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PHASE TRANSITIONS IN DOPED AND UNDOPED LEAD ZIRCONATE TITANATE PIEZOELECTRIC MATERIALS

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Abstract

The study of the anelastic behaviour versus temperature at medium and low frequencies for undoped and doped lead zirconatetitanate –PZT- reveals the presence of two peaks P_1 and P_2. According to the phase diagrams established for PZT materials, P_1 peak could be related to the Curie transition between tetragonal ferroelectric phase and the cubic paraelectric phase, whereas the P_2 peak could be related to the morphotropic phase transition between rhombohedral and tetragonal ferroelectric phases. Both $P_1$and P_2 peaks evolutions are in accordance with several existing literature models for explaining the first order phase transition. The introduction of potassium and niobium dopants changes the nature of the phase transition process.

Keywords:PZT ceramics, Mechanical losses, Phase transition, Potassium doping, Niobium doping.

Résumé

L'étude du comportement anélastique en fonction de la température aux moyennes et basses fréquences pour des Zircono-titanates de plomb –PZT non dopées et dopées révèlent la présence de deux pics P_1 et P_2. En se basant sur le diagramme de phase des PZT, le pic P_1 peut être relié à la transition de Curie entre la phase ferroélectrique quadratique et la phase cubique paraélectrique, cependant le pic P_2 peut être relié à la transition morphotropique entre les phases ferroélectriques rhomboédrique et quadratique. Les évolutions des deux pics P_1 et P_2sont en bon accord avec les différents modèles existant dans la littérature et expliquant les transitions de phase du premier ordre. L'introduction des dopants potassium et niobium change la nature du processus de la transition de phase.

Mots clés : Céramiques PZT, Pertes mécaniques, Transition de Phase, Dopage au potassium, Dopage au niobium.

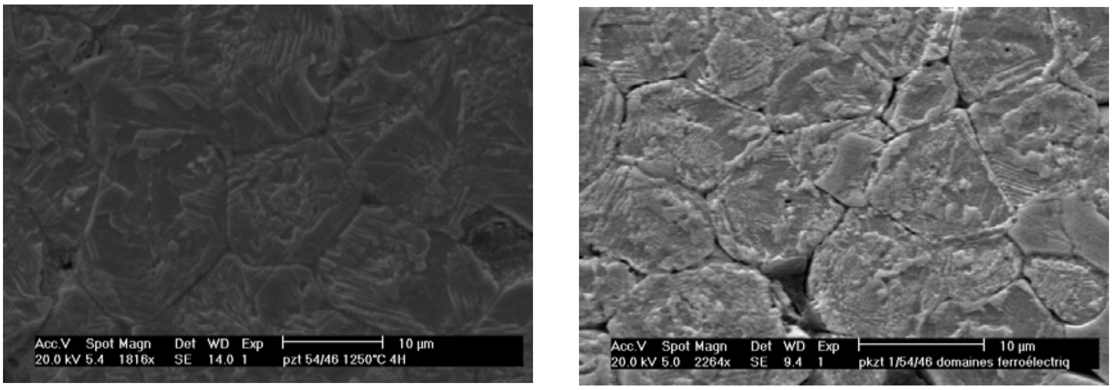
I. INTRODUCTION

Lead zirconatetitanate piezoelectric materials are widely used as sensors and actuators in several daily applications but seldom in their simple chemical formulation. They are rather modified by the introduction of substitutionals in the A or B sites of the perovskite structure ABO_3. The role of these doping agents is generally the improvement of the materials properties for their adaptation to quite specific applications. PZT phase diagrams[1-3] show a zone where the rhombohedral and tetragonal ferroelectric phases coexist which is commonly called morphotropic phase boundary (MPB). Noheda et al.[4,5], Ragini et al.[6] have reported the coexistence of also a monoclinic phase with the tetragonal phase in the MPB.

Most industrial applications are within this zone, because the majority of piezoelectric and dielectric properties present optimal values [7,8].

Previous studies of the anelastic behaviour of PZT near the MPB by mechanical spectroscopy in the Hz frequency range showed relaxation phenomena due to the interaction between ferroelectric domain walls and point defects such as oxygen vacancies[9,10] and the presence of phase transitions[11,12].

The introduction of dopant such as K^{1+} in the A-sites of the perovskite structure as a substitute for Pb^{2+} increases the oxygen vacancies concentration when oxygen ions leave their sites to maintain the electro-neutrality disturbed by the deficit charge in the A-sites. The PZT doped with an acceptor element (of lower valence) are called hard piezoelectric materials.



PZT 54/46 (ϕmoy: 10µm) **PKZT 1/54/46** (ϕmoy: 5µm)

PNZT 2/54/46 (ϕmoy: 2µm)

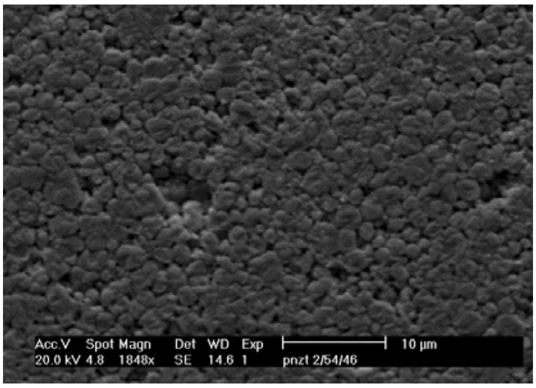


Figure1. SEM Microstructure and average grain size (ϕmoy) of processed materials.

While the introduction of Nb^{5+} in substitution of the $(Zr,Ti)^{4+}$ couple in the B-sites of the perovskite structure decreases the oxygen vacancies concentration. The PZT doped with a donor element (of higher valence) are called soft piezoelectric materials.

In the present paper, mechanical losses and associated Young/ Shear moduli are studied at low and medium frequencies for undoped PZT 54/46, PKZT 0.5/54/46 and PKZT 1/54/46 doped respectively with 0.5 at. % and 1 at. % of potassium, PNZT 1/54/46 and PNZT 2/54/46 doped respectively with 1 at. % and2 at.% of niobium.

II. MATERIALS PROCESSING AND EXPERIMENTAL PROCEDURE

By the solid reaction method undoped, potassium doped and niobium doped materials with a chemical formulation (Zr/Ti = 0.54/0.46) close to the morphotropic phase boundary (MPB) were processed. The starting powders of PbO, ZrO_2, $TiO_2$and (K_2CO_3 or Nb_2O_5) are mixed and calcined at 900 °C, the obtained powder is isostatically compacted and sintered at 1250 °C for four hours in the presence of lead zirconate as an atmosphere powder[13] in order to avoid the PbO loss at high temperatures during the sintering.

The mechanical losses Q^{-1} and Young's modulus M as function of temperature have been measured by an experimental system at medium (kilohertz range) frequencies by the transversal flexion vibration.

The mechanical losses Q^{-1} and associated shear modulus G versus temperature were measured in the Hz frequency range respectively at 1; 0.3; 0.1 Hz by using a torsion inverted pendulum, under vacuum between 25 and 500 °C at a heating rate of 1 °C/min. The samples for both medium and low frequencies experiments were rectangular bars with dimensions of $40*5*1$ mm^3. More details on the measurement method could be found in our previous publications [14,15].

III. RESULTS

III.1 Materials characterisation

The relative density and the average grain size for both processed materials are showed in **Table.1**. Both potassium and niobium have an inhibitory effect on the grain size growth (Fig.1).

X-ray patterns were carried out at room temperature with a step of 0.05° and a scanning speed of 2°/min from 2θ equal 20° to 70°. The

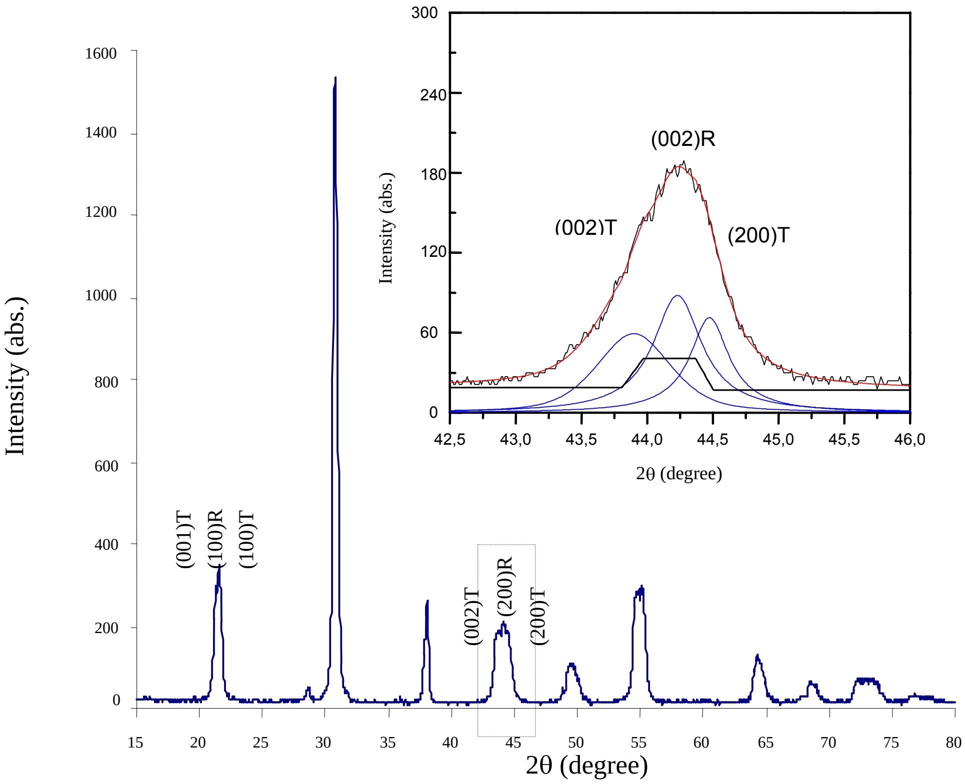


Figure 2. XRD patterns of undoped PZT.
T : tetragonal phase ; R : rhombohedral phase

diffraction lines were split into triplets indicating the coexistence of both tetragonal and rhombohedral ferroelectric phases for both compositions as expected from the phase diagram.[16,17](see **Fig.2** for undoped PZT).

Table1. Relative density and average grain size for processed materials.

Materials	Relative Density (%)	Average grain size (µm)
PZT 54/46	94.7	10
PKZT0.5/54/46	94.2	7
PKZT1/54/46	93.5	5
PNZT1/54/46	95.2	4
PNZT2/54/46	95.8	2

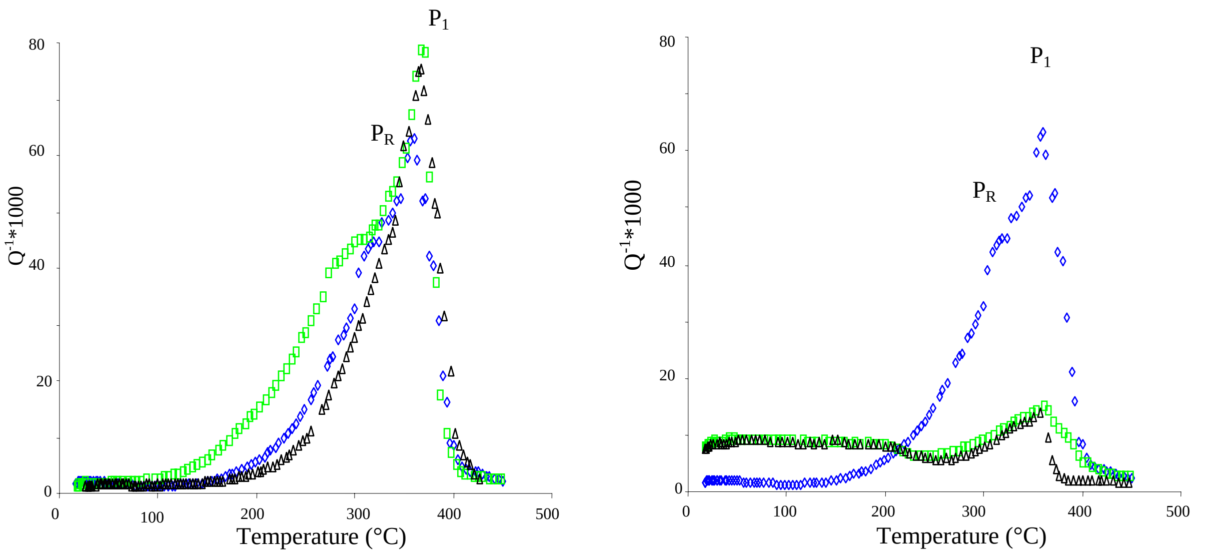
III.2 Anelastic behaviour at medium frequencies

The mechanical losses $Q^{-1}(T)$ and associated Young's modulus M(T) for both materials (**Fig.3**), show a sharp peak P_1 and a corresponding Young's modulus sharp M_1 minimum. The P_1 peak is preceded by a P_R shoulder. No peak on the $Q^{-1}(T)$ curve corresponds to the smooth Young's modulus M_2 minimum.

According to the minima temperatures on one part and to the Jaffe phase diagram[3] and its revisited version[14,16] on the other part, the M_1 minimum could be related to the Curie transition between cubic paraelectric phase and

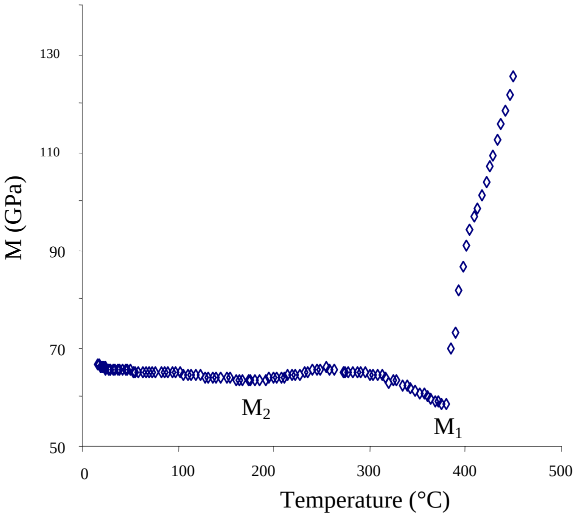
Table 2Phase transition temperatures deduced from M(T) curves and tetragonal ΔT_{tetr}).

Materials	$T_{(C\text{-}T)}$ (°C)	$T_{(T\text{-}R)}$(°C)	(ΔT_{Tetr}) = $T_{C\text{-}T}$-$T_{T\text{-}R}$ (°C)
PZT 54/46	380	175	205
PKZT 0.5/54/46	370	153	217
PKZT 1/54/46	373	125	248
PNZT 1/54/46	360	200	160
PNZT 2/54/46	345	210	135



a) Potassium doping effect on Q^{-1} (T).
◊ : PZT 54/46 ;□ : PKZT 0.5/54/46; Δ : PKZT 1/54/46.

b) Niobium doping effect on Q^{-1} (T).
◊ : PZT 54/46 ;□ : PNZT 1/54/46 ; Δ : PNZT 2/54/46.



c) Young modulus for PZT 54/46

Figure 3. Mechanical losses Q^{-1} (T) and Young modulus M (T) measured in the medium frequency range.

tetragonal ferroelectric phase, whereas, the M_2 minimum could be related to the morphotropic phase transition between tetragonal and rhombohedral ferroelectric phases. (**Table.2**)

III.2.1 Potassium doping effect

The introduction of potassium increases slightly the height of the P_1 peak while the peak temperature remains stable. The P_R shoulder remains stable in height, but it shifts towards the low temperatures by doping with 0.5 at. % and shifts towards high temperatures by few degrees when the potassium doping with 1 at. %. (**Fig.3**).

The introduction of potassium increases the width of the tetragonal ferroelectric phase range.

III.2.2 Niobium doping effect

Niobium introduction decreases strongly the level of both P_1 peak and P_R shoulder. Whereas, at temperature under 200 °C the mechanical losses of niobium doped materials are more important than those of undoped materials. (**Fig.3**)

The introduction of niobium decreases the width of the tetragonal ferroelectric phase range.

III.3 Anelastic behaviour at low frequencies

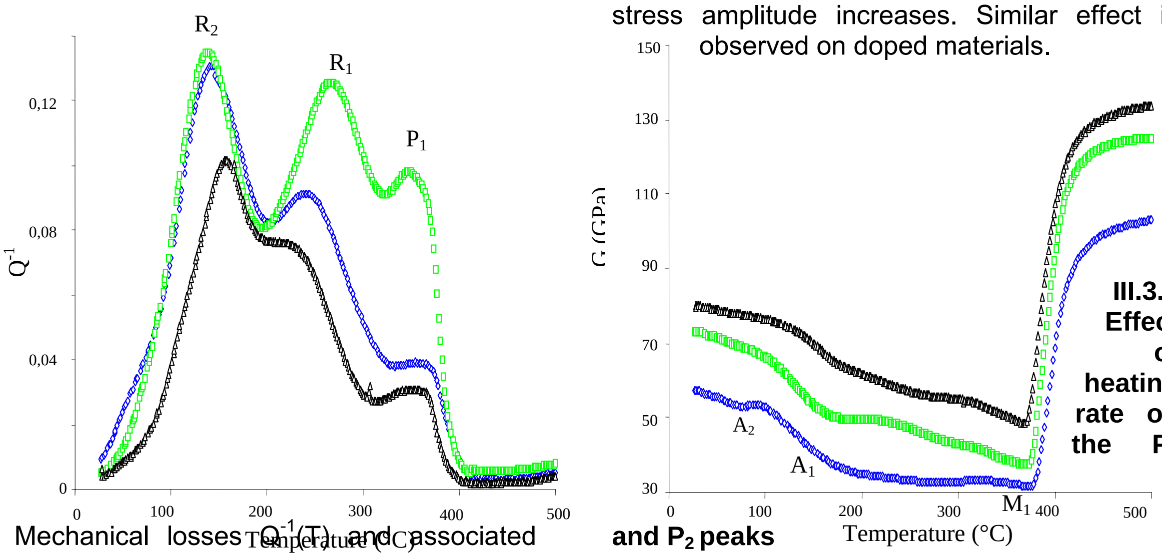


Figure 4. Potassium doping effect at 1Hz.
◊ : PZT 54/46, □ : PKZT 0.5/54/46, Δ : PKZT 1/54/46.

Mechanical losses $Q^{-1}(T)$ and associated shear modulus G(T) for undoped PZT and potassium doped (**Fig.4**), shows the Curie transition peak P_1 and its correlated modulus minimum M_1, and two other peaks R_1 and R_2 with two associated modulus anomalies A_1 and A_2. **Fig.5** for undoped PZT and niobium doped materials, shows the P_1 peak and its correlated modulus minimum M_1, the R_1 peak and its associated modulus anomalies A_1, and the morphotropic phase transition P_2 peak – between tetragonal and rhombohedral ferroelectric phases- and its correlated modulus minimum M_2. R_1 and R_2 peaks are relaxation phenomena due to the interaction between ferroelectric domain walls and point defects such as oxygen vacancies[9,10,15]. In the present study we are interested only by the evolution of P_1 and P_2 peaks.

III.3.1 Effect of frequency on the P_1 and P_2 peaks

When the solicitation frequency increases, the height of both peaks decreases and they remain stable in temperature. **Fig.6** shows the evolution of $Q^{-1}_{max.}(P_1)$ and $Q^{-1}_{max.}(P_2)$ as a function of the frequency inverse (1/f) for the undoped PZT. Similar effect is observed on doped materials.

III.3.2 Effect of stress amplitude on the P_1 and P_2 peaks

Fig.7 represents the evolution of $Q^{-1}_{max.}(P_1)$ and $Q^{-1}_{max.}(P_2)$ as a function of the applied stress amplitude $\sigma_{max.}$for the undoped PZT. The height of both P_1 and P_2 peaksincreases when stress amplitude increases. Similar effect is observed on doped materials.

III.3.3 Effect of heating rate on the P_1 and P_2 peaks

When the heating rate increases, the height of both P_1 and P_2 peaksincreases.**Fig.8** shows the evolution of $Q^{-1}_{max.}(P_1)$ and $Q^{-1}_{max.}(P_2)$ as a function of heating rate ($\dot{T}$) for the undoped PZT. Similar effect is observed on doped materials.

IV. DISCUSSION

Our discussion will treat only the phase transition peaks P_1 and P_2.

The height of both P_1 and P_2 peaksis directly proportional to stress amplitude and heating rate but inversely proportional to frequency. Such evolution is very similar to that of the first order phase transition.

Among the several theoretical models existing in literature to describe the first order phase transition reviewed by Fantozziet al.[18], one can notice a qualitative agreement of the evolution of our P_1 and P_2 peaks with the theoretical models of Zhang et al.[19], De Jonghe et al.[20]

Zhang et al., proposed a model for explaining the transition peak in $BaTiO_3$ semi-conducting materials and in which it is suggested that the mechanical losses are the result of two components:

- A transitory component, measured during heating and cooling, Q_t^{-1}. This component depends on frequency and heating rate and associated to the phase mobile interfaces.
- An equilibrium (or stationary) component Q_s^{-1}, measured at a fixed temperature ($\dot{T}$ = 0) and associated to the phase immobile interfaces.

The total internal friction is given by the following relation:

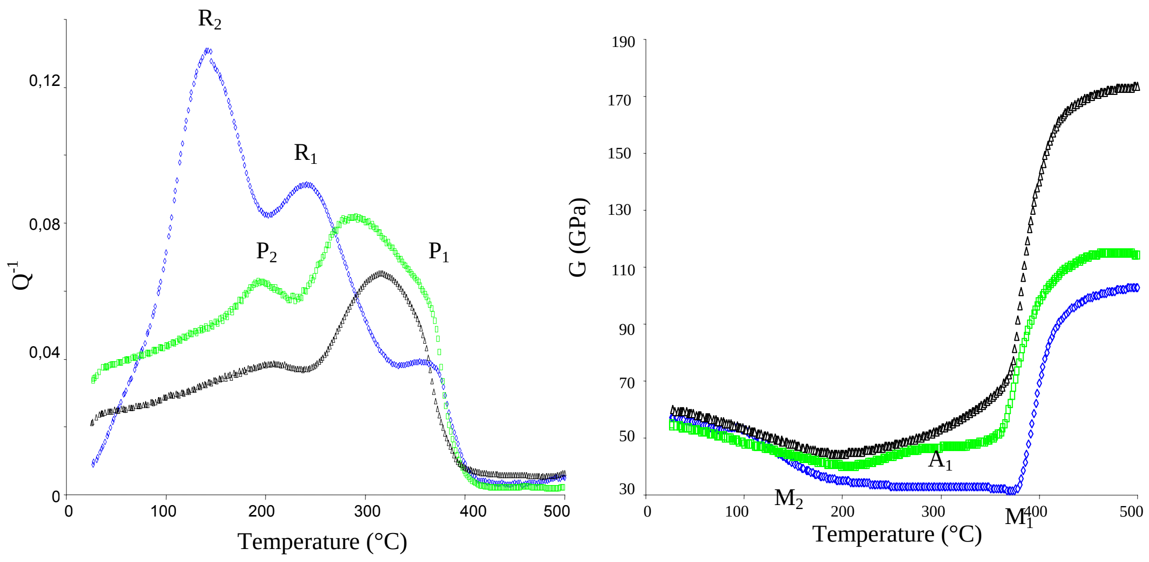


Figure 5. Niobium doping effect at 1Hz.
◊ : PZT 54/46 ;□ : PNZT 1/54/46 ; Δ : PNZT 2/54/46

$$Q^{-1} = Q_t^{-1} + Q_s^{-1} = A'(F)\,\alpha^2(\omega)(\dot{T}/\omega)^n + B'(F)\,\alpha^2(\omega)\,\omega \quad (1)$$

Where F is the volume fraction of the produced phase,

and $\alpha(\omega)$ could be written like following:

$$\alpha(\omega) = (2\varepsilon_0 Q^{-1})/(\Delta M/M) = \alpha'\omega^{-P} \quad (2)$$

With ($0 < P < 1$)

α' is a constant,

ε_0 represents the transitory phase deformation,

$\Delta M/M$ is the change in modulus.

In our case, the evolution of $Q^{-1}_{max.}(P_1)$ and $Q^{-1}_{max.}(P_2)$ function of ($\dot{T}/\omega$)is in agreement with the proposed formulation (**Fig.8**).

So the Zhang et al. model takes into account frequency and heating rate but not stress amplitude.

De Jonghe et al. proposed a model in which the quantity of transformed phase per unit of time take into account both heating rate $\dot{T}$ and applied stress amplitude σ, however the stress contribution is not available before a critical stress σ_C.

The quantity of transformed phase per unit of time ($\dot{m} = f(\dot{T}, \sigma)$) is given by the relation :

$$\frac{dm}{dt} = \frac{\partial m}{\partial T}\frac{\partial T}{\partial t} + \frac{\partial m}{\partial \sigma}\frac{\partial \sigma}{\partial t}$$

The following relation is proposed to assess the internal friction:

$$Q^{-1} = \frac{A}{2\pi}\left[\frac{\partial m}{\partial T}\cdot\frac{\partial T}{\partial t}\cdot\frac{1}{f} + \frac{4}{3}\cdot\sigma_0\cdot\frac{\partial m}{\partial \sigma}\cdot\left\{1-\left(\frac{\sigma_c}{\sigma_0}\right)^3\right\}\right]$$

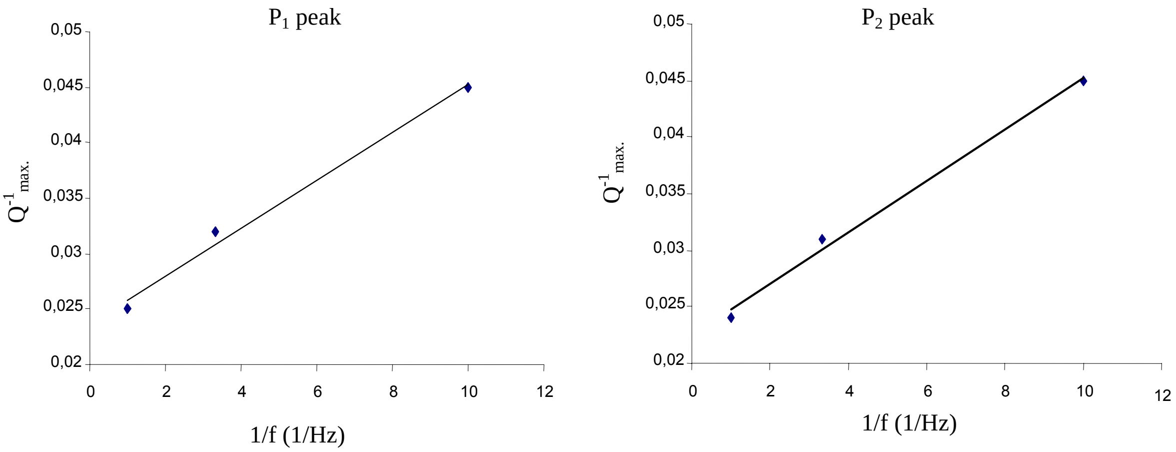


Figure 6.Q^{-1}max.evolution versus (1/f) for P_1 and P_2 peaks for undoped PZT.

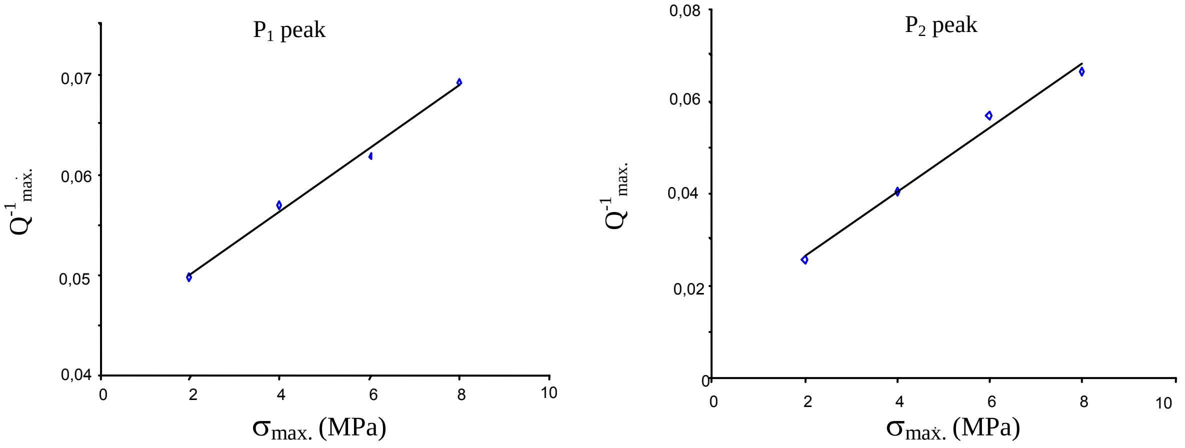


Figure 7.Q^{-1}max.evolution versus stress amplitude ($\sigma_{max.}$) for P_1 and P_2 peaks for undoped PZT.

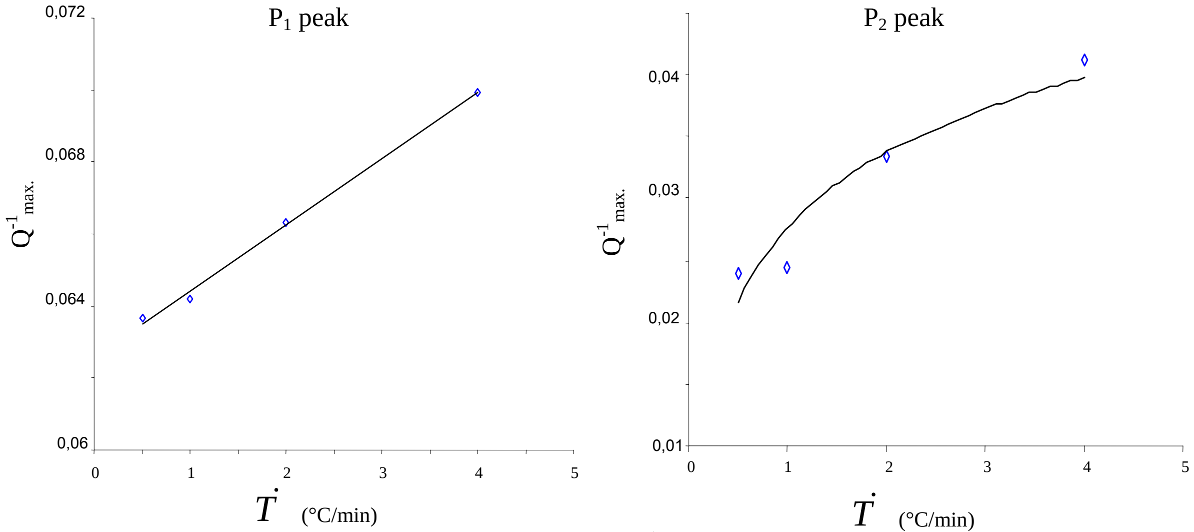


Figure 8.Q^{-1}max.evolution versus heating rate ($\dot{T}$) for P_1 and P_2 peaks for undoped PZT.

Where:

A is a material constant,

$\frac{\partial m}{\partial T}$ Represents the relative transformed phase variation per unit of time,

$\frac{\partial T}{\partial t}$ is the heating rate,

fis the frequency,

$\sigma_0$is the applied stress amplitude,

$\frac{\partial m}{\partial \sigma}$ Represents the relative transformed phase variation per unit of stress; this term is rather related to the interfaces mobility.

Accordingly to the above models, the effect of potassium and niobium doping could be interpreted by the change of the nature of the transformed phase when doping. The change in the chemical composition of the starting transformed phase unit (or cell) by the introduction of aliovalent dopants could have as a result the change of the kinetic and the strength of the phase transition process.

The presence of the P_R shoulder is not clearly understand, we thought that it could be related to the anelastic phenomena represented at low frequencies by one or both R_1 and R_2 peaks. Further investigations are needed to better understand the P_R shoulder.

V. CONCLUSION

According to the P_1 and P_2 peaks temperatures and to the phase diagrams established for PZT solid solutions, one can notice the following considerations:

- The P_1 peak is attributed to the Curie transition –between cubic paraelectric phase and tetragonal ferroelectric phase-accompanied losses.

- The P_2 peak is attributed to the losses occurring during the phase transition between tetragonal and rhombohedral ferroelectric phases or to a more complex transition where the monoclinic phase coexist with the tetragonal phase as shown by Noheda et al.[4,5] and ,Ragini et al[6].

- Both P_1 and P_2 peaks present a great similitude with a first order phase transition internal friction peak.

The introduction of potassium and niobium dopants changes the chemical composition of the starting transformed phase unit (or cell) and induces as a result the change of the nature of the phase transition process but the transition remains of first order.

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