The International Conference on Technologies and Materials for Renewable Energy, Environment and Sustainability, TMREES14

Sintering and 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 ferroelectric ceramics doped with P_2O_5

Louanes Hamzioui [a,b], Fares Kahoul [a,b], Ahmed Boutarfaia [a,b,]*

a Université Kasdi Merbah Ouargla, laboratoire de génie des procédés, Faculté des sciences appliquées, Ouargla 30000 Algérie
b Département de chimie, laboratoire de chimie appliquée, Université de Biskra B. P. 145, RP-Biskra 07000, Algérie

Abstract

The effect of phosphorus additions on the structure, microstructure and dielectrics properties of the $Pb_{0.98}Ca_{0.02}$ [$(Zr_{0.52}Ti_{0.48})_{0.98}(Cr^{3+}_{0.5}$, $Ta^{5+}_{0.5})_{0,02}]_{1-x}P_x$ O_3 (x ranged from 0.01 to 0.12) ceramics have been investigated. All of the samples were prepared by a high-temperature solid-state reaction technique. AFM analysis of the compounds suggests that the average grain size increases with increasing sintering temperature which is characteristic of a ceramic material. Until that it reaches maximum values for the simple doped with 4 Wt. % of P_2O_5 at a sintering temperature of 1050 °C. Dielectric studies of the compounds as a function of frequency (from 1 to 200 KHz) sintered at different sintering temperatures (1000, 1050, 1100, 1150 and 1180 ° C) show that the compounds undergo a phase transition of diffuse type. The transition temperature shifts towards higher side with increase in frequency a typical characteristic of a relaxor material.

Keywords: PZT, AFM, frequency, grain size, dielectrics proprieties

1. Introduction

Lead zirconate titanate ($Pb(Zr_{1-x}Ti_x)O_3$ or PZT) ferroelectric ceramic and its derivatives are widely used in

* Corresponding author. Tel.: +213 29 717 070; fax: +213 29 715 161.
  E-mail address: hamzioui_louanes@yahoo.fr, Aboutarfaia@yahoo.fr

transducers, actuators, and sensors and other electromechanical devices because of their high dielectric coefficients [1,4]. However, the structure of PZT is the point of discussion till today. For many years, the crystal structure of PZT was thought to be as indicated by the well known phase diagram published by Jaffe et al. [5]. The morphotropic phase boundary (MPB) region mostly defined in the range $0.4 < x < 0.6$. Most of the research interest has been devoted in this region, because of the extremely high piezoelectric response which has numerous technological applications [6, 8]. Commercially available PZT ceramics were modified with either acceptor dopants such as ions of K^+, Na^+, P^{5+} (at A-site) and Fe^{3+}, Al^{3+}, Mn^{3+} (at B-site) creating oxygen vacancies in the lattice [9,10] are known as hard PZT, or donor such as ions of La^{3+} (at A-site) and Nb^{5+}, Sb^{3+} (at B-site) leading to the creation of A-site vacancies in the lattice are known as soft PZT. Compared with the undoped composition, hard PZT often shows lower but more stable properties after ageing. In contrast, soft PZT shows higher properties and insensitivity to ageing. The difference in properties between the soft and hard PZT ceramics is rather large, even though the doping level is limited to a very low value (on the order of 1 mole %). The large difference of the physical properties between them mainly originates from the contributions from domain wall motion rather than properties of the crystal lattice. A hard PZT is usually used for high power applications while a soft PZT is used for sensors or low power transmitter applications [11,14]. The present work aims, to synthesize new materials of the formula $Pb_{0.98}Ca_{0.02}$ $[(Zr_{0.52}Ti_{0.48})_{0.98}(Cr^{3+}_{0.5}, Ta^{5+}_{0.5})_{0.02}] O_3$ and see the effect of P_2O_5 on the sintering and properties.

2. Experimental procedures

During the preparation of modified PZT compounds, it is necessary to control the lead oxide content during sintering. The loss of lead oxide and the resultant variation in the composition affects greatly the dielectric properties. According to D. Wang and S. Zhang [15], when PZT solid solution is fired, lead oxide tends to evaporate and its vapor pressure becomes very important in sintering temperature. This volatility of lead oxide often leads to an unbalanced stoichiometry. The optimization of the operating conditions concerns the sintering temperature and atmosphere. Keeping this in mind, the compounds were synthesized by a conventional oxide mixing technique. The compositions used for the present study were $Pb_{0.98}Ca_{0.02} [(Zr_{0.52}Ti_{0.48})_{0.98}(Cr^{3+}_{0.5}, Ta^{5+}_{0.5})_{0.02}] O_3$ added xP_2O_5 with x varying as 0, 2, 4, 6, 8, 10 and 12 Wt.% respectively. The appropriate amounts of Pb_3O_4 (99.9%), TiO_2 (99.9%), ZrO_2 (99.0%), Ta_2O_5 (99.9%), CaO (99.9%), Cr_2O_3 (99.9%) and P_2O_5 (99.9%) powders were weighed and mixed by ball milling with partially stabilized zirconia balls as media in isopropyl alcohol for 6 h. After drying, the mixture was calcined in a covered alumina crucible at 800 °C for 4 h. The calcined powders were again mixed by ball milled for 4 h. The resulting powders were uniaxially compacted into pellets of 10 mm in diameter at a pressure of 5 MPa, followed by isostatically pressing at 150 MPa. To investigate their sintering behavior, the specimens were sintered in a sealed alumina crucible at temperatures ranging from 1000°C to 1180 °C for 2 h. Excess PbO (2 wt%) was taken to compensate the lead loss during sintering. Microstructural features such as a grain size and pores were characterized by means of atomic force microscopy (AFM). The fractured surfaces were used for grain size and morphology determination. The size distribution of the grains was measured and the results compared with each other. The size distribution of the pores and the total value of porosity were determined on a polished cross-section of the samples with an image analyzer. The dielectric response was measured at room temperature by using an automatic LCR meter as a function of frequency for all samples with different sintering temperatures.
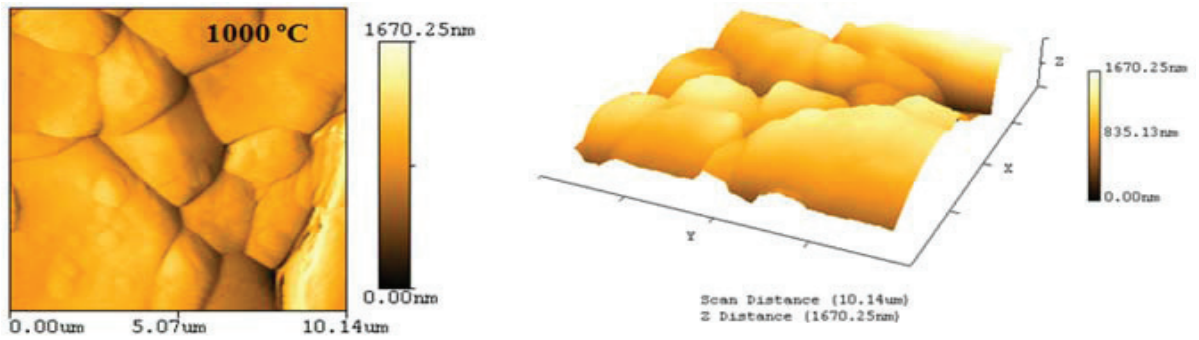
3. Results and discussion

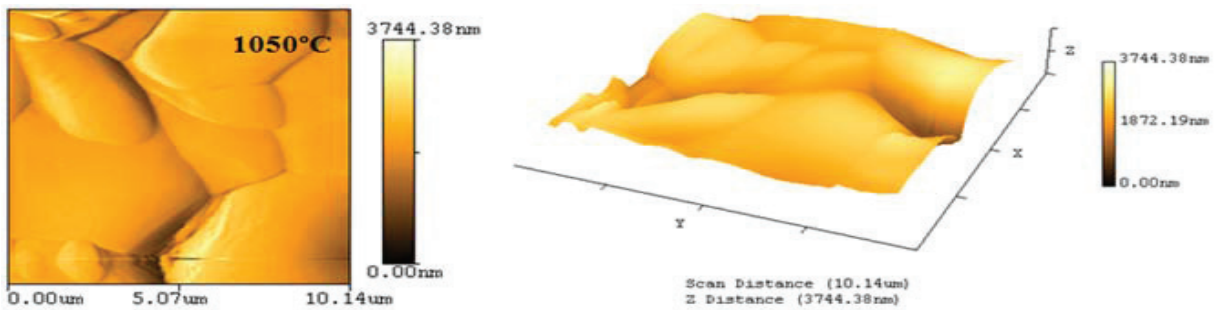### 3.1. Microstructure and crystallinity

3.1.1. AFM analysis

The surface morphology of ceramics was examined by contact mode atomic force microscopy (AFM), which is able to detect single tiny crystallites before XRD or SEM detect crystalline phases. The fig. 1 shows the morphology of PZT-CCT in two and three dimensions to the different simples doped in phosphorus: a) 4 Wt. %, b) 6 Wt. % and
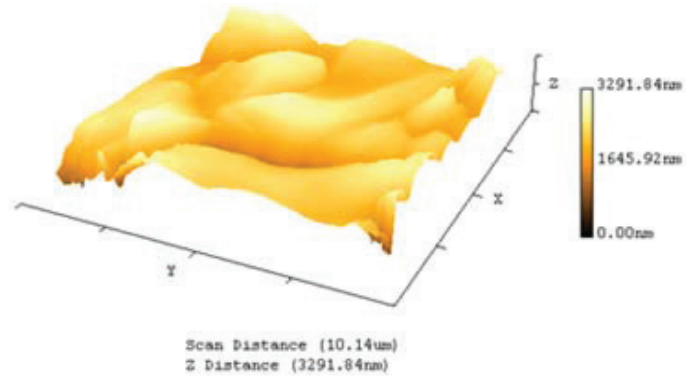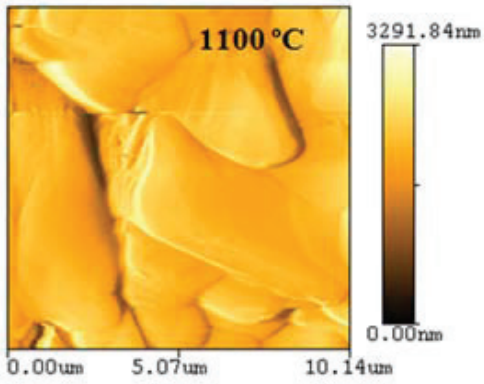
b) 8 Wt. % sintered at 1000, 1050 and 1100 °C for 2 hours. Analyzes were carried out on surfaces equal 10.14 µm × 10.14 µm. The observation of the surface reveals the presence of large grains with boundaries clearly marked.
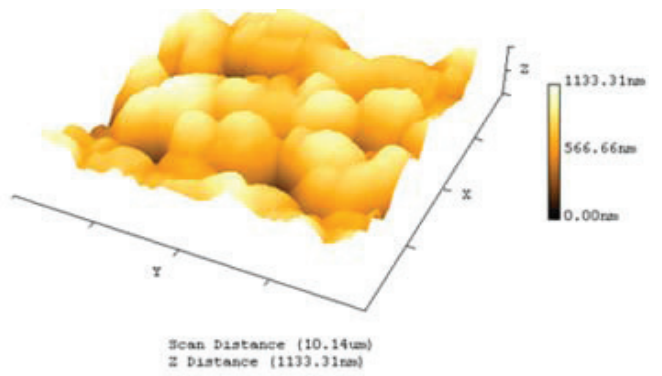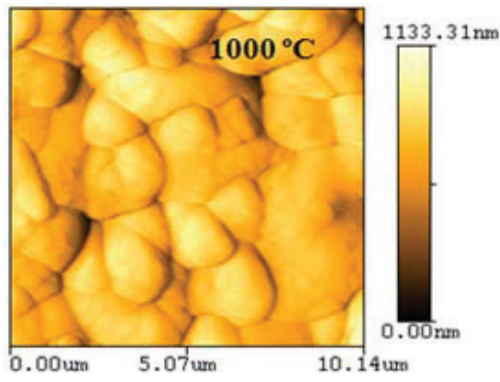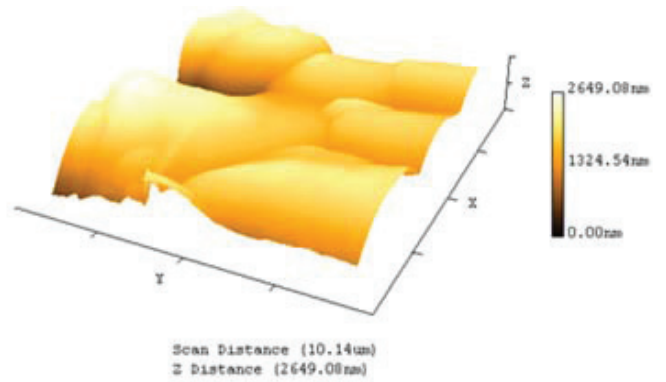

(a)

(a)

1100 °C

3291.84nm

0.00nm

0.00um   5.07um   10.14um

z 3291.84nm

1645.92nm

0.00nm

Scan Distance (10.14um)
Z Distance (3291.84nm)

(a)

1000 °C

1133.31nm

0.00nm

0.00um   5.07um   10.14um

z 1133.31nm

566.66nm

0.00nm

Scan Distance (10.14um)
Z Distance (1133.31nm)

(b)

1050 °C

2649.08nm

0.00nm

0.00um   5.07um   10.14um

z 2649.08nm

1324.54nm

0.00nm

Scan Distance (10.14um)
Z Distance (2649.08nm)

(b)

(b)

(c)
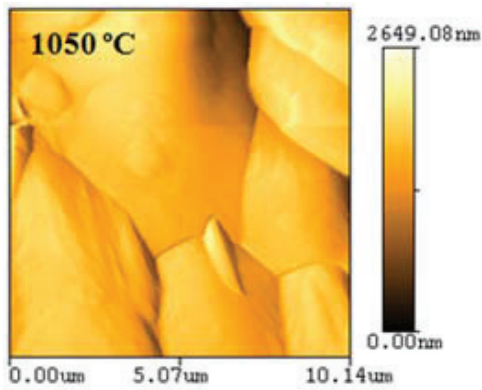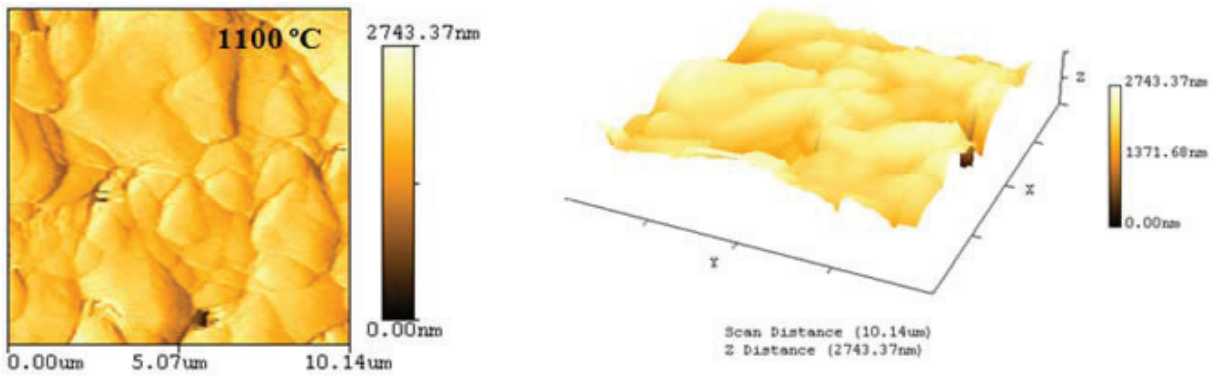
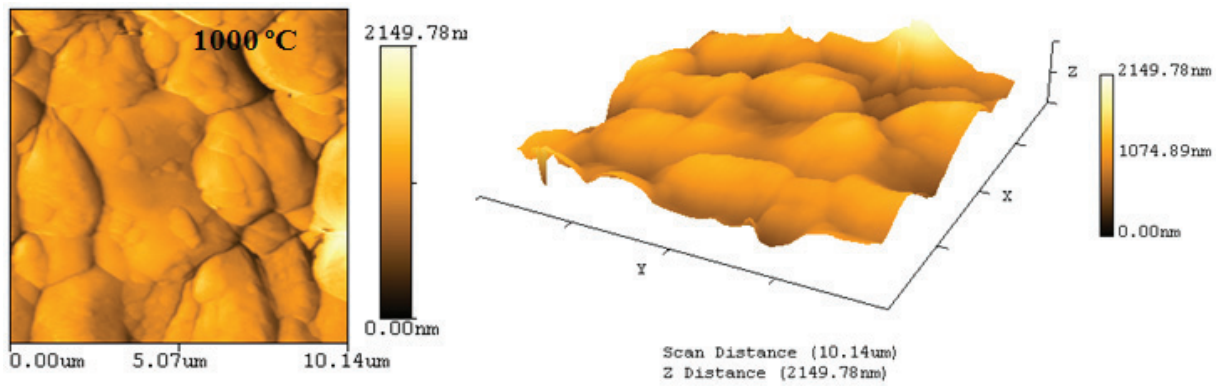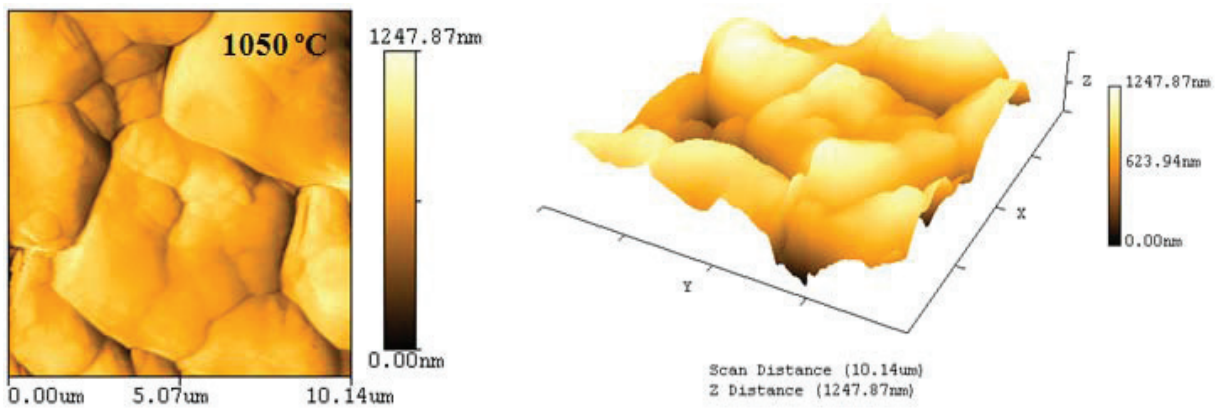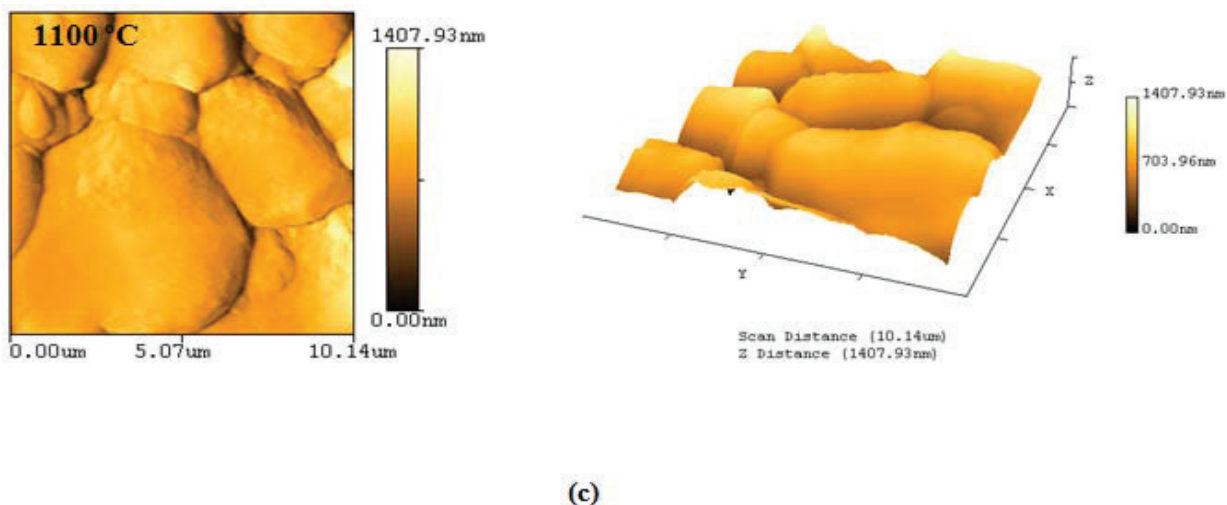**(c)**

(c)

Fig. 1. AFM topographical images left and right 3D of PZT-CCT doped with P_2O_5: a) 4 Wt. %, b) 6 Wt. % and c) 8 Wt. % sintered at 1000, 1050 and 1100 ° C.

From these images, we see that the average grain size increases with increasing sintering temperature which is characteristic of a ceramic material. Until that it reaches maximum values at a sintering temperature of 1050 °C for all the samples a, b and c. Then this size decreases slightly to 1100 ºC (Table 1). This evolution can be explained, by the coalescence of these nodules and better crystallization, which is generally, accompanied by enlargement of the grain size with increasing sintering temperature. All the samples showed an intergranular fracture mechanism indicating that the grain boundaries are mechanically weaker than the grains. The values of measured grain size for all samples (a, b and c) sintered at 1000, 1050 and 1100 °C are listed in Table 1.

Table 1. Evolution of the average grain size of PZT-CCT doped by P_2O_5: 4 Wt.% b) 6 Wt.% c) 8 Wt.% depending on the sintering temperature.

Sample	1000 °C		1050 °C		1100 °C	
A	2,24	(µm)	2,80	(µm)	2,51	(µm)
B	2,10	(µm)	2,71	(µm)	2,26	(µm)
C	2,17	(µm)	2,64	(µm)	2,36	(µm)

From this table, the simple doped with 4 Wt. % of P_2O_5 and sintered at temperature of 1050 ° C become much denser (has better crystallization).

The topographical images (Fig. 1), show the evolution of the average roughness (Rms) depending on the composition: the roughness of samples sintered at 1000 ° C increases from 176.9788 nm for the sample doped with 4 Wt.% P_2O_5 up to 252.7602 nm for the sample doped with 6 Wt.% P_2O_5 , then a slight decrease to reaches a value of 240.51 nm for the sample doped with 8 Wt.% P_2O_5. For the samples sintered at 1050 °C , the roughness changes from 147.22 nm for the sample doped with 4 Wt.% of P_2O_5 up to 164.54 nm for the sample doped with 6 Wt.% P_2O_5 , then a slight decrease to a value of 208.07 nm for the sample doped with 8 Wt.% P_2O_5. The samples sintered at 1100 °C , their roughness increases from 205.212 nm for the sample doped with 4 Wt.% P_2O_5 up to 402.7422 nm for the sample doped with 6 Wt.% , then a slight decrease to reach a value of 361.145 nm for the sample doped with 8 Wt. % P_2O_5. AFM observations shows that the roughness varies slightly as a function of sintering temperature for

the sample doped with 4 Wt.% P_2O_5 , it reaches a minimum value of 164.54 nm at 1050 ° C, which is consistent with the increase of the densification of specimens (the crystallization has reached its limits).

3.2. Dielectrics properties

3.2.1. Variation of ε_r as a function of frequency

Fig. 2 show the variation of dielectric permittivity (ε_r) of all the samples sintered at different sintering temperatures (1000, 1050, 1100, 1150 and 1180 ° C) with frequency at room temperature.
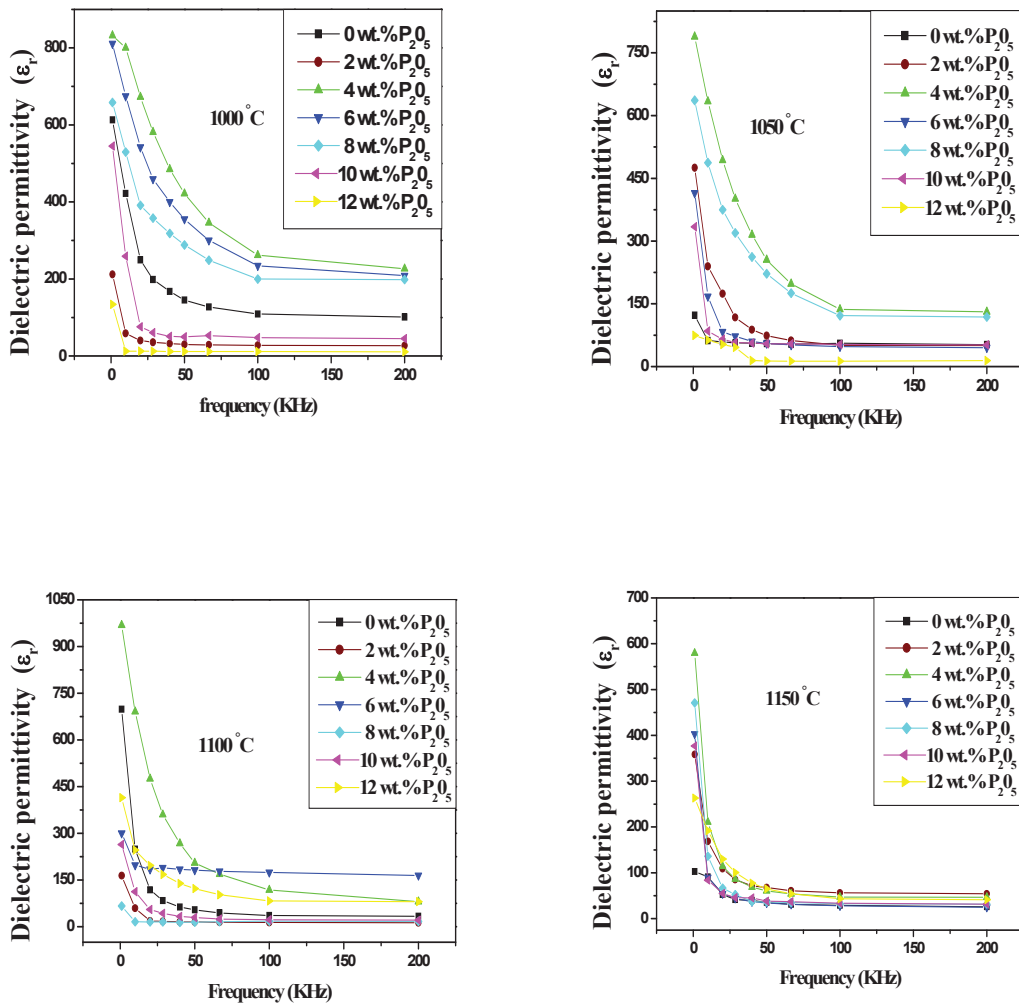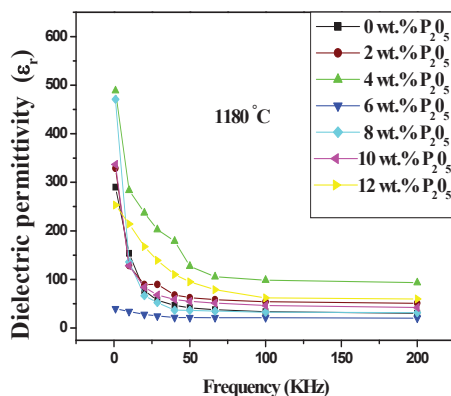
Fig. 2. Variation of dielectric permittivity as a function of frequency for all samples with different sintering temperatures.

It may be noted that in all samples, there is an increase in the dielectric constant with decreasing frequency, which is a typical characteristic of normal dielectric [14]. The decrease in dielectric constant arises from the fact that polarization does not occurs instantaneously with the application of the electric field because of inertia. The delay in response to wards the impressed alternating electric field leads to loss and decline in dielectric constant. At low frequencies, all the polarizations contribute. As frequency is increased, those with large relaxation times cease to respond and hence the decrease in dielectric constant [16, 20]. From these results, we can consider the PZT-CCT ceramic doped with P_2O_5 as a soft ceramic (depolarizes easily) and it can be used at high frequencies in transmission technology.

4. Conclusion

The crystal structure, microstructure, and dielectrics properties of the $Pb_{0.98}Ca_{0.02}$ $[(Zr_{0.52}Ti_{0.48})_{0.98}(Cr^{3+}_{0.5}, Ta^{5+}_{0.5})_{0,02}]_{1-x}P_x$ O_3 (x ranged from 0.01 to 0.12) ceramics have been investigated. The crystal structure and microstructure varied with the increase of P_2O_5 content. It has been found that the sample doped with 4 Wt. P_2O_5 and sintered at 1050 °C for 4 h exhibiting better homogeneity and formation of pure perovskite structure. Coincidentally, the P_2O_5 addition gave rise to a lower lead loss, and the dielectric constant increase with decreasing frequency, so we can consider the PZT-CCT ceramic doped with P_2O_5 as a soft ceramic (depolarizes easily). This investigation may be useful in the fabrication of electronic/electrical devices which used in transmission technology.

References

[1] R.C. Pohanka and P.L. Smith, in: L.M. Levinson (Ed.), Electronic Ceramics, Marcel Dekker, New York, 1988, p. 45.
[2] A.J. Moulson and J. M. Herbert, Electroceramics: Materials, Properties, Applications, Chapman & Hall, London, 1990, p. 265, 281.
[3] B. Jaffe, W. R. Cook and H. Jaffe, Piezoelectric Ceramics, Academic Press, New York, 1971, p. 148.
[4] A. Mansingh, Ferroelectrics, Vol. 102, 1990, p. 69.
[5] B. Jaffe, W.R. Crook, H. Jaffe, Piezoelectric Ceramics, Academic Press, New York, 1971.
[6] C. Prakash, O.P. Thakur and Pran Kishan, Improvement in material figure of merit of PLZT by samarium substitution, Ferroelectrics 263 2001, p.61–66.
[7] O.P. Thakur, C. Prakash and A.R. James, Enhanced dielectric properties. Ceramics through improved processing, J. Alloys Compd. 470 2009, p. 548, 551.
[8] P. Novak, J. Kunes, L. Chaput and W.E. Pickett, Exact exchange for correlated electrons, Phys. Stat. Sol. B 243, 2006, p. 563,572.
[9] T. B. Weston, A. H. Webster and V. M. Mcnamara, J. Am. Ceram. Soc., Vol. 54, 1969, p. 253.

[10] N. Uchida and T. Ikeda, Jap. J. Appl. Phys., Vol. 6, 1967, p. 1292.

[11] TB. Weston, AH. Webster and VM. Mcnamara., J. Am. Ceram. Soc., 1969; 52:253–7.

[12]L. Jin, Z. He and D. Damjanovic, Appl. Phys. Lett., 2009, 95:012905.

[13] CY. Chen and HL. Lin, Ceram. Int., 2004; 30:2075–9.

[14] P. Winotai, N. Udomkan and S. Meejoo, Sensor Actuators Phys., Vol. 122, 2005, p. 257.

[15] D. Wang , M. Cao and S. Zhang, Investigation of ternary system Pb(Sn,Ti)O3–Pb(Mg1/3Nb2/3)O3 with morphotropic phase boundary compositions, Journal of European ceramic society, Vol 32, 2012, p.441, 448.

[16] G. Schmidt, Ferroelectrics, Vol. 78, Issue 1, 1988, p.199, 206.

[17] C. G. Koops, On the Dispersion of Resistivity and Dielectric Constant of Some Semiconductors at Audiofrequencies, Phys. Rev. 83, 1951, p. 121, 124.

[18] L. E. Cross, Relaxor Ferroelectrics, Vol. 76, Issue 1, 1987, p. 241.

[19]Z. He, J. Ma, R. Zhang and T. Li, PZT-based materials with bilayered structure: preparation and ferroelectric properties, J. Eur. Ceram, Soc., Vol. 23, (2003), 1943-1947.

[20]Y. Xu, Ferroelectric materials and their applications, North-Holland, Amsterdam, (1991).