Scientific
Research

Synthesis and Dielectric Properties of (0.80 − x)Pb(Cr$_{1/5}$,Ni$_{1/5}$,Sb$_{3/5}$)O$_3$-xPbTiO$_3$-0.20PbZrO$_3$ Ferroelectric Ceramics

Abdelhek Meklid[1*], Ahmed Boutarfaia[1,2], Zelikha Necira[1], Hayet Menasra[1], Malika Abba[1]

[1]Laboratory of Applied Chemistry, Materials Science Department, Mohamed Kheider University of Biskra, Biskra, Algeria; [2]University of Ouargla, Ouargla, Algeria.
Email: *abdelhek.meklid@yahoo.fr, aboutarfaia@yahoo.fr

ABSTRACT

Perovskite PZT variants were synthesized from stoichiometric oxide ratios of Pb, Zr, Ti, Cr, Ni and Sb. The oxide powders were mixed mechanically and calcinated, and then sintered to form the desired perovskite phase. The detailed structural and ferroelectric properties were carried out for sintered specimens. The results of X-ray diffraction showed that all the ceramics specimens have a perovskite phase. The multi-component ceramic system consists of the (0.80 − x)Pb(Cr$_{1/5}$,Ni$_{1/5}$,Sb$_{3/5}$)O$_3$-xPbTiO$_3$-0.20PbZrO$_3$ (PZT-CNS), with $0.30 \leq x \leq 0.42$, and the ternary system near the rhombohedral/tetragonal morphotropic phase boundary(MPB) was investigated by X-ray diffraction and dielectric properties. In the present system, the MPB that coexists with the tetragonal and rhombohedral phases is a narrow composition region of x = 0.38 - 0.42. The scanning Electron Microscopy (SEM) showed an increase of the mean grain size when the sintering temperature was increased. A sintered density of 92.93% of the theoretical density was obtained for Ti = 42% after sintering at 1180˚C. Ceramics sintered at 1180˚C with Ti = 42% achieve excellent dielectric properties, which are as follows ε$_r$ = 4262.48, and Tc = 340˚C.

Keywords: PZT; Calcination; Dielectric Properties; MPB; Ceramic; X-Ray Methods

1. Introduction

Lead zirconate titanate (PZT) with the perovskite structure is the most popular ferroelectric material, which plays a remarkable role in modern electroceramic industry [1]. Moreover, PZT has high dielectric constant, high electromechanical coupling and high piezoelectric coefficient and has been employed as sensors, actuators and transducers [2-6]. The PZT are often modified by the introduction of the doping agents into the sites A or/and in the sites B of perovskite ABO$_3$ structure. The principal role of the doping agents is generally the improvement of the physical and mechanical properties of these materials. Substitutions in the crystal lattice called doping are often led with the aim to improve the specific properties of the PZT or sometimes to adapt them to specific applications. These properties are generally improved by the additions of one or more cations which will replace Pb^{2+} in site A and/or couple (Zr^{4+}/Ti^{4+}) in

site B of perovskite structure (ABO$_3$) [7]. The selection of dopants or substitutions to tailor some physical properties of PZT was based on many factors which are the following: 1) charge neutrality, 2) tolerance factors, 3) ionic radius, and 4) solubility/miscibility. However, the sintering of PZT at high temperatures gives rise to a lead loss, which drastically degrades the device performance. Generally, a lead loss at high temperatures can be prevented by atmosphere controlled sintering of PZT. However, such composition requires sintering at a high temperature (>1250˚C) in a controlled atmosphere to contain lead volatilization so as to avoid a shift in composition. To get around the problem, different sintering aids have been tried by various workers [8-10]. However, for practical applications, such sintering aids need proper selection so that the electrical and piezoelectric properties of the ceramics do not degrade. The width and the properties of the coexistence region are associated with the occurrence of the compositional fluctuation of Ti^{4+} and Zr^{4+}

*Corresponding author.

ions in the PZT materials [11]. The compositional fluctuation, which is due to a non-uniform distribution of Titanium and Zirconium ions, leads to a broad variation in the dielectric constant accompanied with a Titanium concentration in the MPB region [12]. The width of this coexistence region and the structure of the PZT ceramics were greatly affected by the firing time and temperature [13].

In this study, $(0.80 - x)Pb(Cr_{1/5},Ni_{1/5},Sb_{3/5})O_3$-$xPbTiO_3$-$0.20PbZrO_3$ piezoelectric ceramics were investigated near the MPB by varying the ratio of Zr/Ti. The purpose of this work was to study the phase structure, the dielectric, and the piezoelectric properties of these ceramics near the MPB in detail.

2. Experimental Procedure

The compositions used for the present study were $(0.80 - x)Pb(Cr_{1/5},Ni_{1/5},Sb_{3/5})O_3$-$xPbTiO_3$-$0.20PbZrO_3$ with x varying as 30, 33, 36, 39 and 42 wt% respectively. The samples were prepared by a conventional oxide mixing technique. The starting materials were Pb_3O_4 (99.90%), ZrO_2 (99.90%), TiO_2 (99.90%), Cr_2O_3 (99.6%), Sb_2O_3 (99.90%) and NiO (99.6%).

Raw materials were mixed in acetone medium by using a magnetic stirrer during two hours. The obtained paste is being dried at 80°C in a drying oven for two hours, and then crushed in a mortar out of glass during six hours. After crushing, the obtained powder is compacted in a form of pastilles with a pressure of 300 kg/cm². Then, a preliminary calcination with 800°C is carried out during two hours with a heating rate of 2°C/mn. The calcined mixture is crushed for a second time during four hours, and then was quickly crushed in a form of pellets with a pressure of 1000 kg/cm². These pellets are agglomerated at various temperatures of sintering (1100°C, 1150°C, 1180°C, and 1200°C) during two hours. It is important to note that a lead loss is possible by evaporation of PbO which is very volatile in T ≥ 900°C. To limit this effect; an atmosphere rich in PbO was maintained with the powder of $PbZrO_3$ to the minimum to reduce this loss during sintering. The pastilles are metalized by using a thin layer of silver paste on the two faces.

X-ray diffraction (XRD, Siemens D500) was used to determine the crystalline phases present in the powder. The compositions of the PZT phases were identified by the analysis of the peaks [(002)T, (200)R, (200)T] in the 2θ range 43° - 46°. The tetragonal (T), rhombohedral (R) and tetragonal-rhombohedral phases were characterized and their lattice parameters were calculated. The rhombohedral lattice parameter was calculated on the assumption that the rhombohedral distortion was constant (unit cell angle α_R = 89.9°) [14,15]. In order to ensure an ac-

curate determination of the lattice parameters, the X-ray peaks were recorded gradually with 0.01° steps.

Electronic micrographs scanning (SEM) were taken from fractured as well as chemically etched surfaces. A section of the sintered sample was etched in a 5% HCl solution for 3 minutes. 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. To investigate the electrical properties, the electrodes were made by applying a silver paste on the two major faces of the sintered disks followed by a heat treatment at 750°C for thirty minutes. The dielectric constant ε was calculated from the capacitance at a frequency of one kHz. It was measured at temperatures ranging from 25°C to 450°C with a heating rate of one °C/minute by using an impedance analyzer (HP 4192A, Hewlett-Packard).

3. Results and Discussion

3.1. Phase Analysis and Microstructure

Sintered powders were examined by X-ray diffractometry to ensure phase purity, and to identify the crystal structure. The coexistence of tetragonal and rhombohedral phases near the morphotropic phase boundary implies the existence of compositional fluctuations which can be determined from the width of the X-ray diffraction peaks. However, determination of the compositional fluctuation for samples near the morphotropic phase boundary is difficult. XRD patterns of PZT powders were analyzed for detecting the characteristic rhombohedral and tetragonal splittings. The (2 0 0) reflections form a doublet in the tetragonal phase while (1 1 1) is a singlet. For the rhombohedral phase, (1 1 1) is a doublet while the (2 0 0) is a singlet. The powder X-ray patterns of $(0.80 - x)Pb(Cr_{1/5},Ni_{1/5},Sb_{3/5})O_3$-$xPbTiO_3$-$0.20PbZrO_3$ ceramics with different x values are shown in **Figure 1**. For x in the range of 0.39 - 0.42, the diagram indicates that a mixture of phases should be present, which is illustrated by the (0 0 2) and (2 0 0) tetragonal doublet enclosing the (2 0 0) rhombohedral line. For x in the range of 0.30 - 0.36 there is a little evidence of the (2 0 0) R peak, indicating a virtually single-phase tetragonal structure. It is evident from "**Figure 1**" that as the Ti content increases, the morphotropic phase becomes more prominent whereas the tetragonal decreases.

Figure 2(a) shows the variation of density with sintering temperature. The density increases in the initial period with sintering temperature and saturates beyond 1180°C. From these results, the optimum firing temperature for the maximum density, ρ, of the ceramic is be-
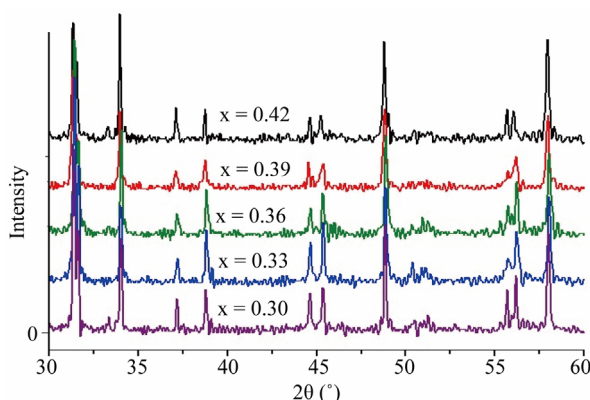
Figure 1. X-ray diffraction patterns of $(0.80 − x)Pb(Cr_{1/5},Ni_{1/5},Sb_{3/5})O_3-xPbTiO_3-0.20PbZrO_3$ ceramics sintered at 1180°C for 2 h with $0.30 \leq x \leq 0.42$.
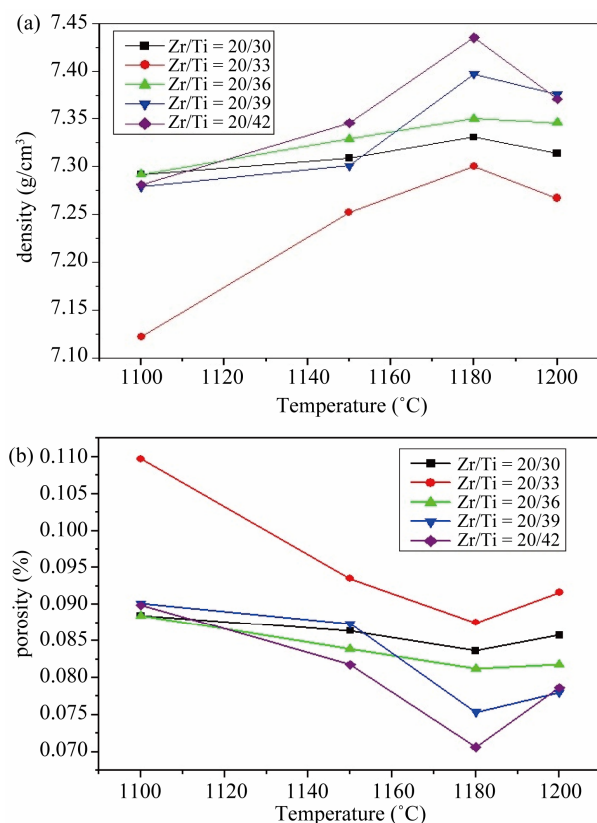

Figure 2. Density and porosity versus sintering temperature of PZT-CNS ceramics (sintering time 2 h).

tween 1150 and 1200°C. At 1180°C and Ti = 42%, 92.93% of the theoretical value was achieved. Sintering at 1200°C caused the density to decrease. The optimum value of the sintering temperature was affected by the additions of impurities and other processing parameters, such as the rate of heating, time of thermal treatment, and composition of the protecting atmosphere. The optimum sintering temperature was taken as the point when the PbO vapor pressure evaporation-recondensation equilib-

rium for the reaction: PbO-PbO (vapor)-Pb(vapor) + 1/2 O_2 was established [16]. Increase of the porosity for temperatures higher than the optimum can, therefore, be attributed to a greater rate of evaporation of PbO compared to that recondensed. Additions of different oxides to PZT-type ceramics influence the densification and the grain size. The process involves a decrease in the number and size of the pores together with an increase in the grain sizes. The porosity, determined by means of the image analyzer as a function of sintering temperature, is given in **Figure 2(b)**.

Figure 3 shows the lattice constant at room temperature as function of x. It can be seen that the tetragonal lattice parameter a_T increases linearly with increasing x, while the c_T parameter decreases linearly to a smaller extent. In all the composition range where the tetragonal phase is present, c_T and a_T are closing to gather a_T when Ti content increases, particularly inside the co-existence region, meaning that the structure is approaching the cubic geometry. The rhombohedral lattice parameter aR appears to oscillate between 4.023 and 4.024 Å. According to these results, we find that there is a region where the two phases tetragonal (T) and rhombohedral (R) co-exist. This region is detected for compositions: Ti = 39%, Ti = 42%. As against the compositions correspond to Ti $\leq$ 36%, show that the material obtained is of tetragonal structure. The influence of the substitution of Zr/Ti ratio on the structure of the parameters can be explained by the difference between the ionic rays of Zr and Ti (0.68 and 0.79 Å, respectively). This cannot provide a total homogeneity in the solid solutions containing both tetragonal and rhombohedral phases.

Figures 4(a)-(c) shows the SEM images of PZTCNS (20/36), PZTCNS (20/39) and PZTCNS (20/42) ceramics sintered at 1180°C. All the sintered ceramics appear to be very dense and of a homogeneous granular structure. At first sight, the three compositions seem homogeneous and there do not seem to be grains of the pyrochlore
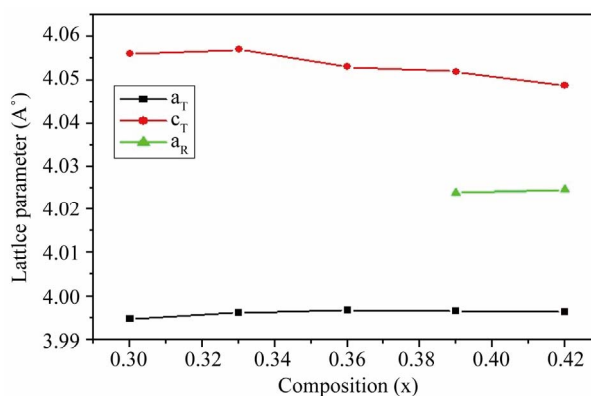
Figure 3. Variation of the unit cell dimensions as a function of composition (Ti%).

(a)

(b)

(c)
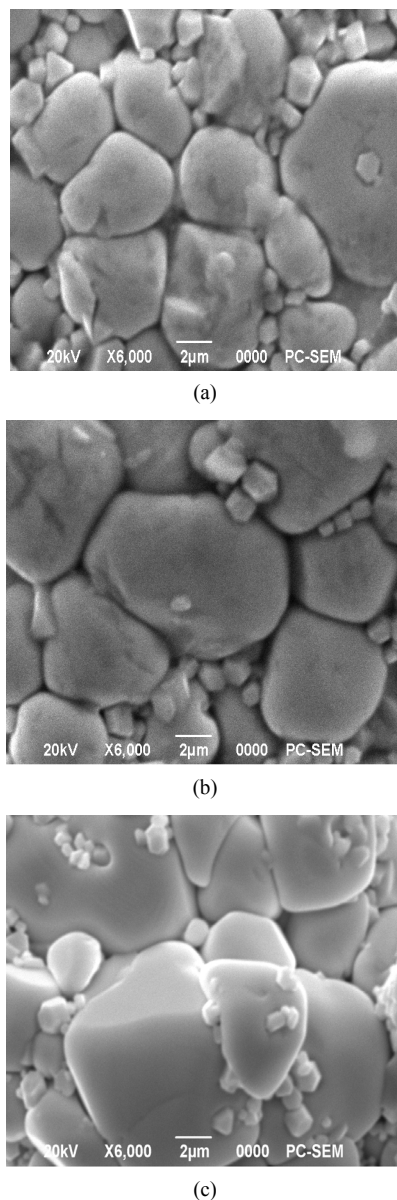
Figure 4. Microstructure of (0.80 − x)Pb(Cr$_{1/5}$,Ni$_{1/5}$,Sb$_{3/5}$)O$_3$-xPbTiO$_3$-0.20PbZrO$_3$ ceramics sintered at 1180°C for 2 h, (a) Ti = 36; (b) Ti = 39; (c) Ti = 42.

phase which are identifiable by their pyramidal form. The ruptures with the grain boundaries are synonymous with a good sintering. It is noticed that the average diameter of the grains increases significantly with increasing TiO$_2$. The intermediate size of the grains is 1.842 μm for the sample "**Figure 4(a)**" with Ti = 36%. For cons, the intermediate size of sample "**Figure 4(b)**" of the grains is larger (2.283 μm). In the case of ceramics "**Figure 4(c)**" with Ti = 42%, the intermediate size of the grains is larger than that of "**Figure 4(a)**" and "**Figure 4(b)**" (of the order 2.521 μm); and the broader the granulo-metric distribution "**Figure 4(c)**", the more the size of the grains gets bigger [17].

3.2. Dielectric Properties

Figure 5 shows the variation of the dielectric constant as a function: of composition and of temperature at sintering temperatures 1100°C, 1150°C and 1180°C. For the three temperatures of sintering 1100°C, 1150°C and 1180°C, observed that the permittivity increases gradually with the increase in the composition of x and takes a maximum of 290,15 for the sample with Ti = 42% included in the morphotropic phase boundary (MPB) at the temperature 1180°C. This maximum of dielectric activity can be explained by the presence of several directions of spontaneous polarization relating to the existence of the two structures rhombohedral and tetragonal. Sample No. 4 (20/39/41) at the sintering temperature of 1180°C has an exception in the evolution of ε_r (T). The dielectric constant increases continuously as a function of temperature, so this sample does not have a Curie temperature to a temperature between (0, 450°C) [18,19].

4. Conclusion

The compounds of the solution solid zirconate-titanate lead, noted PZT, general formula (0.80 − x)Pb (Cr$_{1/5}$,Ni$_{1/5}$,Sb$_{3/5}$)O$_3$-xPbTiO$_3$-0.20PbZrO$_3$ as x varies from 0.30 to 0.42 by setup of 0.03, and it has been prepared from a mixture of oxides by the method ceramics. The
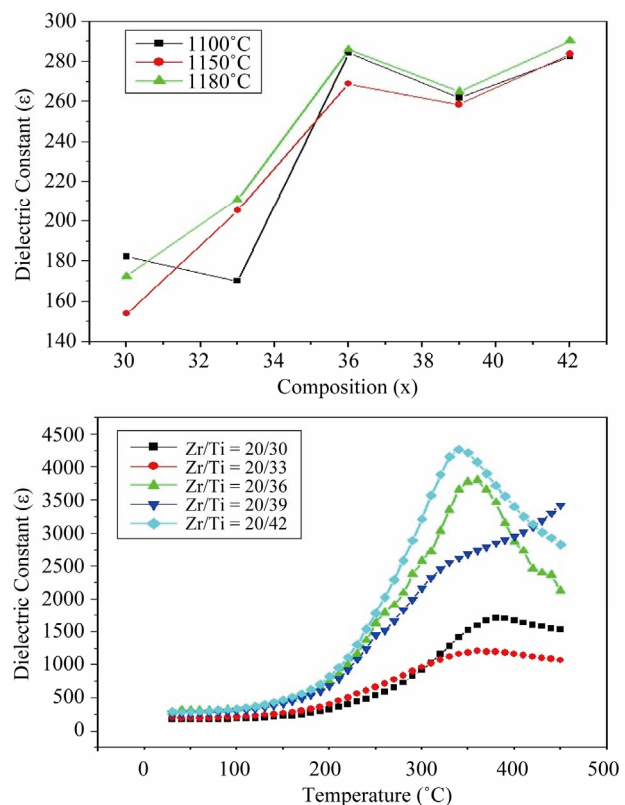
Figure 5. Dielectric constant (ε) according to the variation of x (Ti) in the composition and temperature.

effect of sintering temperature on density and porosity was studied to achieve the optimum sintering temperature corresponding to the maximum density and minimum value of porosity, because this temperature (1180°C) corresponds to a better quality product. The parameters of the lattice: a_T and c_T of the tetragonal structure and a_R of the rhombohedral structure were found to change when composition is modified. The $0.20PbZrO_3$-$0.42PbTiO_3$-$0.38Pb(Cr_{1/5},Ni_{1/5},Sb_{3/5})O_3$ ceramics sintered at 1180°C exhibit good Dielectric properties at the new MPB $\varepsilon_r = 4262.48$, and $Tc = 340°C$.

REFERENCES

[1] Z. He, J. Ma and R. Z. Hang, "Investigation on the Microstructure and Ferroelectric Properties of Porous PZT Ceramics," *Ceramics International*, Vol. 30, No. 7, 2004, pp. 1353-1356.
http://dx.doi.org/10.1016/j.ceramint.2003.12.108

[2] R. E. Newnham and A. Amin, "Smart Systems: Microphones, Fish Farming, and Beyond-Smart Materials, Acting as Both Sensors and Actuators, Can Mimic Biological Behavior," *Chemtech*, Vol. 29, No. 12, 1999, pp. 38-47.

[3] K. Uchino, "Materials Issues in Design and Performance of Piezoelectric Actuators: An Overview," *Acta Materialia*, Vol. 46, No. 11, 1998, pp. 3745-3753.
http://dx.doi.org/10.1016/S1359-6454(98)00102-5

[4] R. Ranjan, R. Kumar, B. Behera and R. N. P. Choudhary, "Effect of Sm on Structural, Dielectric and Conductivity Properties of PZT Ceramics," *Materials Chemistry and Physics*, Vol. 115, No. 1, 2009, pp. 473-477.
http://dx.doi.org/10.1016/j.matchemphys.2009.01.017

[5] S. T. Lau, K. W. Kwok, H. L. W. Chan and C. L. Choy, "Piezoelectric Composite Hydrophone Array," *Sensors and Actuators A*: *Physical*, Vol. 96, No. 1 ,2002, pp. 14-20.
http://dx.doi.org/10.1016/S0924-4247(01)00757-9

[6] T. Zeng, X. L. Dong, S. T. Chen and H. Yang, "Processing and Piezoelectric Properties of Porous PZT Ceramics," *Ceramics International*, Vol. 33, No. 3, 2007, pp. 395-399. http://dx.doi.org/10.1016/j.ceramint.2005.09.022

[7] S. S. Chandratreya, R. M. Fulrath and J. A. Y. Pask, "Reaction Mechanisms in the Formation of PZT Solid Solutions," *Journal American Ceramic Society*, Vol. 64, No. 7, 1981, pp. 422-425.
http://dx.doi.org/10.1111/j.1151-2916.1981.tb09883.x

[8] S. Y. Cheng, S. L. Fu, C. C. Wei and G. M. Ke, "The Properties Low-Temperature Fixed Piezoelectric Ceramics," *Journal of Materials Science*, Vol. 21, No. 2, 1986, pp. 571-576. http://dx.doi.org/10.1007/BF01145525

[9] H. G. Lee, J. H. Choi and E. S. Kim, " Low-Temperature Sintering and Electrical Properties of $(1-x)Pb(Zr_{0.5}Ti_{0.5})$-$O_3$-$xPb(Cu_{0.33}Nb_{0.67})O_3$ Ceramics," *Journal of Electro-ceramics*, Vol. 17, No. 2-4, 2006, pp. 1035-1040.
http://dx.doi.org/10.1007/s10832-006-0384-1

[10] R. Mazumder, A. Sen and H. S. Maiti, "Impedance and Piezoelectric Constants of Phosphorous-Incorporated Pb-$(Zr_{0.52}Ti_{0.48})O_3$ Ceramics," *Materials Letters*, Vol. 58, No. 25, 2004, pp. 3201-3205.
http://dx.doi.org/10.1016/j.matlet.2004.06.011

[11] A. V. Turik, M. F. Kupriyanov, E. N. Sidorenko and S. M. Zaitsev, "Behavior of Piezoceramics of Type $Pb(Zr,Ti)O_3$, near the Region of the Morphotropic Transition," *Soviet Physics-Technical Physics*, Vol. 25, No. 10, 1980, pp. 1251-1254.

[12] K. Kakegawa, J. Mohri, T. Takahashi, H. Yamamura and S. Shirasaki, "A Compositional Fluctuation and Properties of $Pb(Zr, Ti)O_3$," *Solid State Communications*, Vol. 24, No. 11, 1977, pp. 769-772.
http://dx.doi.org/10.1016/0038-1098(77)91186-3

[13] S. A. Mabud, "The Morphotropic Phase Boundary in PZT Solid Solution," *Journal of Applied Crystallographic*, Vol. 13, 1980, pp. 211-216.
http://dx.doi.org/10.1107/S0021889880011958

[14] P. Ari-Gur and L. Benguigui, "X-Ray Study of the PZT Solid Solutions near the Morphotropic Phase Transition," *Solid State Communications*, Vol. 15, No. 6, 1974, pp. 1077-1079.
http://dx.doi.org/10.1016/0038-1098(74)90535-3

[15] A. Boutarfaia and S. E. Bouaoud, "Tetragonal and Rhombohedral Phase Co-Existence in the System: $PbZrO_3$-$PbTiO_3$-$Pb(Fe_{1/5}, Ni_{1/5},Sb_{3/5})O_3$," *Ceramics International*, Vol. 22, No. 4, 1996, pp. 281-286.
http://dx.doi.org/10.1016/0272-8842(95)00102-6

[16] R. B. Atkin and R. M. Fulrath, "Point Defects and Sintering of Lead Zirconate-Titanate," *Journal of American Ceramic Society*, Vol. 54, No. 5, 1971, pp. 265-270.
http://dx.doi.org/10.1111/j.1151-2916.1971.tb12286.x

[17] O. Ohtaka, R. Von Der Mühll and J. Ravez, "Low-Temperature Sintering of $Pb(Zr,Ti)O_3$ Ceramics with the Aid of Oxyfluoride Additive: X-Ray Diffraction and Dielectric Studies," *Journal American Ceramic Society*, Vol. 78, No. 3, 1995, pp. 805-808.
http://dx.doi.org/10.1111/j.1151-2916.1995.tb08251.x

[18] H. R. Rukmini, R. N. P. Choudhary and D. L. Prabhakara, "Sintering Temperature Dependent Ferroelectric Phase Transition of $Pb_{0.91}(La_{1-z/3}Liz)_{0.09}(Zr_{0.65}Ti_{0.35})_{0.9775}O_3$," *Journal of Physics and Chemistry of Solids*, Vol. 61, No. 11, 2000, pp. 1735-1743.
http://dx.doi.org/10.1016/S0022-3697(00)00040-8

[19] W. Chaisan, R. Yimnirun, S. Ananta and D. P. Cann, "Phase Development and Dielectric Properties of $(1-x)Pb(Zr_{0.52}Ti_{0.48})O_3$-$xBaTiO_3$ Ceramics," *Materials Science and Engineering B*, Vol. 132, No. 3, 2006, pp. 300-306.
http://dx.doi.org/10.1016/j.mseb.2006.04.033