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Dielectric and piezoelectric properties of tetragonal PMNT 65/35 piezoelectric single crystal

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Three planes of PMNT 65/35 single crystal were investigated and it was concluded that the (110) orientation was most promising in terms of high dielectric constant and high mechanical coupling factor: ε_{33}^T » 8000 and k'_{33} » 83% in sliber mode. The dielectric constant was almost temperature independent up to the Curie temperature of about 175°C. The mechanical coupling factor k'_{33} showed a decrease of about 15% in the temperature region of 20-70°C. In order to quantify the material with the best overall performance a Figure of Merit (FOM) was introduced. Calculations showed that PMNT 65/35 had an improvement of about 30% over PZT ceramic and therefore is a very promising material for application in a piezoelectric transducer.

Key words: PMNT single crystal, piezoelectric property, dielectric property, orientation

1. INTRODUCTION

In medical pulse-echo ultrasonic imaging, the piezoelectric transducer is the link between the human body being imaged and the processing electronics [1], therefore the choice of the piezoelectric materials is very important. Piezoelectric materials and its characteristics have to be chosen to match with the design of the imaging device. For medical ultrasonic imaging, it is desirable to use a broad-bandwidth transducer to obtain maximum resolution at maximum penetration depth of the human tissue. This can be accomplished by a well-designed electrical and acoustic impedance matching. In the case of array transducers, the dimensions of the transducer are small (typical 0.2x0.4x12mm), which results in relatively small capacitance of the array. Therefore, for array transducers, materials with a high dielectric constant are preferred to achieve electrical impedance matching. Acoustic impedance matching can be optimized by using front matching layers. In order to achieve simultaneously high sensitivity and bandwidth for an ultrasonic probe there are five piezoelectric properties that have to be considered: coupling factor, dielectric constant, losses, depoling temperature and velocity [2].

Ceramic piezoelectrics like lead zirconate titanate (PZT ceramic) are most commonly used for ultrasonic probes because they offer relatively high electromechanical coupling, wide range of dielectric constants and low dielectric losses. However, the performance of PZT ceramics has not significantly been improved over the last two decades [3].

In 1982 Kuwata et al. [4] discovered exceptionally high electromechanical coupling (k_{33} > 0.9) in the solid solution of lead zinc niobate and lead titanate (PZNT). These relaxor ferroelectric crystals have a Perovskite structure and take a cubic non-piezoelectric structure for temperatures over the Curie Temperature T_c, typical 180°C. As the temperature is lowered the crystal departs slightly from cubic to tetragonal symmetry, at even lower temperatures the crystal exhibits rhombohedral symmetry [2]. The temperatures at which the transitions occur are a function of composition and are usually represented in the form of a phase diagram (Fig.1). For relaxor-based single crystals the dielectric constant and the coupling factor is reported to be highest on the rhombohedral side of the phase boundary. This effect is the result of enhanced polarizability arising from the coupling between two equivalent energy states, i.e., the tetragonal and rhombohedral phases, allowing optimum domain reorientation during the poling process [5].

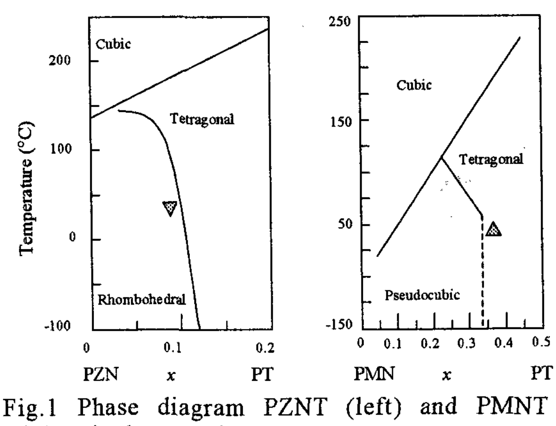

Fig.1 Phase diagram PZNT (left) and PMNT (right) single crystal.

The elastic, piezoelectric and dielectric constants of $(1\text{-}x)Pb(Zn_{1/3}Nb_{2/3})O_3\text{-}xPbTiO_3$ (PZNT) and $(1\text{-}x)Pb(Mg_{1/3}Nb_{2/3})O_3\text{-}xPbTiO_3$ (PMNT) have been investigated by several groups. Kuwata et al. [4] investigated the dependence of the transition temperature and the concentration ratio x in the solid solution between PZN, with rhombohedral symmetry and PT, with tetragonal symmetry. Multiple phase

transitions in the $0.91Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.09PbTiO_3$ single crystal were observed as a function of the temperature. Shrout et al. [6] characterized the morphotropic phase boundary (MPB) separating the rhombohedral (pseudo cubic) and the tetragonal phases in PMNT. The MPB was reported to occur at
$x = 0.33$ PT and the piezoelectric coefficient d_{33} was found to be 1050 – 1500 pC/N for the (100) direction and 300 – 550 pC/N for the (111) direction.
Zhang et al. [7] investigated the properties of $0.67Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.33PbTiO_3$ domain engineered single crystal and it was confirmed that it had a large electromechanical coupling coefficient k'_{33} of about 94% and a piezoelectric constant d_{33} of about 2800 pC/N when poled in the (001) direction, consistent with values reported earlier [5].
In order to realize ultrasonic array probes using single crystal materials, two important practical conditions have to be considered: the growth of sufficiently large single crystals and the fabrication of array probes from the relatively mechanically fragile crystal structure. Recent research successfully demonstrated the growth of homogenous and large PZNT single crystals by the self-flux Bridgman method using PbO-flux [8]. Other work [9] revealed that a PZNT 91/9 single-crystal phased array probe indeed has advantages over a ceramic probe. Improved sensitivity and broader bandwidth for echocardiography were demonstrated.
High piezoelectric constants k_{33} and d_{33} of PMNT and PZNT make them very attractive for medical imaging. However, previous work has focused primary on the (100) orientation of compositions in the rhombohedral phase near the MPB. There are still many questions on material properties of other composition and orientations. Recently, Chen et al. [10] found a very high mechanical coupling factor (> 0.9) for the (110) and (111) orientations of a PMNT 69/31, but no dielectric constant data was shown.
In order to quantify a Figure of Merit for the application of these materials to ultrasonic transducers both the coupling factor and dielectric constant are important.
Y. Lu et al [11] reported both these properties for PMNT 67/33, for various planes, but only for rhombohedral PMNT. Although the mechanical coupling factor k_{33} is reported to be highest on the rhombohedral side of the MPB, this doesn't mean that rhombohedral PSC is necessarily the most appropriate composition of PSC for medical ultrasonic transducers. For a high efficiency of a transducer a high coupling factor, high dielectric constant, low acoustic impedance and low frequency constant of the longitudinal mode are important as well. Since there is little data available on the piezoelectric properties of PMNT compositions in the tetragonal phase near the MPB, this paper we will discuss the material properties of PMNT 65/35 PSC, which is in the tetragonal phase, for (111), (110) and (100) crystal orientation. A figure of merit will be presented and used to compare the performance to other piezoelectric materials.

2. EXPERIMENTAL PROCEDURE

For the experiments, plate samples of PMNT were used and cut in the desired dimensions using a disco DAD-2H/6T automatic dicing machine. Because the PMNT single crystal samples were not equipped with an electrode, a thin film of gold (~200 nm) was sputtered on the plate sample. In order not to influence the dielectric constant of the material, the thickness of the electrodes on the plate samples needed to be substantially less than the thickness of the plate [12], hence a thin film sputtering technique was used (TOKUDA CFS-8EP sputtering machine). Dimensions of the plate samples were typical in the order of (l x w) 25 mm x 10 mm, with various thickness. Experiments were performed for both plate mode and sliber mode samples, in the latter case the width of the sample was much smaller than its length, as is indicated in Fig.2. The dicing was done on all samples with the same type of blade.

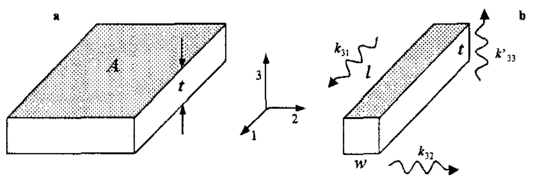

Fig.2 Plate and sliber mode of piezoelectric material and its dimensions. Plate samples (a) were cut into sliber samples (b).

Experiments were concentrated on sliber mode of the samples. Impedance resonance and dielectric constant resonance were used to measure material properties (Fig.3). Before starting the experiments the plate samples and sliber samples were poled at room temperature for about 5 minutes at an electric field of 1kV/mm. The impedance resonance method is often used because it simple and rather accurate, it uses the coupling relation to calculate material properties based on the resonance and anti-resonance frequencies. With this method the electromechanical coupling factors k_t and k'_{33} were determined using a network/spectrum analyzer (HP 4195A).

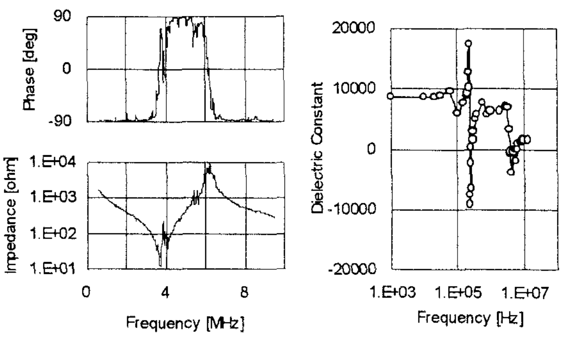

Fig.3 Impedance resonance (left) and dielectric constant resonance (right) for PMNT 65/35 (110) sliber sample.

By using a small electric oven, the same method was used to measure the temperature dependence of k'_{33}. In order to determine the transverse vibration k_{31}, the admittance resonance in the lower frequency region was used instead of the impedance curve.
Dielectric constants and dielectric losses were measured using a LF impedance analyzer (YHP 4192A) from
1 kHz to 13 MHz. Using the dielectric resonance method, the dielectric constant at 1 kHz (ε_{33}^T), at two times the

resonance frequency f_r of the length-mode vibration (ε_1) as well as the dielectric constant at two times the anti-resonance frequency f_a of the thickness-mode vibration (ε_2) were measured. From this data, as verification, the coupling factor k_{31} and k'_{33} were also calculated. By using a small oven, the temperature dependence of the dielectric constant for plate mode was determined as well.

3. RESULTS

The PMNT 65/35 PSC ingot used for the experiments was prepared. Three types of different planes (100), (110) and (111) were cut from the ingot. The cut plate-shaped crystal used for the experiments had a thickness of about 0.40 mm, length of 10 mm and width of 10 mm. Several samples with different crystal orientation were chosen to determine the material properties of PMNT 65/35 in plate mode.

The dielectric constant was recorded as a function of the temperature for different plate samples with (100), (110) and (111) crystal orientation. The graph of the most promising composition (110) is presented in Figure 5. The Curie temperature for the PMNT samples was found to be typically 185°C for (100) crystal orientation, 175°C for (110) orientation and 170°C for (111) orientation. Since it is difficult to manufacture the PMNT samples at exactly the 65/35 proportion, the Curie temperature can be used as a non-destructive method to roughly estimated the concentration of lead magnesium niobate and lead titanate. The theoretical Curie temperature of PSC, if the T_c obeys the Vegard Law, is presented in Table I.

Table I Theoretical T_c and predicted PMNT content

		T_c [°C]	samples
$PbTiO_3$		490	
PMNT	61/39	185	(100)*
	62/38	180	(110)*
	64/36	170	(111)*
	65/35	165	
$Pb(Mg_{1/2}Nb_{2/3})O_3$		-10	

The Curie temperature of the samples is slightly higher (5 – 10%) than the theoretical value of 165 °C which corresponds to a larger content of lead titanium as is indicated in Table I (* for predicted composition).

Two important characteristics of the temperature dependent dielectric graphs are: the relatively high dielectric constants of the (110) and (111) crystal orientations (typically 7000) in plate mode and the absence of any phase transition in the temperature region up to the Curie Temperature, corresponding to an almost constant dielectric constant up to T_c.

Other properties of the plate mode sample are presented in Table II.

Table II Plate mode PMNT 65/35, poling conditions 1kV/mm, room temperature

Orient.	T_c [°C]	ε_{33}^T	k_t [%]	d_{33} [pC/N]	Z_t [Mrayls]
100	185	100	60	400	36
110	175	7000	65	1000	42
111	170	6500	55	450	42

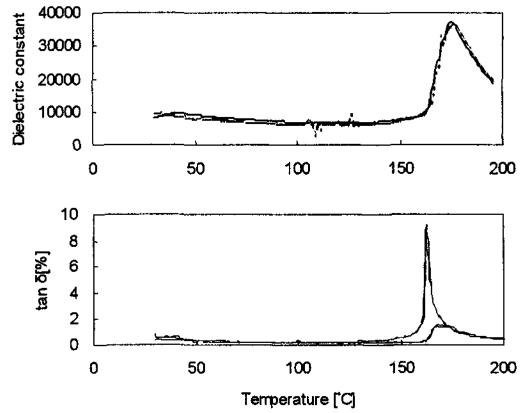

Fig.5 Dielectric constant and tangent losses of 110 orientated PMNT 65/35 crystal as a function of temperature, plate mode.

Since the results on the (110) and (111) orientated crystal looked most promising, because of the higher dielectric constant and because the mechanical properties of the (100) samples were very poor (fragile), it was decided to only cut the (110) and (111) samples into the sliber mode. The plate mode samples were cut to slibers with typical dimensions of 7.0 x 0.16 x 0.40 mm. The experimental results on the sliber samples are summarized in Table III.

Table III PMNT 65/35 sliber, poling conditions 1kV/mm, room temperature

Orient.	ε_{33}^T		ε_1	ε_2
110	8000		6000	2000
111	10000		6000	3000
	k_{31} [%]	k'_{33} [%]	N'_{33a} [Hzm]	Z'_{33} [Mrayls]
110	50	82	2500	40
111	63	71	2500	40

The dielectric constant of the (110) single crystal is about 8000 with a k'_{33} of 82%, the dielectric constant of the (111) sample is very large at 10000, however, the corresponding k'_{33} is only 71%. Based on these results it was judged that although the (111) orientation has a higher dielectric constant, the combination of ε_{33}^T and k'_{33} is most promising for (110) orientated PMNT 65/35 single crystal.

The temperature dependence of the mechanical coupling factor for the practical temperature operation range of 20 – 70°C was studied and the results for PMNT 65/35 (110) in sliber mode are depicted in Fig.6.

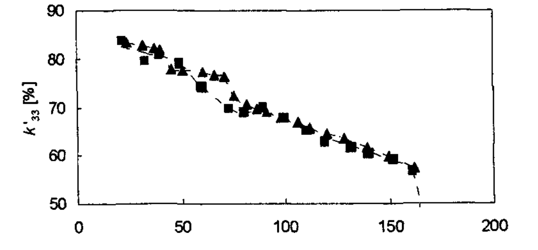

Fig.6 Temperature dependence of mechanical coupling factor k'_{33} of (110) single crystal PMNT in sliber mode.

As can be seen from Fig. 6, k'_{33} shows a large variation in the temperature range of 20 - 70℃, with a non-monotone decrease of about 15%. The step like decrease of k'_{33} suggested a phase transition in this area, however, this was verified by checking the temperature dependence of the dielectric constant of the sliber sample and no such phase transition was observed.

4. CONCLUSIONS

The choice of the most optimal piezoelectric material is very important for medical pulse-echo ultrasonic imaging. In this report the dielectric and piezoelectric properties of tetragonal PMNT 65/35 are discussed.

Three crystal planes of PMNT 65/35 were investigated and it was concluded that the (110) orientation was most promising in terms of high dielectric constant and high mechanical coupling factor: ε_{33}^T » 8000 and k'_{33} » 83% in sliber mode. The dielectric constant was almost temperature independent at a value of 8000 up to the Curie temperature of about 175°C. The mechanical coupling factor k'_{33} showed a relatively large temperature dependence, a decrease of about 15% was observed in the temperature region of 20-70°C.

In order to quantify the material with the best overall performance a Figure of Merit (*FOM*) was used, which is expressed in Equation 1.

$$FOM = \frac{\left(k'_{33}\right)^2 \varepsilon_1}{Z'_{33} N'_{33a}} \qquad \text{(Equation 1)}$$

Equation 1 was used to compare the *FOM* of PMNT 65/35 from this experiment and PZT. The data of the transducers is summarized in Table IV.

Table IV Piezoelectric properties of studied materials.

Material	k'_{33} [%]	ε_{33}^T	ε_1
PMNT 65/35	83	8000	6000
PZT ceramic	70	5000	4000
	Z'_{33} [Mrayls]	N'_{33a} [Hzm]	
PMNT 65/35	40	2500	
PZT ceramic	31	2000	

With use of Equation 1 and the data in Table IV, the figure of merit for the different materials is calculated and the results are presented in Table V.

Table V Figure Of Merit (FOM) calculated for the different materials.

Material	Phase	Orient.	*FOM**
PMNT 65/35	tetragonal	110	4.1
PZT ceramic	ceramics	-	3.2

*unit: s/Mrayls・m

The calculated *FOM* showed that PMNT 65/35 had a Figure of Merit of about 30% larger than the advanced PZT ceramic material and therefore is a very promising material for application in a piezoelectric transducer.

5. REFERENCES

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