NON LINEAR BEHAVIOUR OF PIEZOELECTRIC MATERIALS WITH GRADED ELECTROMECHANICAL PROPERTIES

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Abstract.
In this paper, we present the implementation of a multilayered KLM model with electromechanical properties of the ceramic that can vary as a function of the thickness. Electromechanical thickness mode measurements on new KNN piezoelectric materials having non-linear behaviour are reported and discussed according the theoretical results of a gradient of properties. Electroacoustic performances of a single-element transducer based on this material are also reported and the potential of this material for ultrasonic linear and non-linear applications is discussed.

Introduction.
The development of lead-free or low lead content materials in electronic industry has become a goal of major importance not only in Europe but also in Japan, in order to protect health and environment. Ceramic manufacturers are developing new compositions with properties close to those of PZT materials. In particular, Potassium Sodium Niobate (KNN) compositions that were investigated in the seventies [1] reniew interest as it has been shown that this material can compete with lead-based ceramics. In addition, these materials can exhibit non-linear behaviour that is currently not explained.
In this paper we present a theoretical and experimental study of this unusual behaviour. The electroacoustic KLM model of transducers that takes into account mechanical and dielectric losses was modified in order to take into account graded electromechanical properties [2]. Effect of the amplitude of the gradient and of the shape is theoretically investigated. Experimental measurements of the electrical input impedance on KNN ceramic samples that present second harmonics are reported and discussed according theoretical predictions. Finally, first result on a single element transducer based on KNN are given.

Theory.
The transducer characteristics (i.e. transfer function, electrical input impedance, electroacoustic response…) were calculated using a multilayered KLM model. Here the piezoelectric ceramic has been divided into *N* piezoelectric layers, the properties of which are independent (figure 1). According to the KLM scheme, a layer, *i*, is separated into two half thickness propagation lines, the front layer is connected to layer *i*+1 and the rear layer is connected to layer *i*-1. All layers have a serial electrical connection. The first layer is loaded by the backing; the front layer (layer *N*) is loaded by a matching layer and water. The transfer matrix, from which the characteristics of the transducer are calculated results from the product of the composition the hybrid functions of each layer.

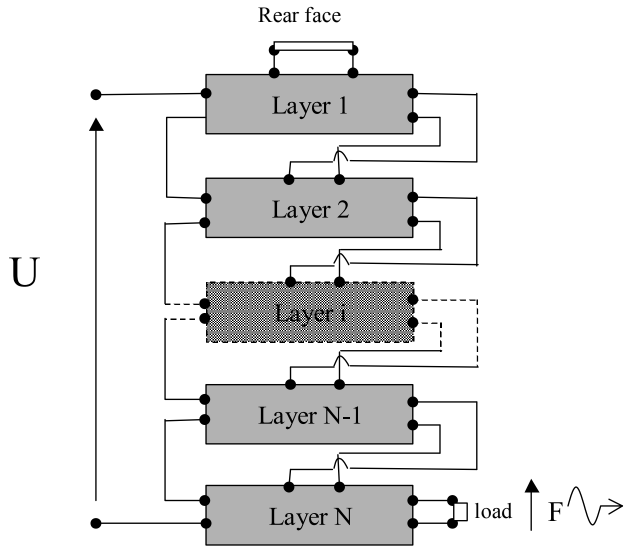

Figure 1 : Multilayered KLM scheme.

The modelling of a transducer using the electroacoustic models requires a large number of ceramic properties that all can vary as a function of the thickness. However, the gradient of properties was applied to main characteristics : velocity, dielectric constant and coupling coefficient respectively. First simulations were performed on the basis of the data published in literature [3] that report velocity variations on a PZT around 10%, relative dielectric constant around 60% and coupling coefficient variations around 80 %.
Simulations of linear gradient applied on the velocity, dielectric constant and thickness coupling coefficient of a 10 mm diameter, 5 MHz KNN ceramic resonator were carried out. The average properties of the KNN ceramic and gradient characteristics used for calculations are given in table I. For calculations, the gradients on velocity and coupling coefficient are of the same sign, opposite to gradient on dielectric constant. Gradient for each property represents 10%, 60% and 80 % for velocity, dielectric constant and coupling coefficient respectively. Eleven layers have been considered in the calculations.

Table I : average properties used for simulation

Material	*KNN type.*
Density (kg/m3)	4200
Velocity (m/s)	5800 (5510-6090)*
Relative dielectric constant ε_{33}^{S}	270 (189-351)*
Coupling coefficient	0.35 (0.21-0.49)*
Mechanical losses	0.03
Dielectric losses	0.03

Minima and maxima of gradients are indicated in bracket

Table II : Gradient characteristics.

Material (KNN type)	*Constant gradient*	*Linear gradient**	*Parabolic gradient**
Coupling coefficient	0.35	0.5-0.20	0.53-0.23

*Minima and maxima of gradients are indicated

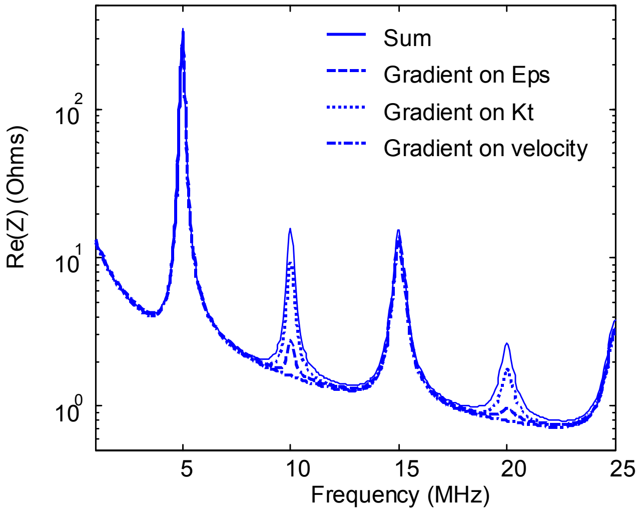

Figure 2 : Simulated real part of the electrical impedance of the ceramic with graded material properties.

When gradients are applied on the three properties, even harmonics are observed (figure 2 solid line). These results are in agreement with those already published in the literature [3-7]. Here the multilayered KLM scheme allows not only the calculation of the electrical input impedance, but also the electroacoustic response of transducer based on this type of materials. The amplitude of the second resonance peak is measured to be 18 Ω. However, when one examines the contribution of each gradient property to the second resonance peak, the most significant contribution is given by the gradient on the coupling coefficient. Indeed, during the poling process of piezoceramics, this property can be drastically modify according to the poling conditions. The velocity that cannot present very large variations in properties has a very little contribution. For the dielectric constant, a 60% variations on the property leads to a second resonance peak of 1.5 Ω showing that this property moderately contributes to the amplitude of the second harmonic.

Now if the amplitude of even harmonics is examined for different gradient variations (figure 3), it can be seen that even harmonics increase as a function of amplitude gradient.

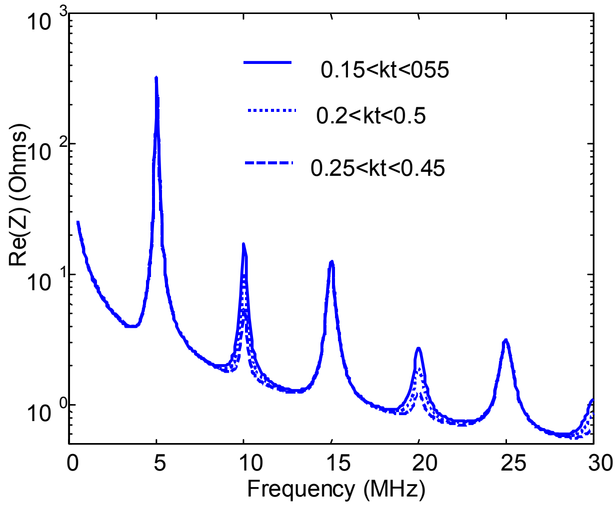

Figure 3 : Simulated real part of the electrical impedance of the ceramic with graded coupling coefficients (other properties remain constant).

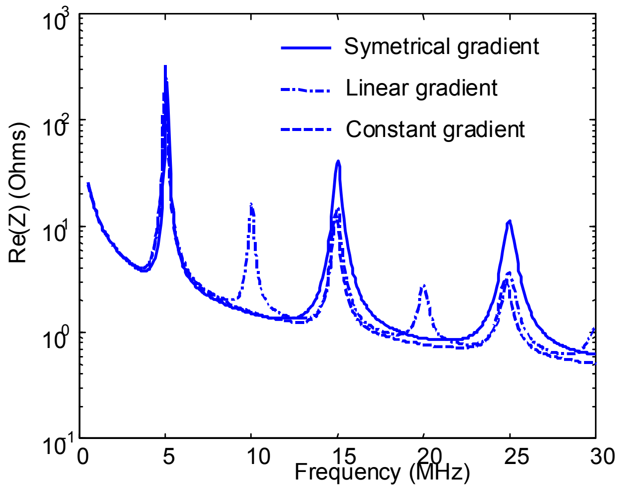

Figure 4 : Theoretical real part of a 5 MHz lead free ceramic with graded material properties for various shapes of gradient.

The shape of the gradient was also studied. A linear and a symmetrical parabolic gradients were applied to the coupling coefficient (table II). Simulation results of a 10 mm diameter, 5 MHz fundamental resonant frequency are shown figure in 4. A constant gradient is equivalent to a non-graded piezoceramic. When a symmetrical gradient is applied, odd harmonics of the fundamental are observed as predicted by theory of classical piezoelectric resonator, but due to the symmetry of the gradient along the thickness second harmonics are not present. When the linear gradient is applied an asymmetry in the material is created that allow the presence of second harmonic vibration peaks.

Experimental results.

Sr-doped potassium sodium niobate (KNN-Sr) of the composition $K_{0.5-x}Na_{0.5-x}Sr_xNbO_3$ (x < 0.02) was prepared by a conventional solid-state synthesis. To begin with, K_2CO_3, Na_2CO_3, $SrCO_3$ and Nb_2O_5 were mixed in 2-propanol, dried and then calcined twice (800 °C, 4 h). After the second calcination, the KNN-Sr powder was ball-milled in water using ZrO_2 milling media of 3 mm diameter to obtain a median particle size $d_{0.5}$ < 1 µm. Binder was added by spray drying and the powder was pressed uniaxially at 100 MPa to obtain discs. The discs were sintered at 1110 °C for 4 h and a bulk density of 4.21 g/cm^3 (93 % relative density) was measured. After lapping, the thickness of the discs was ~1.35 mm and the diameter was ~ 9.6 mm. Silver electrodes were applied by screen printing, and finally the discs were poled at a field of 2.8 kV/mm and a temperature of 60 °C for 15 min. Resonant frequencies are close to 2 MHz.

The linear properties of the ceramic samples were deduced from electrical impedance measurements that were carried out on a HP 4195A impedance analyser. Due to the lateral mode, spurious resonances were observed on the first harmonic, measurements were then made on the third overtone. In order to obtain the material properties the input parameters of a one layer KLM model that predicts the electrical impedance of the ceramic were fitted to experimental data. Fitting parameters are : velocity, thickness coupling coefficient, dielectric constant, dielectric and mechanical losses. A result of the curve fitting is given on figure 5. Material properties of the three ceramic samples are given in table III.

Table III: linear electromechanical properties of KNN samples

Material(KNN type)	*Sample #1*	*Sample #2*	*Sample #3*
Thickness (mm)	1.35	1.38	1.35
Diameter (mm)	9.65	9.6	9.65
Density (kg/m3)	4210	4210	4210
Velocity (m/s)	5848	5738	5787
Coupling coefficient	0.30	0.36	0.34
Relative dielectric constant ε_{33}^S	280	275	276
Mechanical losses	-	0.023	0.022
Dielectric losses	-	0.071	0.045

KNN ceramics have low density compared to conventional lead zirconate titanate ceramics (PZT) Density is around 4280 kg/m^3. This benefit on the acoustical impedance of the ceramic is partially compensated by a very high longitudinal velocity compared to PZT (5800 m/s). This leads to an acoustical impedance of the ceramic around 24 MRayl, which is an advantage for immersion transducer applications. In KNN materials, velocity is close to that of lithium niobate. The absence of lead is such that the inertia of the crystalline network is much lower than in PZT ceramic. Crystalline response to external sources such as mechanical vibration is fast, the velocity is higher. The dielectric constant is of 275 which makes this property suitable for the fabrication of single element transducer. Mechanical and dielectric losses are relatively high which also makes this material suitable for low power applications such as echography or flaw detection. In particular, the low acoustical impedance and the high velocity make this material particularly suitable for high frequency applications. The coupling coefficient around 0.35 is intermediate between that of lead metaniobate ceramics and PZT ceramics. Improvement in the fabrication process of these KNN ceramics should allow to expect thickness coupling coefficient greater than 0.4.

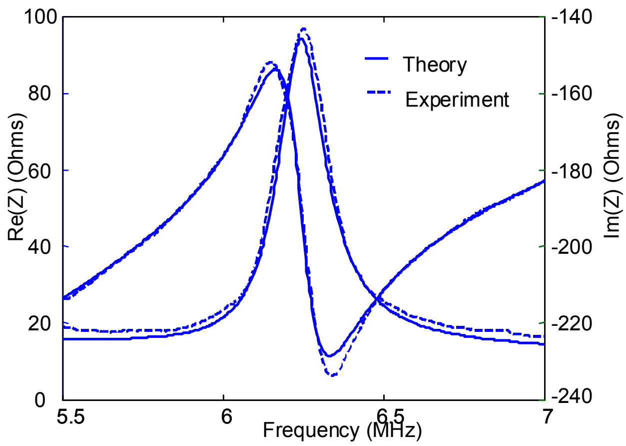

Figure 5 ; Real part and imaginary part of the electrical input impedance of the ceramic #2.

Figure 6. shows the theoretical and experimental real part of the electrical input impedance of the ceramic #2 for a large frequency span. A linear gradient was applied to calculate the theoretical electrical impedance. With mean properties equal to that measured on the third harmonic, velocity varies by ±150 m/s around 5738 m/s, relative dielectric constant varies by ± 75 around 275, and coupling coefficient varies by ± 0.16 around 0.36.

Experimentally, a second resonance peak, the amplitude of which is larger that the third resonance peak, is observed. The chosen gradient of properties leads to a general behaviour close to that observed by the experiment, however discrepancies appear for low and high frequencies. At low frequency, the predicted resonant frequency is very much higher than the one observed experimentally. This latter is perturbed by lateral resonances. At present the origin of the gradient in the material is not explained. A hypothesis that is currently investigated could be in the presence of free electrons in the material. During poling they concentrate to the positive electrode by diffusion mecanism. This inhomogeneous distribution leads non uniform ceramic properties especially on the coupling. To confirm this, experiments have to be conducted, such as measuring the electromechanical properties as function of the thickness.

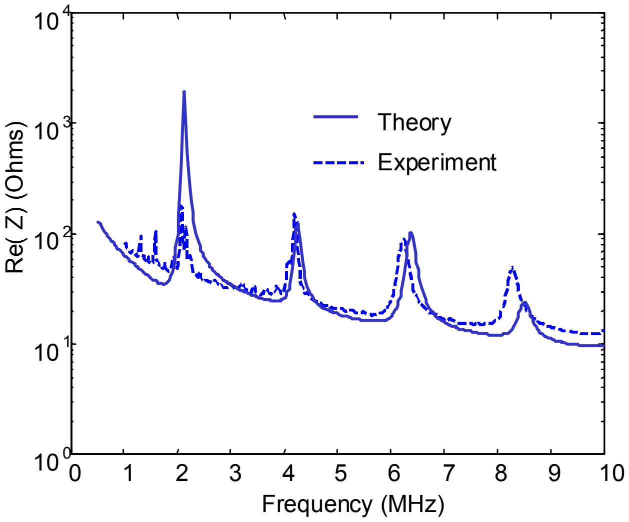

Figure 6 : Real part of the electrical input impedance of the ceramic #2

On the basis of these results, ceramic #1 was used to fabricate a simple single-element transducer. The goal was to take advantage of the presence of the second harmonic to fabricate a very wide-band transducers. The ceramic was glued on an epoxy tungsten backing material of 10 MRayl and an echo was produced on an aluminium block of thickness 20 mm. Figure 7 shows the frequency and time response of the transducer when excited by Panametric 5055 PR. A very sharp pulse is obtained. The centre frequency around 7 MHz suggests that the transducer preferably operates on the third harmonic instead of the first. Due to the large damping on both faces of the ceramic the transducer can operate in a very wide band, here the bandwidth is 140 % which makes this transducer suitable for flaw detection or harmonic imaging. The presence of the second harmonic in the ceramic allows the transducer to operate at usually cut off frequencies 4 and 8 MHz and partially explains this behaviour.

Conclusion.

In this paper, the non-linear electromechanical behaviour of new potassium sodium niobiate ceramics have been explained on the basis of a multilayered electroacoustic KLM model that allows to take into account gradient of properties. Theoretical results show that the coupling coefficient has the strongest influence on the amplitude of the second resonance peaks. Experimental measurements on KNN single-element transducer show that very wide band transducers can be manufactured with such material.

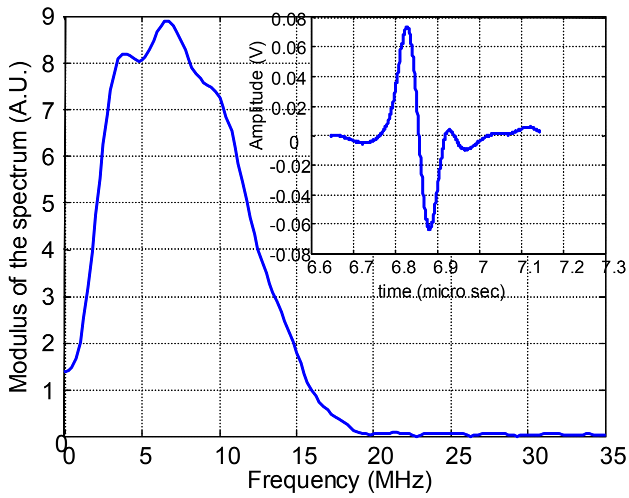

Figure 7 Frequency. and time response of single element transducer KNN based (pulse echo mode).

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