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The Structure and the Electrical Properties of $Pb_{0.95}La_{0.05}[Zr_xTi_{(0.95-x)}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$ Ferroelectric Ceramics

Malika Abba[1], **Ahmed Boutarfaia**[1,2*]

[1]Laboratoire de Chimie Appliquée, Université de Biskra, RP-Biskra, Algérie; [2]Département de Sciences de la Matière, Université de Ouargla, RP-Ouargla, Algérie.
Email: *aboutarfaia@yahoo.fr

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ABSTRACT

The structural, the dielectric, and the piezoelectric properties of new ferroelectric $Pb_{0.95}La_{0.05}[Zr_x,Ti_{(0.95-x)}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$ $(0.46 \le x \le 0.55)$ *ceramics have been investigated. All the samples were being sintered at a temperature ranging from* 1000 *to* 1180 °*C after being compacted in circular discs. 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 phase structure of* $Pb_{0.95}La_{0.05}[Zr_xTi_{(0.95-x)}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$ *ceramics was transformed from the tetragonal to the rhombohedral, with an increase in the ratio of Zr/Ti in system. In the present system the MPB that coexists with the tetragonal and rhombohedral phases is a narrow composition region of* $x = 0.50 - 0.51$. *The scanning Electron Microscopy (SEM) showed an increase of the mean grain size when the sintering temperature was increased. The dielectric constant* ε *and the coupling factor* K_p *reached the maximum values, while the mechanical quality factor* Q_m *and the loss tangent reached the lowest values when* $x = 0.50$. *For the composition where* $x = 0.50$, *these properties include* $\varepsilon = 5414$ *(at the Curie temperature),* $tang\delta = 0.039$, $K_p = 0.67$, $Q_m = 20$ *and a Curie temperature of* 335 °*C.*

Keywords: *MPB, Sintering, Piezoelectric, Dielectric, Zr/Ti Ratio, Ceramic*

1. Introduction

The lead zirconate titanate materials $Pb(Zr_xTi_{1-x})O_3$ (PZT) of a perovskite-type represented by the formula ABO_3, have been extensively used for the piezoelectric applications such as capacitors, sensors, actuators and other high piezoelectric devices. In the PZT materials, the dielectric, the ferroelectric, and the electromechanical characteristics have been modified when several substitutions were being done on the A- or/and B-sites, and also by varying the ratio of Zr/Ti [1-6]. Since the discovery of the behavior of the relaxor in $Pb(Mg_{1/3},Nb_{2/3})O_3$ [7], $Pb(Zn_{1/3},Nb_{2/3})O_3$ [8], and $Pb(Ni_{1/3},Nb_{2/3})O_3$ [9], the studies of the ferroelectrics of the relaxor with $Pb(B'_{1/3},B''_{2/3})O_3$–type perovskites have attracted much attention because of their excellent dielectric and electromechanical properties. In a conventionally prepared PZT ceramics with compositions near the morpho-tropic phase boundary (MPB), the tetragonal, and the rhombohedral phases always coexist [9]. The width and the properties of the coexistence region are associated with the occurrence of the compositional fluctuation of Ti^{4+} and Zr^{4+} ions in the PZT materials [10]. 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 Zirconium concentration in the MPB region [11]. The width of this coexistence region and the structure of the PZT ceramics were greatly affected by the firing time and temperature [12]. 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. The substitution of lanthanides and the different doped material at Pb-sites and Zirconium at the Ti-sites with a different ratio of Zr/Ti have produced many solid solutions with interesting properties for wide industrial applications. The understanding of the relationships between the variations in the physical properties and the phase coexistence with a composition is very important because, first, they produce a great influence on the characteristics of the PZT ceramics; and, second, they stabilize the temperature and the time in the region of the phase transition between the tetragonal and the rhombohedral phases.

In this study, $Pb_{0.95}La_{0.05}[Zr_xTi_{(0.95-x)}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$ 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 polycrystalline samples with a general compositional formula $Pb_{1-z}La_z[Zr_xTi_y(Mo_{1/3},In_{2/3})_{1-(x+y)}]_{1-z/4}O_3$ with $z = 0.05$, $(x + y)= 0.95$ and $0.46 \leq x \leq 0.55$ were being prepared by a conventional dry ceramic method to form the solid solution of a composition that follows: $Pb_{0.95}La_{0.05}[Zr_xTi_{(0.95-x)}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$. The reagent grade oxide of PbO, ZrO_2, TiO_2, La_2O_3, MoO_3 and In_2O_3 were used as starting materials in a stoichiometric ratio. The powders were, first, ball-milled for twelve hours; and, then, calcined at 800˚C for two hours at the following heating and cooling rates: 2˚C/min. After calcination, the mixture was, first, ball-milled for twenty-four hours; and then, dried and granulated with PVA as a binder. After drying, the powders were pressed into discs of a diameter of thirteen millimeters and of a thickness of about one millimeter. The compacted discs were being sintered at a temperature ranging from 1000˚C - 1180˚C for two hours in air. To prevent PbO volatilization from the pellets, a PbO atmosphere was controlled with a bed of $PbZrO_3$ powder placed in the vicinity of the pellets.

The X-ray diffraction (XRD, Simens D500) was used to determine the crystalline phases present in the powder. The compositions of PZT phases were identified by the analysis of the peaks [(002)T, (200)R, (200)T] in the twenty range 43˚ - 46˚. The Cu Kα radiation with a step of 0.01˚ was used. The bulk densities of the sintered ceramics were being measured by the Archimedes method. The micrographs of the fractured samples were taken on a JEOL scanning electron microscope. The average grain size of the samples was determined from the micrographs by the linear intercept technique. 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 400˚C with a heating rate of one ˚C/minute by using an impedance analyzer (HP 4192A, Hewlett-Packard). The piezoelectric samples were, first, being poled in a silicone oil bath at 120˚C by applying a d.c. field of thirty kV/cm for thirty minutes; and, then, were being cooled under the same electric field.

They were aged for twenty-four hours before testing. The electromechanical coupling factor K_p, along with the mechanical quality factor Q_m were determined by the resonance and anti-resonance technique from the equations [13]:

$$K_p = \left[\frac{2.51 \times \left(f_a^2 - f_r^2\right)}{2f_a^2}\right]^{1/2}$$

$$Q_m = \left[4\pi \times \left(f_a - f_r\right) \times RC\right]^{-1}$$

where:

f_a: anti-resonant frequency (Hz)

f_r: resonant frequency (Hz)

R: resonant resistance (ohms)

C: *capacity* (*faraday*)

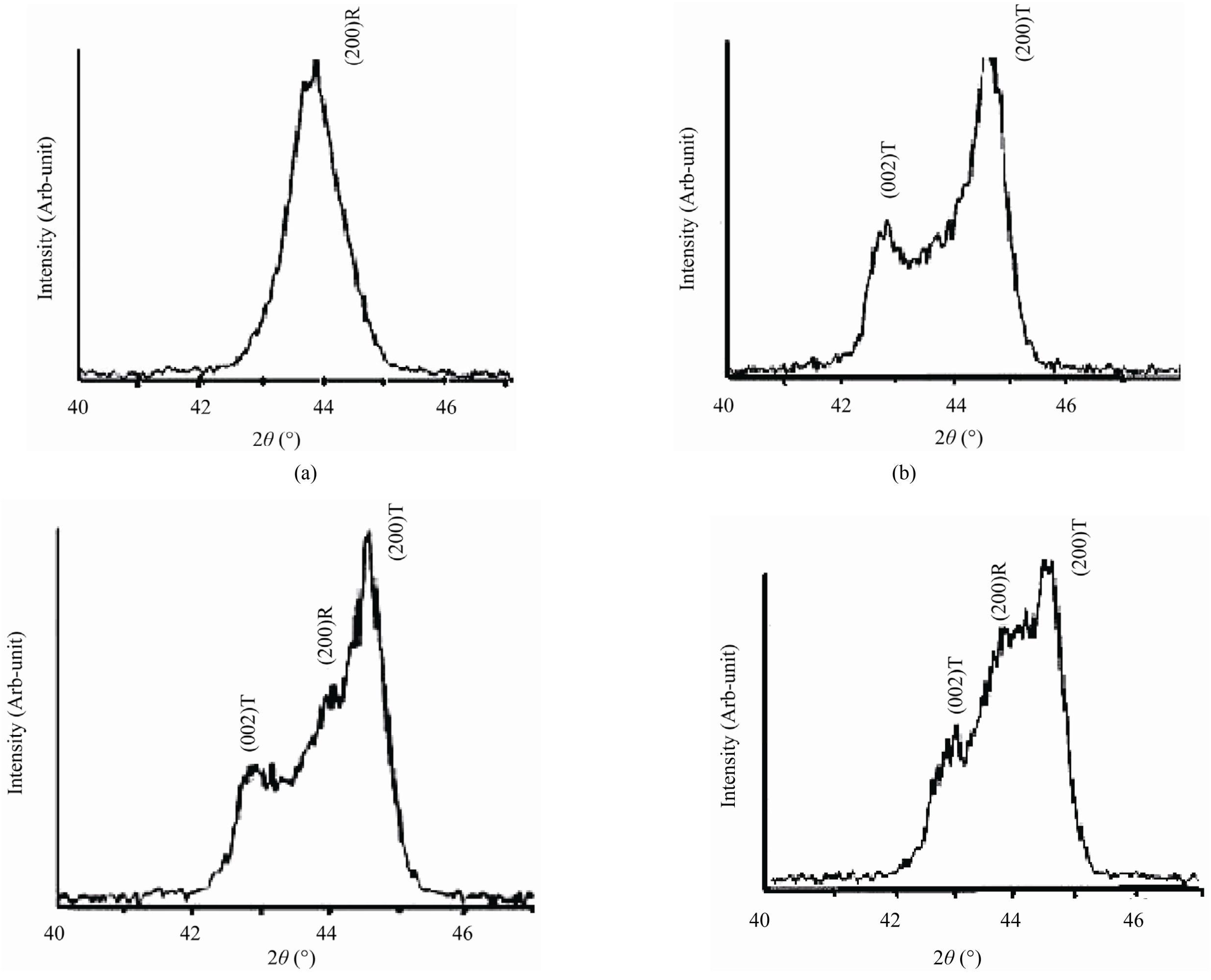
3. Results and Discussion

The analysis of the phase was performed from the XRD (at a room temperature) patterns over a range of $2\theta = 43^\circ$ to 46˚, where the tetragonal phase displays two peaks, $(002)_T$ and $(200)_T$, and the rhombohedral phase displays one peak, $(200)_R$. There was a broad region where the two phases, the rhombohedral and the tetragonal, coexisted. This indicated a typical morpho-tropic phase behavior (MPB). The typical patterns of the X-ray diffraction of $Pb_{0.95}La_{0.05}[Zr_xTi_{(0.95-x)}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$ compositions is shown in **Figure 1**. The samples obtained in this study are summarized in **Table 1**. At 1150˚C, a typical tetragonal phase was observed at a room temperature when $x_T > 0.50$. The $(002)_T$ and $(200)_T$ peaks split into the $(200)_R$ peak as the ratio of Zr/Ti was increased. The rhombohedral phase can be obtained when $x_R < 0.51$. A transition from the tetragonal to the rhombohedral phase was observed as the ratio of Zr/Ti was increased. The Rhombohedral and the tetragonal phases coexisted at $x = 0.50 - 0.51$, and demonstrated that the ceramic resided at the morpho-tropic phase boundary (MPB) [14]. The parameters of the lattice were, then, determined from the triplets (200) by using a non-linear least squares method [15]. The a_R-parameter of the rhombohedral phase and the a_T-parameter, c_T-parameter, and the tetragonality (c_T/a_T) of the tetragonal phase of $Pb_{0.95}La_{0.05}[Zr_x,Ti_{(0.95-x)}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$ ceramics are plotted as a function of the ratio of Zr/Ti in **Figure 2**. The results showed that the parameters of the lattice of the tetragonal phase changed when the ratio of Zr/Ti was modified. While the value of the a_T parameter increased, the one of c_T parameter decreased, and the a_R parameter of the rhombohedral phase increased along

Table 1. Series of compositions and crystal structure.

	Crystal structure			
Sample	**1000˚C**	**1100˚C**	**1150˚C**	**1180˚C**
$Pb_{0.95}La_{0.05}[Zr_{0.46}Ti_{0.49}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$	T	T	-	-
$Pb_{0.95}La_{0.05}[Zr_{0.47}Ti_{0.48}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$	T + R	T	T	-
$Pb_{0.95}La_{0.05}[Zr_{0.49}Ti_{0.46}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$	T + R	T + R	T	T
$Pb_{0.95}La_{0.05}[Zr_{0.50}Ti_{0.45}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$	T + R	T + R	T + R	T + R
$Pb_{0.95}La_{0.05}[Zr_{0.51}Ti_{0.44}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$	T + R	T + R	T + R	T + R
$Pb_{0.95}L_{0.05}[Zr_{0.52}Ti_{0.43}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$	T + R	T + R	R	R
$Pb_{0.95}L_{0.05}[Zr_{0.54}Ti_{0.41}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$	T + R	T + R	R	-
$Pb_{0.95}La_{0.05}[Zr_{0.55}Ti_{0.40}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$	R	R	-	-

T = Tetragonal; R = Rhombohedral; T-R = Tetragonal-Rhombohedral.



(a) (b)

(c) (d)

Figrue 1. XRD patterns of $Pb_{0.95}La_{0.05}[Zr_xTi_{(0.95-x)}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$ ceramics sintered at 1150˚C for 2h: (a) $x = 0.52$, (b) $x = 0.46$, (c) $x = 0.50$ and (d) $x = 0.51$.

with the sintering temperature in the coexistence region. The resulting values of the parameters of the lattice of the tetragonal phase showed that the c_T/a_T axial ratio decreased as a_T increased and c_T decreased. The values of the parameters of the lattice were revealed to be practically the same as those previously studied [16, 17].

Figure 3 shows the SEM micrographs of $Pb_{0.95}La_{0.05}[Zr_{0.50}Ti_{0.45}(Mo_{1/3}, In_{2/3})_{0.05}]_{0.9875}O_3$ ceramics sintered at different temperatures. It can be observed

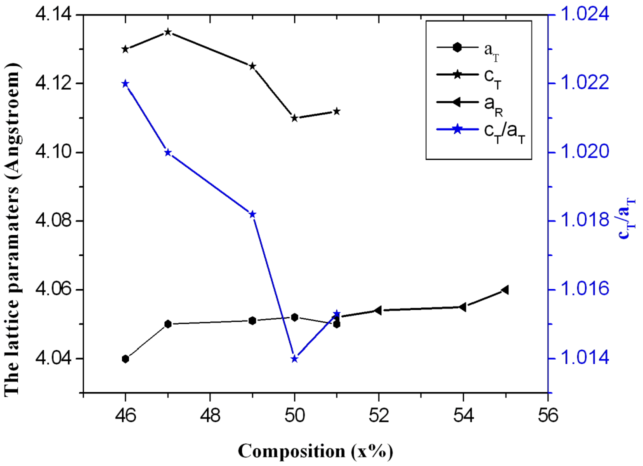


Figure 2. The parameters of the lattice of $Pb_{0.95}La_{0.05}[Zr_xTi_{(0.95-x)}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$ ceramics as a function of composition (for a sintering temperature about 1150˚C) .

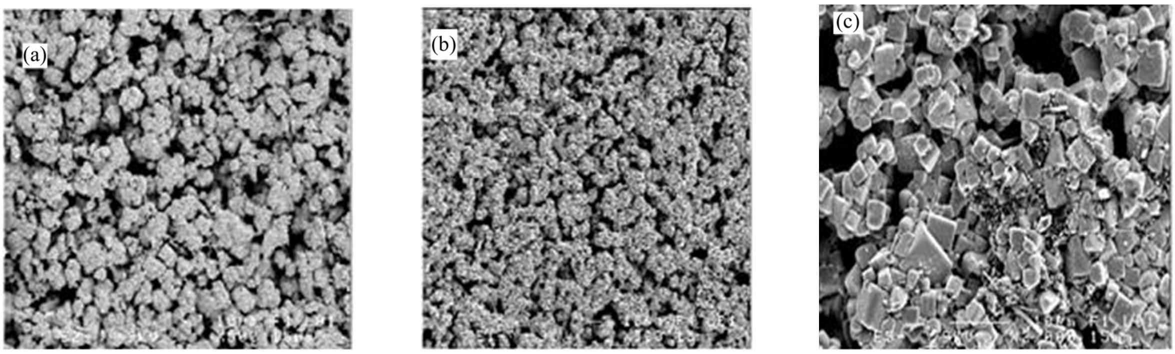


Figure 3. SEM micrographs for $Pb_{0.95}La_{0.05}[Zr_{0.50}Ti_{0.45}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$ ceramics sintered at (a)1000˚C, (b) 1100˚C and (c) 1150˚C.

that many distinct pores exist on the surface of the $Pb_{0.95}La_{0.05}[Zr_{0.50}Ti_{0.45}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$ ceramics sintered at 1000˚C and the average grain size is under 9 µm. When the sintering temperature is increased, the pores can hardly be observed and the grain size is about 9 µm. This indicates that a high sintering temperature promotes a grain growth process. The obtained images show a slight difference in the particle size and also give rise to the different phases, viz. the tetragonal, the rhombohedral, and the tetragonal-rhombohedral. In addition to the morphological modification of grains, different grain sizes could be noticed for these samples. In this way, the coexistence region of the tetragonal-rhombohedral phases was demonstrated.

The values of the room temperature of the dielectric constant (ε) and the dissipation factor (tan δ) at 1 kHz for all samples are given in **Figure 4**. It can be seen that the ε curve appears to be parabolic, and the values of ε increase sharply from 46/49 to 50/45; and, also, large dielectric constants are obtained at the compositions of 50/45 ($\varepsilon = 430$ at 1 kHz) and 51/44 ($\varepsilon = 390$ at 1 kHz). It, then, follows a decreasing trend when the ratio of Zr/Ti is increased further. The present results verify the conclusions about the dielectric constant peak in MPB. The increase in Zr content induces the microstructure transition of $Pb_{0.95}La_{0.05}[Zr_xTi_{(0.95-x)}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$ from the rhombohedral to the tetragonal phase within the MPB region, as indicated by the above XRD investigations. The tanδ shows an inverse trend and reaches the minimum value of 3.9% when $x = 0.50$. Thus the compositions at 50/45 and 51/44 are at the center of the MPB.

Figure 5 reveals the dielectric constant ε as a function of temperature for the $Pb_{0.95}La_{0.05}[Zr_xTi_{(0.95-x)}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$ ceramics ($x = 0.50$ and $x = 0.51$) sintered at 1150˚C, which were measured at a frequency of 1 kHz. As it might be known, two peaks are observed on the dielectric constant versus temperature curves in the measured temperature which ranges between 265˚C and 330˚C for a sample of a ceramic 50/45. The first dielectric peak corresponds to the transition temperature T_{R-T}, of the rhombohedral to the tetragonal phase, but the second peak, which results at a

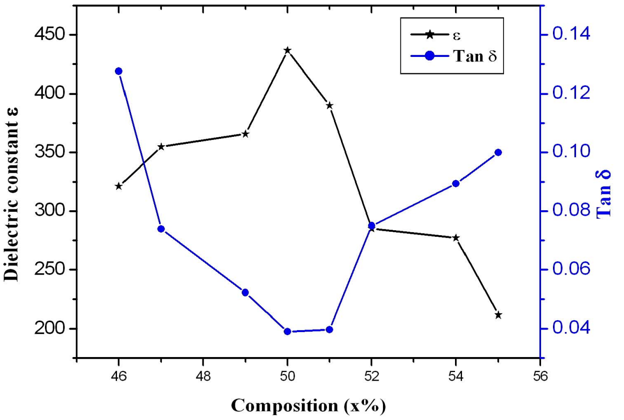


Figure 4.The dielectric constant ε and the loss tangent (at room temperature, 1 KHz) for $Pb_{0.95}La_{0.05}[Zr_x,Ti_{(0.95-x)}(Mo_{1/3}, In_{2/3})_{0.05}]_{0.9875}O_3$ ceramics as a function of composition.

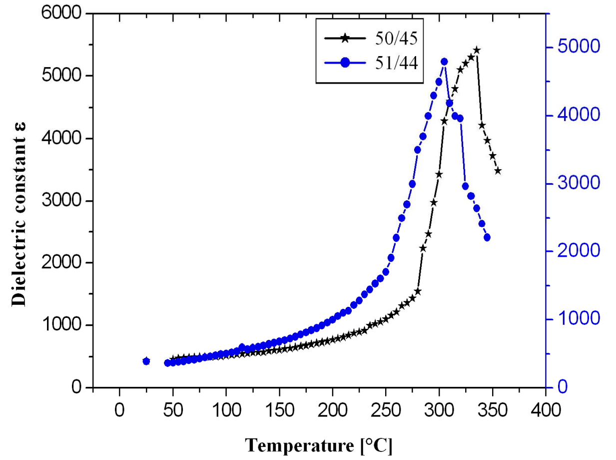


Figure 5. The dielectric constant ε (at 1 KHz) for $Pb_{0.95}La_{0.05}[Zr_xTi_{(0.95-x)}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$ ceramics as a function of temperature.

higher temperature, is the Curie temperature T_c. The broadening in the transition phase is attributed to the structural disorder and the compositional fluctuation present in the arrangement of cation at A-site and B-site with lattice vacancies. This results in a microscopic heterogeneity in the composition and the distribution of different local Curie points [18].

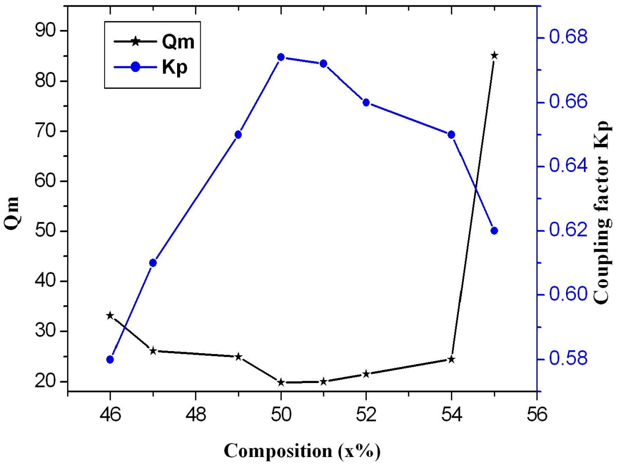


Figure 6. The Coupling factor K_p and Q_m for $Pb_{0.95}La_{0.05}[Zr_xTi(_{0.95-x})(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$ ceramics sintered at 1150˚C as a function of composition (x).

Figure 6 shows the variation of the electromechanical coupling factor K_p and the mechanical quality factor Q_m for $Pb_{0.95}La_{0.05}[Zr_xTi_{(0.95-x)}(Mo_{1/3}, In_{2/3})_{0.05}]_{0.9875}O_3$ ceramics. It is observed in **Figure 6** that as the ratio of Zr/Ti increases, the value of kp increases; and, subsequently, represents a peak of 0.67 at the ratio of Zr/Ti of 50/45; but, when the ratio of Zr/Ti is further increased, the value of K_p decreases. Q_m continues to decrease; and, finally, shows the minimum value when the ratio of Zr/Ti is 50/45 (Q_m = 20). This is due to the fact that the structure of the phase of $Pb_{0.95}La_{0.05}[Zr_xTi_{(0.95-x)}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$ ceramics changes, first, from the tetragonal phase to the coexistence of both the tetragonal and the rhombohedral phases; and, then, changes to a single rhombohedral phase when the ratio of Zr/Ti is increased.

4. Conclusions

The aim of this study was to investigate the structure and the behavior of the electrical properties in $Pb_{0.95}La_{0.05}[Zr_xTi_{(0.95-x)}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$. The phases of the sintered samples were examined by X-ray diffractometry. The structure of the phase of the system was changed from the tetragonal to the rhombohedral as the ratio of Zr/Ti was increased. The XRD results reveal that an MPB with the co-existence of the rhombohedral and the tetragonal for the ceramics lies in the range of x = 0.50 – 0.51. 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 $Pb_{0.95}La_{0.05}[Zr_{50}Ti_{45}(Mo_{1/3},In_{2/3})_{0.05}]_{0.9875}O_3$ ceramics sintered at 1150˚C exhibit good piezoelectric properties: K_p = 0.67, Q_m = 20 and T_C = 335˚C. This means that this system is a promising candidate for the lead-free piezoelectric applications.

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