The influence of vacuum pressure on the electrical properties of $PbTiO_{3-\delta}$ ceramics

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ABSTRACT

$PbTiO_{3-\delta}$ ceramics were successfully prepared by the traditional solid state reaction method using different vacuum pressures during calcinations step and then sintered at 1150 °C/2h. The present study was focused on the influence of vacuum pressure variation on the electrical properties of $PbTiO_{3-\delta}$ ceramics. The room temperature XRD patterns indicate the crystallization of the perovskite structure for all the ceramics. The dielectric permittivity is increasing with decreasing of vacuum pressure due to the increasing of oxygen vacancies with reaching the high vacuum. Resistivity decreased with temperature increasing which proves the semiconductor character of present $PbTiO_{3-\delta}$ ceramics. The electrical characterization indicates that $PbTiO_{3-\delta}$ ceramics prepared using three different vacuum pressures during calcinations step are suitable for room temperature applications in microelectronics.

1. Introduction

In the last few years, many researchers have been reported the functional properties of the $PbTiO_3$ (PTO) system because is one of the simplest perovskite [1], that presents stable properties in a wide range of temperature and frequencies and possess a high spontaneous polarization: 75 µC/cm^2 from experiment [2] and 88 µC/cm^2 from first-principles calculation [3]. Owing to its interesting properties, PTO is very used in many practical applications in microelectronics and optoelectronics, such as surface acoustic wave devices, infrared sensors, and high frequency transducers, ferroelectric random access (DRAM) memories, capacitors etc. [4–6]. Recently, it has been demonstrated that electrical properties, such as conductivity or resistivity can be controlled by the presence of the defect in the sample, as oxygen vacancies [7,8]. In order to enhance the electrical conductivity, the oxygen vacancies can be introduce in the PTO perovskite materials by controlling the oxygen partial pressure, the hydrogen reduction or the vacuum pressure during preparation process of the sample [7–10]. It was observed in the last few years, an increasing attention on the PTO powder synthesis using different methods that require a calcinations step: by solid state reaction [11], by sol-gel [12] and molten-salt [13] or by hydrothermal method [14]. Because the calcinations parameters of the precursor's powders are very important for the successful

preparation of the ceramic materials, the vacuum used in this step of the ceramics processing represents a new method for preparation PTO powders with excellent sinterability. The Vacuum Calcination Method (VCM), developed by Uno et al. [10] in 1988, was used in the present study: (i) to reduce the residual carbon carried over from reacting of the raw materials; (ii) to avoid the formation of undesirable phases in order to obtain calcined powder of high purity and (iii) to create oxygen vacancies and induce mobile charge carriers in order to improve electrical performance of the PTO system. An oxygen vacancy represents a kind of system self-doping without introducing any kind of chemical elements that helps to preserving intrinsic crystal structure of the PTO material.

The objective of this study was to investigate the influence of the vacuum pressure on the structural, microstructural and electrical properties (dielectric properties, electrical resistivity and electrical conductivity) of the sintered PTO ceramics prepared by solid-state reaction method. In this work, the control of the amounts of oxygen vacancies was performed by varying the vacuum pressure in the calcinations step of the $PbTiO_{3-\delta}$ ceramics synthesis. To the best of our knowledge, a study of the influence of the vacuum pressure on the electrical properties of the oxygen deficient $PbTiO_{3-\delta}$ has not been reported in the literature so far.

2. Experimental details

Ceramics of oxygen deficient $PbTiO_{3-\delta}$ were prepared by solid state reaction, using commercial raw materials of high purity: PbO (Alfa Aesar, purity > 99.9%, average particle size of 3–5 µm) and Ti_3O_5 (Alfa Aesar, purity > 99.9%, average particle size between 10 and 200 µm). The weighted powders were well-mixed in an agate mortar for 2 h by a wet homogeneous technique using ethanol. The optimization of the calcinations temperature on the $PbTiO_{3-\delta}$ phase was reported in a previous paper [15] and reveals the pure phase for 800 °C temperatures. Consequently, the mixed powders were calcinated in a furnace equipped with a vacuum pump by using the 800 °C/4h thermal treatment temperature and different vacuum pressures varying from 100 Pa to 10^{-4} Pa and 10^{-6} Pa. After the calcination step, the powders were pressed by uniaxial pressing at ~150 MPa into pellets (length ~2–3 cm, diameters of ~1 cm) and then sintered in air at 1150 °C/2h, with a heating rate of 5 °C/min. The samples were then slowly cooled down with 1 °C/min to the room temperature. The perovskite phase formation of the ceramics was checked by XRD analysis using PANalytical Empyrean X-ray diffractometer with CuKα radiation (λ = 1.5406 Å), with scan step increments of 0.06° and counting time of 10 s/step for 2θ between 10° and 60°. The identification of the phase was performed using the HighScore database software. The average crystalline size was calculated from X-ray principal peak broadening using the Scherer formula [16,17]. The microstructures of fractured surfaces of the this ceramics were examined by using a using scanning electron microscope (SEM) analysis performed with a JEOL JSPM 5200 type microscope. The bulk density for all ceramics was determined by Archimedes method in water taking into account the theoretical density (7.6 g/cm³) of the $PbTiO_3$ system. The densities of ceramic samples sintered at 1150 °C/2h were found to be: 94.12% (for the 100 Pa vacuum pressures used in the calcination step), 94.44% (for 10^{-4} Pa) and 96.63% (for 10^{-6} Pa). The complex impedance measurements at room temperature in the frequency range $1–10^6$ Hz, were performed by using a Solartron 1260A Impedance Analyzer on Ag-electroded ceramic pellet. The electrical resistivity measurements were conducted under a direct current bias of 200 V on the obtained ceramics in the temperature range of 20–450 °C.

3. Results and discussion

3.1. X-ray diffraction analysis

In order to investigate the phase purity and to determine the lattice parameters, crystallize size and degree of tetragonality, the XRD patterns of sintered ceramics were recorded at room temperature. The recorded room temperature X-ray patterns of the prepared $PbTiO_{3-\delta}$ ceramics are presented in the Fig. 1. These results evidenced the crystallization of the perovskite structure for all the ceramics, with small amounts of impurity for the 100 Pa pressures that disappear with the reaching of the high-vacuum. According to previously reported results [15], the diffraction patterns were identified to belong to the tetragonal P4/mm symmetry. As vacuum pressure is decreasing, the peaks are more sharpened which suggest the increase in the crystallite size.

The structural parameters calculated for the $PbTiO_{3-\delta}$ ceramics prepared with vacuum pressure variation during calcinations are listed in the Table 1. Both *a* and *c* lattice parameters are modified at vacuum pressure variation. At the normal vacuum pressure (100 Pa) the tetragonal distortion is $c/a = 1.052$ and as the pressure decreasing to 10^{-4} Pa and 10^{-6} Pa, the tetragonal distortion increase up to 1.062 value. The results of the crystallization calculation are characterized by the increase of the crystallite size from ~22 nm to ~48 nm with vacuum pressure decreasing from 100 Pa to 10^{-6} Pa, which is in accordance with the peaks sharpens of each ceramics XRD pattern.

Fig. 2 shows the fracture-cross section SEM images of the $PbTiO_{3-\delta}$ ceramics sintered at the same temperature of 1150 °C/2h. It is observed
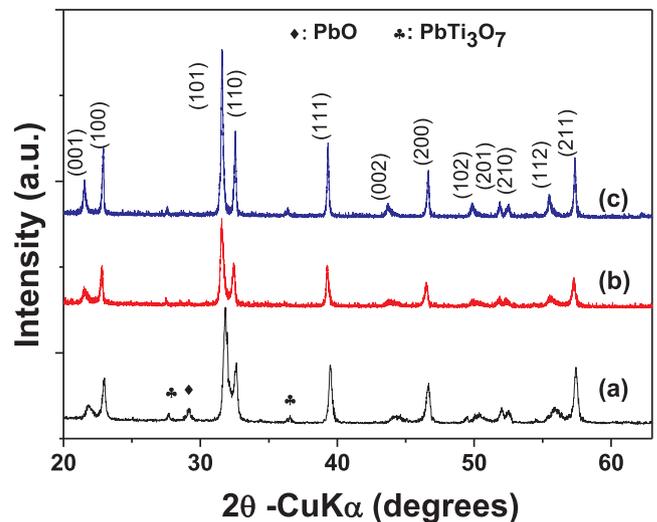

Fig. 1. XRD patterns of the $PbTiO_{3-\delta}$ ceramics produced with different vacuum pressure during calcinations: (a) 100 Pa, (b) 10^{-4}Pa and (c) 10^{-6}Pa.

Table 1
The structural parameters calculated from the XRD patterns for $PbTiO_{3-\delta}$ ceramics.

Samples	Lattice a(Å)	Parameters c(Å)	Distorted ratio c/a	Cell volume V(Å³)	Crystallite size A (nm)
100 Pa	3,876	4,078	1,052	61,285	22,9
10^{-4} Pa	3,900	4,113	1,054	62,596	30,5
10^{-6} Pa	3,885	4,129	1,062	62,341	48,5

that by using different vacuum pressure in powder calcinations step, the microstructure and the grain size are different in the final ceramic product. For the normal vacuum pressure of 100 Pa used in the calcinations step, the ceramic microstructure presents a certain degree of porosity and grains with faceted aspect and 2 µm average grain size. As vacuum pressure is decreasing to 10^{-4} Pa (in the powder calcinations step), the sintered ceramic present an heterogeneous microstructure described mostly from the small grains of 1–6 µm but are formed also large and non-uniform grains with average size about 8–16 µm. For the lowest used pressure of 10^{-6} Pa, the morphology investigation show a homogeneous dense microstructure with grains more rounded as shape and average sizes between 1 and 4 µm.

3.2. Comparative analysis of the dielectric properties

Fig. 3 shows the room temperature dielectric properties measured at low frequency $1–10^6$ Hz for the PTO ceramics that were obtained using different vacuum pressure during calcinations and sintered at 1150 °C/2h. Fig. 3(a) shows the frequency dependence of real part of permittivity. All the ceramics presents high values of permittivity by the order of ~ (800–1250) in the low frequency region (< 10 Hz) and values of ~ (100–400) in the high frequency region (> 10^3 Hz) that can be considered as intrinsic values characteristic for oxygen deficient $PbTiO_{3-\delta}$ system. The decreasing of the dielectric constant with frequency increasing is a normal behavior of the dielectric/ferroelectric materials [18]. The reduction of the real part of permittivity with increasing frequency for all the ceramics can be explained as a combination of complex dielectric relaxation and/or locally uncompensated space charge Maxwell-Wagner phenomena which most probably are due to the oxygen vacancies presence, that were induced by vacuum pressure variation. It can be also observed that with decreasing of vacuum pressure the permittivity is increasing and this can be explained also by the increasing of oxygen vacancies with reaching the high vacuum. The
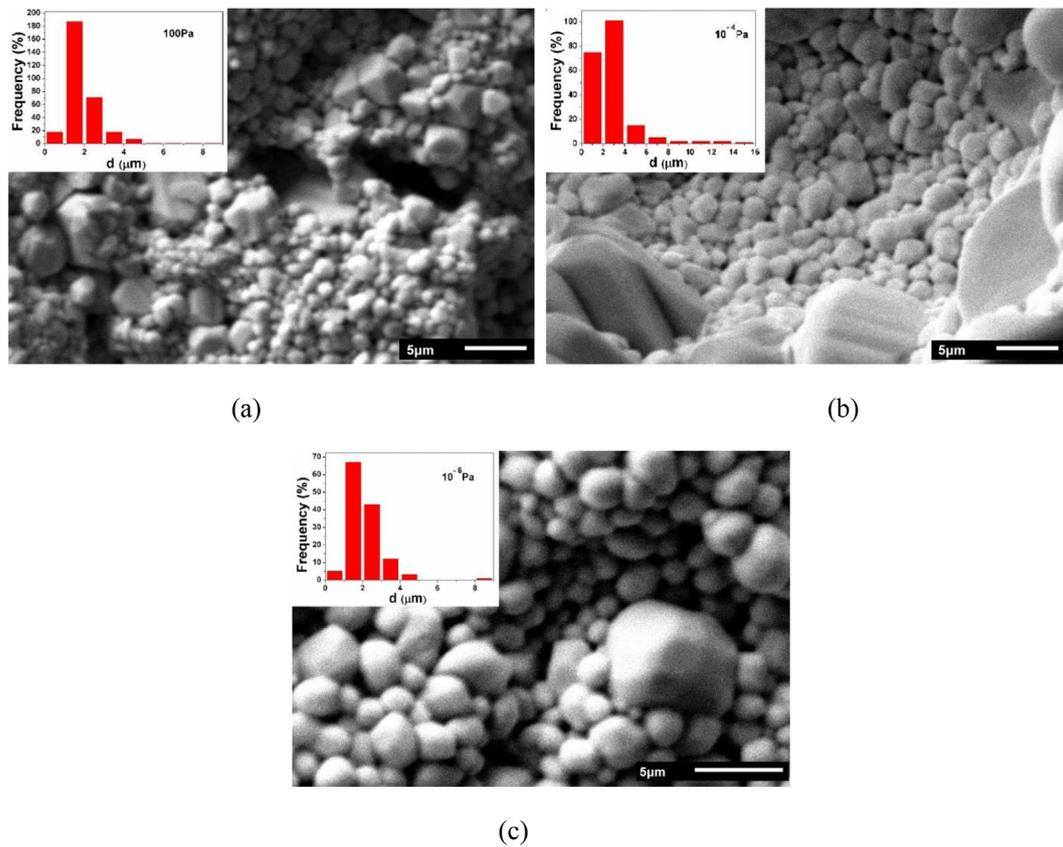
(a)

(b)

(c)

Fig. 2. Fracture SEM images of the PbTiO$_{3-\delta}$ ceramics prepared with vacuum pressure variation during calcinations: (a) 100 Pa, (b) 10^{-4}Pa and (c) 10^{-6}Pa. Inset: corresponding grain size distribution.

dielectric losses at room temperature are presented in the Fig. 3(b). The ceramics presents dielectric losses that are below unity in the whole range of frequency and reach smaller values between 0.01 and 0.06 at 1 MHz. The tendency toward intrinsic values is also observed in the case of tangent losses, for which losses due to the conductivity typical at low frequencies are strongly reduced.

The comparative analysis of the ac-conductivity (Fig. 3(c)) shows a similar trend of increasing with frequency increasing and values between 10^{-3} and 10^{-8} (S/m). Even the complex impedance plot (Fig. 3(d)) shows an apparent single component that explain a good dielectric homogeneity (which means that the oxygen vacancies are not segregated at the grain boundaries), a difference between the conductivity inside the ceramic grain and on the grain boundary most probably exist and it is demonstrated by the multiple conductivity component that characterize the PbTiO$_{3-\delta}$ ceramics. The multiple conduction components are more obvious in the conductivity response of the PbTiO$_{3-\delta}$ ceramic prepared from powder calcined at the normal vacuum of 100 Pa for which three regions can be observed. In the case of other two ceramics, the conductivity presents apparently only two components. The calcinations in vacuum was used in order to induce a higher concentration of oxygen vacancies in the system but it is also known that a higher sintering temperature (> 1000) leads to the increasing of the oxygen vacancies necessary for the charge compensation due to the Pb volatilization [19].

The contributions of the oxygen vacancies to the conductivity response can be explained taking into account that:

(i) the ionization of the oxygen vacancy creates conducting electrons in the perovskite oxides as given in the following equation:

$$V_o \Leftrightarrow V_o^{\cdot} + e'$$
$$V_o^{\cdot} \Leftrightarrow V_o^{\cdot\cdot} + e' \tag{1}$$

where $V_o^{\cdot}$ and $V_o^{\cdot\cdot}$ are single-ionized and double –ionized oxygen vacancies, respectively. These electrons can move by hopping at short-range, equivalent to reorientation of the dipole which is responsible by dielectric relaxation in the system [20].

(ii) different levels of oxygen deficiency in different spatial regions within the sample lead to electric heterogeneity (even in single phase materials) that is given rise to interfacial polarization (Maxwell–Wagner or space charge relaxation mechanism) [21].

The complex impedance spectra of the investigated ceramics (Fig. 3(d)) are characterized by an apparent single component. The impedance pattern is changing with vacuum pressure modification, but the fact that there is no visible difference between the properties of the grain boundary and grain bulk demonstrates a good dielectric homogeneity.

3.3. Electrical resistivity study

The electronic behavior was investigated in the temperature range of 20–450 °C. Fig. 4(a) shows the resistivity measurement results for the PTO ceramics that were obtained using different vacuum pressure during calcinations and sintered at 1150 °C/2h. It can be observed two regions in the resistivity dependences vs. temperature: (i) a low temperature regions with high resistivity that can be explained by an ordered ferroelectric state with oxygen vacancies that presents low mobility and (ii) a region with almost linearly decreasing resistivity at the increase in temperature which is typically behavior for a semiconductor system. As the temperature increase, the electrons absorb thermal energy necessary to become free electrons that creates conduction. Thus, the conduction of the material is also increased and the resistivity of the material is decreased due to the mobile defects present in the system.
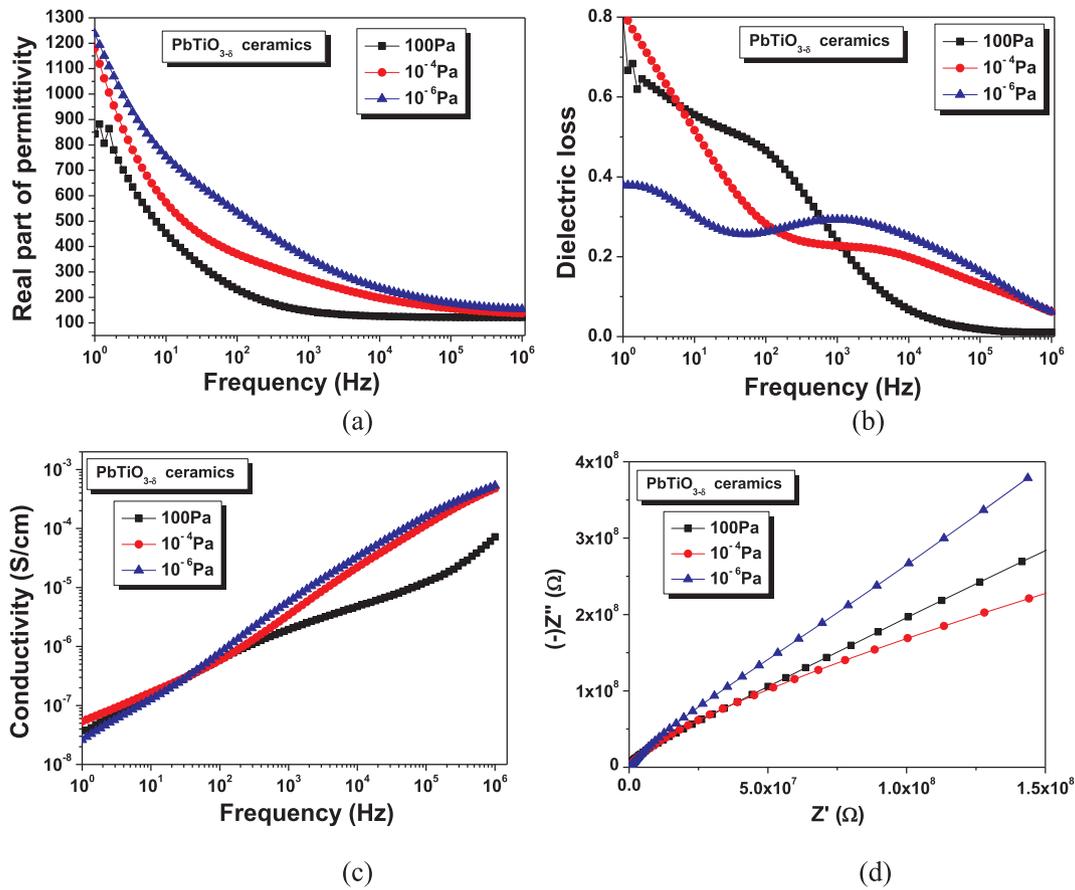
Fig. 3. Frequency dependences of the dielectric properties recorded at room temperature for PbTiO₃₋δ ceramics prepared with vacuum pressure variation during calcinations: (a) real part of dielectric permittivity; (b) dielectric losses and (c) ac-conductivity; Complex impedance spectra (d).

As already mentioned, the oxygen vacancies plays an important role in the conduction process since are the most mobile charge carriers in oxide ferroelectrics [18]. The decrease of the vacuum pressure leads to the increase in oxygen vacancies concentration and consequently to the increase of the charge carriers which will decrease the resistivity. The highest resistivity was obtained for the 10^{-6} vacuum pressure used for the calcinations step and was equal to 1.35×10^{10} Ω cm.

In order to determine the type of the oxygen vacancies that are responsible for the variations in resistivity behavior, the Arrhenius Law was employed. The activation energy was calculated using the following Arrhenius equation:

$$\ln\rho = \ln\rho_0 + \left(-\frac{E_a}{K_B T}\right),$$

(2)

where ρ_0 represents the pre-exponential factor, E_a is the activation energy and K_B is the Boltzmann constant.

Fig. 4(b) shows the Ln(ρ) vs. (1/T) dependences for the PTO ceramics that were obtained using different vacuum pressure during calcinations and sintered at 1150 °C/2h and the activation energies were extracted after fitting the experimental data with the Arrhenius equation. The linear fit gave the following values for the activation energies: Ea = 0.89 eV, Ea = 1.17 eV and Ea = 1.4 eV corresponding to the
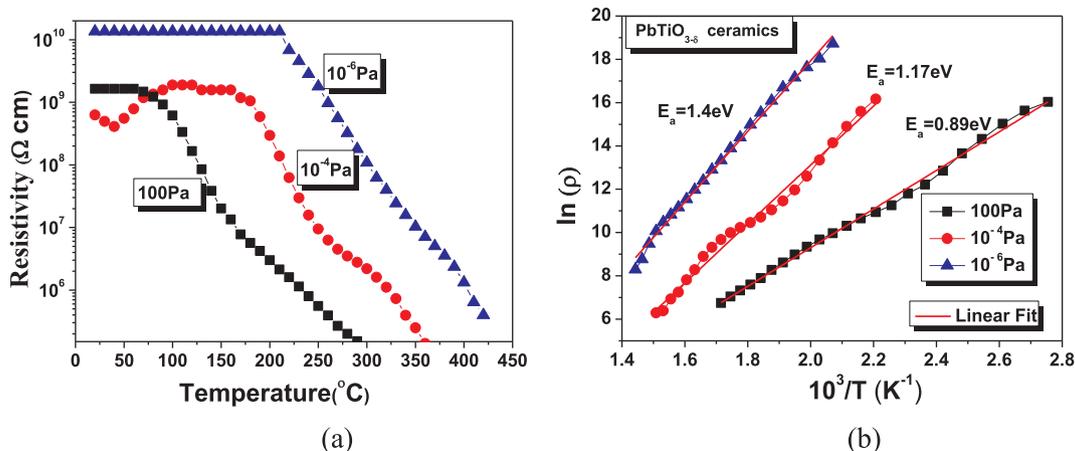

Fig. 4. (a) Temperature dependences of the resistivity for PbTiO₃₋δ ceramics prepared with vacuum pressure variation during calcinations; (b) Arrhenius plot of the resistivity dependences at various temperatures.

vacuum pressures used during calcinations equal to 100 Pa, 10^{-4} Pa and 10^{-6} Pa, respectively. Peláiz-Barranco et al. [22] reported that oxygen vacancies exist in single ionized state with activation energy values in the range of $0.3 \div 0.4$ eV, while the activation energy values in the range of $0.6 \div 1.2$ eV are commonly associated to double-ionized oxygen vacancies. Therefore, our values of activation energies indicate contributions to the ionic electrical conduction process related to the double ionized oxygen vacancies. The decreasing of the vacuum pressure results in the generation of more oxygen vacancies and leads to an increase in the long-range hopping of the charged carriers, which in fact increase the conductivity. The decrease in resistivity is also due to the hopping movements of the double ionized oxygen vacancies.

4. Conclusions

In conclusion, the present paper reports original results about the influence of the vacuum pressure used in the calcinations step on the electrical behavior of the PbTiO$_{3-\delta}$ ceramics sintered at 1150 °C/2h. PbTiO$_{3-\delta}$ ceramics were prepared successfully by the traditional solid state reaction method using three different vacuum pressures during calcinations step. The XRD patterns indicate the crystallization of the perovskite structure for all the ceramics, with small amounts of impurity for the 100 Pa pressures that disappear with the reaching of the high-vacuum. The morphology investigation reveals that the vacuum pressure has important influence on the ceramics microstructures: by using different vacuum pressure in powder calcinations step, the microstructure and the grain size are different in the final ceramic product. The real part of permittivity presents high values in the low frequency range due to the Maxwell-Wagner phenomena which were induced by the oxygen vacancies presence at vacuum pressure variation during calcinations and values of $\sim$ (100–400) in the high frequency region ($> 10^3$ Hz) that can be considered as intrinsic values characteristic for oxygen deficient PbTiO$_{3-\delta}$ system. The complex impedance spectra pattern is changing with vacuum pressure modification and reveals a good dielectric homogeneity for all ceramics demonstrated by the single-component in the Cole-Cole plot. Conductivity presents important contribution from the oxygen vacancies and shows an increasing trend with frequency increasing with values between 10^{-3}-10^{-8} (S/m). The higher values of the activation energy determined using the Arrhenius equation indicates that the electrical conduction was due to the double ionized oxygen vacancies and their hopping movement leads to the resistivity decreasing. The overall electrical characterization of the PbTiO$_{3-\delta}$ system prepared using different vacuum pressures in the calcinations step indicates that PTO ceramics are suitable for room temperature applications in microelectronics.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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