Physicochemical Characteristic of BaTi$_{0.95}$Zr$_{0.05}$O$_3$

LAMIAE MRHARRAB[1]*, ABDELHALIM ELBASSET[2] and SALAHEDDINE SAYOURI[1]

[1]LPTA Department of Physics, University Sidi Mohamed Ben Abdellah,
Faculty of Sciences D-M, B.P.1796, Fes-Atlas Morocco.
[2]LSSC Department of Electrical Engineering, Faculty of Science and Technology (FST),
University Sidi Mohamed Ben Abdellah, Fes, Morocco.
*Corresponding author E-mail: mrharrab_lamiae@yahoo.fr

ABSTRACT

Physical and chemical properties of BaTiO$_3$ (BT) and BaTi$_{0.95}$Zr$_{0.05}$O$_3$ (BZT0.05) ceramics have been studied. These powders are prepared by the Sol-gel process and calcined at different temperatures [500°C-1000°C]. X-Ray Diffraction (XRD) showed a crystallization of BT and BZT0.05 powders in the perovskite phase after a calcination temperature at 600°C, during 4 hours, but in the presence of some traces of zirconium oxide for the doped powder. Also, the effect of zirconium addition on dielectric properties to BT is analyzed. Indeed, dielectric measurements carried out have shown the presence of a second anomaly for Zr doped material at 60°C; an anomaly that has been attributed to structural transition.

Keywords: Sol-gel Process/ XRD/ Dielectric Measurements/ Anomalies.

INTRODUCTION

Barium titanium oxide, BaTiO$_3$ (BT), was discovered for the first time during World War II in 1941[1]. This compound which crystallizes in the perovskite structure was widely used because it's enhanced dielectric permittivities[2]. BT presents a transition temperature of about 120°C[3], and for T<Tc, it shows a tetragonal structure, with a ferroelectric behavior. It is also known that the dielectric properties are granulo-dependent[4].

Substitution of another element in a pure matrix produces remarkable effects, either on structural characteristics such as crystalline phase, grain size and number of active phonon modes, or on physicochemical characteristics such as dielectric properties, dielectric constant, transition temperature and dielectric loss[5-6-7-8].

There is various method of preparation of the ceramic or the powder fine perovskite[9]. We chose to work with the sol-gel method since it is known that this method produces powder with small grain sizes[10].

In this work, we focus on the role of zirconium substituted in the BT material. Physical and chemical properties are studied. We worked on a percentage of 5% of Zr; $BaTi_{0.95}Zr_{0.05}O_3$ (BZT0.05) material.

With the help of X-ray diffraction (XRD), we have studied the effect the Zr on the temperature crystallization and on the quality of the prepared powder. The dielectric measurements of sintered pellets are carried out between 30 to 200°C, with the HP4284A impedance measuring bridge having a frequency range of 100 Hz to 2 MHz. The parallel faces of the samples are covered with electrodes conductive silver lacquer to form a parallel plate capacitor. The dielectric tests also showed the influence of Zr which is noted on several parameters that we will discuss later.

Procedure

The following precursors were used to prepare the BTZ0.05 powders: barium acetate (Ba(CH3CO2)2; 3H$_2$O, purity 99:9%, Johnson Matthey GmbH Alfa, Karlsrube, Germany), zirconium acetate (Zr(CH3CO2)4; xH$_2$O) (purity 99.9%, x = 1.5, Johnson Matthey GmbH Alfa, Karlsrube, Germany), and titanium alcoxide (97 % (Assay) Johnson Matthey GmbH Alfa, Karlsrube, Germany). Distilled water was used as solvent. Preparation of the samples was needed two steps. The first step consisted of a preparation of a colloidal solution of TiO$_2$. Titanium alcoxide was added to 0.5 M lactic acid aqueous solutions. A white precipitate was then obtained under stirring, at 60°C, during 20 hours, which transforms into a clear solution. The latter was adjusted, by adding water, to 1M the solution. A rapid stirring was necessary to obtain a homogeneous solution (colloidal solution). In a second step were added to the latter colloidal solution, in stoichiometric amounts, barium and zirconium acetates as we have shown in other work[11]. Phase identification of the samples was performed using X-ray diffraction (Cu K ray, λ = 1.5418 Å). Dielectric measurements were carried out in the frequency range of 100 Hz to 2 MHz using an inductance capacitance resistance (LCR) bridge (HP, Model 4284 A).

RESULTS AND DISCUSSION

The first difficulty was to find the proper calcination temperature value for the complete crystallization, and without any secondary phase, for powder to prepare, which is verified by XRD analyzes.

Figure. 1 shows the XRD spectra of the sample BTZ 0.05 calcined at different temperatures [500°C to 1000°C for 4 hours]. These spectra
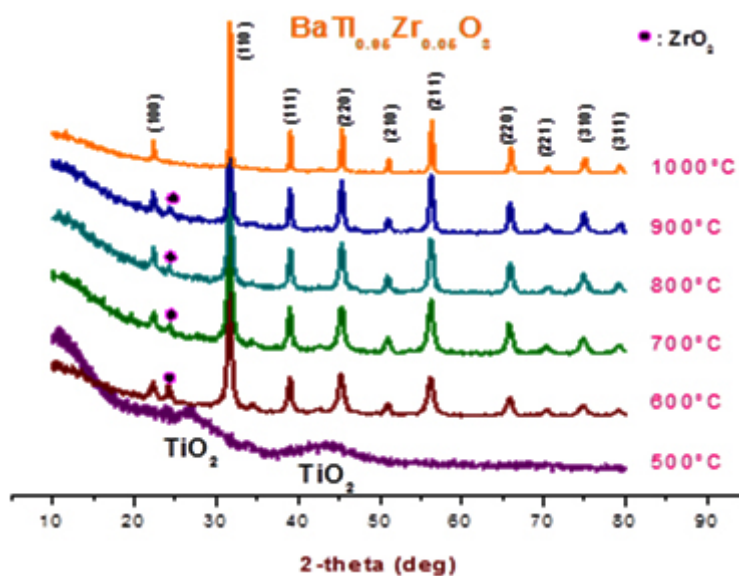

Fig. 1: Evolution of the XRD spectra of the BZT0.05 powder, calcined for 4 hours, depending on the temperature

clearly show the effect of increasing temperature on the quality of the prepared powder. In fact, the XRD pattern of the calcined powder at 500°C is substantially amorphous, apart diffuse diffraction peaks and intense which was identified as peaks of reflection characteristics of the TiO_2 precursor, no crystalline phase is apparent. However, at 600°C the peak characteristic of the reflection phase TiO_2 decreases almost completely and also registers the

birth of the characteristic reflection peaks of BTZ0.05 phase. Too we noted that the powder is completely crystallized into the perovskite phase, at 600 °C, with the presence of a secondary phase (ZrO_2) at $2\theta \approx$ 24°, this crystallization temperature is significantly lower than other processes like classical pathway and the solid coprecipitation[12-13-14] and also for sol-gel preparation method[15]. On the other hand, the intensity of the secondary phase decreases with
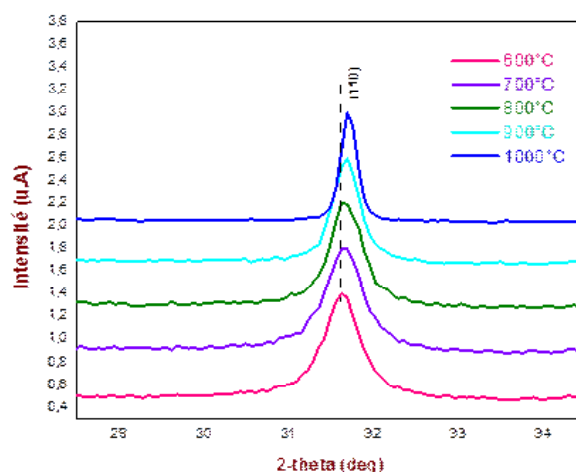

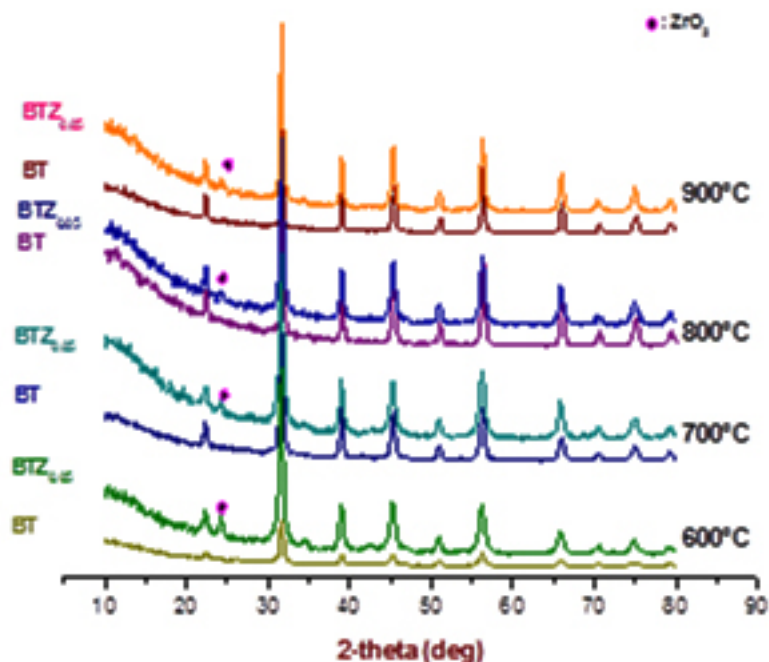**Fig. 2: The zoom peak (110) in the range 28°< 2θ < 35°**

Fig. 3: X-ray diffraction of pure BaTiO$_3$ and doped, calcined at different temperature for (4h)
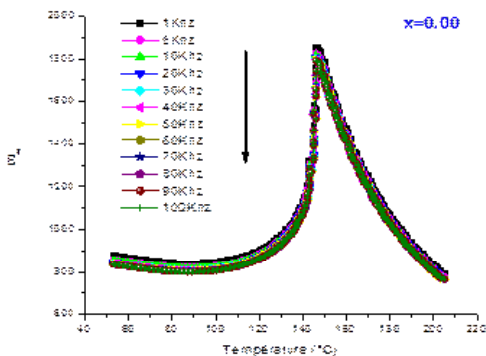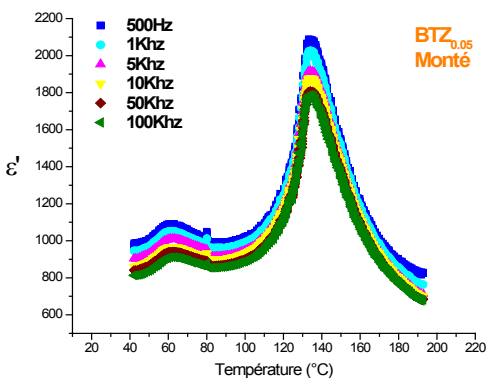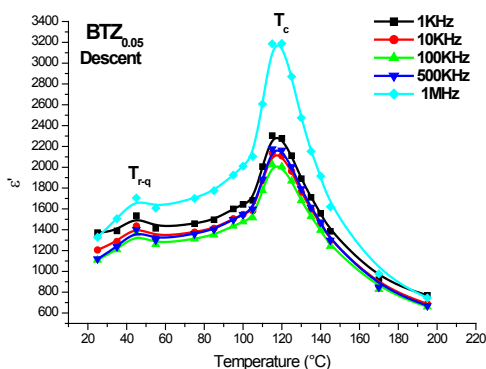
Fig.4.a

Fig.4.b

Fig.4.c

Fig. 4: Dielectric constant as a function of the temperature of the pure sample and of the BZT0.05 sample

increasing calcination temperature. Thereby, powder calcined at 1000°C for 4 h, led to a solid solution BTZ0.05 pure and without secondary phase. Also we observed, from Fig.2, the crystallization peak of the perovskite phase becoming narrower when the calcination temperature increases and the reflection peaks of ZrO_2 phase disappears completely. This shows a better crystallization of the phase.

Even if, we see that the spectrum of the powder calcined at 1000°C, for 4 h, is virtually a reproduction of the XRD spectrum corresponding to the calcined powder at 600°C. However, from Fig.2, there is a displacement of the position of the peak (110) to the highest angles, reflecting the effect of the calcination temperature on the crystallization of the $BTZ_{0.05}$ powder.

In order to make a comparison of the XRD spectra of the pure BT powder calcined at the same temperature values that the $BTZ_{0.05}$ sample, we proceed to develop a pure BT powder (Fig.3). Fig. 3 shows that, BT spectra are isotype of that BTZ0.05. Indicating that pure perovskite phase, without the presence of secondary phase, is fully attained at the calcination temperature 600°C. However, it may be noted two major differences between powders BT and BZT: First to 600°C, even 900°C, spectrum of BTZ0.05 also shows the presence of the ZrO_2 phase while for BT the secondary phase (TiO_2) has completely disappeared at 600°C, indicating that the zirconium doping increases the calcining temperature of the pure perovskite phase. This is due to the atomic number of zirconium size which is larger or the nature of the bonds. These results are in good agreement with those found in the literature[16-17]. And second, With regard to the spectrum of the BT powder calcined at 600°C, we see that the intensity of the reflection peaks, characteristics of pure perovskite phase, is smaller than that of BTZ0.05. This can be interpreted by the effect of atomic radius of Zr ($R_{Zr} > R_{Ti}$).

In other words the substitution of Ti by Zr can increase the intensity peaks at certain crystallization temperatures. In the same way, to highlight the influence of zirconium on the structural state of $BaTiO_3$ we calculated the lattice parameters a and c of BTZ0.05 by the use of CMPR program. The parameters a and c and their ratio c/a (quadracite)

and their difference is illustrated in Table.1. Doping zirconium thus produced a reduction in quadracite and growth in volume. The Scherrer equation enabled us to determine the size of the powder grains PTZ0.05 we found a value of 24.72 nm.

The results of dielectric analyzes performed on pellets sintered at 1100°C (8H) are shown schematically in Fig.4 .The shape of the dielectric constant as a function of the temperature of the pure sample (Fig.4.a) shows an increase in the dielectric constant values a function of the temperature to a

maximum at a temperature of the order 150°C with a maximum value of about 1900. This transition temperature is independent of the frequency; confirming that it is the Curie ferroelectric-paraelectric transition. The curves of Fig.4 .b and Fig.4.c of the dielectric permittivity ε_r which corresponds to the BZT0.05 show a similar trend to that observed in the case of $BaTiO_3$ (pure sample), although the values of the dielectric permittivity measured at different frequencies are different. In addition, it is noted that the value of the transition temperature (Tc) decreases sharply. However, doping Zr produces a
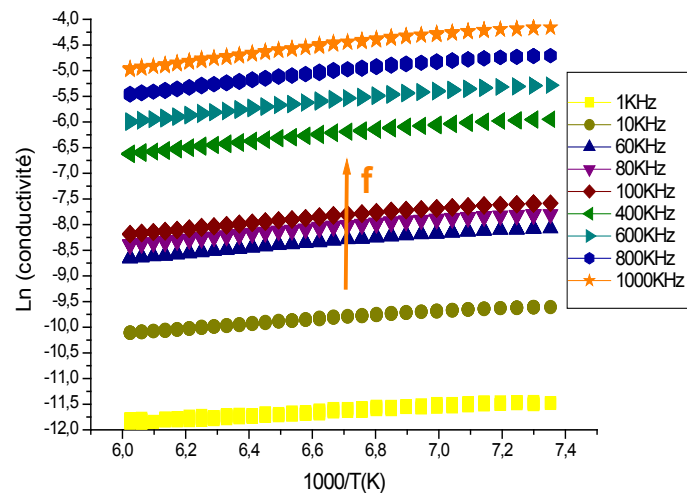

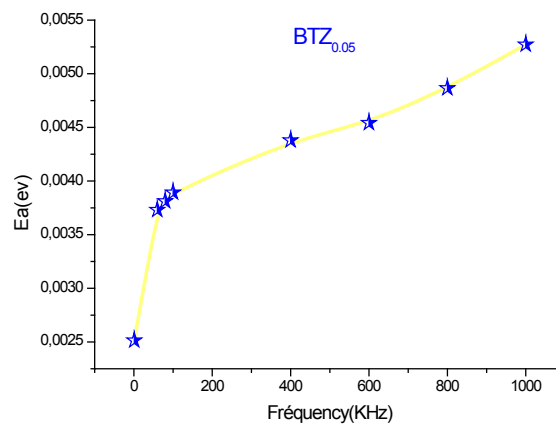**Fig. 5: Arrhenius law applied to the sample BTZ 0.05 to different frequencies**

Fig. 6: Evolution of the activation energy as a function of the frequency

Table 1: Parameters of mesh and quadracite of BTZ0.05 (1000 °C (4h))

Rate Zr (%)	Parameters a and c		Quadracite (c/a)	c-a (Å)	Volume (Å^3)
x	c (Å)	a (Å)	c/a		
0	4,0421	4,0014	1,0102	0,0407	64,7189
5	4,0423	4,0029	1,0098	0,0394	64,7718

Table 2: Sintering time of effect on the dielectric properties of BZT0.05

	Sintering time (h)	ε'_{max} at T_c	T_c
BZT$_{0.05}$	4	2976	130°C
BZT$_{0.05}$ (mounted)	8	6740	120°C

second anomaly at 60°C (Fig.4 b). And the Fig.4.c shows the persistence of the second anomaly during cooling. Indeed, the work done by Baptisa *et al.*[18] we confirm that it is a structural transition and that such anomalie can not be allocated to the vacant oxygen sites in the crystal structure. But recently Nanakorn *et al*[14-15-19] have mounted that it is a orthorhombic-tetragonal structural transition (To-q).

The choice of 1100°C for 8 hours in the sintering step is not random, but after a study of function the sintering time. In fact, we prepared two samples one sintered at 1100°C for 4 hours and the other at 1100°C for 8 hours. The table 2 shows the result of this study. It is thus observed that sintering at 1100°C for 8 hours improves the dielectric constant obtained about 113% relative to the sintered for 4 h.

And on the other hand, to study the transport mechanism in BZT, we plotted the variation of the conductivity as a function of temperature under different frequencies. The conductivity was calculated from the measurements carried out, according to the relation below:**.**

$$\sigma = \omega\varepsilon_o\varepsilon'' = \omega\varepsilon_o\varepsilon'\tan(\delta)$$

When the temperature increases, and below Tc, the conductivity follows the Arrhenius law:

$$\sigma = \sigma_0 e^{-\frac{E0}{K_B T}}.$$

With E_a the activation energy, T absolute temperature in Kelvin and K_B is Boltzmann's constant. The curves representing $Ln(\sigma) = f(^1/_T)$, being straight (Fig.5) , the thermal activation energy can be easily calculated using different frequencies. The activation energy (Fig.6) shows an increase as a function of frequency in the frequency base region (f <100 kHz), followed by an almost linear increase in frequency above 100 kHz. These values remain low confirming that the BTZ0.05 is a conventional ferroelectric material[20].

CONCLUSION

The addition of zirconium produced intense effects on properties of the pure powder BT, keeping the same phase as the latter, whatsoever on the value of proper calcination temperature or on the quality and purpose of reflection peaks of the perovskite phase. More, there is an appearance of a second anomalie in the spectrum of the dielectric permittivity as a function of temperature for the sample doped with Zr, an anomalie attributed to the structural phase transition within the material under the effect of the temperature variation. This anomalie persists during the cooling step thus leaving the hypothesis prophesy it is not a question of the vacant oxygen sites. The measurements of the conductivity as a function of the temperature at different frequency values, confirms that pure BT and doped of Zr are conventional ferroelectrics materials.

REFERENCES

1. Randall, C.A.; Newnham, R.E. and Cross, L.E. "History of the First Ferroelectric Oxide, BaTiO$_3$, Materials Research Institute", *The Pennsylvania State University, University Park, PA 16802 USA.*

2. Bertin, M.; Faroux, J.P. and Renault, J. *Electromagnetisme 4, cours de physique, Dunod* **Ed.1994**,.70.

3. NENEZ, S. "Céramiques diélectriques commandables pour applications micro-ondes: composites à base de titanate de baryum-Strontium et d'un oxyde non ferroélectrique", *Thèse de Doctorat, Université de Bourgogn* **2001**.

4. Bernaben, N.; leriche, A.; Thierry, B. and Niepce *J.C. Electroceramics* **1995**, *5*, 203-210.

5. Chi Man Lau, Xiao Wu Xu, K.W.Kwok *Applied Surface Science* **2015**, *336*, 314-320.

6. Li, W.L.; Cao, W.P.; Xu, D.; Wang, W.; Fei, W.D. *Journal of Alloys and Compounds* **2014**, *613*, 181-186.

7. Yantao Liu, Wei Ren, Jinyan Zhao, Lingyan Wang, Peng Shi, Zuo-Guang Ye *Ceramics International* **2015**, *41*,(1), 259-S264

8. Wanwilai Chaisan, Rattikorn Yimnirun, Supon Ananta *Ceramics International* **2009**, *35*(1), 121-124.

9. Lamiae MRHARRAB, doctoral thesis, "Etude des propriétés physico-chimiques de PbZr$_x$Ti$_{1-x}$O$_3$ (0 d" x d" 0,91) et de PbTiO$_3$ pur et dopé (V, Cu, Bi, Mn, Mg, La, Ca) élaborés par voie solide", *University Sidi Mohammed Ben Abdellah Morocco* **2014**.

10. Abdelhalim ELBASSET," Synthèse et Caractérisation de matériaux de Titanate de Baryum purs et dopés au Strontium et au Zirconium"*, Thèse de doctorat à la FST Maroc* **2014**.

11. Elbasset, A.; Lamcharfi, T.; Abdi, F.; Mrharrab, L. and Sayouri, S. *Indian Journal of Science and Technology* **2015**, *8*(12), 56348

12. Chen, H.; Yang, C.; Fu, C.; Shi, J.; Zhang, J.; Leng, W. *J. Mater. Sci.* **2008**, *19*(4), 379-382.

13. Kuang, S.J.; Tang, X.G.; Li, L.Y.; Jiang, Y.P.; Liu, Q.X. *Scr. Mater.* **2009**, *61*, 68-71.

14. Nanakorn, N.; Jalupoom, P.; Vaneesorn, N.; Thanaboonsombut, A. *Ceram. Int.* **2008***, 34,* 779-782.

15. Julphunthong, P.; Bongkarn, T. *Current Applied Physics* **2011**, *11*(3), 60-65.

16. B. Jaber, *Thèse de l'université de Valenciennes et du Hainaut-Cambresis* **1995**.

17. T. Lamcharfi, "Elaboration par voie hydrothermale et caractérisation des céramiques ferroélectriques de type pérovskite PZT dopé au lanthane Pb$_{1-y}$La$_y$(Zr$_x$Ti$_{1-x}$)O$_3$" *Doctorat national*, *Université Sidi Mohamed Ben Abdellah Maroc* **2005**.

18. Ang, C.; Yu, Z. and Cross, L.E. *Phys. Rev. B* **2002***, 62,* 228-236.

19. Kumar, M.; Garg, A.; Kumar, R. and Bhatnagar, M.C. *Physica B: Condensed Matter* **2008**, *403* (10), 1819-1823.

20. Smolenskii, A.," Ferroelectrics and Related Materials", *Gordon and Breach*, *New York* **1984**, 589-606.