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EFFECT OF P_2O_5 ADDITION ON THE MICROSTRUCTURE AND DIELECTRIC PROPERTIES OF $Pb_{0.98}Ca_{0.02}[(Zr_{0.52}Ti_{0.48})_{0.98}(Cr^{3+}_{0.5}, Ta^{5+}_{0.5})_{0.02}]O_3$

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Abstract

We can note that the sintering temperature of the piezoelectric $Pb_{0.98}Ca_{0.02}[(Zr_{0.52}Ti_{0.48})_{0.98}(Cr^{3+}_{0.5}, Ta^{5+}_{0.5})_{0.02}]O_3$ can be reduced after the addition of phosphor without compromising the dielectric properties. A sintered density of 96 % of the theoretical density was obtained for 4 wt. % P_2O_5 addition after sintering at 1050 °C for 2 h. Ceramics sintered at 1050 °C with 4 wt. % P_2O_5 achieve excellent properties, which are as follows: ε_r= 18808, tan δ = 0.0094 and T_c = 390°C.

Keywords: Dielectric properties, Electronic materials, Methods physicochemical of analysis, PZT, Piezoelectricity.

Résumé

On peut constater que la température de frittage du piézo-électrique $Pb_{0.98}Ca_{0.02}[(Zr_{0.52}Ti_{0.48})_{0.98}(Cr^{3+}_{0.5}, Ta^{5+}_{0.5})_{0.02}]O_3$ peut être réduite après l'addition du phosphore sans compromettre les propriétés mécaniques. La densité frittée de 96 % de la densité théorique a été obtenue pour l'addition de 4 wt.% de P_2O_5 après le frittage à 1050 °C pendant 2h. Céramiques frittées à 1050 °C avec 4 wt.% de P_2O_5 atteindre d'excellentes propriétés, qui sont les suivantes: ε_r= 18808, tan δ = 0.0094 and T_c = 390°C.

Mots clés *:* Propriétés diélectriques, Matériels électroniques, Méthodes physicochimique d'analyse, PZT, Piézoélectricités.

1- INTRODUCTION

Since their discovery (early 50s), ceramic materials piezoelectric lead zirconate titanate (PZT), have known a very important period of flourishment as evidenced by the growing number of articles and international scientific events devoted to these materials every year [1-4]. These piezoelectric ceramics are currently used as transducers, sensors, ultrasonic motors, actuators…. etc. [5-7]. This is due to their different properties: insulation, dielectric, electromechanical and ferroelectric [8–11]. Within the frame of our work, we are interested in substituting: Pb^{2+} with the Ca^{2+}, couple (Zr^{4+} / Ti^{4+}) with (Cr^{3+}, Ta^{5+}) and see the effect of P_2O_5 on the dielectric properties of the solid solution: $Pb_{0.98}Ca_{0.02}[(Zr_{0.52}Ti_{0.48})_{0.98}(Cr^{3+}_{0.5}, Ta^{5+}_{0.5})_{0.02}]O_3$

2- EXPERIMENTAL

The compositions studied are summarized in Table 1. These compositions have been synthesized by chemical reaction in the solid state. Raw materials were mixed and ground for six hours. After grinding, obtained powder is compacted in the form of pellets at a pressure of 7.50 MPa. Then a preliminary calcination at 800 °C is done for 2 hours with a heating rate of 2 °C / min. The calcined mixture is ground again for 4 hours then molded into pellets under 30 MPa and sintered to 1000, 1050, 1100, 1150 and 1180 °C for 2 h.

The pellets are metalized with the help of a thin layer of dough silver on both of their surfaces. After drying, metallic pellets undergone calcinations at 750 °C for thirty minutes. The sintered compounds are carefully ground, then analyzed by X-ray diffraction (Diffract meter SIEMENS D500, λ Cu Kα: 1.54056 Å) to establish crystallographic phases: tetragonal, rhombohedral and tetragonal-rhombohedral (Morphotropic). The scanning electron microscopy (SEM) is a technics for estimating the size distribution, the average size of grains after sintering and qualitatively assesses the presence of porosity. The micrographics are made using a Microscope JMS 6400. The variation of the dielectric constant ε_r, resistivity and also the angle of the losses were examined by using a multi-analyzer LCR meter combined with a programmable oven (25 degrees C-1200°C) with a heating rate of 2 degrees Celsius per minute and at a frequency of 1kHz.

Table 1: Different compositions prepared for our study.

Sample N°	Formula
1	$Pb_{0.98}Ca_{0.02}[(Zr_{0.52}Ti_{0.48})_{0.98}(Cr^{3+}_{0.5}, Ta^{5+}_{0.5})_{0.02}]O_3$
2	$Pb_{0.98}Ca_{0.02}[\{(Zr_{0.52}Ti_{0.48})_{0.98}(Cr^{3+}_{0.5}, Ta^{5+}_{0.5})_{0.02}\}_{1-0.02}P_{0.02}]O_3$
3	$Pb_{0.98}Ca_{0.02}[\{(Zr_{0.52}Ti_{0.48})_{0.98}(Cr^{3+}_{0.5}, Ta^{5+}_{0.5})_{0.02}\}_{1-0.04}P_{0.04}]O_3$
4	$Pb_{0.98}Ca_{0.02}[\{(Zr_{0.52}Ti_{0.48})_{0.98}(Cr^{3+}_{0.5},Ta^{5+}_{0.5})_{0.02}\}_{1-0.05}P_{0.05}]O_3$
5	$Pb_{0.98}Ca_{0.02}[\{(Zr_{0.52}Ti_{0.48})_{0.98}(Cr^{3+}_{0.5}, Ta^{5+}_{0.5})_{0.02}\}_{1-0.08}P_{0.08}]O_3$
6	$Pb_{0.98}Ca_{0.02}[\{(Zr_{0.52}Ti_{0.48})_{0.98}(Cr^{3+}_{0.5}, Ta^{5+}_{0.5})_{0.02}\}_{1-0.1}P_{0.1}]O_3$
7	$Pb_{0.98}Ca_{0.02}[\{(Zr_{0.52}Ti_{0.48})_{0.98}(Cr^{3+}_{0.5}, Ta^{5+}_{0.5})_{0.02}\}_{1-0.12}P_{0.12}]O_3$

3- RESULTS AND DISCUSSION

3.1- Analysis by X-ray diffraction

The results of X-rays on the samples sintered at 1050 °C are illustrated in Fig. 1.
According to this figure, samples doped with P_2O_5 and non-doped have a coexistence of two phases tetragonal and rhombohedral.

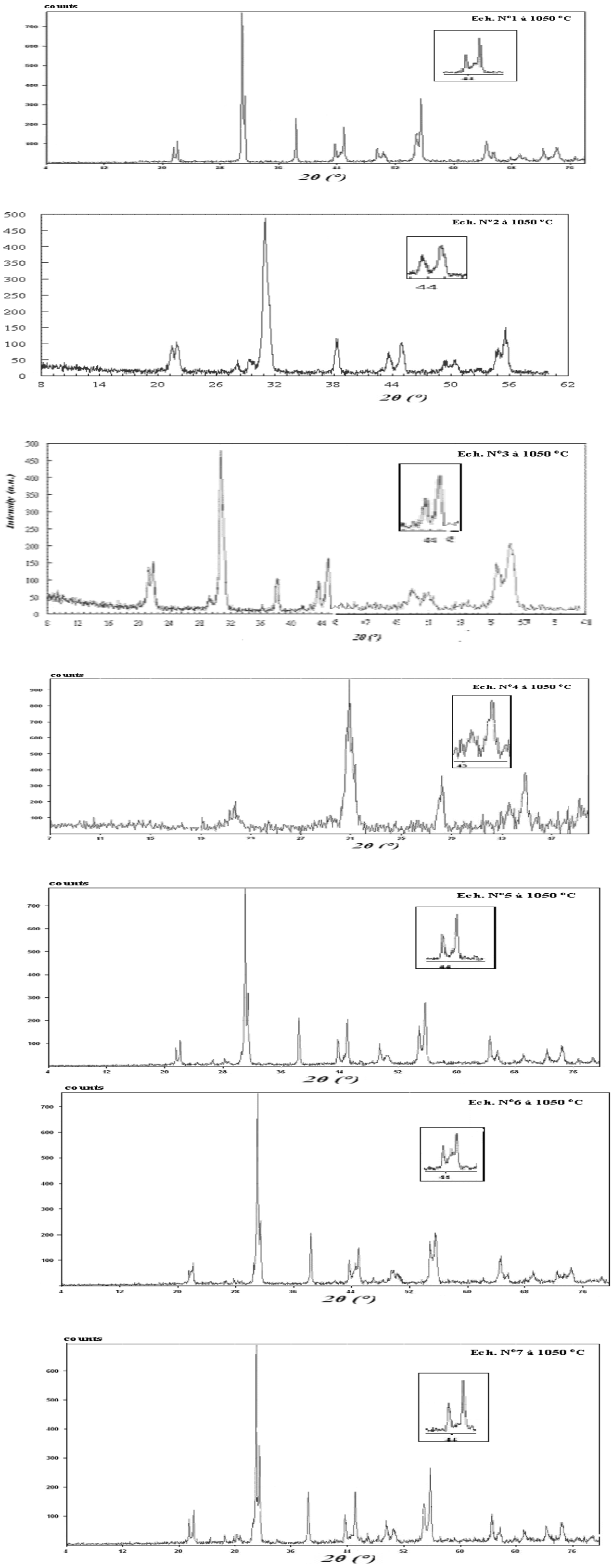


Fig.1: *Diffractogrammes X-ray for the samples sintered at 1050°C.*

3.2- morphological Study

Fig. 2 shows the SEM image of the fractured surface of $Pb_{0.98}Ca_{0.02}[(Zr_{0.52}Ti_{0.48})_{0.98}(Cr^{3+}_{0.5}, Ta^{5+}_{0.5})_{0.02}]O_3$ doped by 4 wt.% of P_2O_5 at different sintering temperatures (1000 °C, 1050 ºC and 1100 ºC).

At first glance, the three compositions seem homogeneous and there do not appear to have grains of pyrochlore phase that are identifiable by their pyramidal shape [12]. The ruptures with the grain boundaries are synonymous with a good sintering.

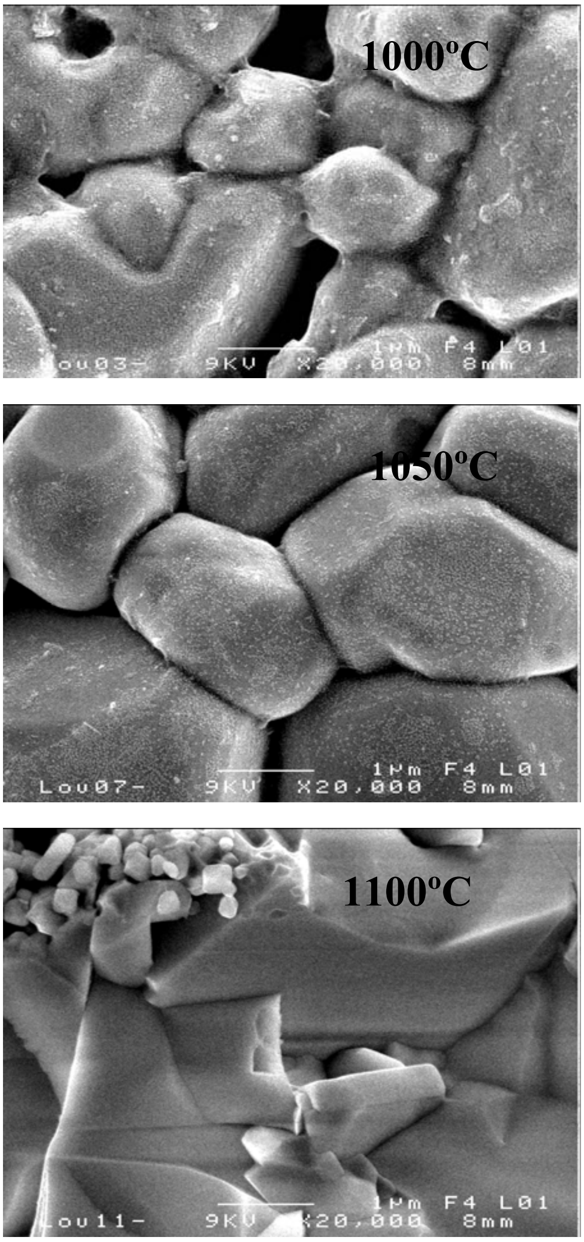


***Fig. 2**: Photographs taken by the scanning electron microscope for the composition - $Pb_{0.98}Ca_{0.02}[(Zr_{0.52}Ti_{0.48})_{0.98}(Cr^{3+}_{0.5}, Ta^{5+}_{0.5})_{0.02}]O_3$ doped by 4 wt.% of P_2O_5 at different temperatures.*

These samples appear very dense, no pores being evidenced on SEM microstructures. It is noted that the average grain size increases with increasing sintering temperature for 2 μm at 1000 ºC up to 2.671 μm at 1050 °C to form a denser and therefore non-porous. Then this size decreases slightly to 1100 °C to reach the value of 2.51 μm. The increase in grain size may have led to the decrease of oxygen vacancies in PZT [13].

3.3- The density

3.3.a- Evolution of the density depending on the sintering temperature

Fig. 3 shows the variation of density with sintering temperature and the amount of P_2O_5 addition. It can be seen variation trend with increasing sintering temperature. The density of specimens sintered at 1050 °C showed the maximum value of 7.52 $g.cm^{-3}$ at 4 wt. % P_2O_5 and then was decreased after the maximum value. This variation is mainly attributed to the formation of liquid phase of excess PbO that improves densification of the ceramics. However, a large amount of this liquid phase leads to low density which may result from the formation of voids.

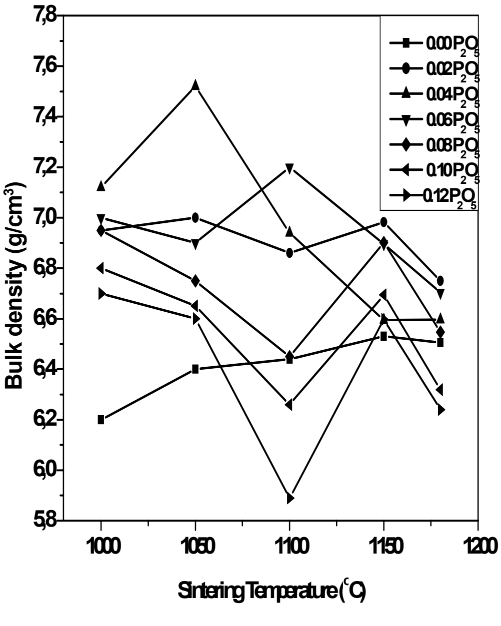


***Fig. 3**: Evolution of the density depending on the sintering temperature.*

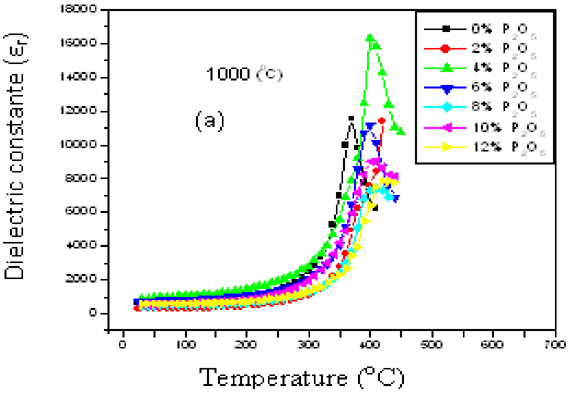
3.4- Study of dielectric properties

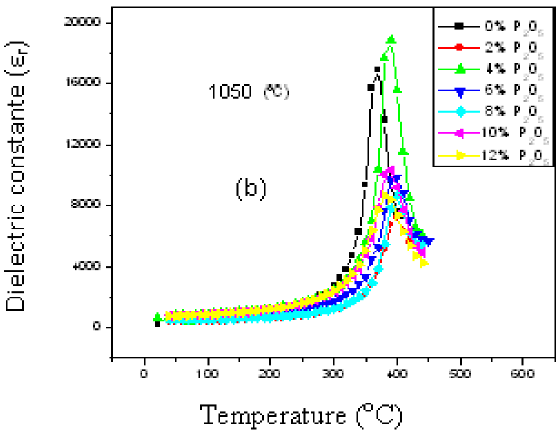
For study the dielectric properties, it is preferably chosen a material not polarized, because it provides a high resistivity, high dielectric constant and low dielectric loss.

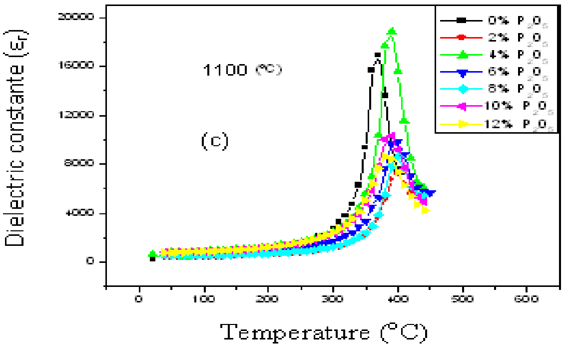
3.4.1- The dielectric constant (ε_r)

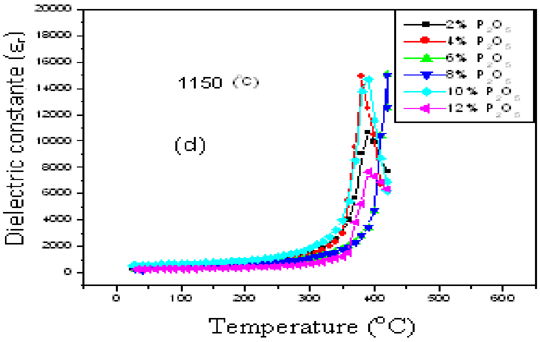
3.4.1.a- Evolution of the dielectric constant as a function of temperature

Fig. 4(a, b, c, d and e) shows the variation of the dielectric constant as a function of temperature at sintering temperatures 1000, 1050, 1100, 1150 and 1180 ^{o}C. The curves of different samples have virtually the same form; they differ from each other only by the position of their maximum. The introduction of 4 wt. % P_2O_5, increases greatly the value of the dielectric constant until 18808 at the transition temperature of 390 °C and at the frequency of measurement 1kHZ for the sample sintered at 1050 ^{o}C. This maximum of dielectric activity can be explained by the presence of several direction of a spontaneous polarization relating to the existence of the two structures: rhombohedral and tetragonal. However, the introduction of (2, 6, 8, 10 and 12 wt. %) P_2O_5 lowers the value of the dielectric constant for the same frequency of measurement.









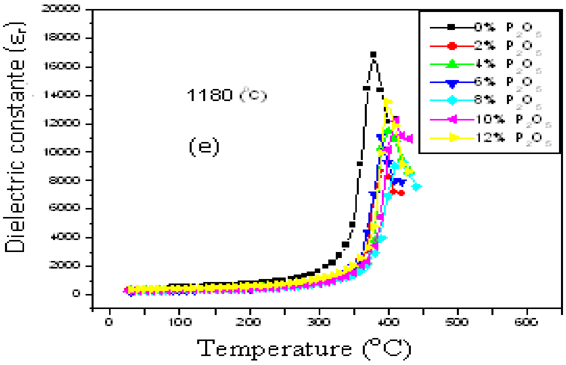


***Fig. 4**: Evolution of the dielectric constant as a function of temperature for all samples:*
a) 1000 °C, b) 1050 °C, c) 1100 °C, d) 1150 °C and e) 1180 °C.

Below the transition temperature (T_c), the distortion of the structure perovskite is accompanied by a relative movement of ions. This creates major part of the spontaneous polarization at the level of the lattice. Thus, the ions Ti^{4+}, Zr^{4+} and Pb^{2+} respectively do not occupy the centre and the summits of the lattice; they are shifted in one of the main directions of the crystal lattice. This gives rise to a spontaneous polarization to achieve maximum value for T_c. These changes of the polarization with T_c explain the value of ε_r at this temperature. The transition temperature T_c corresponds to the maximum peak of the dielectric constant.

3.4.1.b- Evolution of the dielectric permittivity depending on the frequency

The effect of frequency dielectric constant of the compound doped by 4 wt. % P_2O_5 is presented in Fig. 5. From the curve, we find that ε_r shows a decrease when the frequency increases up to 30 KHz and stability from 30 kHz to 100 kHz. According to these results, we can consider the compound doped by 4 wt. % P_2O_5 as a soft ceramic and can be used at high frequencies in the transmission technology. Some authors: Z. He et al. (2004), Y. Xu et al. (1991) explain the maximum value of the dielectric constant at room temperature by the existence of different types of polarization [14–15].

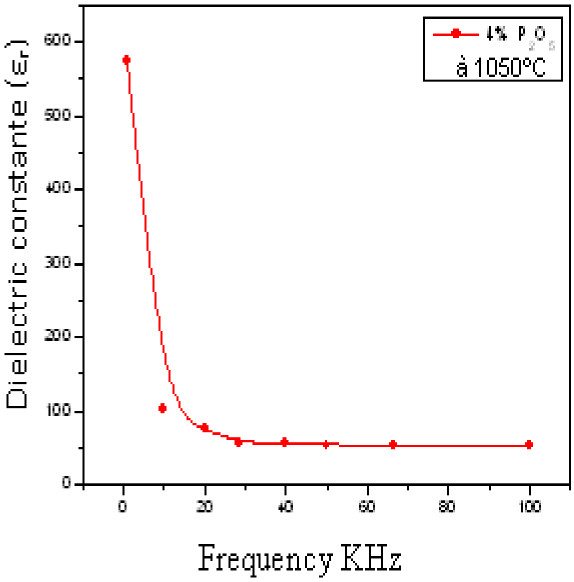


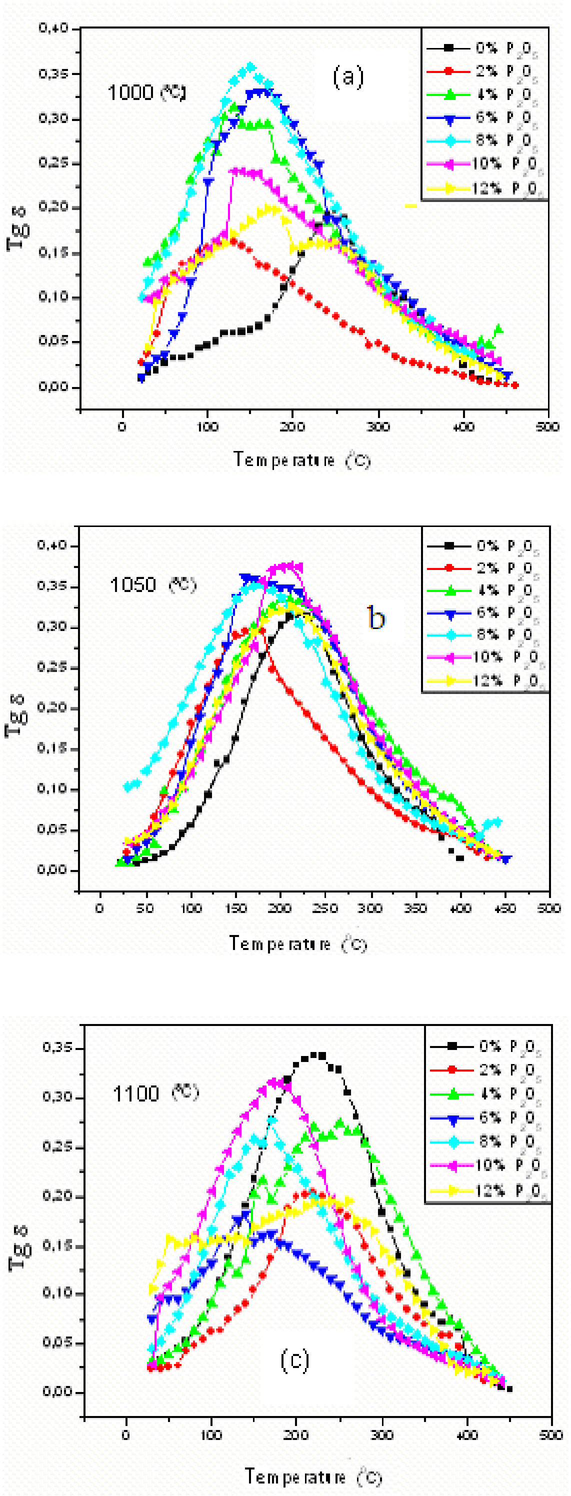
***Fig. 5**: Evolution of the dielectric constant depending on the frequency for the sample doped by 4 wt. % of P_2O_5 at room temperature.*

3.4.2- Dissipation factor (dielectric losses tgδ)

This factor that varies depending on temperature and frequency plays an important role especially in high frequency circuits.

3.4.2.a- Evolution of tgδ as a function of the temperature

The curves in Fig. 6 (a, b, c, d and e) shows the change in the dissipation factor as a function of temperature for all samples sintered at different temperatures (1000, 1050, 1100, 1150 and 1180 °C). The curves giving variations tgδ=f(T) retain the same form for different sintering temperatures. The dissipation factor increases with increasing temperature until it reaches a maximum value which reflects a maximum loss dielectric mixture, which is due to movement of the dipole moments and then declines. This decrease caused by the increase in temperature leads to a deterioration in the material properties.



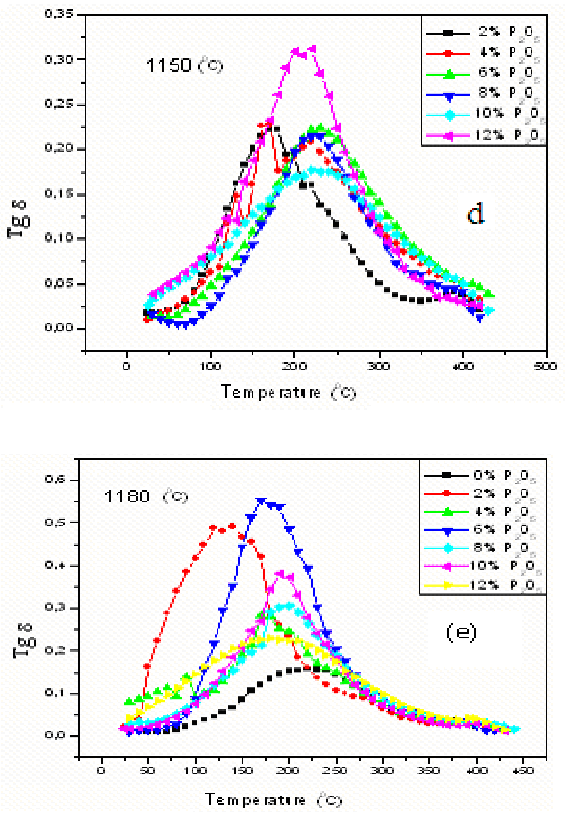


***Fig. 6**: Evolution of factor dissipation as a function of temperature for all sintered samples: a) 1000 °C, b) 1050 °C, c) 1100 °C, d) 1150 °C and e) 1180 °C.*

3.4.2.b- Study of dissipation factor as a function of P_2O_5

The effect of composition on the evolution of dielectric losses is represented in Fig. 7.

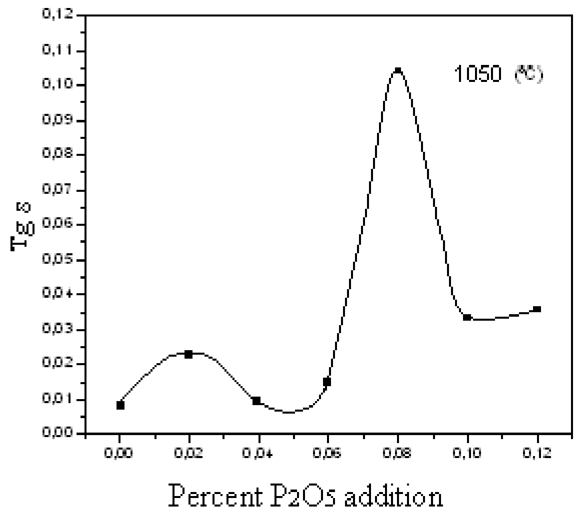


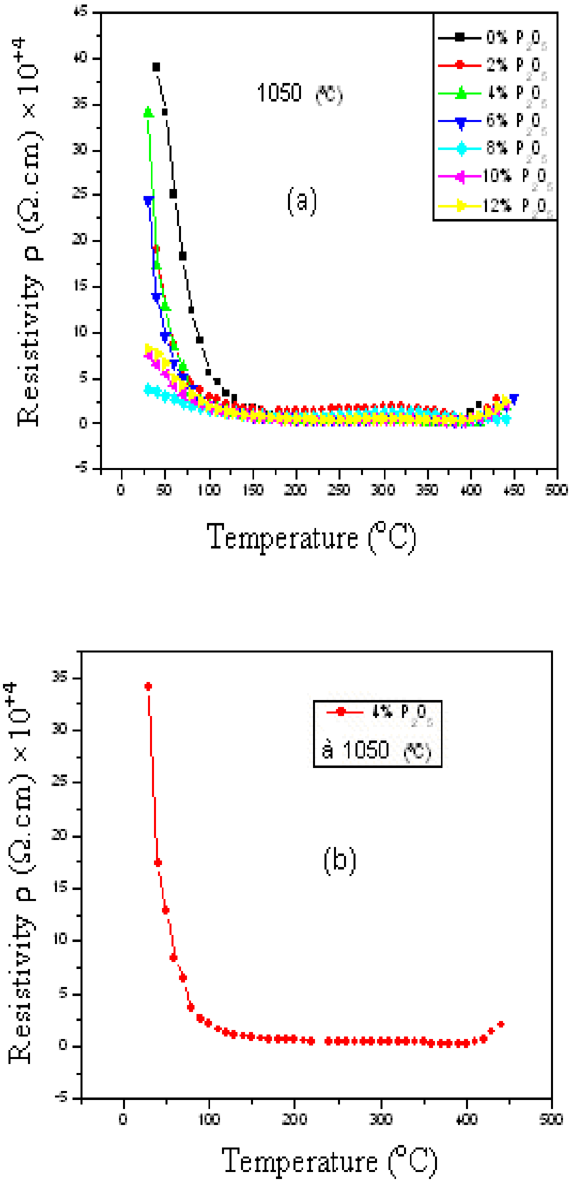
***Fig. 7**: Evolution of dissipation factor as a function of P_2O_5.*

It is noticeable that there is a variation of the dielectric losses with increasing concentration of P_2O_5. These losses may reach a minimum value of 0,942 % to 4 wt. % of P_2O_5 and a maximum value of 10,376 % to 8 wt. % of P_2O_5. This indicates that the compound doped with 4 wt. % of P_2O_5 is denser than other compound doped and non-doped by P_2O_5.

3.4.3- Resistivity (ρ)

3.4.3.a- Study of resistivity and conductivity as a function of temperature

The study of the variation of resistivity and conductivity as a function of temperature is illustrated in Fig. 8.



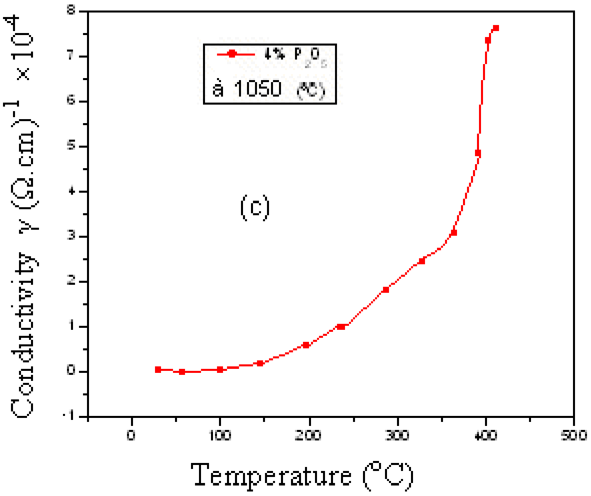


***Fig. 8**: Variation of resistivity and conductivity as a function of temperature.*

The curves of this figure shows that there is a relationship between the relative change in temperature and the two electrical factors (conductivity and resistivity).

The resistivity of each sample decreases with the increases of temperature (Figure 8.a). At 1kHZ we find that resistivity shows a decrease, for the sample doped with 4 wt. % P_2O_5, the resistivity decrease for 35 ×10^{+4} (Ω.cm) at T = 50 °C until it reaches the value 0.09 × 10 $^{+4}$ (Ω.cm)at 350 °C (Figure 8.b). This is due to the fact that high-temperature thermal energy may be sufficient to break some connections or ionic and covalent causes some mobility of ions. However, the electrical conductivity varies in the opposite direction of resistivity; it grows with the increase of temperature (Figure 8.c). It can reach a maximum value of 7.5×10^{-4} (Ω.cm)$^{-1}$ at a temperature of 350 °C.

4- CONCLUSION

In the present work we have reported the P_2O_5-doped $Pb_{0.98}Ca_{0.02}[(Zr_{0.52}Ti_{0.48})_{0.98}(Cr^{3+}{}_{0.5}, Ta^{5+}{}_{0.5})_{0.02}]O_3$ ceramic with composition z = 0.0, 0.02, 0.04, 0.08, 0.10, 0.12 prepared by mixed oxide method. X-ray diffraction studies confirmed coexistence of two phases tetragonal and rhombohedral for the synthesized compound. The effect of temperature sintering on the density and porosity has been studied to achieve the optimum sintering temperature which corresponds to the maximum density and the minimum value of the porosity, because this temperature (1050 °C) corresponds to the product of better quality. The study of dielectric properties of our solid compound state depending on the temperature allows us to have high values of the dielectric constant, such as density of 7.6 g.cm^{-3}, dielectric constant of 18808, Dissipation factor of 0.0094 and resistivity of 0.09 × 10 $^{+4}$ (Ω.cm), were found at 4 wt. % P_2O_5 substituted $Pb_{0.98}Ca_{0.02}[(Zr_{0.52}Ti_{0.48})_{0.98}(Cr^{3+}{}_{0.5}, Ta^{5+}{}_{0.5})_{0.02}]O_3$ ceramics sintered at 1050 °C.

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