

A new synthesis technique and structural, microstructural and dielectric properties of BaTiO₃ nanopowder

Abdelaziz Salhi^a, Salaheddine Sayouri^{a,*}, Lahoucine Hajji^b and TajEddine Lamcharfi^c

^aLPTA, Department of Physics, Faculty of Sciences-DM, B.P. 1796, Fez-Atlas, Morocco

^bLMCN, F.S.T.G. University Cadi Ayyad Marrakech, Morocco

^cLSSCFST-Fès B.P. 2202-Route d'Imouzzar, Fès, Morocco

Nanocrystalline barium titanate (BT) was synthesized by the sol gel method. The dry gel obtained was first treated in the microwave (MW) and then calcined at different temperatures. A pure tetragonal phase was obtained under heat treatment at 750 °C which is a relatively low temperature. SEM image reveals a fairly dense and uniform microstructure. Dielectric measurements performed on the sintered BaTiO₃ sample at 1200 °C revealed the presence of the resonance phenomenon at frequencies lower than 2 MHz and the existence of a weak positive temperature coefficient of resistivity (PTCR) just above the Curie temperature. Electric impedance analysis shows the predominance of the grain boundary (gb) contribution and enables determination of activation energies of the gb and the bulk effect and their relative capacitance and resistance elements.

Key words: Nanocrystalline BaTiO₃, Sol gel process, Microwave, PTCR, Resonance.

Introduction

Barium titanate (BT) has been one of the best known materials for a variety of electrical and electronical applications [1], due to its excellent dielectric, ferroelectric and piezoelectric properties. Pure BaTiO₃ shows a ferro-to-paraelectric transition at about 120 °C depending on its grain size and purity. The microstructure control using non-conventional techniques of elaboration is the key for improving the BaTiO₃ ceramics electrical performances. The reactivity of precursors is greatly improved by increasing their effective surface areas; thereby the processing temperature can be reduced significantly [2]; mechano-chemical processing technique like high-energy planetary milling is one example that confirms this. Heat treatment of ceramics by the application of microwave energy is gaining prominence due to its multiple benefits [2]. Due to their ability to absorb microwaves, BT based dielectric ceramics materials may be volumetrically heated up in shorter period [3]. Microwave processing of BT ceramics was investigated by Takahashin et al. [4]. By taking into account the advantage of the microwave processing, we have in this paper studied the combined effect of the microwave and oven on the calcination temperature and the electric characteristics of sol gel processed BT powder.

Experimental Procedure

The sample BaTiO₃ was synthesized by the sol gel method using titanium isopropoxide (Ti(OCH(CH₃)₂)₄, 97% min Aldrich), barium acetate (Ba(CH₃COO)₂ >= 99% Aldrich) as precursor, and distilled water, acetic and lactic acids were used as solvents. Details of the procedure of preparation of titanium sol are given in refs [5,6]. Barium acetate was dissolved in aqueous solution of acetic acid. Ti sol was then added to this solution with adequate proportions and a transparent sol was obtained. A gel dry was obtained by drying transparent sol in an oven at 80 °C. The gel dry obtained was heat-treated in microwave (MW, power 500 W-14 min) in an opened crucible. The porous product was ground in an agate mortar, which led to a very fine powder, and then calcined for two hours in an oven at different temperatures at a heating rate of 5 °C/min. The calcined powder was uni-axially pressed into pellets of ~ 12 mm diameter without need of a binder. Sintering was performed, in air, at 1200 °C for 6 hrs, with a heating rate of 5 °C/min followed by cooling to room temperature.

The structural and microstructural properties of the sample were determined using X-ray diffraction (XPRT-PRO diffractometer with Cu-K α radiation (λ = 1.5405980 Å). Raman spectroscopy was also used to investigate, at room temperature, the existing phase of the synthesized BaTiO₃ powder with a Senterra Dispersive Raman Microscope over the scan range of (90-3200 cm⁻¹) using the 785 nm exciting wavelength.

Scanning electron microscopy (SEM) analysis was

*Corresponding author:
Tel : +212-6-73-78-52-88
Fax: +212-5-35-73-33-49
E-mail: ssayouri@gmail.com

carried out using Quanta 200 FEI device (resolution 3.5 nm, accelerating voltage 0.5-30 kV).

Dielectric measurements were carried out using the LCR-meter HP 4284A having a sensitivity of 0.05% that allows to measure the capacity and the loss factor of the sample at frequencies ranging from 200 Hz to 1 MHz. Before measurements, silver electrodes were deposited on the circular faces of the ceramic to get capacitor shaped samples.

Results and Discussion

Structural and microstructural studies

Fig. 1 shows the room temperature XRD patterns of BaTiO₃ powders preliminary submitted to microwave treatment (MW) (Fig. 1(a)) and then heat treated at 650 °C (Fig. 1(b)) and 750 °C (Fig. 1(c)). It is clear from Fig. 1(a) that MW treatment of BaTiO₃ powder favours appearance of the crystalline phase as indicated by the presence of X ray reflections at 22,13; 31,52; 38,84; 45,18; 50,90; 56,13; 65,87. After calcination at 650 °C in the furnace it is observed that the powder crystallizes in the pseudo cubic phase with few BaCO₃ impurities; the latter are not detected as revealed by the XRD pattern (Fig. 1(c)) of the powder calcined at

750 °C which is a relatively low temperature compared to that found in other studies (Table 1). This shows that microwave treatment followed by calcinations can significantly reduce the crystallization temperature of BaTiO₃. This could be due to the large specific surface of the fine powder obtained after treatment with microwave, thus facilitating the reactivity of the reagents. Fig. 1(d) shows the XRD pattern of the BT ceramic sintered at 1200 °C, the split of the peaks (002) and (020) indicates that the tetragonal BT phase is dominant in the ceramic sintered at 1200 °C. Lattice parameters (a,c), tetragonality (c/a), cell volume (V₀) and crystallite size (d) of the BT powder and BT ceramic are given in Table 2; the latter was calculated from the X ray peak broadening of the peak (111) using the Scherrer's equation; $d = (0.94 \cdot \lambda / (\beta \cdot \cos(\theta)))$, where λ is the wave length of CuK α (1.5405980 Å), β is the full width at half maximum (FWHM) of the peak and θ is the diffraction peak

Table 1. Comparative table.

Method of preparation	Sol gel [8]	Pechini process PPM [9, 10]	Sol gel + MW (Our method)
Calcination temperature	1000 °C- 4h	(500 °C-4 h) + (700 °C-4 h) + (900 °C-2 h)	MW+ (750 °C-2 h)

Table 2. Lattice parameters (a,c), tetragonality (c/a), cell volume (V₀) and crystallites size (d) of the BT powder and BT ceramic.

	a (Å)	c (Å)	c/a	V ₀ (Å ³)	d(nm)/pic (111)
BT powder	3.9935	4.0263	1.0081	64.21	33.7
BT ceramic	3.9956	4.0354	1.0099	64.42	51.2

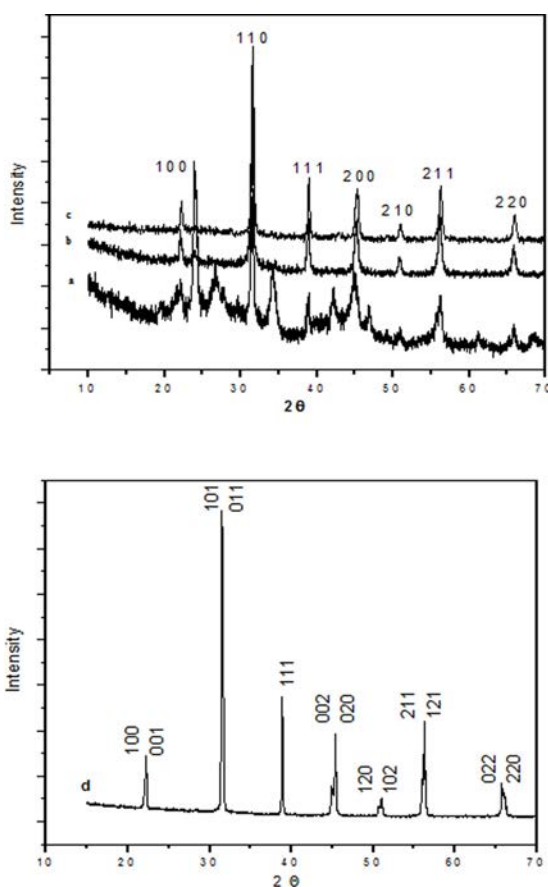


Fig. 1. XRD spectra, up of BT powders heat treated: (a) MW, (b) at 650 °C-2 hrs after MW, (c) at 750 °C-2 hrs after MW, (d) at 1200 °C-6 hrs.

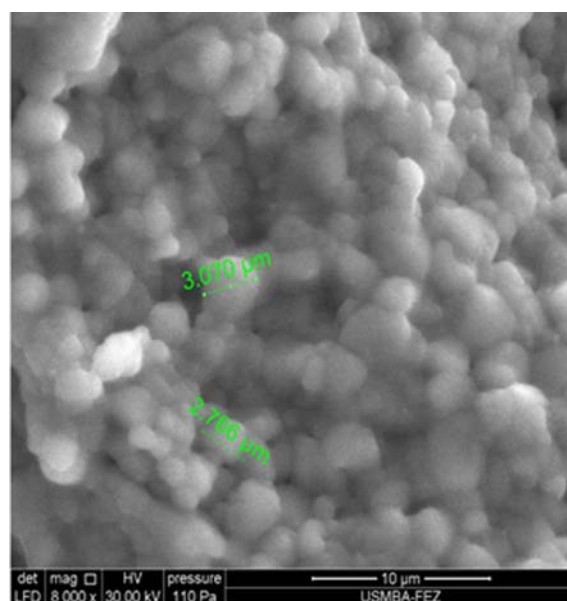


Fig. 2. SEM micrograph of the BaTiO₃ sintered at 1200 °C-6 hrs and furnace cooled under ventilation.

Table 3. Grain size and relative density of the BaTiO₃ ceramic.

Sintered temperature (°C)	Average grain size (μm)	Relative density (%)
1200	2	91.2

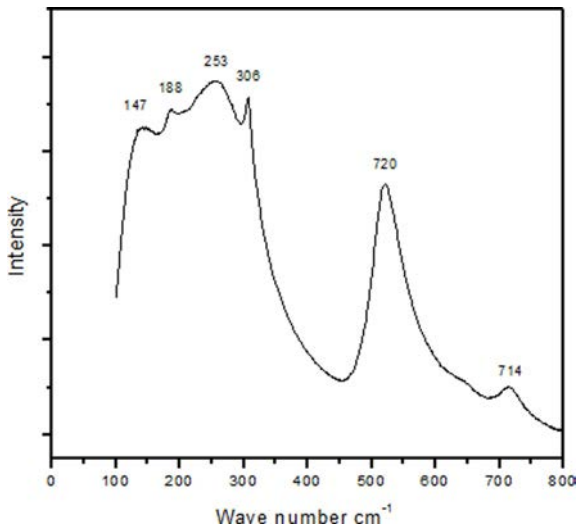


Fig. 3 Raman spectrum of the BaTiO₃ nanopowder calcined at 750 °C-2 hrs after MW.

Fig. 2 shows SEM image of the BaTiO₃ ceramic sintered at 1200 °C-6 hrs. The microstructure is fairly dense and uniform (Table 3). We can conclude that this elaboration process may favour good density of ceramics at relatively low temperature.

Raman analysis

Raman spectroscopy is a highly sensitive technique to probe the local structure of atoms in materials. BaTiO₃ has fifteen degrees of freedom per unit cell. In cubic phase (Pm3m) the 15 degrees of freedom divided into the optical representations 3F_{1u} + F_{2u}. F_{1u} and F_{2u} are not Raman active modes in BaTiO₃ cubic phase, however in tetragonal phase Raman active modes are 4E_g (TO + LO) + 3A_{1g}(TO + LO) + B_{1g}(TO + LO). Each of the three F_{1u} modes splits into A₁ + E while the F_{2u} mode splits into B₁ + E.

Fig. 3 shows the Raman spectra of BaTiO₃ nanoparticles. It is known that the sharp bands around 188 cm⁻¹ A₁(LO₁), 306 cm⁻¹ [B₁, E (TO + LO)] and 714 cm⁻¹ A₁(LO), E(LO) are the characteristics peaks of the tetragonal phase of BaTiO₃ [10, 11]. This justifies that the BaTiO₃ nanopowder prepared with this technique has a tetrahedral structure confirming the results obtained by X-ray analysis. It is also well known that the two bands at 306 and 714 cm⁻¹ disappear above the tetragonal-cubic phase transition point, which are considered as the signature of the tetragonal phase.

Dielectric studies

Thermal variations of the permittivity, ϵ_r , and losses,

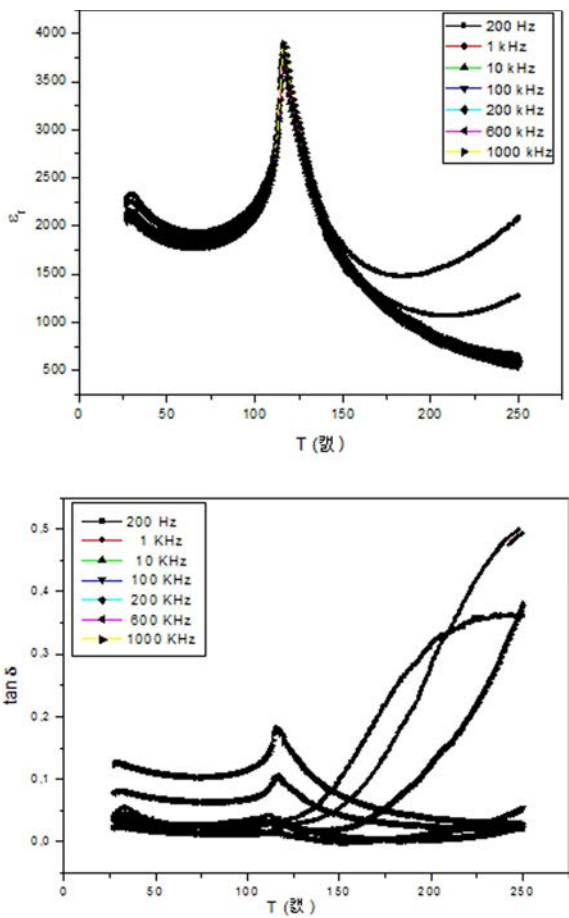


Fig. 4. Temperature dependence of the dielectric constant (ϵ_r) and dielectric loss ($\tan\delta$) of the BaTiO₃ ceramic sintered at 1200 °C-6 hrs.

Table 4. Dielectric constant at Tc(ϵ_m) and Room temperature (ϵ_r (RT)) compared to other Works.

	M.M. Vijatovic et al. [9]	W.Li et al. [10]	A.Elbasnet et al. [8]	Our method
Sintered temperature	1200 °C- 8 h	1200 °C- 8 h	1100 °C- 8 h	1200 °C- 6 h
ϵ_m at 1 kHz	1336	1750	2850	3775
ϵ_r (RT) at 1 kHz	730	1082	~ 140	2205

$\tan\delta$, for frequencies ranging from 200 Hz to 1 MHz, of BaTiO₃ ceramic sample sintered at 1200 °C/6H, are given in Fig. 4. It is observed that the sample shows no significant frequency dispersion of the permittivity around the temperature corresponding to its maximum at which the structure of the sample changes from pseudo cubic phase to cubic one; this transition of the first order is characterized by sharp peaks as habitually observed for BaTiO₃ ceramics. The maximum, ϵ_m , of ϵ_r , which values vary between 3642 and 3900, occurs at 116 °C for all frequencies. These recorded values are relatively high compared to those found in other works (Table 4). It can also be seen on Fig. 4 and Fig. 5(a) that the maximum of the permittivity decreases with frequency

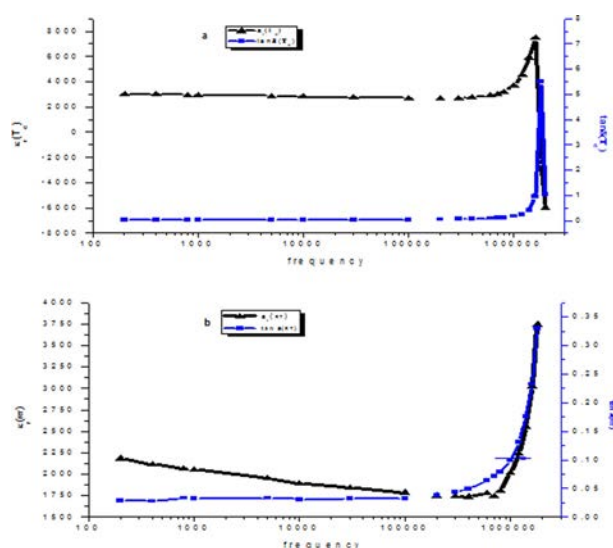


Fig. 5. Plot of ϵ_r and $\tan \delta$ vs frequency at (a) Currie temperature $\epsilon_r(T_c) - \tan \delta(T_c)$ and (b) room temperature $\epsilon_r(RT) - \tan \delta(RT)$.

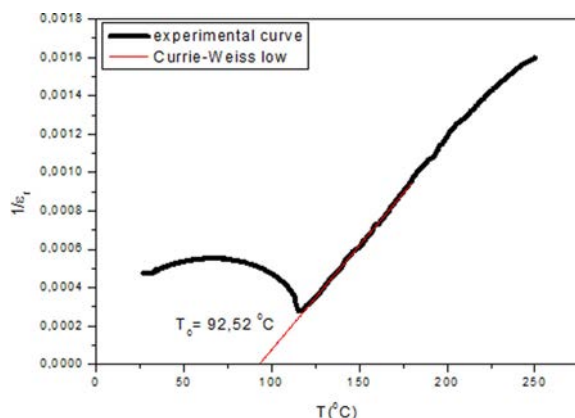


Fig. 6. Plot of $1/\epsilon_r$ vs temperature at 10 kHz.

until 200 kHz and then increases continuously with increasing frequency to give rise to the resonance phenomenon at the frequency 1.6 MHz; accompanied with a strong dissipation effect as revealed by the maximum of $\tan \delta$ at 1.8 MHz (Fig. 5(a)); for frequencies higher than 200 kHz, atoms, valence electrons and inner electrons are expected to resonate successively and make their contribution to the permittivity [13].

Fig. 5(b) displays variations of the permittivity and losses at room temperature, no resonance is observed at room temperature in the interval of frequencies studied. This curve shows the effect of temperature on the behaviour of ϵ_r and $\tan \delta$. Plot of $1/\epsilon_r$ vs. temperature at 10kHz is shown in Fig. 6. The normal ferroelectric

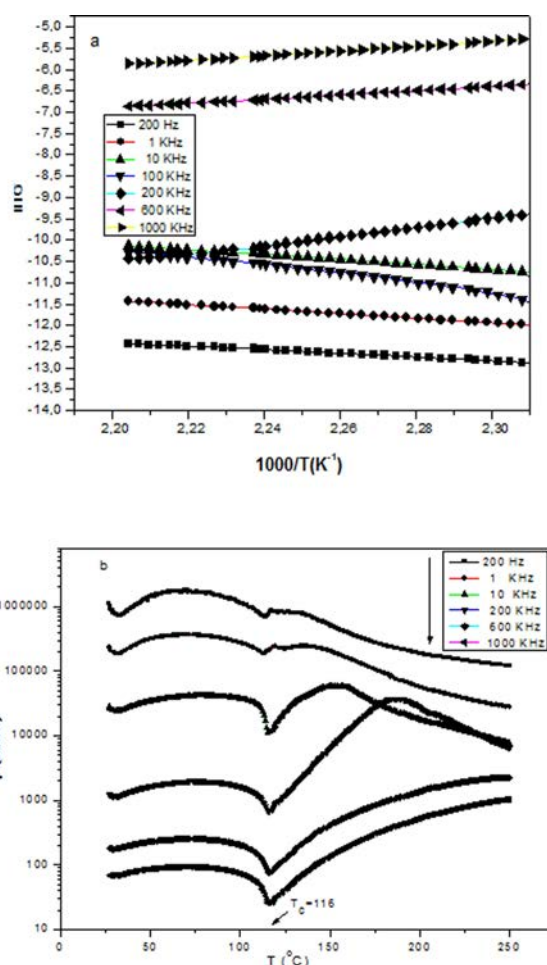


Fig. 7. (a) Conductivity vs. $1000/T$ (b) Resistivity as a function of temperature at various frequencies of the BT pellet sintered at 1200 °C - 6 hrs and furnace-cooled with ventilation.

character of BaTiO₃ is evident. In Table 5, we have reported the values of T_0 (Curie-Weiss temperature) and C (Curie Weiss constant) for different frequencies.

Conductimetric study

The conductivity σ of the sample has been evaluated using the relation: $\sigma = 2\pi f \epsilon_0 \epsilon_r \tan \delta$, where f is the frequency, ϵ_0 the permittivity of vacuum. Fig. 7(a) shows the variation of $\ln \sigma$ vs. $10^3/T$ at different frequencies, where T is the absolute temperature considered in the range 423-453 Kelvin. The behaviour of $\ln \sigma$ observed on Fig. 7(a) is in conformity with those of ϵ_r and losses below and above 200 kHz, and may be explained as due to the existence, above the ferro-to-paraelectric transition temperature, of weak PTCR effect as shown

Table 5. Values of Curie-Weiss temperature (T_0) and Curie Weiss constant (C) for different frequencies.

Frequency (Hz)	200	10^3	10^4	10^5	2×10^5	6×10^5	10^6
C (°C)	139407,56	105443,51	92676,38	94564,07	89500,65	99535,47	94309,74
T_0 (°C)	75,92	88,44	92,51722	91,95	95,77	91,44	94,28

Table 6. Activation energy of conduction at different frequencies.

Frequency (Hz)	200	1000	10000	100000
Ea (eV)	0,39	0,43	0,49	0,77

on Fig. 7(b) representing the variation of the resistivity as a function of the temperature in the interval 27-250 Celsius. Indeed, above the Curie point a very weak PCTR effect arises for frequencies inferior to 200 kHz, and then a somewhat pronounced increase is observed as the frequency approaches the resonance interval; the resistivity shows broad maxima that shift towards high temperature region as the frequency increases. Above these maxima the resistivity decreases (increasing conductivity). To our knowledge, this behaviour has not been reported in the literature. Below the frequency 200 kHz the conductivity increases (Normal behaviour) slightly and gradually with rise in temperature (Fig. 7(a)), suggesting a thermally activated process in the sample, and follows the Arrhenius law $\sigma = \sigma_0 \exp(-E_a/K_b T)$, where E_a is the activation energy of conduction which is calculated from the slope of $\ln \sigma$ with $10^3/T$ curve and reported in Table 6.

Impedance studies

Fig. 8 shows a set of Nyquist plots (Z'' as a function of Z') over a wide range of frequency (1 Hz-1 MHz) at different temperatures. This figure clearly shows the presence of two depressed semicircles suggesting the existence of both bulk and grain boundary effects that can be represented by combinations of resistances and constant phase elements (CPE) associated to these effects (Fig. 9). Extracted values of resistances and CPE parameters (R_b (bulk resistance), CPE_b (bulk CPE), R_g (grain boundary resistance) and CPE_g (grain boundary CPE)), for different temperatures, are gathered in Table 7; as the temperature increases the total resistance of the sample drops, leading to an increase of conductivity which is a manifestation of

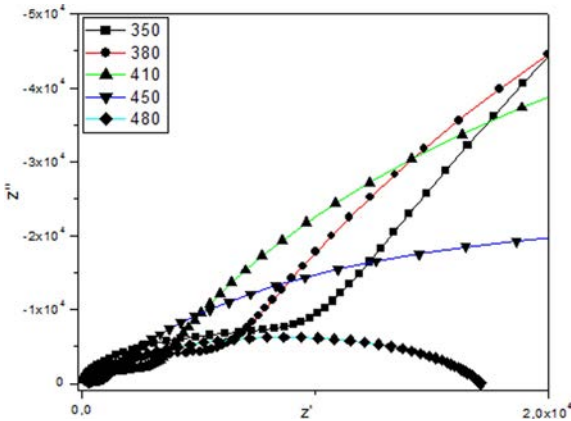


Fig. 8. Impedance curves of the sample at various temperatures.



Fig. 9. Equivalent circuits used for fitting the experimental data.

Table 7. The resistance and capacitance of bulk and grain boundary at high temperature.

T (°C)	C _g (F)	R _g (Ω)	C _{gb} (F)	R _{gb} (Ω)
350	4.9310 ⁻¹⁰	9000	5.3710 ⁻⁹	1.0710 ⁶
380	5.4410 ⁻¹⁰	5870	5.1710 ⁻⁹	395320
410	4.7310 ⁻¹⁰	3133	4.8810 ⁻⁹	165800
450	4.0810 ⁻¹⁰	942	5.5810 ⁻⁹	50706
480	2.6410 ⁻¹⁰	319	5.5010 ⁻⁹	16749

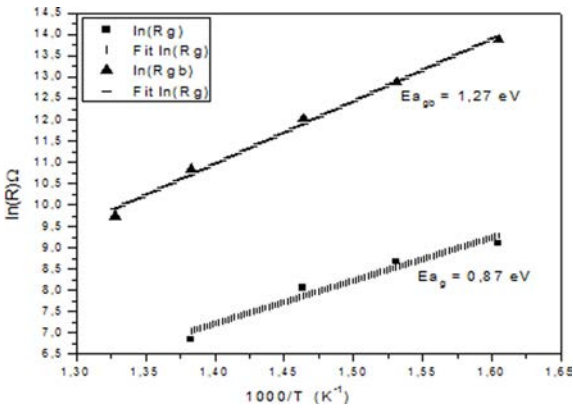
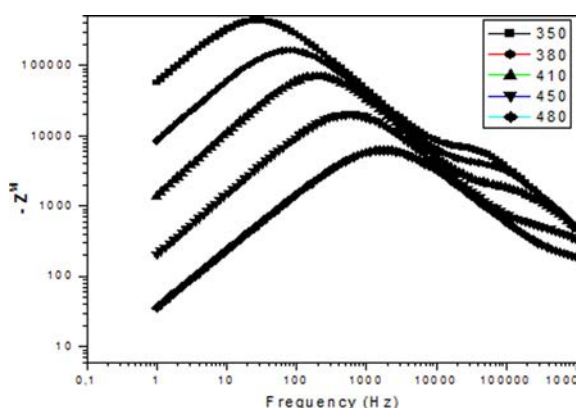


Fig. 10. Temperature dependence of grain and grain boundary resistances.

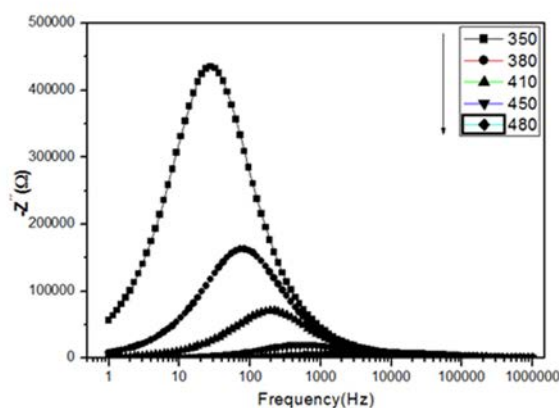
high temperature ionic conductors. Fig. 10 gives the plots of $\ln R$ for bulk and grain boundary contributions as a function of $1000/T$ (Fig. 10) in the temperature range 350-480 °C. From these plots activation energies for the two contributions have been determined: $E_b = 0.87$ eV, $E_{gb} = 1.27$ eV, suggesting a hopping-type process. Moreover, these semicircles have their centers lying under the real axis (Z' axis) indicating the existence of continuously distributed relaxation times.

Frequency dependence of Z''

The variation of imaginary part of impedance (Z'') with frequency at different temperatures is shown in Fig. 11(a) (enlarged scale). Clearly, two distinct temperature dependent peaks at a characteristic frequency are observed in the temperature range considered. At the temperature 480 °C, the second peak of Z'' lies outside the measured frequency window. A strong dispersion of Z'' is also observed accompanied with a decrease of magnitude of Z'' and a shift of the position of the Z'' peaks towards the higher frequency region on increasing temperature. The width of the peaks may indicate a possible distribution of relaxation times, in conformity with impedance results.



(a)



(b)

Fig. 11(a). Frequency dependence of Z' at various temperatures showing the two contributions of grain and grain boundary (enlarged scale).

Fig. 11(b). Frequency dependence of Z'' at various temperatures (Z'' in linear scale).

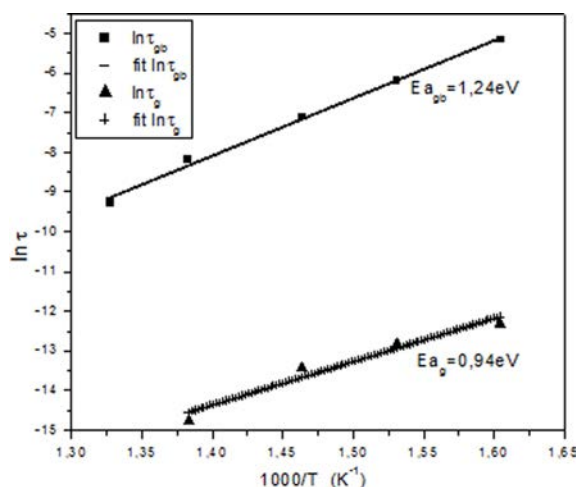


Fig. 12. Temperature dependence of relaxation times for grain and grain boundaries.

The lower frequency peak is ascribed to the grain boundary relaxation and the higher frequency peak to the

grain relaxation. Relaxation time, τ , may be evaluated from Table 7. As the relaxation is thermally activated the relaxation time follows Arrhenius law $\tau = \tau_0 \exp(E_a/k_b T)$, where τ_0 is the pre-exponential factor, k_b is the Boltzmann constant and E_a is the activation energy. Moreover, it is observed that all the curves (Fig. 11(b)) merge in the high frequency region which may be indicative of the possibility of release of space charge as a result of reduction in the grain boundary potential height.

Fig. 12 displays $\ln(\tau_g)$ and $\ln(\tau_{gb})$ as a function of the inverse of temperature, where τ_g and τ_{gb} represent time relaxations for grains and grain boundaries, respectively, determined from Table 7. The values of activation energy for bulk and grain boundary were found to be 0.94 and 1.24 eV respectively.

Conclusions

Single phase pseudo cubic BaTiO₃ powders were prepared by the sol gel process followed by a thermal preheating in the microwave before calcination in the furnace. The calcination temperature was found to be relatively low compared to those reported in the literature using other methods of synthesis. Raman spectroscopy analysis confirmed the pseudo cubic structure of the sample. Thermal variations of the permittivity and losses of the sample, heat treated at 1200 °C during 6 h, in the frequency range 100 Hz–1 MHz, showed a ferro-to-paraelectric transition at about 116 °C and a relatively high value of the corresponding maximum of the permittivity and revealed the presence of the resonance and dissipation phenomena at the frequency 1.6 MHz; to our knowledge such behaviour has not been reported. The calculated conductivity showed a normal behaviour below the frequency 200 kHz as displayed by Arrhenius plots in the temperature range 423 K–453 K. Increasing the frequency revealed the presence, just above the Curie point, of a weak positive temperature coefficient of resistivity (PTCR), as confirmed by the observed thermal behaviour of the resistivity, which explained the behaviour of the conductivity for frequencies superior to 200 kHz. Complex impedance studies showed the presence of both bulk and grain boundary effects; the latter being predominant compared to the bulk one, and permitted extraction of the corresponding resistances and constant phase elements (CPE) parameters associated with bulk and grain boundaries contributions. Existence of these two contributions was also confirmed by the frequency behaviour of the imaginary part of the impedance (Z''). Moreover, the behaviour of Z'' suggested a distribution of relaxation times (τ) as expected from Nyquist plots. The parameter τ was shown to follow an Arrhenius law and the corresponding activation energies of bulk and grain boundary contributions were determined.

References

1. L.B. Kong, J. Ma, H. Huang, R.F Zhang and W.X. Que, J. Alloys Comp. 337[1] (2002) 226-230.
2. J. Xue, J. Wang and D. Wan, J. Am. Ceram. Soc. 83 (2000) 232-234.
3. C.Y. Fang, C.A Randal, M.T. Lanagan and D.K. Agrawal, J. Electroceram. 22 (2009) 125-130.
4. H. Takahashi, Y. Numamoto, J. Tani, K. Matsuta, J. Qui and S. Tsurekawa, Jpn. J. Appl. Phy. 45 (2006) 30-32.
5. M. Kellati, S. Sayouri, N. El Mouden, M. Elaammani, A. Kaal and M. Taibi, Mater. Res. Bull. 39(6) (2004) 867-872.
6. L. Kadira, A. Elmesbahi, S. Sayouri, M. Zenkour, A. Kherbahe, M. Echa-chamikh and M. Lotfi, Ann. Chim. Sci Mat. 28[4] (2003) 75-82. doi:10.1016/S0151-9107(03) 00097-7.
7. A. Elbasset, T. Lamcharfi and F. Abdi and S. Sayouri, Advances in Physics Theories and Applications 30 (2014) 45-54.
8. M.M. Vijatovic, B.D. Stojanovic, J.D. Bobic, T. Ramoska and P. Bowen, Ceramics International 36 (2010) 1817-1824.
9. Wei Li, Zhijun Xu, Ruining Chu, Peng Fu and Jigong Hao, Journals of Alloys and Compounds 482 (2009) 137-140.
10. U. Venkateswaran, V. Naik and R. Naik, Phys. Rev. B 58 (1998) 14256.
11. P. Hermet, M. Veithen and P. Ghosez, J. Phys. Condens. Matter 21 (2009) 215901.
12. S. Roberts, Barium titanate and barium-strontium titanate as nonlinear dielectrics, Massachusetts Institute of Technology <http://hdl.handle.net/10945/46911> (1946).