

RECENTLY DEVELOPED PIEZOCERAMIC MATERIALS FOR NEW APPLICATIONS

W. W. WOLNY

Ferroperm Piezoceramics A/S, Hejreskovvej 18A, 3490 Kvistgaard, Denmark
<http://www.ferroperm-piezo.com>

Abstract - For more than 40 years, PZT family has been the best established group of piezoelectric ceramics, with a wide variety of compositions, optimised for different applications. It has been divided into hard and soft materials, each of the main groups divided again into subgroups, standardised and widely available in these classical types. The recent developments within the medical field, includes besides 3D diagnostics, new therapeutical applications using high intensity focused ultrasound (HIFU), requires for the latter a hard material type to handle necessary signal level. However, it is also desirable to have, at the same time, higher dielectric constant in order to match electrical impedance. Besides electrical matching, acoustic properties of ceramics are important in order to optimise performance of transducers based on PZT. Mismatch between acoustic properties of PZT and environments, in which transducers have to work, have been overcome by adding matching layers and/or backing and creating composite structure using time consuming and costly dice and fill processes or similar. Finally, high content of lead in PZT has in the light of EU's environmental policy towards sustainable materials, a substantial effort was made to replace PZT by lead free materials. This paper presents besides, two new hard materials with dielectric constant of 1900 and 2800, also an additional version of these materials with engineered structure, where the acoustic impedance has been reduced to approx. 15 MRayleigh. Typical properties for the new materials, incl. lead free ceramics will be presented.

1. Introduction

Lead titanate lead zirconate ceramics family has been developed over more than 4 decades. The basic composition was modified by a number of different substituents in order to meet requirements of a growing number of applications.

Technology based on mixed oxides method, still dominating in industry, has been upgraded by improved powder processing routes and by pressure assisted densification.

New market signals indicate that sustainability has become a part of the strategy for a new product generation and requirements for design and materials. At the same time, global competition makes it necessary to sharply monitor cost of manufacturing, forcing industry to reject some of the possible candidates for innovation, being materials or technologies, due to high cost either of capital

investment or chemical ingredients.

Time to the market is another factor defining return of the costly development effort. Close collaboration with end users and fast response time to the marked needs are conditions for success and ensure more efficient introduction of new products. Recently, new emerging products within HIFU (high intensity focused ultrasound) created interest for a new generation of hard materials, optimised for this application. Examples of such new materials will be given in this paper.

To comply with the demand for sustainable products the lead content in PZT can be either completely eliminated or significantly reduced. Both routes will be illustrated in the paper.

Cost, performance and timing define success criteria for development of the new product. High cost of composites consisting of PZT and polymer phase, manufactured by dicing and filling method together with their relatively narrow operating temperature range have been limiting the use of such materials despite their satisfying performance. Alternative composite manufacturing process has been developed resulting in significantly lower cost materials with extended operating temperature range. As these engineered structure materials do not contain the soft polymer phase, they can be also attractive when prepared from hard type PZT for high signal operation. Properties of the engineered structure soft and hard type piezoceramics are shown in the paper.

2. Sustainable piezoceramics

Reduced effect of lead on environment can be obtained either by eliminating or reducing the content of lead in the product or by improving the products performance. As a result, volume of the hazardous substance, necessary to maintain the correct function of a given device, containing such a product, will be reduced. Finally, cost of components is an important, often a key factor in design of new devices. The cost factor limits therefore, practically, the use of pressure assisted densification methods, such as hot pressing, hot isostatic pressing or forging a/o, if using those means significantly increased cost.

To eliminate lead totally, compositions of piezoelectric materials alternative to PZT, have to be considered. At present, however, no ideal replacement for PZT has been found. None of the investigated candidates such as barium titanate or bismuth titanate offers properties even close to those of PZT (see Table 1). In addition, neither bismuth nor barium, is a completely safe alternative to lead. Ferroperm Piezoceramics working within 5th Frame Project LEAF² (Lead -free piezoelectric ceramics based on alkaline niobates) took a different approach and focused on materials consisting of ingredients completely non-toxic. Alkaline niobates have been known since the sixties¹, however, due to a problematic densification, they were not common among users of piezoceramics. The number of compositions tested and reported in literature was limited and reported mainly for compositions densified by means of hot pressing. Properties were only attractive when compared to lead metaniobate, another porous, highly anisotropic ceramic used mainly for non-destructive testing (NDT) transducers.

Table 1: Comparison of various types of piezoelectric ceramics. Typical values.

Parameter	ρ (g/cm^3)	$\epsilon_{3,r}$	$\tan \delta$	T_c ($^{\circ}C$)	k_p	k_t	d_{33} ($10^{-12}C/N$)	Q_M
PZT Type 1 (Pz26)	7.70	1300	0.003	330	0.57	0.47	290	>1000
PZT Type 1 (Pz27)	7.70	1800	0.017	350	0.59	0.47	425	80
Barium titanate	5.70	1450	0.02-0.10	130	0.36	0.38	190	600
Bismuth titanate (K15, PZ 46)	7.20	145	0.010	>600	0.06	0.15	>18	100
Lead metaniobate (K81, PZ 35)	6.20	300	0.01	400	<0.10	0.30	85	N/A
Lead-free (Pz61)	4.30	600	0.030	400	30	40	60-80	20-30

3. Lead free ceramic

PZ 61 is the potassium sodium niobate composition selected after the recent completion of LEAF project for commercialisation. It offers attractive properties when compared to lead metaniobate, both for low frequency and resonant applications as d_{33} and k_t have same or higher values than those of K81 or PZ 35, two commercial compositions. (see Table 1). Its relatively high sound velocity affects acoustic properties of KNN, which is not an advantage in terms of matching transducer acoustically to most of environments (see Figure 1). On the other hand, it makes it easier to manufacture components for high frequencies, when compared with porous and mechanically weak lead metaniobate. The work carried out during the project indicates possibilities to extend this niobate family by additional compositions e.g. with higher dielectric constant² to create a choice of materials optimised for different applications. Still, based on present experience, properties cannot be expected to provide a direct replacement for PZT family.

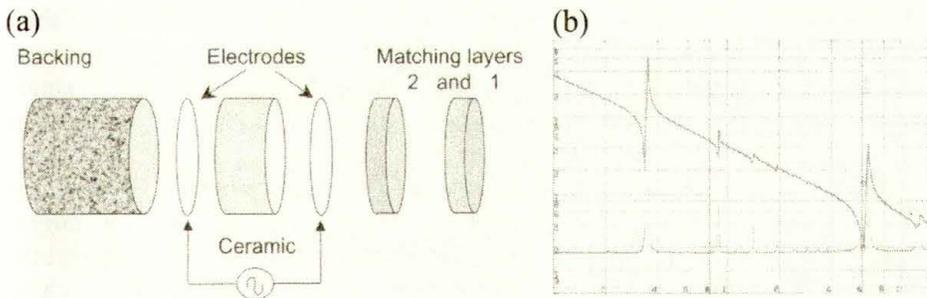


Fig. 1: (a) Schematic representation of KNN based transducer for medical applications. Impedance plot for a circular Pz61 disc. Dimensions are OD 9,6 mm TH 0.45 mm. (b) The frequency sweep is from 100 kHz to 15 MHz.

4. Modified PZT compositions with improved performance properties by means of innovative technologies

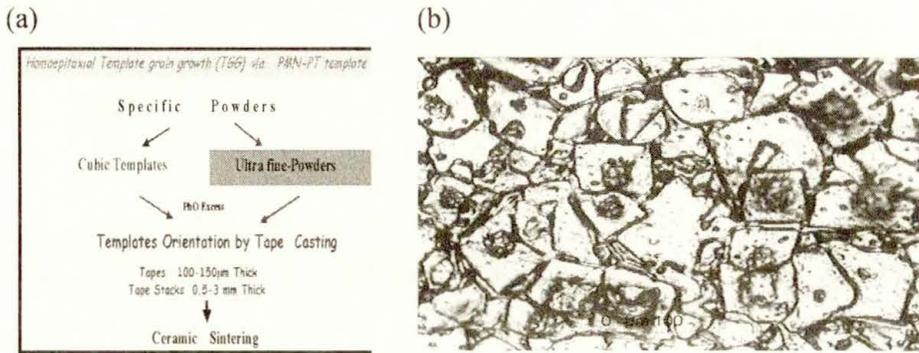


Fig. 2: (a) Textured ceramic process. (b) Microscope picture of a textured ceramics.

Medical arrays for 2D diagnostics, are often based on so-called 1-3 composites, i.e. ceramic plates are produced by dice and fill method and cut into elements sometimes as small as 50 micrometer.

Their commercialisation, approx. 10 years ago, triggered development of ceramics with very high dielectric constant in order to compensate for the tiny size of individual elements and their very low capacitance. 3203HD from CTS³ became market standard and reference, offering besides very good piezoelectric properties, high dielectric permittivity and nice dense microstructure, another feature important for materials to be cut.

Single crystals PMN-PT and PZN-PT could be alternative, offering a/o electromechanical coupling of 90% and more³ together with other attractive features, however, high cost and until recently poor reproducibility put limitations on their commercialisation. The idea of improving technology of ceramics, so that thanks to a higher degree of ordered structure, properties closer to those of relaxor single crystals would be obtained, led to investigations on textured ceramics^{5, 7,8} (see Figure 2) and sinter forging⁶ (see Figure 3).

Both technologies result in materials with improved properties. Textured ceramics, however, still require further work on process parameters such as degree of texturing, which is a function of volume and orientation of seed crystals and the remaining ceramic tape, but also more conventional process parameters such as densification of these structures. Forging, one of pressure assisted sintering techniques, whilst resulting in improved properties, adds substantial cost to the product.

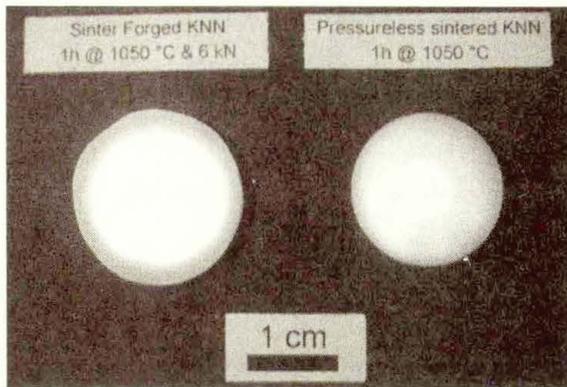


Fig. 3: Comparison of sinter forged KNN and conventionally sintered KNN (High density is here shown by a higher degree of translucency)

The application driven development depends on the market's interest and will often be based on a push-pull relationship between the end user and the supplier. Medical devices market is a good example how such a relationship affects the material development.

The medical market works on the next generation of diagnostic devices- 3D arrays, leading to a demand for even higher dielectric permittivity of 5-6000. The challenges here are to maintain Curie temperature, which usually drops as material is modified in order to increase permittivity, at min. 160- 170 °C, and to have sufficiently high coercive field in order to avoid depolarisation during e.g. assembly. The more general trend goes towards miniaturisation of devices based on piezoceramics. This market includes medical devices as well, single element transducers. The medical market for diagnostic arrays is less price sensitive and is relatively low volume and opens therefore for using expensive raw materials such as scandium and indium to obtain desired properties. Other medical applications will challenge the material suppliers, working on ceramics for new requirements, to modify their products by mainly process improvements.

5. New materials for therapeutic applications

Whilst ultrasound based medical diagnostics devices are well established and cover, besides already mentioned arrays systems for e.g. obstetrics, gynaecology, cardiology a/o, small often portable equipment for bloodflow and heart rate control. As new countries develop their welfare, new health care units are organised to serve local societies. Well-established societies in Europe and Japan are ageing, creating a need for costly hospitalisation to increase. This situation has created an increasing interest for new treatment methods, based on use of ultrasound and replacing traditional surgery. Ultrasound therapy based on the principle of high intensity focused ultrasound (HIFU) is in many situations expected to replace surgery, thus minimising the impact of the operation on human body and reducing the hospitalisation time needed after treatment, which will minimise additional

cost emerging from social development. The reported experiments show positive effect of ultrasound on treating cancer tumours and healing of wounds or broken bones. HIFU in treatment of prostate tumours, another old age disease, is already developed and commercialised.

Table 2: Comparison of new HIFU materials (Pz52, Pz54) with a standard PZT type I material (www.ferroperm-piezo.com)

Parameter	ρ (g/cm^3)	$\epsilon_{3,r}$	$\tan \delta$	T_C ($^{\circ}\text{C}$)	k_p	k_t	d_{33} (10^{-12}C/N)	Q_M
Pz26 (Type I)	7.70	1300	0.003	330	0.57	0.47	290	>1000
Pz52 (HIFU)	7.30	1900	0.003	250	0.61	0.53	420	550
Pz54 (HIFU)	7.80	2800	0.003	225	0.59	0.48	500	1500

The traditional group of hard PZT materials, developed for maritime or industrial applications, was optimised for relatively low frequency and bulky devices. The new medical applications require materials with different properties. At the same time, as the new therapeutic devices follow the general trend towards miniaturisation, their structure has to be fine grained. Low dielectric and mechanical losses are to be maintained in order to handle the energy needed during the ultrasonic treatment, however, significantly higher dielectric permittivity than that of Type I materials is desired to match electronics. Finally, the operating temperature range should not be significantly reduced, which again, limits the possible degree of freedom in modifying the basic compositions (see Table 2 & Figure 4).

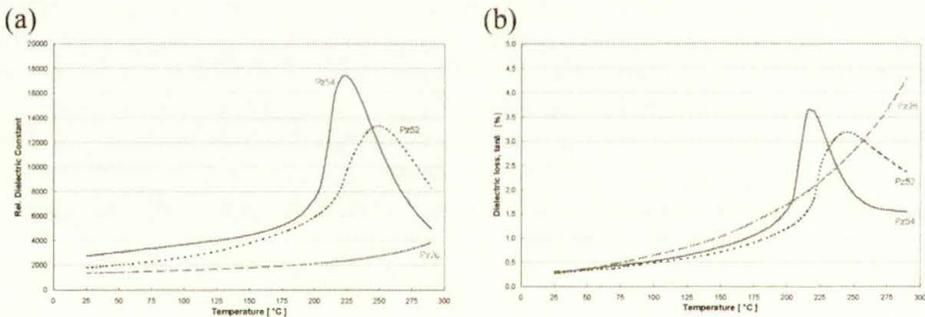


Fig. 4: Temperature dependence of the free dielectric constant, ϵ_r , (a) and dielectric loss tangent, $\tan \delta$, (b) of Pz52 and Pz54 in comparison with a traditional Type 100 high-power material (Pz26).

6. Engineered structure ceramics

Engineered structure ceramics⁹ are an example for modifying properties by process modification. By using a carefully controlled volume of a combustible additive to the powder, the resulting content of porosity in otherwise fully densified ceramic, can be defined in advance, both with regard to the volume percent and pore size. The process opens for possibilities to modify more or less any traditional bulk

ceramic, offering physically lighter components.

Table 3: Comparison of lead metaniobate Pz35 with new low acoustic impedance materials Pz36, Pz37 (www.ferroperm-piezo.com)

Parameter	ρ (g/cm^3)	$\epsilon_{3,r}$	$\tan \delta$	T_c ($^{\circ}C$)	k_p	k_t	d_{33} ($10^{-12}C/N$)	Q_M
Pz35	5.70	220	0.006	500	0.05	0.34	100	15-20
Pz36	5.70	610	0.003	350	0.26	0.52	230	500
Pz37	5.70	850	0.017	350	0.25	0.50	340	50

As a result the acoustic impedance of such a modified material is significantly lower and the number of matching layers, needed in transducers in order to obtain better signal transmission to a human body, is reduced. Again, transducer assembly is simplified and the overall cost reduced. Engineered structure ceramics are not a complete replacement for 1-3 composites prepared by the dicing and filling technique, but they do offer a good alternative in many applications. Besides much lower cost, they have a wide operating temperature range as they do not contain polymer phase and can be used with standard screen printed silver electrodes. As materials are modified already at powder stage, piezoceramic components can be formed by pressing into, more or less, any shape. Following manufacturing steps are similar to those of standard ceramics and do not involve additional cost. Engineered structure ceramics have good mechanical properties and can be machined and handled exactly as conventional piezoceramics (see Table 3 & Figure 5).

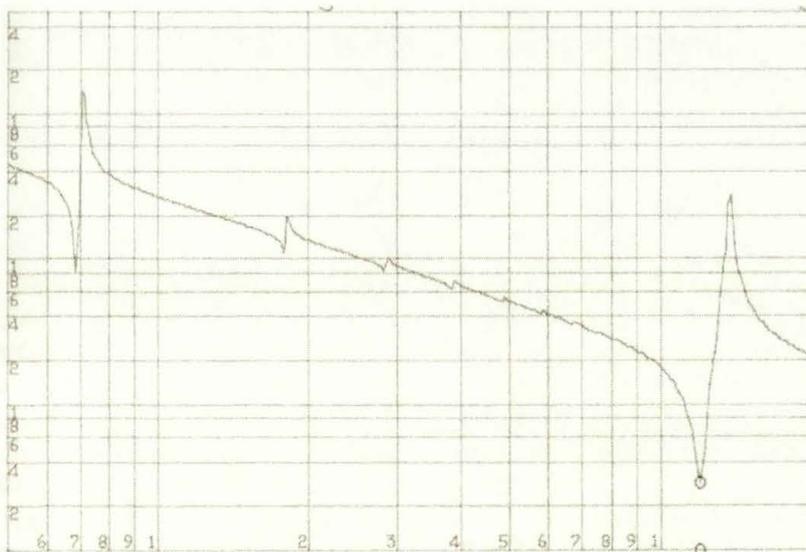


Fig. 5: Impedance plot for a circular Pz39 disc. Dimensions are OD15 mm TH 1 mm. The frequency sweep is from 50 kHz to 2 MHz.

7. Piezoceramics in miniaturised integrated devices.

Miniaturisation supports sustainable development policy. It can be implemented by means of a devices based on the principle identical to the traditional devices, just smaller. Miniaturised catheters are good examples of such products (see Figure 6). They use traditional high quality piezoceramics, extensively machined and assembled. They are an example of a highly sophisticated product.

Another example can be a simple disposable doppler (bloodflow measurement) device used to monitor patients after surgery. Here, its cost is a crucial factor for its implementation, even that benefit seems to be obvious, reduced risk of acquiring contagious disease during hospitalisation.

In a small device smaller volume of harmful substances is used. This simple fact requires, however, extensive development of material technology, if the performance of miniaturised devices has to be comparable to the traditional devices.

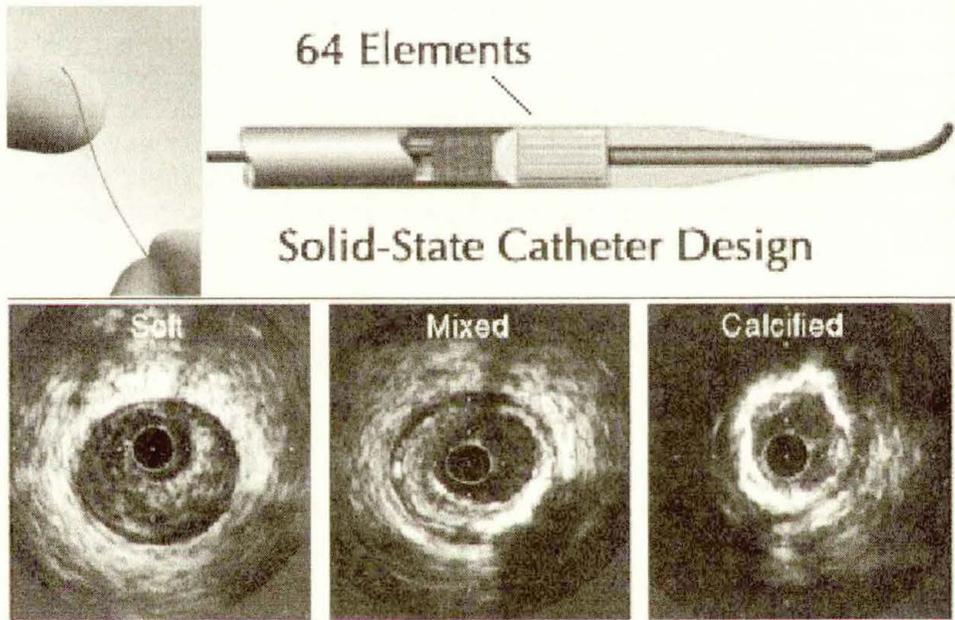


Fig. 6: Jomed¹⁰ transducer. Miniaturized, high-frequency medical ultrasound which in this case is shown by an Intravascular Catheter.

Market drive is towards lower cost products enabling implementation of disposable, preferably small, transducers. To achieve that, new technologies such as thick films¹¹ have to be introduced. Screen printing technology, traditionally used for e.g. depositing metal layers or similar, can also be used for depositing ceramic layers to create thick film (see Figure 7). It also offers benefit of integration of other components on a substrate. Altogether, technology has been known for many years, the challenge however, is to adapt piezoceramics for this technology. PZT contains highly reactive lead and requires relatively high temperatures of 1200 °C or higher for densification.. To make it possible to deposit PZT on. e.g. silicon substrate,

powder has to be modified in order to densify below 800 °C and barrier layers blocking migration of lead have to be developed.

LTCC (low temperature co-fired ceramics) have been developed for integrated circuits, however, without active components such as PZT transducers. Technologically, LTCC integration presents similar challenges to those related to silicon substrates.

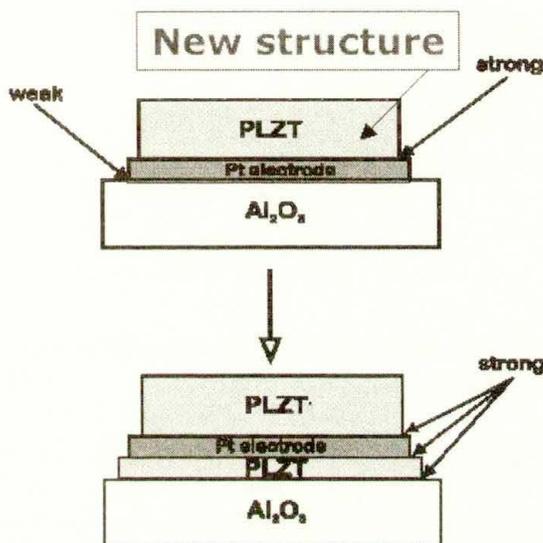


Fig. 7: Thick film structure.

8. Conclusions

The examples of applications given in this paper are based on development in the medical device market. It could be as well hardware technology, sensor- automotive market or robotics. Miniaturisation is a general trend, no matter the application. At the moment, the focus is on material development, however, in the future, implementation of new or improved materials in the devices based on technologies enabling integration is to take place. Thick film technology is a good candidate to provide a feasible and relatively fast route to commercialisation. The principle is the same everywhere- timing, cost reduction coupled with improved or at least comparable performance. Close collaboration with end users is to mutual benefit.

The development has not been identical in different parts of world. Whilst in Europe and Japan the environmental aspects were dominating, improved performance was the most important factor affecting material or technology choice in United States.

Acknowledgments

The author wishes to acknowledge inspiring discussions with my professional colleagues and friends, often taking place at Polecer (G5RT-CT-2001 – 05024) workshops and conferences.

References

- [1] B. Jaffe, W. Cook, H. Jaffe. Piezoelectric Ceramics. Academic Press Inc.
- [2] LEAF project: G5RD-CT-2001-00431. EC 5th Framework Programme, GROWTH. 2001-2004.
- [3] CTS... <http://www.ctscorp.com/components/Datasheets/PZT.pdf>.
- [4] Park, S.-E. & Shrout, T. R., Characteristics of Relaxor-Based Piezoelectric Single Crystals for Ultrasonic Transducers. *IEEE Trans. Ultrason., Ferroelect., Freq. Contr.*, 1997, **44** [5], 1140-1147.
- [5] PIRAMID project: G5RD-CT-2001-00456. EC 5th Framework Programme, GROWTH. 2001-2004.
- [6] Pithan, C., Pressure Assisted Consolidation of Electroceramics. In *Processing of Electroceramics, Conference Notes*, ed. Kosec, M., Kuscer, D. & Malic, B. (POLECER Symposium). Jozef Stefan Institute, Ljubljana, 2003, pp. 181-198.
- [7] Pham-Thi, M., Holc, J. & Kosec, M., Textured $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ Ceramics by Homoepitaxial TGG. In *Processing of Electroceramics, Conference Notes*, ed. Kosec, M., Kuscer, D. & Malic, B. (POLECER Symposium). Jozef Stefan Institute, Ljubljana, 2003.
- [8] Sabolsky, E. M., James, A. R., Kwon, S., Trolier-Mckinstry, S. & Messing, G. L., Piezoelectric Properties of Textured $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ Ceramics, *Appl. Phys. Lett.*, 2001, **78** [17], 2551-2553
- [9] Galassi, C., Development and Characterization of Porous Piezoelectric Materials. In *Processing of Electroceramics, Conference Notes*, ed. Kosec, M., Kuscer, D. & Malic, B. (POLECER Symposium). Jozef Stefan Institute, Ljubljana, 2003, pp. 267-281.
- [10] <http://www.jomed.com>
- [11] Kosec, M., Ferroelectric Thick Films: Composition, Fabrication Processes and Structural Characterisation. In *Proc. of Material Technology and Design of Integrated Piezoelectric Devices*, ed. Feuillard, G. et al. (POLECER Symposium).
- [12] <http://www.ferroperm-piezo.com>
- [13] A. Ando, M. Kimura, K. Syratsuyu, Y. Sakabe. Murata, Alkaline Niobate piezoelectric Ceramics. Polecer WP9, Euro Asian Environmental Meeting, China November 2003.
- [14] T. Takanaka. Ferroelectric and Piezoelectric Properties of $\text{Sr}_2\text{Bi}_{14}\text{Ti}_{15}\text{O}_{18}\text{-Ca}_2\text{Bi}_{14}\text{Ti}_{15}\text{O}_{18}$ Solid State Solution Ceramics. AMF4, December 2003.
- [15] Damjanovic, D., F. Brem, N. Setter. Crystal Orientation dependence of the d_{33} coefficient in tetragonal BaTiO_3 as a function of temperature: *Appl. Phys. Letters*, vol. 80, 652-654, 2002

- [16] J. Cheng, R.E.Eitel, N.Li & L.E.Cross. Structural and Electrical Properties of $(1-x)\text{Bi}(\text{Ga}_{1/4}\text{Sc}_{3/4})\text{O}_3\text{-xPbTiO}_3$ Piezoelectric Ceramics. *J of Applied Physics*, 94(1) 605-609, 2003.