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smart engineering for extreme environments

# High frequency transducer based on lead free piezoceramic thick film

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# Outline

- Lead free legislation
- Lead free candidates
- KNN ceramic
- KNN thick film
- KNN thick film transducer
- Conclusion

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# Lead free legislation (ROHS)

13.2.2003 EN Official Journal of the European Union L 37/19

**DIRECTIVE 2002/95/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL**

**of 27 January 2003**

**on the restriction of the use of certain hazardous substances in electrical and electronic equipment**

THE EUROPEAN PARLIAMENT AND THE COUNCIL OF THE EUROPEAN UNION,

Having regard to the Treaty establishing the European Community, and in particular Article 95 thereof,

Having regard to the proposal from the Commission ([1]),

Having regard to the opinion of the Economic and Social Committee ([2]),

Having regard to the opinion of the Committee of Regions ([3]),

Acting in accordance with the procedure laid down in Article 251 of the Treaty in the light of the joint text approved by the Conciliation Committee on 8 November 2002 ([4]),

Whereas:

(1) The disparities between the laws or administrative measures adopted by the Member States as regards the restriction of the use of hazardous substances in electrical and electronic equipment could create barriers to trade and distort competition in the Community and may thereby have a direct impact on the establishment and functioning of the internal market. It therefore appears necessary to approximate the laws of the Member States in this field and to contribute to the protection of human health and the environmentally sound recovery and disposal of waste electrical and electronic equipment.

(2) The European Council at its meeting in Nice on 7, 8 and 9 December 2000 endorsed the Council Resolution of 4 December 2000 on the precautionary principle.

(3) The Commission Communication of 30 July 1996 on the review of the Community strategy for waste management stresses the need to reduce the content of hazardous substances in waste and points out the potential benefits of Community-wide rules limiting the presence of such substances in products and in production processes.

(4) The Council Resolution of 25 January 1988 on a Community action programme to combat environmental pollution by cadmium ([5]) invites the Commission to pursue without delay the development of specific measures for such a programme. Human health also has to be protected and an overall strategy that in particular restricts the use of cadmium and stimulates research into substitutes should therefore be implemented. The Resolution stresses that the use of cadmium should be limited to cases where suitable and safer alternatives do not exist.

(5) The available evidence indicates that measures on the collection, treatment, recycling and disposal of waste electrical and electronic equipment (WEEE) as set out in Directive 2002/96/EC of 27 January 2003 of the European Parliament and of the Council on waste electrical and electronic equipment ([6]) are necessary to reduce the waste management problems linked to the heavy metals concerned and the flame retardants concerned. In spite of those measures, however, significant parts of WEEE will continue to be found in the current disposal routes. Even if WEEE were collected separately and submitted to recycling processes, its content of mercury, cadmium, lead, chromium VI, PBB and PBDE would be likely to pose risks to health or the environment.

(6) Taking into account technical and economic feasibility, the most effective way of ensuring the significant reduction of risks to health and the environment relating to those substances which can achieve the chosen level of protection in the Community is the substitution of those substances in electrical and electronic equipment by safe or safer materials. Restricting the use of these hazardous substances is likely to enhance the possibilities and economic profitability of recycling of WEEE and decrease the negative health impact on workers in recycling plants.

(7) The substances covered by this Directive are scientifically well researched and evaluated and have been subject to different measures both at Community and at national level.

(8) The measures provided for in this Directive take into account existing international guidelines and recommendations and are based on an assessment of available scientific and technical information. The measures are necessary to achieve the chosen level of protection of

([1]) OJ C 365 E, 19.12.2000, p. 195 and OJ C 240 E, 28.8.2001, p. 303.
([2]) OJ C 116, 20.4.2001, p. 38.
([3]) OJ C 148, 18.5.2001, p. 1.
([4]) Opinion of the European Parliament of 15 May 2001 (OJ C 34 E, 7.2.2002, p. 109), Council Common Position of 4 December 2001 (OJ C 90 E, 16.4.2002, p. 12) and Decision of the European Parliament of 10 April 2002 (not yet published in the Official Journal). Decision of the European Parliament of 18 December 2002 and Decision of the Council of 16 December 2002.
([5]) OJ C 30, 4.2.1988, p. 1.

([6]) See page 24 of this Official Journal.

1. Member States shall ensure that, from 1 July 2006, new electrical and electronic equipment put on the market does not contain **lead**, mercury, cadmium, hexavalent chromium, polybrominated biphenyls (PBB) or polybrominated diphenyl ethers (PBDE). National measures restricting or prohibiting the use of these substances in electrical and electronic equipment which were adopted in line with Community legislation before the adoption of this Directive may be maintained until 1 July 2006.

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# Lead free legislation (ROHS)

13.2.2003 EN Official Journal of the European Union L 37/23

ANNEX

**Applications of lead, mercury, cadmium and hexavalent chromium, which are exempted from the requirements of Article 4(1)**

1. Mercury in compact fluorescent lamps not exceeding 5 mg per lamp.
2. Mercury in straight fluorescent lamps for general purposes not exceeding:
   - — halophosphate 10 mg
   - — triphosphate with normal lifetime 5 mg
   - — triphosphate with long lifetime 8 mg.
3. Mercury in straight fluorescent lamps for special purposes.
4. Mercury in other lamps not specifically mentioned in this Annex.
5. Lead in glass of cathode ray tubes, electronic components and fluorescent tubes.
6. Lead as an alloying element in steel containing up to 0,35 % lead by weight, aluminium containing up to 0,4 % lead by weight and as a copper alloy containing up to 4 % lead by weight.
7. — Lead in high melting temperature type solders (i.e. tin-lead solder alloys containing more than 85 % lead),
   - — lead in solders for servers, storage and storage array systems (exemption granted until 2010),
   - — lead in solders for network infrastructure equipment for switching, signalling, transmission as well as network management for telecommunication,
   - — lead in electronic ceramic parts (e.g. piezoelectronic devices).
8. Cadmium plating except for applications banned under Directive 91/338/EEC ([1]) amending Directive 76/769/EEC ([2]) relating to restrictions on the marketing and use of certain dangerous substances and preparations.
9. Hexavalent chromium as an anti-corrosion of the carbon steel cooling system in absorption refrigerators.
10. Within the procedure referred to in Article 7(2), the Commission shall evaluate the applications for:
    - — Deca BDE,
    - — mercury in straight fluorescent lamps for special purposes,
    - — lead in solders for servers, storage and storage array systems, network infrastructure equipment for switching, signalling, transmission as well as network management for telecommunications (with a view to setting a specific time limit for this exemption), and
    - — light bulbs,

    as a matter of priority in order to establish as soon as possible whether these items are to be amended accordingly.

**Applications of lead, mercury, cadmium and hexavalent chromium, which are exempted from the requirements of Article 4(1)**

— lead in electronic ceramic parts (e.g. piezoelectronic devices).

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# Lead free candidates

| Material | $d_{33}$ (pC/N) | $\varepsilon_{33}^T/\varepsilon_0$ (meas. freq) | $k_p$ (%) | $P_r$ ($\mu C/cm^2$) | $E_c$ (kV/mm) | $T_c$ (ºC) | Reference |
|---|---|---|---|---|---|---|---|
| $[Bi_{0.5}(Na_{1-x}K_x)_{0.5}]$ $TiO_3$<br>x = 0.16<br>x = 0.20 | - | (100 kHz)<br>635<br>1,030 | <br>31.4<br>27.0 | - | - | - | [54] |
| $[Bi_{0.5}(Na_{1-x}K_x)_{0.5}]$ $TiO_3$<br>x = 0.22 | 192 | 1,007 | 32.5 | 19.5 | - | - | [55] |
| $0.94Bi_{0.5}Na_{0.5}TiO_3$–<br>$0.06K_{0.5}Na_{0.5}NbO_3$ | ~94 | - | ~26 | 37 | 3.6 | - | [56] |
| $0.97(Na_{0.5}K_{0.5})$ $NbO_3$–<br>$0.03(Bi_{0.5}Na_{0.5})$ $TiO_3$ | 195 | - | 43 | - | - | 375 | [57] |
| $0.995(Bi_{1/2}Na_{1/2})$ $TiO_3$–<br>$0.005BiFeO_3$ | - | 530–700<br>(1 MHz) | - | 33.6 | 6 | 340 | [61] |
| $(Bi_{1/2}Na_{1/2})_{0.94}Ba_{0.06}TiO_3$ | 125 | 580 (10 kHz) | - | 20 | - | 288 | [58] |
| $(0.9)(Bi_{1/2}K_{1/2})$ $TiO_3$–$0.1BaTiO_3$<br>electric field applied parallel to<br>tape stacking direction | 84.5 | 560 (1 kHz) | - | - | - | - | [62] |
| 0.90 $(K_{0.48}Na_{0.48}Li_{0.04})$ $NbO_3$–<br>$0.10BaTiO_3$ | 206 | ~530 | ~38 | - | - | ~38<br>0 | [65] |
| 0.95 $(Na_{0.5}K_{0.5})$ $NbO_3$–$0.05BaTiO_3$ | 225 | 1,058 | 36 | - | - | - | [63] |
| 0.92NBT-0.06BT-0.02KNN | 30<br>576* | 2,320<br>(10 kHz) | - | 16 | 1.3 | - | [66] |
| 0.93NBT-0.05BT-0.02KNN | 98<br>276* | 2,060<br>(10 kHz) | - | 32 | 3.1 | - | [66] |
| $(0.90)(Bi_{1/2}Na_{1/2})TiO_3$–<br>$0.05(Bi_{1/2}K_{1/2})$ $TiO_3$–$0.05BaTiO_3$ | 148 | 700 (1 kHz) | 34 | 35.9 | - | - | [70] |
| $0.852(Bi_{1/2}Na_{1/2})$ $TiO_3$–<br>$0.028BaTiO_3$–$0.12(Bi_{1/2}K_{1/2})$ $TiO_3$ | 191 | 1,141<br>(1 kHz) | 33 | - | - | 301 | [69] |
| 0.88NBT–0.08KBT–0.02BT<br>(MPB) | 181 | - | - | - | - | 300 | [68] |
| 0.78NBT–0.146KBT–0.074BT<br>(tetragonal) | 128 | - | - | - | - | 300 | [68] |
| $(Bi_{1/2}Na_{1/2})_{0.78}$ $(Bi_{1/2}K_{1/2})_{0.22}TiO_3$–<br>$0.03(Na_{0.5}K_{0.5})$ $NbO_3$ | 167 | - | 35.5 | 27.6 | 2.79 | 340 | [71] |

*Values are measured under large driving signals.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Pz26 NAVY Type I | 290 | 1300 | 57 | - | - | 360 | - |

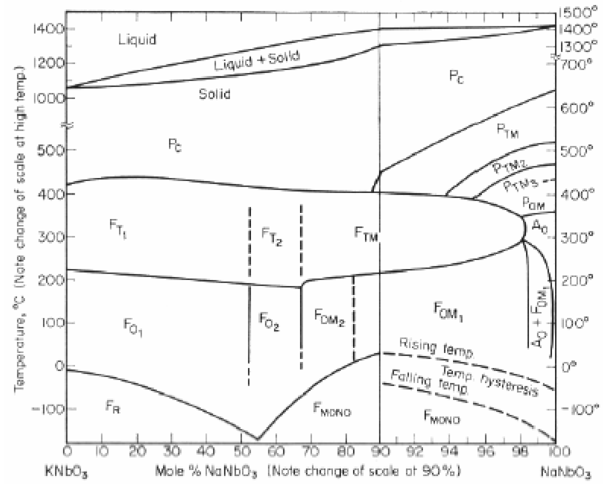
**Elena Aksel and Jacob, L. Jones,** *Sensors* **2010**, *10*, 1935-1954; doi:10.3390/s100301935

# Lead free candidates

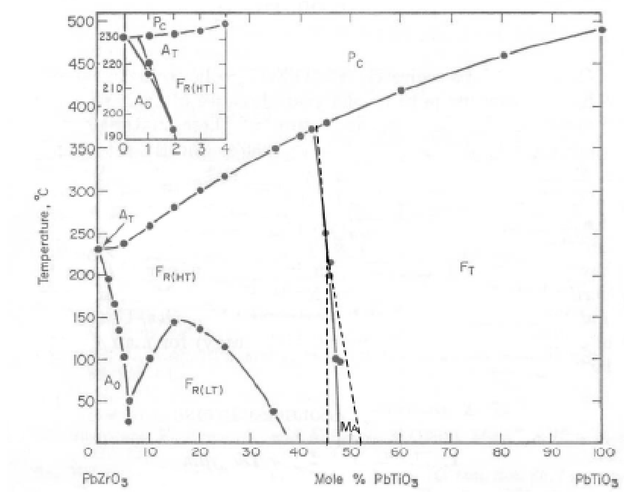
- BT first ceramic system used and is attractive for underwater acoustics, however $T_c$ is around 120 ℃ only
- NBT has higher coupling, but depolarises even below 200 ℃
- KBT and KNN have attractive properties, but are difficult to process
- Adding dopants to KBT and KNN improves the processing and properties

**Elena Aksel and Jacob, L. Jones,** *Sensors* **2010**, *10*, 1935-1954; doi:10.3390/s100301935

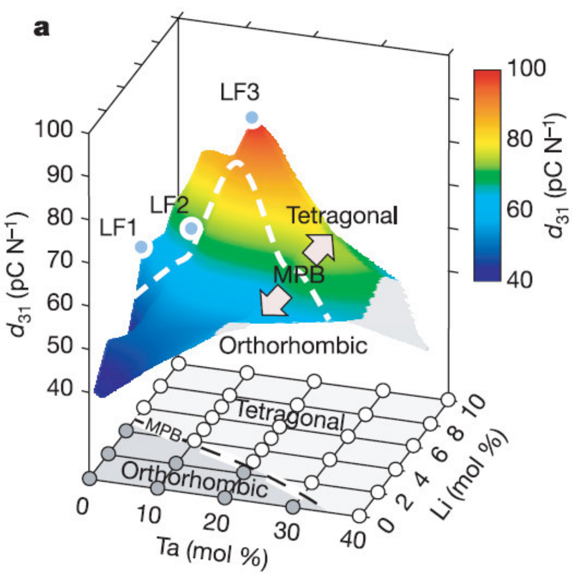
# New lead-free piezo-ceramics, KNN…




Phase diagram of (K,Na)$NbO_3$ [1]




Cf. phase diagram of PZT… [1]




| | | KNN.. | Pz27 |
|---|---|---|---|
| $\varepsilon_{33,r}{}^{\sigma}$ | | 1000-1600 | 1800 |
| $d_{33}$ | (pC/N) | 250-400 | 425 |
| $k_p$ | | 0.35-0.60 | 0.59 |
| $T_C$ | (ºC) | 250-400 | 350 |

1. Jaffe, Cook & Jaffe: Piezoelectric ceramics, 1971

2. Saitoh et al.: Lead-free piezoceramics, *Nature*, 2004

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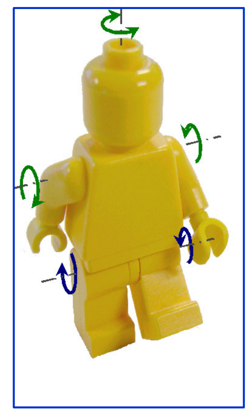
# Work carried out within Ferroperm

- European project LEAF 2004
  - Project dedicated to lead free compositions
- European project MINUET 2007
  - A continuation on the work carried out within LEAF
- European project IMMIDIATE 2007
  - Project on up-scaling of lead free manufacturing
- MIND NoE 2010
- Commercial projects
  - Confidential
- Strategic projects



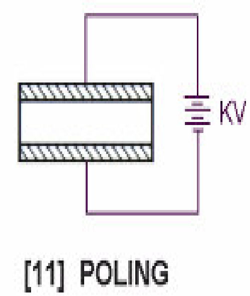
# Work with Ex61

Challenges

- Processing using carbonates which absorb water
- Sintering
- Poling

Solutions

- Drying powders carefully before mixing
- Adding dopants and Cold Isostatic Pressing (CIP)
- Poling in controlled environment

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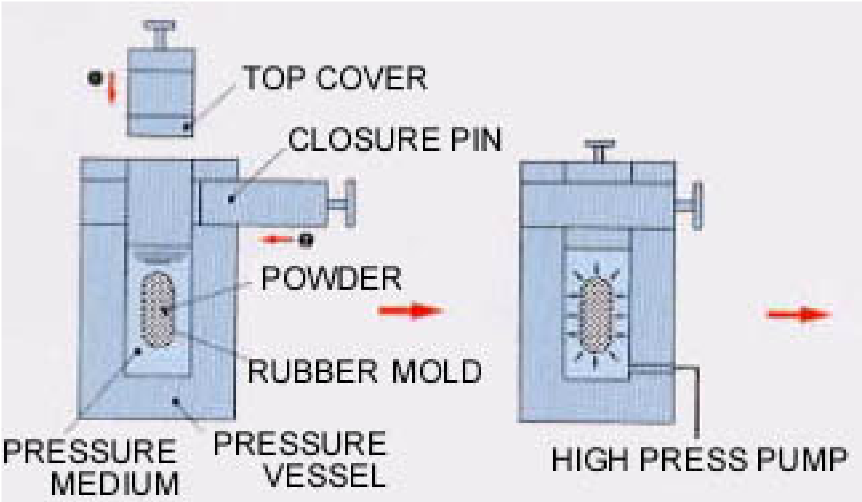
# Cold Isostatic Press, CIP

- High pressure, max 200 MPa
- Processing optimization
  - lenses
- Functionally Graded Materials
  - Density profile in thickness mode

- High density materials


http://www.nikkiso.co.jp/e-c_seihin/sangyo/kouatu/cip/images/cip.jpg

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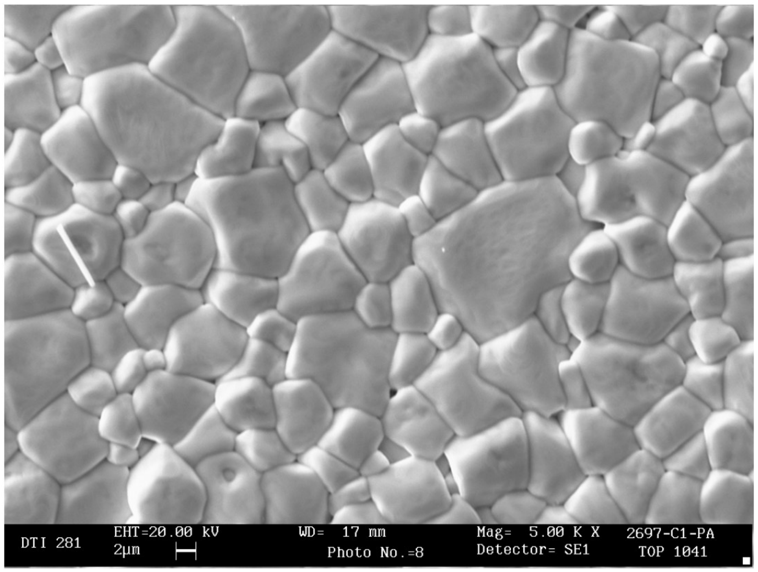
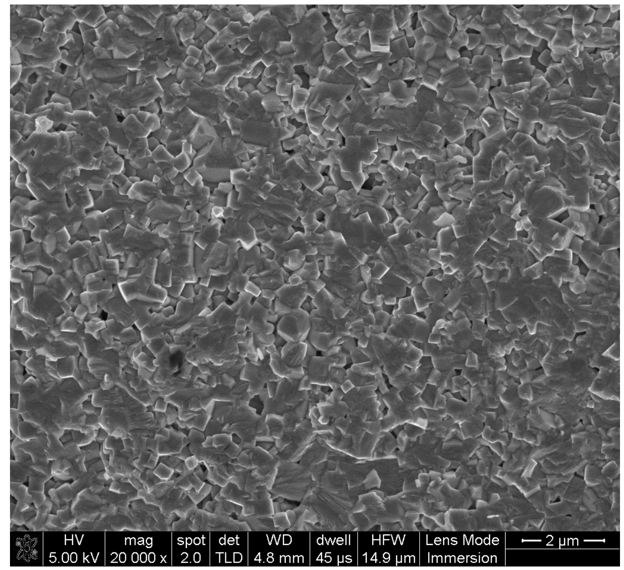
# Properties of Ex61 (KNN)




Pz26 bulk




Ex61 bulk

| | $\varepsilon_r$ | $\tan\delta$ % | $k_t$ % | $N_t$ Hz·m | $k_p$ % | $N_p$ Hz·m | $d_{33}$ pC/N |
|---|---|---|---|---|---|---|---|
| Pz26 | 1300 | 0.3 | 47 | 2040 | 57 | 2230 | 290 |
| Ex61 | 950 | 3 | 42 | 2550 | 36 | 2950 | 160 |

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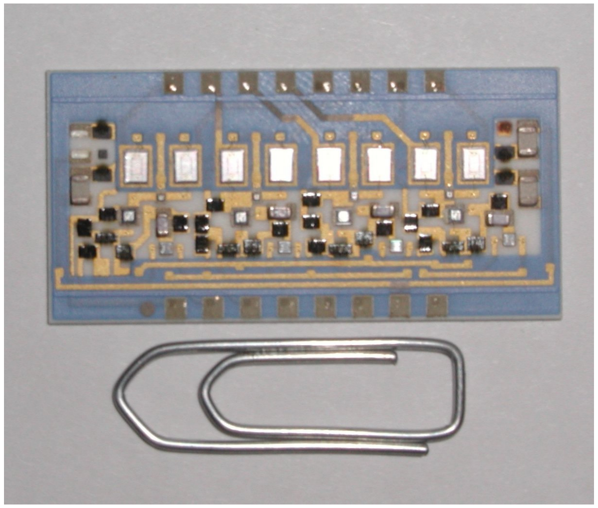
# Thick film

- Ceramic on a substrate
    - Ceramic
    - Silicon
    - Stainless steel
- Thickness: 10-100 µm

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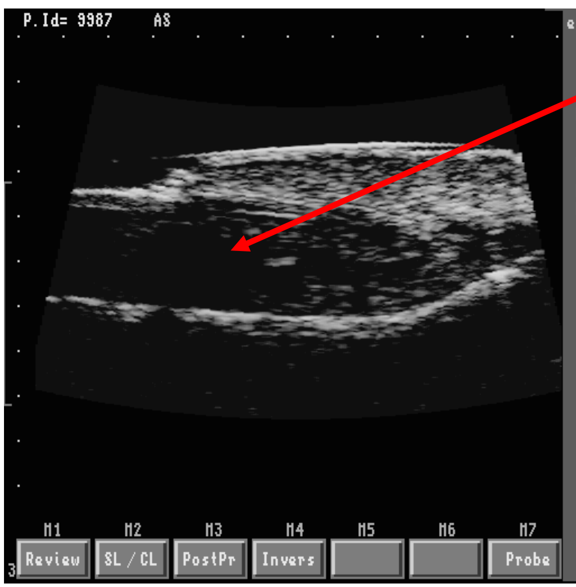
# PZT thick film

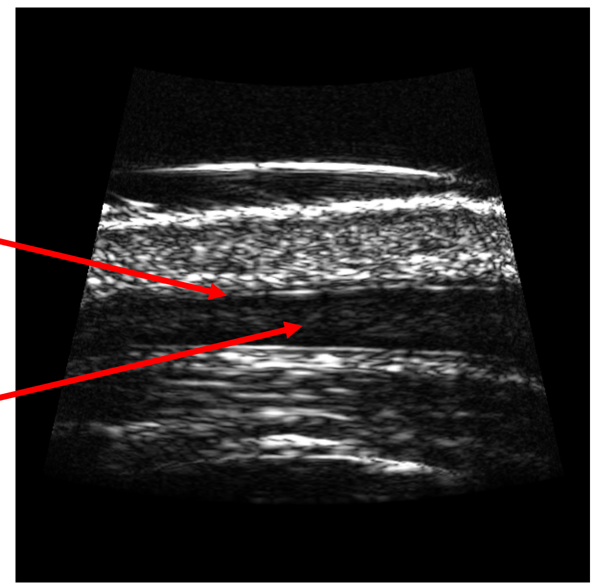
MINUET




Nail

Vessel wall

Red blood cells



Med IFTR, Warszawa (PL)

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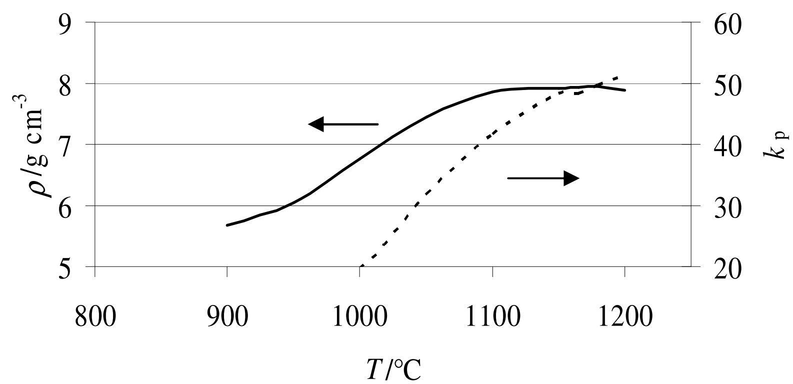
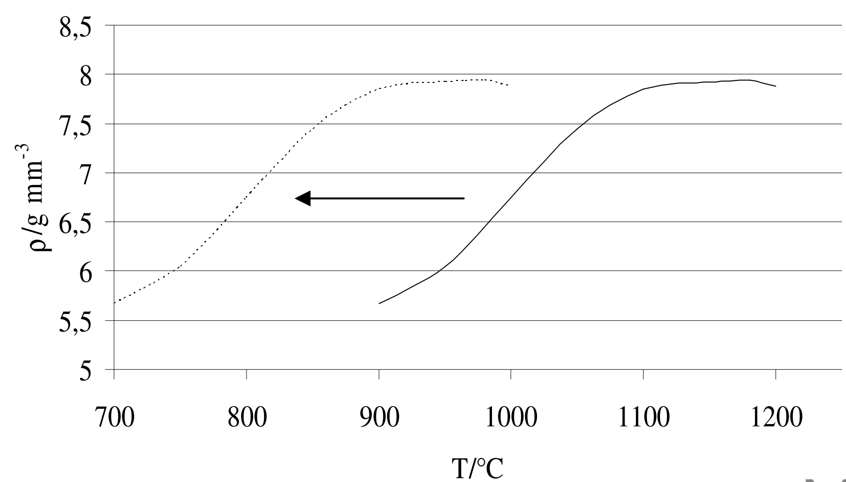
# Transferring processing of bulk KNN to thick film

- Lowering sintering temperature by adding sintering aids
- Making paste for screen or pad printing
- Cold Isostatic Pressing

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# KNN thick film properties

- $\varepsilon_r \approx 290$, tan $\delta \approx 1.6$ % (alumina substrate)
- $d_{33,app} \approx 80$ pC/N

| BULK | $\varepsilon_r$ | tan$\delta$ % | $k_t$ % | $N_t$ Hz·m | $k_p$ % | $N_p$ Hz·m | $d_{33}$ pC/N |
|---|---|---|---|---|---|---|---|
| Ex61 | 950 | 3 | 42 | 2550 | 36 | 2950 | 160 |


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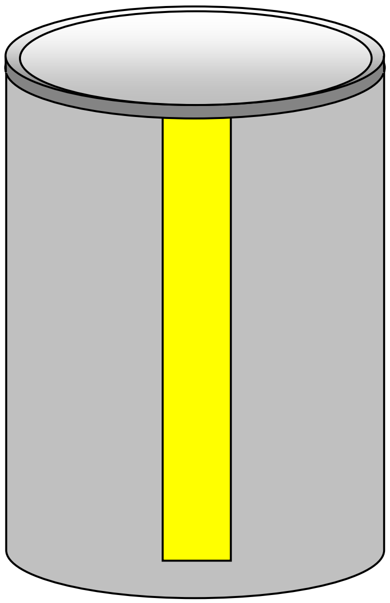
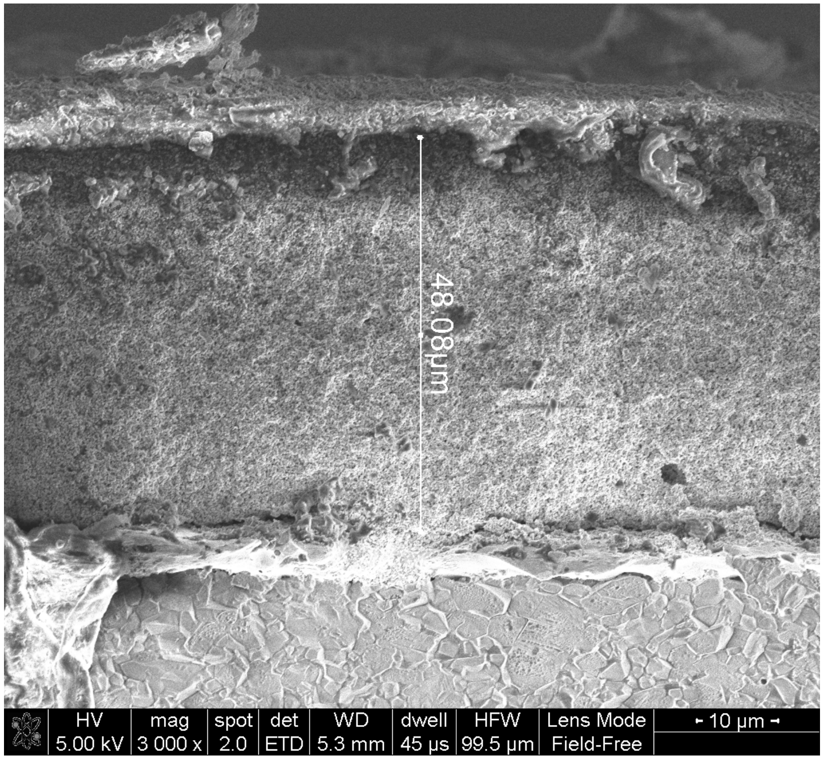
# KNN thick film transducer

- Porous KNN backing
- Gold bottom electrode
- KNN thick film
- Silver top electrode



# KNN thick film transducer

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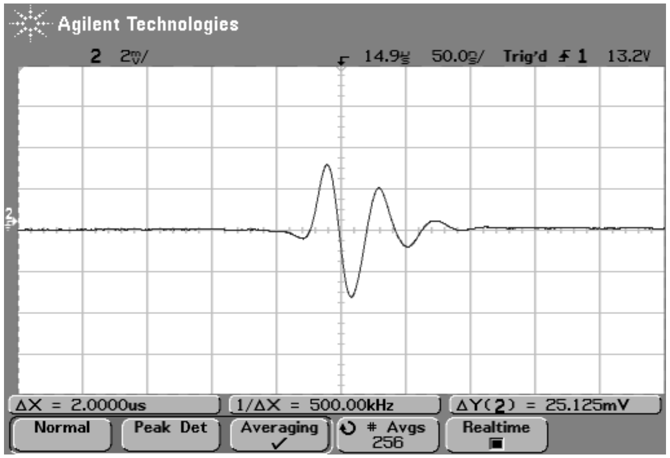
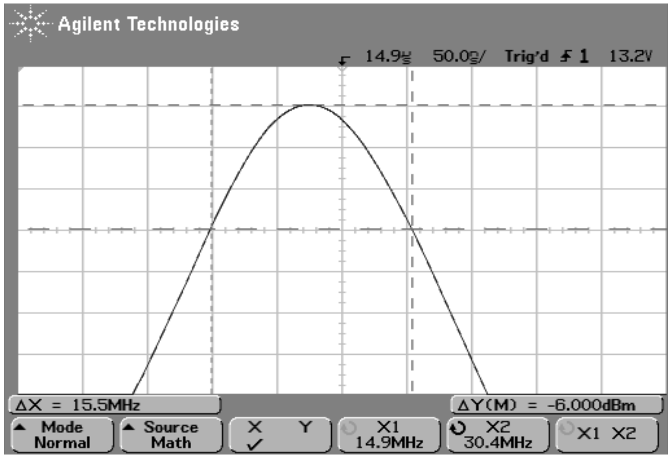
# Measurements, pulse echo




- Pulse echo in water tank using a steel reflector
- 70 V pp 4 ns pulse generated by an AVTECH AVG-3A-PS Pulser
- The reflection was received with a RITEC Receiver
- Centre frequency: 25 MHz
- 6 dB bandwidth 62 %

IPPT PAN

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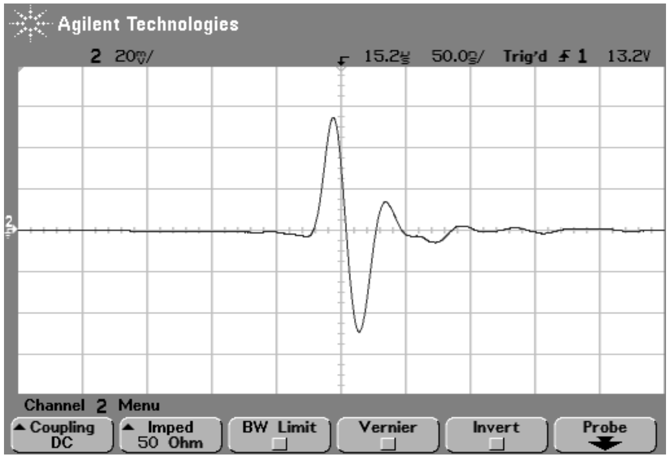
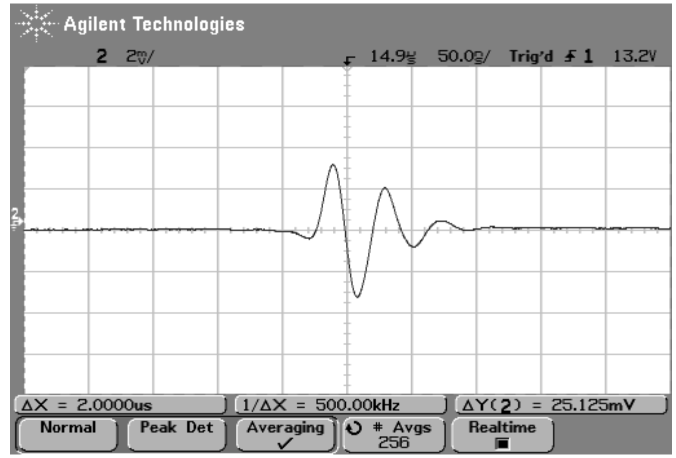
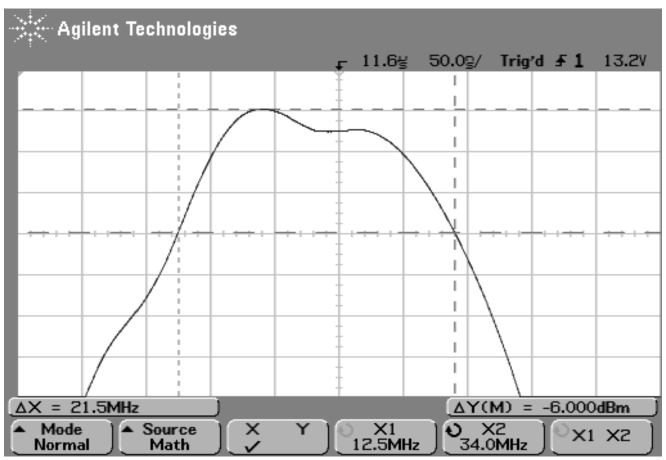
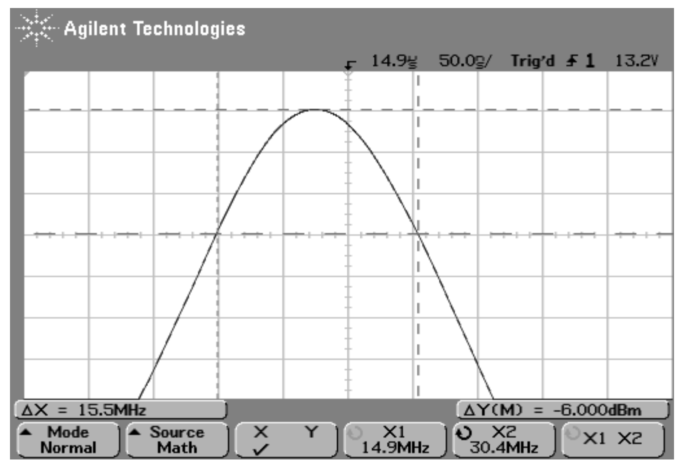
# Measurements, pulse echo




Pz26 based thick film

KNN based thick film

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# Conclusions

- Reproducible results for large scale processing
- Properties are well established
- Customers are now testing materials in commercial devices
- KNN thick film used in high frequency demonstrator

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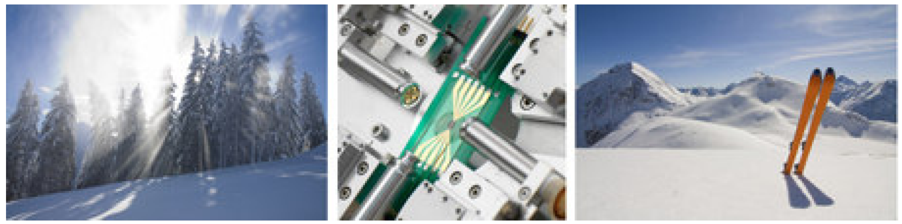
# Piezo 2011

## Piezo 2011: Electroceramics for End-users V



**27 Feb – 2 Mar 2011**
**Sestriere, Italy**

Piezo 2011 will be in Sestriere (northern Italy), the location of Turin's 2006 Winter Olympic Games.

This is the fifth *Electroceramics for End-users* conference, and the second organised by the Piezo Institute. Piezo 2011 will continue the conference's established traditions of presenting the latest piezoelectric materials and devices research; and bringing together the international community for discussion and networking.

There will be seven technical sessions, each with an invited keynote presentation. There will also be industrial training on lead-free processing and performance led by international experts. This will provide unique insights for early stage researchers and those interested in broadening their skills.

Topics that will be explored at the conference include:

- Energy
- Environment (including lead-free materials)
- Security
- Flexible substrates
- Food processing technologies
- Avionics
- Telecommunications/ materials for ICT
- Multiferroics

The call for abstracts is not yet open.

Register your interest to receive updates about the event including the call for abstracts.

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# Thank you

6th EU framework programme

- The MINUET project (Contract No. NMP2-CT-2004-505657)
- MIND Network of Excellence (Contract No. NMP3-CT-2005-515757)

The Danish Foundation of Advanced technology

- The Π-MEMS project

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