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Frequency dependance of electromechanical properties of PZN-xPT single crystals

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Abstract

In this paper, the frequency behaviour of electro-mechanical properties of PZN-xPT single crystals with compositions close to the morphotropic phase boundary is studied at frequencies up to 100 MHz. Properties are deduced from the fit of the electrical input impedance, theoretically calculated with the KLM equivalent circuit model, to experimental data. To measure the electrical impedance of a crystal, its surfaces have first to be metallized. For very thin samples, this metallization may influence the resonances and alter the property identification. A theoretical study is thus performed to quantify the influence of the electrodes on the crystal vibrations. The results show that, even for high frequencies, their effects are negligible. In a second part, the evolution with frequency of the single crystal characteristics is studied. The properties are identified in a frequency bandwidth centered on the resonances, from the fundamental to the 21^{th} harmonic. The study shows the stability of the electromechanical properties versus the frequency. Finally, the mechanical and dielectric loss tangents are quantified.

1 INTRODUCTION

Since the early 90s, relaxor-based ferroelectric single crystals such as PMN-xPT or PZN- xPT have been largely investigated because of their very attractive piezoelectric properties. Indeed, the piezoelectric coefficient, d_{33}, typically reaches values of 2500 pC/N which can lead to a length extensional coupling coefficient, k_{33}, of 90% or higher [1–3]. This feature can be exploited in transducer applications, by combining these materials with a polymer phase to make 1-3 piezocomposites. This ensures the single crystals operate in their length extensional mode instead of their thickness mode, the coupling coefficient of which is around 55%. Currently, most of the research focuses on the optimisation of the PT content [4], on the optimisation of the crystal growth process [5] or on the role of domain orientation on piezoelastic properties of polydomain structures [6, 7], but little attention has been paid to the study of the frequency stability of electromechanical properties of these materials, which is the goal of this paper. Currently, single crystals are characterized in the MHz range. Methods are based on combined approach with both electrical and ultrasonic velocity measurements. This allows reducing the number of single crystal samples for complete tensor characterization. Here, we investigate the electromechanical characterization of PZN-xPT compositions, on the thickness mode, near the morphotropic phase boundary, at frequencies up to 100 MHz. In a first part of the paper, the measurement method based on a fitting process of the electric resonator is presented. Then, effect of electrode thickness on the accuracy of electromechanical characterization is studied for various configurations. In third part, measurements of the velocity, the dielectric constant, the thickness coupling coefficient and losses are reported as a function of frequency. Results are discussed both in terms of PT content and potential use of these materials for high frequency transducer applications.

2 FABRICATION PROCESS OF SINGLE CRYSTALS

In this study, three thin plates are considered: a $440\mu m \times 10mm \times 10mm$ PZN-7PT, a $500\mu m \times 10mm \times 10mm$ PZN-8PT and a $1mm \times 10mm \times 10mm$ PZN-9PT(Mn doped). These PZN-xPT single crystals were grown by the flux method using a PbO flux [8,9]. PZN-7PT and PZN-8PT crystals were commercial materials while the PZN-9PT(Mn doped) plate was processed by Thales. Its PZN-PT/PbO flux ratio was equal to 45/55 (mol%). The largest crystal obtained was about $20mm \times 10mm \times 10mm$. Crystals were oriented by SPMS Laboratory using the Laue diffraction technique. They were cut and polished along [100]/[010]/[001]. Gold electrodes were sputtered on the (001) faces for dielectric and electromechanical measurements. Composition and homogeneity of the samples were controlled by $\mathrm{T_{max}}$ measurement and X-ray diffraction. Samples were poled using the field cooling method with a DC field of 1-3 kV/cm from 200°C to room temperature (RT) or with increasing a DC field from 0 to 6-10kV/cm at RT [10].

3 SINGLE CRYSTAL CHARACTERIZATION

3.1 Characterization protocol

The electro-acoustic response of a piezoelectric structure is modeled using the one dimensional KLM electrical scheme (figure 1). It allows the electrical impedance and admittance of a pure resonator to be computed [11]. Real and imaginary parts of the electrical impedance and admittance of the piezoelectric sample are measured on an HP4395A analyser. 800 points are captured with a bandwidth of 300Hz, and for each measurement the signal is averaged 50 times. As an example, figure 2 shows the real and imaginary parts of the electrical admittance of the PZN-7PT plate, measured on a large bandwidth including resonances from the fundamental ($\mathrm{H_0}$) to the 21^{th} harmonic ($\mathrm{H_{21}}$). Electro-mechanical properties of single crystals are deduced from the fit to experimental data of the electrical input impedance theoretically calculated with the KLM equivalent circuit model. Different properties of thickness mode are identified: longitudinal wave velocity v_{l}, coupling coefficient k_{t}, clamped dielectric constant $\varepsilon_{33}^{\mathrm{S}}$, dielectric $tan(\delta_{\mathrm{e}})$ and mechanical $tan(\delta_{\mathrm{m}})$ losses. Contrary to usual, the real part of the admittance curve increases as a function of frequency (figure 2). This behaviour is due to a serial contact resistance $\mathrm{Z_{serial}}$ of about 2Ω, which will be taken into account in the fit procedure.

3.2 Resonances scanning

To quantify the evolution of v_{l}, k_{t}, $\varepsilon_{33}^{\mathrm{S}}$, δ_{e} and δ_{m} with the frequency, the characterization process is performed on measurements realized at each resonance from $\mathrm{H_0}$ to $\mathrm{H_{21}}$. This procedure is applied to the three different materials. As an example, figure 3 presents the comparison

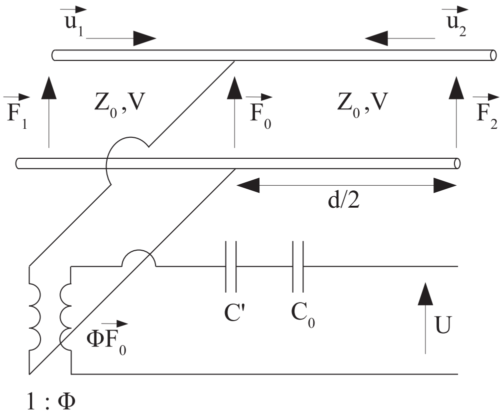

Fig. 1. KLM one dimensional equivalent electrical scheme for a piezoelectric material.

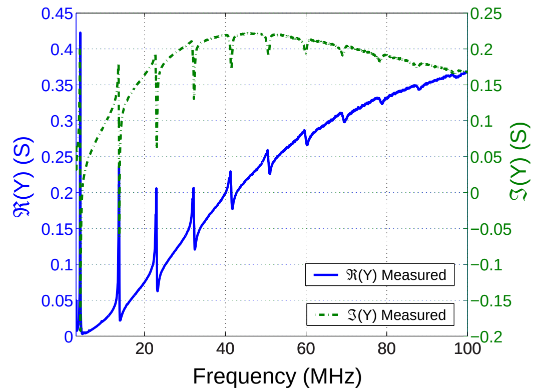

Fig. 2. Real and imaginary parts (solid and dashed line) of the electrical admittance of the PZN-7PT plate from the fundamental resonance to the 21^{th} harmonic.

between the real and imaginary parts of the experimental impedance around the 5^{th} harmonic of the PZN-7PT plate and computations performed after the fit.

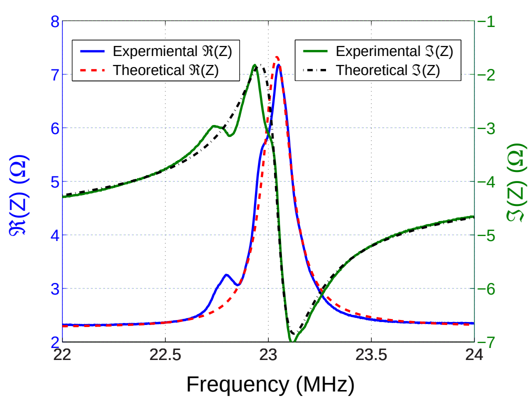

Fig. 3. Real and imaginary parts of the electrical impedance around the 5^{th} harmonic of the PZN-7PT plate (solid lines: experiments; dashed and dash dot lines: computed curves).

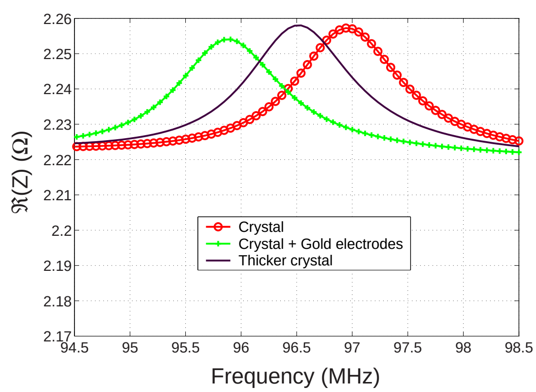

Fig. 4. Influence of a 2 μm error on the thickness (solid line) or of 1 μm gold electrode on each face (crosses) on $\Re(Z)$ computed around the 21^{th} harmonic of a 440 μm thick PZN-7PT plate (circles).

4 ELECTRODES INFLUENCE

Due to the experimental setup, the piezoelectric samples need to be metallized. However, the electrodes may disturb the plate resonances and lead to a misidentification of the material parameters. In this section, their influence on the electrical response of the thinnest plate, where the disturbances are greatest, is studied. The PZN-7PT plate is $440\mu m$ thick and its area is 100 mm^2. Electrodes are $2\mu m$ thick, a typical value for such samples [12]. To quantify the electrode influence on the electro-acoustic response of the sample, three configurations are studied: a $440\mu m$ thick crystal without electrode, a $440\mu m$ thick crystal with $1\mu m$ gold electrodes on each face and a $442\mu m$ thick crystal without electrode, simulating an error on the thickness measurement. Figure 4 presents the real part of the electrical impedance (for harmonic 21) according to the described configurations. It shows that the electrodes introduce a change in the amplitude and in the frequency of the resonance. However, the maximum variation in frequency is 1.2% on the 21^{th} harmonic, and is obtained for the gold electrodes configuration. For the amplitude, only the gold configuration produces a noticable modification of 3.8% (see table 1). In conclusion, $2\mu m$ thicknesses induce negligible modifications on the harmonic 21. Moreover, in practice, it is nearly impossible to reach precisions of $2\mu m$ on the thickness, of 1% on the frequency and of 4% on the magnitude. Consequently in the rest of the paper, electrodes will not be taken into consideration.

Table 1. Relative error on amplitude and frequency position of H_{21} for the metallized and the thicker PZN-7PT plates. Comparison with the $440\mu m$ naked sample.

Thickness	$440\mu m$	$442\mu m$
Electrode	$2\mu m$ Gold	-
Δf	-1.2%	-0.5%
$\Delta\Re(Z)$	-3.8%	+0.8%

Table 2. Electro-mechanical properties of PZN-7PT, PZN-8PT and PZN-9PT(Mn) plates, measured on a large bandwidth (H_0 to H_{21}).

Properties	PZN-7PT	PZN-8PT	PZN-9PT
v_l (m/s)	4055	4117	4166
ε_{33}^S (ε_0)	767	516	392
k_t (%)	50	53	58
δ_e (%)	$2 \rightarrow 5$	$2.5 \rightarrow 4.5$	$1.3 \rightarrow 7.5$
δ_m (%)	0.19	0.13	X

5 RESULTS AND DISCUSSION

This section presents the behaviour, with the harmonic order, from H_0 to H_{21}, of various electro-mechanical properties of the three plates: the $10 \times 10 \times 0.44mm^3$ PZN-7PT (resp. $10 \times 10 \times 0.50mm^3$ PZN-8PT and $10 \times 10 \times 1mm^3$ PZN-9PT (Mn doped)) leading to frequencies up to 100MHz (resp. 100MHz and 50MHz). Most of the properties of PZN-xPT single crystal (near MPB) are stable with frequency (figure 5).

In the three cases, the longitudinal wave velocity identified at the fundamental is about 0.5% lower than the mean value (figure 5 (a)). This can be explained by the effect of radial modes. Furthermore, wave velocity increases with the PT content. Figure 5 (b) shows the stablity of the clamped dielectric constant in thickness mode for the three crystal plates. Unlike the wave velocity, the clamped dielectric constant decreases with the PT content. This property is strongly related to the crystalline structure and to the Curie temperature. It is known that the dielectric constant increase at room temperature is related to a lower Curie temperature. Figure 5 (c) shows that the electro-mechanical coupling coefficient is constant with frequency up to H_{21} for all three materials. The slight decreases observed at the 21^{th} harmonic are due to experimental difficulties caused by low signal to noise ratios. It is seen that the coupling coefficient grows with PT content. The characterization of the losses depends on the quality of the electrical impedance of the sample. Nevertheless, dielectric and mechanical losses are found to be similar whatever the PT content. Figure 5 (d) shows that the dielectric losses increase with frequency. The PZN-7PT and PZN-8PT dielectric losses start to be stable from the eleventh harmonic while the manganese inside the PZN-9PT (Mn doped) material seems to lead to an increase of its dielectric losses. The mechanical losses are very low for the three materials (0.0015 for harmonics higher the fundamental) and relatively constant. PZN-9PT (Mn doped) mechanical losses are higher, at the fundamental, than for other materials. However, the resonance, for this crystal, is neither sharp nor symmetric, leading to difficulties in determination of the mechanical losses. Table 2 presents the average values of v_l ; k_t and ε_{33}^S for the three materials. The coupling coefficient of PZN-9PT (Mn doped) is particularly high : 0.58. This result combined with a low clamped dielectric constant makes this material particularly suitable for high frequency applications. Finally, figure 6 shows, for the PZN-7PT plate, the comparison between the real part of the electrical impedance measured from H_0 to H_{21} and a large bandwidth simulation of $\Re(Z)$ computed from properties identified from measurements performed around H_5. The good agreement between these two sets of data proves the stability of electro-mechanical properties as a function of frequency.

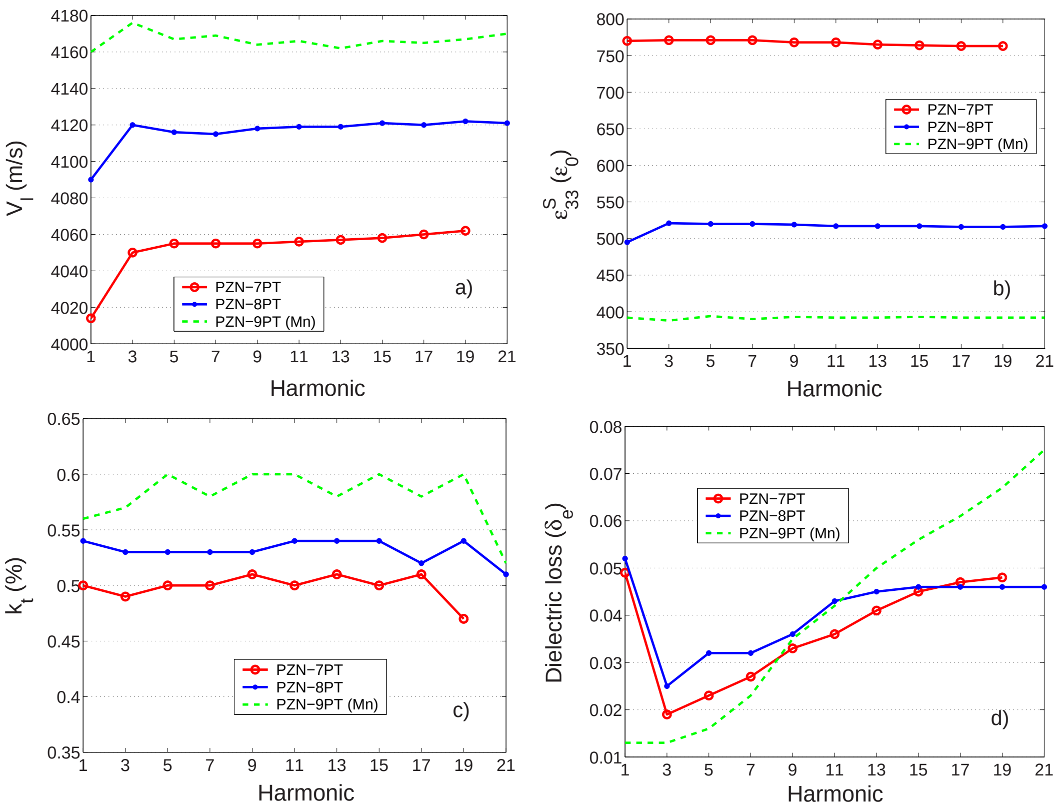

Fig. 5. Evolution, with the harmonic order, of the longitudinal wave velocity (a), the clamped dielectric constant ε_{33}^{S} (b), the electro-mechanical coupling coefficient k_t (c) and the dielectric losses (d).

6 CONCLUSION

Material characterizations were performed on PZN-x%PT single crystal samples with the chemical compositions near the MPB. They show good frequency stability up to 100 MHz showing these materials could be used for high frequency application. Futhermore, PZN-9PT (Mn doped) having a high value of 58% for the coupling coefficient and a low value of $392\varepsilon_0$ for the clamped dielectric constant posseses properties particularly suitable for single element high frequency transducters. Next step will be the design and modelling of a 30 MHz transducer for medical imaging. The relation between PT content and properties is very useful to select a material for a given application. Future work is to extend this study to PZN-4.5PT, PZN-9PT and a PZN-12PT in order to complete the characterisation of the PZN-xPT single crystal phase diagram.

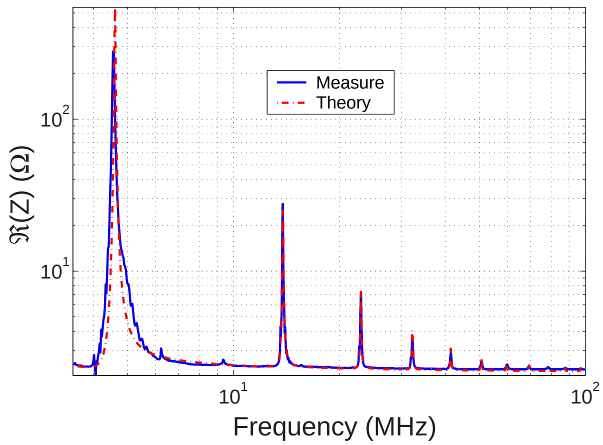

Fig. 6. Real part of the electrical impedance of the PZN-7PT plate in a large bandwidth: experiments in solid line, dashed line is calculated from the properties deduced from the fit on the 5^{th} harmonic.

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