ELSEVIER

Ceramics International 30 (2004) 1079–1083

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

European approach to development of new environmentally sustainable electroceramics

Wanda W. Wolny

Ferroperm Piezoceramics A/S, Hejreskovvej 18A, 3490 Kvistgaard, Denmark

Received 1 December 2003; accepted 18 December 2003

Available online 15 July 2004

Abstract

Environmental policy of European Union aims at elimination or reduction of use of chemically hazardous materials and sustainable use of natural resources and waste. 6th Action Programme defines the strategy of managing risks from chemicals and recommends development and use of most efficient technologies. Piezoceramics, with its most common representative, the lead titanate/lead zirconate family (PZT), is in focus and substantial effort has been dedicated to both the development of new lead free materials and improving manufacturing technologies of existing materials in order to obtain better efficiency and reduce the volume of chemical waste. Preliminary results of this work, supported by the 5th Framework Programme Growth will be presented in the paper.

Keywords: C. Piezoelectric properties; D. PZT; Piezoceramic thick films

1. Introduction

The 5th Framework Programme, with its thematic programme Competitive and Sustainable Growth, was open for proposals 1998–2002. Its strategy was to support development of "efficient and quality-based systems, embedded in agile organisations and producing high quality eco-friendly products". The relevant defined key action has been "innovative products, processes and organisation".

Conditions for obtaining financial support for the planned activity are, besides relevance to areas defined by the Commission, sound scientific subject and a detailed working plan, participation of at least three independent organisations from minimum two European countries, either members of the European Union, candidate countries or associated countries. Industrial participants have to provide 50% of self-financing. The usual success rate for proposals is approx. 15%.

Two selected ongoing R&D projects and one network and preliminary outline of their results are a subject of the paper.

2. Background

PZT family of piezoceramics is the well-known group of ceramic materials represented by several compositions, tailored for specific applications. In general, it is characterised by high sensitivity and wide operating temperature range. They are used in a high number of different devices, many of them like buzzers, igniters, transformers, knock sensors, manufactured in millions of units, i.e. several tons of material, every day.

The commonly used mixed oxide technology is relatively simple and chemicals used in the process have a moderate cost. However, the major part of the volume of chemicals used in the manufacturing process is lead oxide. Lead and its compounds are listed as toxic and hereby hazardous, not only in form of direct pollution originating from the waste produced during the manufacturing process of powders and machining of components but also because products containing PZT based transducers, are not recyclable.

The strategy of the European consortia, whose work is presented here, was to take three different approaches to reduce the use of lead and its compounds:

E-mail address: ww@ferroperm-piezo.com (W.W. Wolny).

0272-8842/$30.00
doi:10.1016/j.ceramint.2003.12.025

(a) Proposal for a project focused on defining and developing a new family of piezoceramic materials to replace PZT whenever possible and based on lead-free compositions [1].
(b) Proposal for a project focused on improving existing manufacturing technology and compositions of PZT in order to obtain higher sensitivity of materials and higher manufacturing process efficiency, thus reducing the toxic impact on environment. In addition, miniaturised device designs were to be pursued further reducing consumption of toxic chemicals [2].
(c) Proposal for a network gathering majority of European industry and academia involved in electroceramics. The network was to prepare a good practice handbook concerning handling of lead based electroceramics including "cradle to grave analysis" [3,4].

All three proposals successfully passed evaluation process and obtained contracts. Work started in early in 2001 and will be completed in 2004. A summary of each project and preliminary results are presented in the following chapters.

3. LEAF—lead-free piezoelectric ceramics based on alkali niobates (G5RD-CT-2001-00431)

Consortium consisting of nine European partners and co-ordinated by Danish manufacturer of piezoceramics Ferroperm Piezoceramics A/S, selected alkaline niobate (sodium potassium niobate KNN and lithium sodium niobate LNN) ceramics to work with. Niobate ceramics are known to be difficult to densify fully, therefore the consortium proposed and investigated innovative powder synthesis routes and ceramic processing methods. The original goals of obtaining relative density of 94% at conventional sintering and 99% relative density at hot forging (sinter forging). The expected piezoelectric properties were electromechanical thickness coupling higher than 20% for LNN and 40% for KNN.

At present, results are close to the original goal. Fig. 1 shows an impedance curve for a sample of KNN developed during the project and Table 1 shows material properties of KNN ceramics in comparison to conventional materials Pz27 (PZT, Type II), Pz34 (modified lead titanate) and Pz35 (lead metaniobate) [5] as a simulation of 10 MHz transducer with two matching layers [6].

Present results of LEAF can lead to preliminary conclusion that alkaline niobate ceramics do not offer a full replacement for PZT, they can be however an attractive alternative to lead metaniobate, e.g. for ultrasonic transducer application in medium and high frequency range. Consortium has investigated a number of compositions showing a wide range of dielectric and piezoelectric properties. The work is on-going, focused at present especially on manufacturing routes in order to obtain higher density and higher thickness coupling, without, however, increasing significantly the cost.

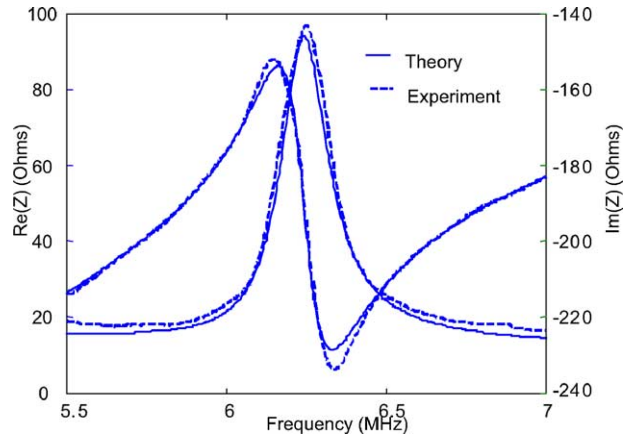


Fig. 1. Real part and imaginary part of the electrical input impedance of a KNN-type ceramic from the LEAF project [6].

4. PIRAMID—high sensitivity novel piezoceramics for advanced applications: textured, thick films and multilayer structures (G5RD-CT-2001-00456)

This project gathers a large consortium of 13 partners and is co-ordinated by G.I.P Ultrasons in France. Whilst staying with PZT materials, the project aims on reducing their impact on environments through improved properties of investigated materials, the improvement obtained by optimising compositions and using new powder processing methods among others controlled dispersion and sol–gel synthesis, attrition and high energy milling. Control of ceramic microstructure through alternative ceramics manufacturing routes such as hot forging, tape casting, textured tape casting and screen printing of thick films should lead to higher process efficiency.

Several compositions have been developed and tested, including PLZT and PMN-PT types.

Table 1
Simulation inputs for a 10 MHz transducer with two matching layers [6]

	KNN-Sr	Pz27[a]	Pz34[a]	Pz35[a]
Ceramic properties				
Density (kg/m^3)	4200	7740	7550	5312
Velocity (m/s)	5850	4380	4700	3145
Z (Mrayl)	24.6	34.34	35.5	16.7
ε^S_{33r}	275	820	180	197
Coupling coefficient	0.36	0.49	0.34	0.32
Mechanical losses	0.02	0.02	0.003	0.07
Dielectric losses	0.07	0.02	0.003	0.08
Matching layer 1				
Thickness (mm)	0.064	0.063	0.063	0.047
Velocity (m/s)	2500	2500	2500	2500
Z (Mrayl)	5.67	5.77	6.10	5.96
Matching layer 2				
Thickness (mm)	0.065	0.063	0.064	0.063
Velocity (m/s)	2500	2500	2500	2500
Z (Mrayl)	2.10	1.94	2.00	2.37

[a] From [5].

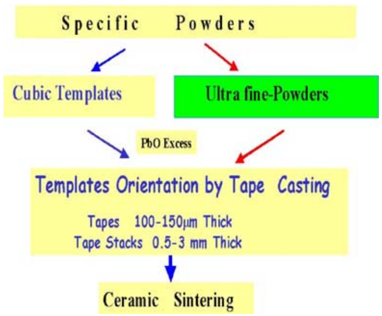


Fig. 2. Homoepitaxial template grain growth (TGG) via PMN-PT template [7].

Inks for screen-printing of piezoceramic layers on a number of different substrates such as alumina, PZT and silicon have been developed. Thus includes inks modified by lead free sintering additives enabling sintering thick films at temperatures as low as 650 °C. Finally, new device configurations, feasible thanks to new technologies have been designed and tested.

Preliminary results demonstrate that along with significant miniaturisation of several devices, mainly sensors and medical transducers, further integration of transducers can be obtained using screen-printing techniques. Examples of the results are given in Figs. 2–6 and Table 2. References for detailed results are given below [7–11].

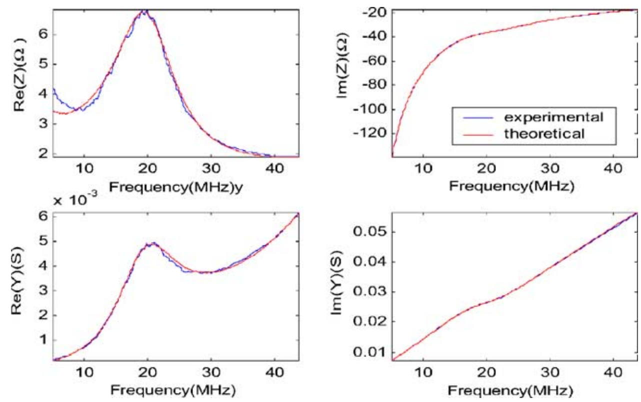
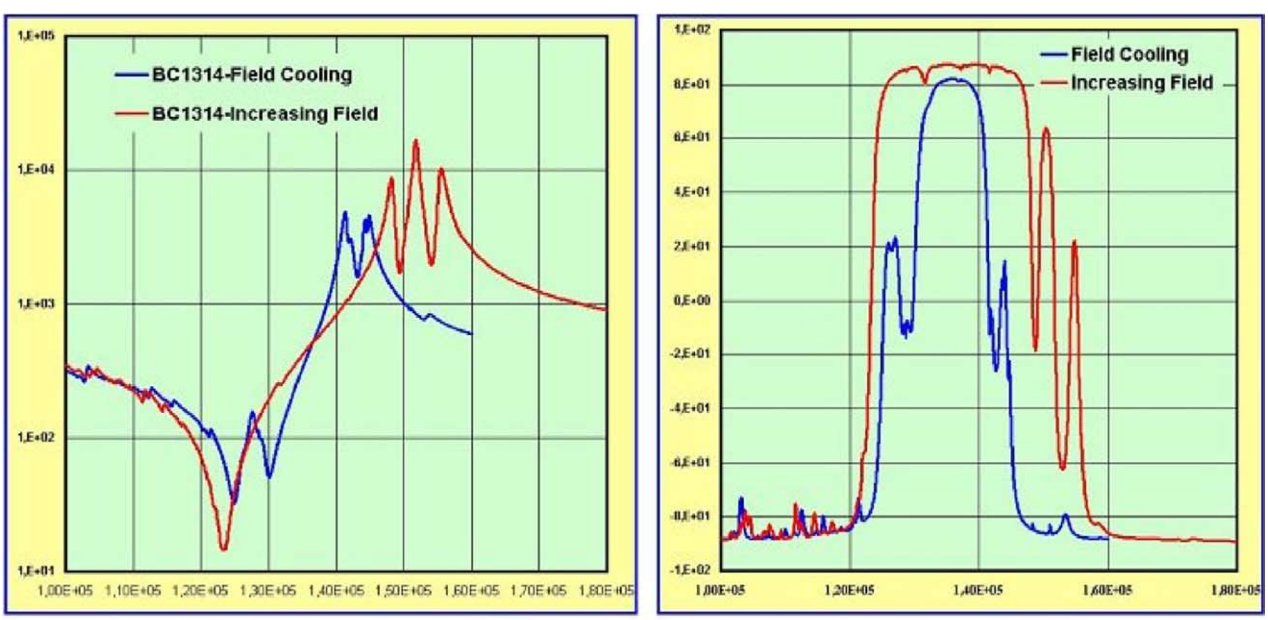


Fig. 4. Theoretical (red lines) and experimental (blue lines) electrical impedance and admittance of a thick film structure [8]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

5. POLECER—polar electroceramics (G5RT-CT-2001-05024)

Whilst the POLECER network does not carry out research, its aim is to support and co-ordinate R&D activities in the field of electroceramics and implementation of emerging technologies, together with dissemination of professional knowledge and best practice within processing of electroceramics. It has at present almost 80 members. In



	k_p	k_t	$_r$(1 kHz) at 30 °C
Disk Ceramic	0.58	0.49	3500-4300
Fine Grain Ceramic	0.52	0.4	-
Tape-Cast Textured Ceramic (f = 0.77)	0.6	-	-
Tape-Cast Textured Ceramic (f = 0.9)	0.66	0.52	3700-4300
Single Crystal (29 % PT)	0.85	0.6	7000

Fig. 3. Impedance spectra and piezoelectric properties of textured PMN-PT ceramic obtained by homoepitaxial template grain growth [7].

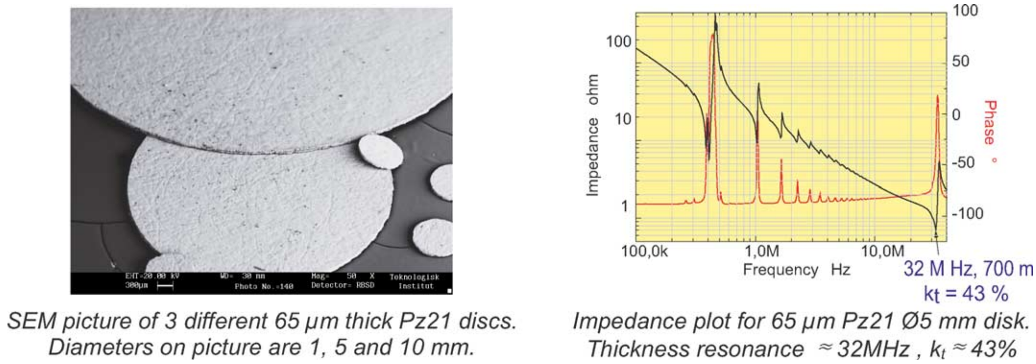


Fig. 5. Examples of thin discs prepared by tape casting, and a corresponding frequency spectrum [5].

Table 2
Data (backing and bottom electrode) and results (thick films) of the multilayer structure

Backing (porous PZT)		Bottom electrode		Piezoelectric thick film				
v_l (m/s)	ρ (kg/m^3)	h_e (μm)	Z_a (MRa)	h_p (μm)	ρ (kg/m^3)	k_t (%)	ε^S_{33r}	$\tan\delta_m$ (%)
3700	6500	10	40	55	6500	28	375	14

h_e and h_p are the thickness of the bottom electrode and the piezoelectric thick film, respectively [8].

accordance with the environmental policy of the European Union, one of its 10 workpackages, WP9, focuses on Environmental Aspects of Electroceramics and is co-ordinated by Prof. P. Gonnard of INSA Lyon, France. One of his reports, “Chemical substances management rank guidelines for polar electroceramics”, is now open for downloading on http://www.polecer.rwth-aachen.de.

The new directives for handling of hazardous and toxic waste exempt electronic ceramic components such as PZT from the list of prohibited substances, however, careful handling of lead compounds and related chemicals, monitoring its consumption, improving the process efficiency and reducing if not eliminating any emission of toxic materials and minimising the volume of waste are a recommended practice. POLECER supports initiatives leading to co-operation within the field.

Fig. 6. Samples for electromechanical characterisations and integrated transducers [8].

6. Conclusions

Environmental issues are not necessarily negative for the future of electroceramics. New materials and especially new and improved technologies leading to higher efficiency and miniaturisation of piezoelectric components open possibilities for new highly integrated devices. As European projects presented in this paper are still ongoing, and their results therefore protected by project consortia mutual confidentiality agreements, only a limited part of their activities and preliminary results could be presented here. Hopefully, despite of this limitation, the paper can serve as an inspiration to a socially responsible development without environmental degradation.

References

[1] Project LEAF, Contract No.: G5RD-CT-2001-00431, Cordis website address: http://dbs.cordis.lu/cordis-cgi/srchidadb?ACTION=D&SESSION=277172001-8-13&DOC=1&TBL=EN_PROJ&RCN=EP_RCN:54909&CALLER=EISIMPLE_EN_PROJ.

[2] Project PIRAMID, Contract No.: G5RD-CT-2001-00456, Cordis website address: http://dbs.cordis.lu/cordis-cgi/srchidadb?ACTION=D&SESSION=280072001-8-13&DOC=5&TBL=EN_PROJ&RCN=EP_RCN:55411&CALLER=EISIMPLE_EN_PROJ.

[3] Thematic Network POLECER, Contract No.: G5RT-CT-2001-05024, Cordis website address: http://dbs.cordis.lu/cordis-cgi/srchidadb?ACTION=D&SESSION=85352003-11-28&DOC=4&TBL=EN_PROJ&RCN=EP_RCN:54970&CALLER=EN_UNIFIEDSRCH.

[4] POLECER website: http://www.polecer.rwth-aachen.de/.

[5] Ferroperm Piezoceramics A/S, website: http://www.ferroperm-piezo.com.

[6] G. Feuillard, V. Loyau, L.P. Tran-Huu-Hue, T. Wurlitzer, E. Ringgaard, W. Wolny, B. Malic, M. Kosec, A. Barzegar, D. Damjanovic, N. Setter, Comparative performances of new KNN lead-free piezoelectric materials and classical lead-based ceramics for ultrasonic

transducer applications, Presented at 2003 IEEE International Ultrasonics Symposium, Honolulu, USA, 5–8 October 2003.
[7] M. Pham Thi, J. Holz, M. Kosec, Textured $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ ceramics by homoepitaxial template grain growth, Processing of Electroceramics, POLECER Symposium, Bled, Slovenia, 31 August–3 September 2003.
[8] J. Holc, F. Levassort, P. Marechal, L.P. Tran-Huu-Hue, M. Kosec, Screen-printed PZT thick film on porous PZT substrate, Abstract Book, Processing of Electroceramics, POLECER Symposium, Bled, Slovenia, 31 August–3 September 2003, p. 61.
[9] S. Gentil, D. Damjanovic, N. Setter, Towards a silicon compatible processing route for relaxor-ferroelectric thick films, Presented at 8th International Conference on Ceramic Processing Science (ICCPS), Hamburg, September 2002.
[10] S. Gentil, P. Maréchal, F. Levassort, M. Lethiecq, D. Damjanovic, Relaxor-ferroelectric curved disks prepared by tape casting for medical imaging applications, Abstract Book, Processing of Electroceramics, POLECER Symposium, Bled, Slovenia, 31 August–3 September 2003, p. 62.
[11] M. Algueró, C. Alemany, B. Jiménez, L. Pardo, Piezoelectric coefficients an losses of high sensitivity $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ ceramics by a non-standard method, Polar Oxides, Properties, Characterisation and Imaging, POLECER Symposium, Capri, Italy, 8–11 June 2003.