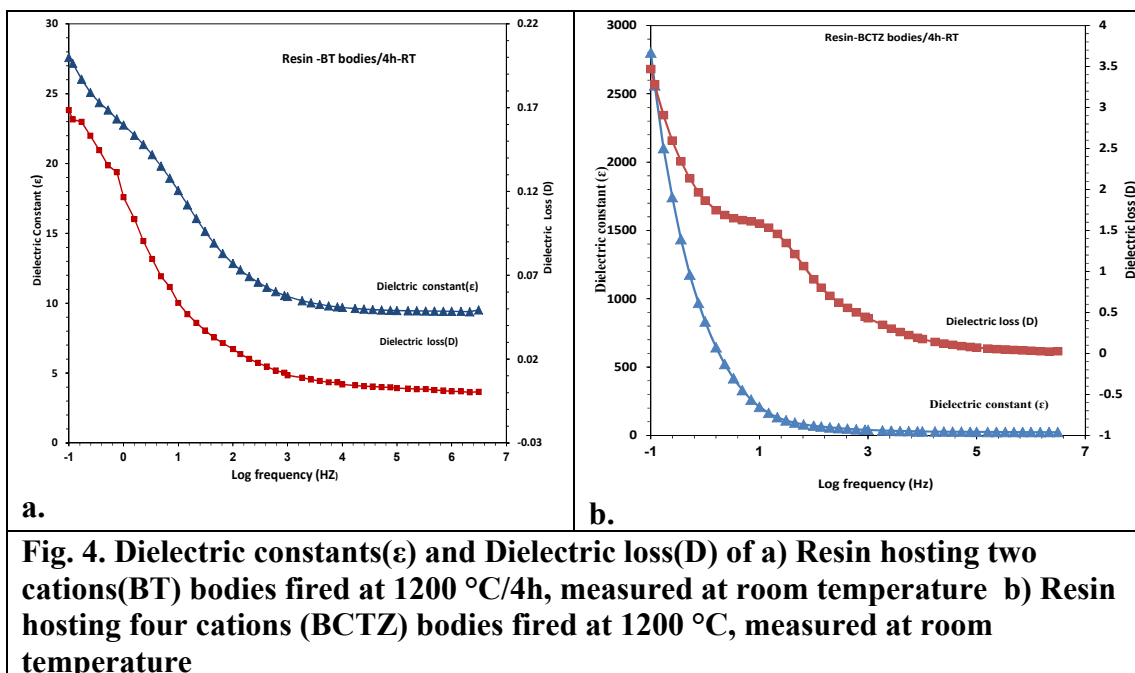
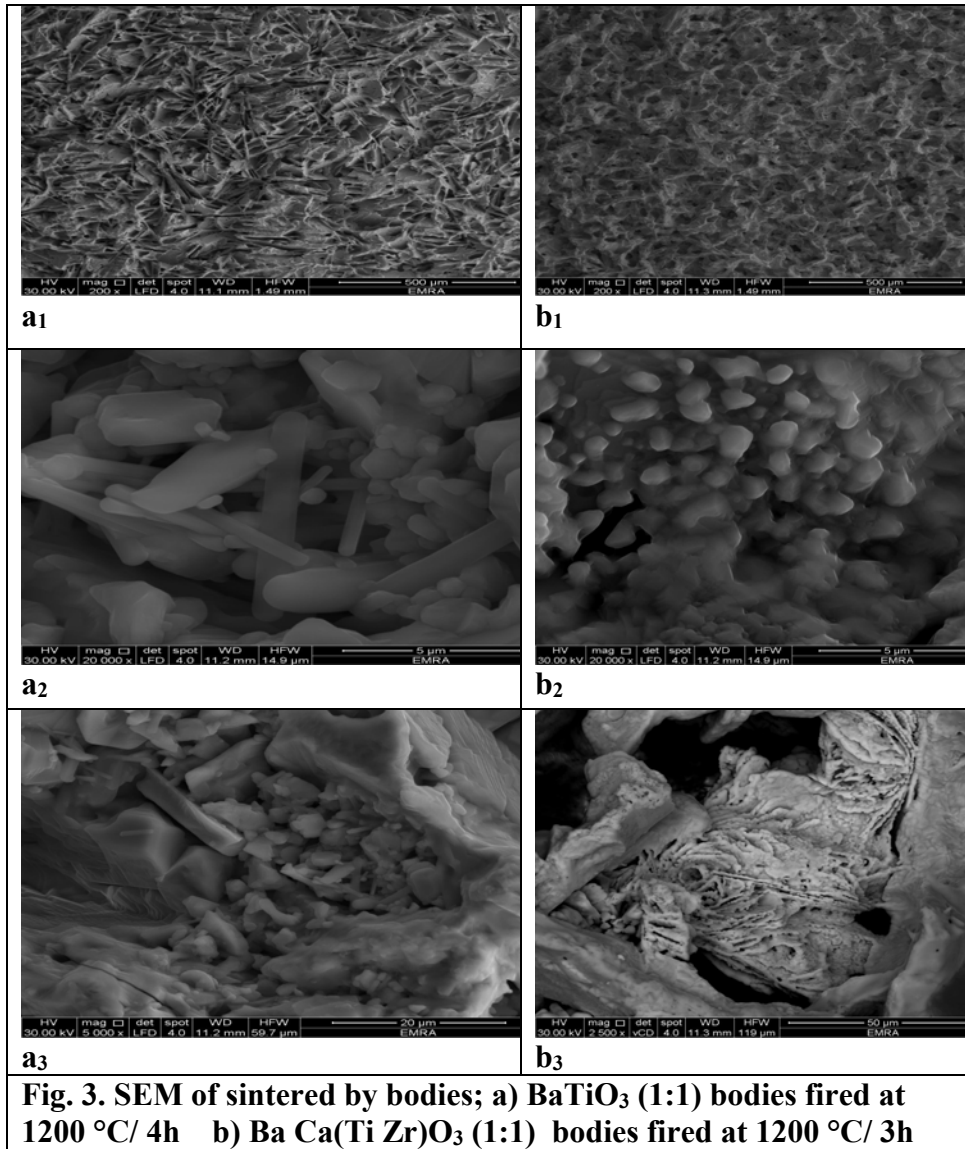


Table 5, Show the results of electrical properties of in terms of dielectric constant (ϵ) and dielectric loss (D) of different barium titanate ceramic phases measured at room temperature prepared by another authors:

Phase structure	Dielectric constant(ϵ)	Dielectric loss (D)	Frequency	Sintering temperature	Average grain size (nm)	Relative density %	Method of preparation	References
BaTiO ₃ Tetragonal ceramic	210 520	0.02 0.02	100 kHz 100 kHz	900 °C/20h 1100 °C/8h	35 120	92 94	modified reverse micellar route	Ahmad and Ganguli, 2005
BaTiO ₃ Tetragonal ceramic	3007	0.00984	10 kHz	1250 °C/10h	60 (μm)	94.5	hydrothermal processing	Nguyen et al., 2007
(Ba _{0.95} Ca _{0.05})(Ti _{0.85} Zr _{0.15})O ₃ (Single phase) ceramic	2000	-	1 KHz	1200°C/2h	-	95	Pechini polymeric precursor	Hsieh et al., 2012
Ba ₄ Ti ₁₃ O ₃₀ (Thin film) Orthorhombic	50	0.0025	1M Hz	-	-	-	laser chemical vapor deposition	Guo et al., (2012)
BaTi ₅ O ₁₁ ceramics	42.8	-	Microwave range	1100°C/4h	-	96	Solid-state	Hsu et al., 2013

Table 6: Major phases of the prepared BT and BCTZ ceramics fired at 1200 °C/4h and the parameter affected the electrical properties in terms of dielectric constant(ϵ) and dielectric loss (D) that measured different frequencies

Batch name	Resulted perovskite BaTiO ₃ Phases of Fired bodies.	Semi quantitative, % of each BaTiO ₃ Phases	x-ray density of BaTiO ₃ Phases	Dielectric constant value(ϵ) at frequency value 0.10Hz-1KHz-10 KHz – 3.12M Hz	Dielectric Loss (D) value at frequency range 0.10Hz-1KHz-10 KHz-3.12M Hz	Bulk density g/cm ³	Relative density %, of the fired samples	Average grain size (nm)
BT	Tetragonal-(BaTiO ₃)	57	5.92	27.592 10.479	0.1685 0.1165			

	Orthorhombic (Ba ₄ Ti ₁₃ O ₃₀)	43	4.64	9.622 9.521	0.0048 0.0005	3.83	83.26	604
BCTZ	Cubic (BaTiO ₃)	59	6.01	2802.250 833.903 28.949	3.4687 1.8654 0.1744	4.25	92.39	804
	Orthorhombic (Ba ₄ Ti ₁₃ O ₃₀)	41	4.64	23.592	0.0255			

starting materials, The dielectric constant was found to increase with sintering temperature (Guo et al., 2012), it was 520 after sintering at 1100 °C/8h and decreased to 210 after sintering 900 °C/20h as presented in Table (5), the dielectric loss how a slight decrease with sintering temperature, this decrease in loss is normally associated with an increase in grain size. A high frequency dispersion of the dielectric constant is seen in the samples prepared by the two polymers BT and BCTZ due to the fine-grained samples (Tang et al., 2004). This phenomena of frequency dispersion appeared in the frequency range between 1.00 (KHz) and 3.12 M Hz, compound by low dielectric loss in all samples, especially in the BCTZ because Zr⁺⁴ with fine-grain size show a transition from a normal ferroelectric to 'relaxor-like' ferroelectric. The relaxor phenomenon has been found in Zr-doped BaTiO₃ ceramics. The fine-grain size in our work resulted from low sinter processing of the samples and the results agreed with Vishnu et al., (2004) and Li et al., (2013). Table (6) summarized the major phases of the prepared BT and BCTZ ceramics fired at 1200 °C/4h and the parameter affected the electrical properties in terms of dielectric constant(ε) and dielectric loss (D) that measured at four frequency value 0.10Hz-

1KHz-10 KHz –3.12M Hz. The resulted major phases of the prepared undoped BT and doped BCTZ, when the secondary phase semi quantitative, % of orthorhombic (Ba₄Ti₁₃O₃₀) increase, the dielectric constant decrease, [Ying and Hsieh, 2007 & Guo et al., 2012]. Also low sintering temperature and porous nature (Zhang et al., 2019) which related to relative density and bulk density, beside the fine grain size reduce the value of dielectric constant for all the prepared samples. Ca and Zr cations as dopant can affect the crystal structure and microstructure as well as dielectric properties of BT by increasing the dielectric constant (ε), 2802.25 recorded by BCTZ [Hsieh et al., 2012; Msouni et al., 2017; Tian et al., (2012) & Zeng et al., 2012].

CONCLUSION

Pure barium polytitanate BT (Tetragonal-orthorhombic), (Cubic-orthorhombic) (BCTZ) ceramic bodies were successfully prepared at low temperature 1200 °C/4h, utilizing dry pressing. Microstructure, phase composition and physical properties and they effect on the electrical properties were studied. Ca and Zr cations as dopant can affect the microstructure and enhanced electrical properties.

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