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New piezoceramic PZT–PNN material for medical diagnostics applications

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Abstract

The development of a new piezoceramic material, Ferroperm Pz21, optimised for use in medical diagnostics applications is described. The requirements to such a material are very high permittivity, sensitivity and coupling factors, and at the same time a relatively high Curie temperature. The structure must furthermore be very dense and fine-grained, since dicing of small sub-elements for medical arrays must be performed without damaging the material. The developed material is a solid solution between a PZT phase and the relaxor phase $Pb(Ni_{1/3}Nb_{2/3})O_3$. A comparison between different production processes is given, and a new solid state route for production of very dense and fine-grained materials is presented. Very positive characteristics are generally observed, and a stable behaviour even at elevated temperatures indicate that the material can find applications not only in the medical market, but also as a more general sensor/actuator. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The market for medical imaging and other related ultrasound diagnostic equipment has seen a remarkable growth in recent years. With a total marked for ultrasound medical imaging systems of 4×10^9 US$ in 1999, and a significant growth in the coming years, the total market value is expected to reach 5.3×10^9 US$ by 2004.[1] A significant increase in demand for piezoelectric materials, which generates the ultrasonic waves, must therefore be expected.

The materials suitable for these applications have very demanding specifications, and existing "traditional" piezoceramic materials, for example known from underwater transducers, are far from optimum in this field. A new family of materials has therefore been developed to fulfil the following general characteristics:

- A relative dielectric constant of 3800 or more.
- A Curie temperature of 200°C or more.
- A k_p of 60% or above.
- A k_t of 45% or above.
- A dense structure with fine-grained and uni-modal crystals.
- High corrosion resistance.

Products with such specifications have until recently only been available from PLZT-based materials. These materials offer most of the desired characteristics, but can unfortunately be sensitive to corrosion, and be difficult to process in a stable manner. It can therefore be necessary to use sintering additives or post-sinter HIP treatment, which increases the price and makes the performance and ageing less reproducible.

The objective of this work has therefore been to find an alternative and more stable material system, which would not only offer the desired material characteristics, but also allow a pure and simple solid-state processing route, where highly predictable results can be obtained from batch to batch.

Several materials systems, which have potential as an alternative for PLZT, have been investigated since the 1960′s. Most work has been concentrated on solid solutions between relaxor phases, e.g. $Pb(Mg_{1/3}Nb_{2/3})O_3$, $Pb(Fe_{1/3}Nb_{2/3})O_3$, $Pb(Sc_{1/3}Nb_{2/3})O_3$, and $PbTiO_3$ (PT) or $Pb(Zr_xTi_{1-x})O_3$ (PZT). The most common system reported are the mixtures between $Pb(Mg_{1/3}Nb_{2/3})O_3$ and PT.[2,3]

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The work in this study has however concentrated on the development of a solid solution between $Pb(Ni_{1/3}Nb_{2/3})O_3$ and PZT (PNN–PZT), hereafter named Pz21, which was found to be easier to process in a reproducible way, and at the same time could give higher Curie temperatures, permittivity and piezoelectric coupling constants.[4–6]

The general ternary phase diagram for the PNN–PZT system is shown in Fig. 1, and an example of the binary phase diagram as a function of temperature for a fixed content of relaxor phase is shown in Fig. 2. It can be noted that the two normal piezoelectric phases, tetragonal and rhombohedral, are stable at temperatures up to 150–200°C, but a transition to a pseudocubic state is possible before the final transition to the non-piezoelectric cubic phase at temperatures above 160–200°C.

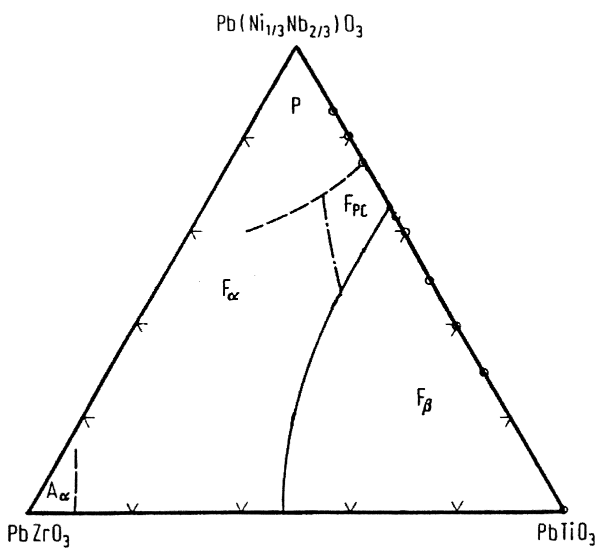

Fig. 1. Ternary phase diagram for the PNN–PZT system. F_α is rhombohedral phase, F_β tetragonal, F_{PC} pseudocubic, P cubic paraelectric, and A_α antiferroelectric.[7]

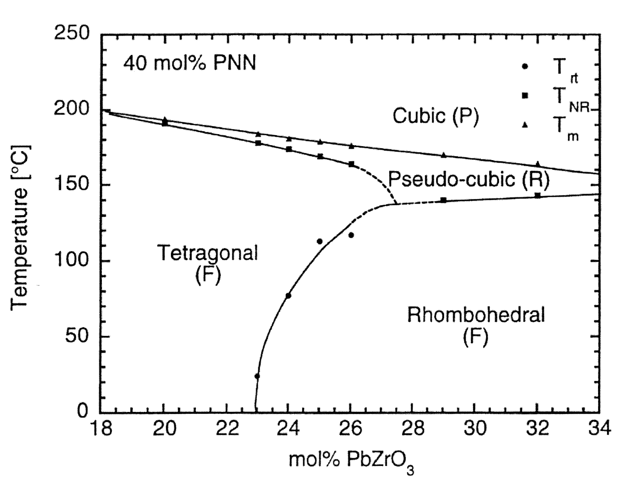

Fig. 2. Example of binary PT–PZT phase diagram in the PNN–PZT system with a 40 mol% PNN content.[5]

Another significant feature of this system is the morphotropic phase boundary between the tetragonal and rhombohedral phase. This boundary generally indicates where the piezoelectric performance peaks, and optimum compositions should be located. In PZT, this boundary is almost vertical, and it is therefore fairly simple to compose materials with stable tetragonal or rhombohedral structure. In the PZT–PNN system, the phase boundary is however not vertical, and a phase transition between tetragonal and rhombohedral phase can thus take place even at very low temperatures. Such a transition is accompanied by abrupt, and therefore unacceptable, changes in the piezoelectric characteristics, and it is therefore necessary to select compositions where this is impossible within the working temperature range.

2. Experimental

Three different processing routes were evaluated in this work: A mixed oxides route, where all oxides are mixed and calcined in one single step; a Columbite route, where a $NiNb_2O_6$ phase is formed before the PbO, TiO_2 and ZrO_2 are added, and a ferroelectric phase is formed in a second calcination step; and finally a new B-oxides route, where all B-oxides (NiO, Nb_2O_5, ZrO_2 and TiO_2) are reacted in an initial calcination before the PbO is added, and the ferroelectric phase formed in a second calcination. Fig. 3 gives a schematic overview of the three different processes. Materials were characterised by conventional IEEE methods using a HP 4278A capacitance bridge (connected with a Delta Design Inc. temperature cabinet), and a HP4192A impedance analyser. Microstructural characterisation was performed on a LEO 435VP SEM.

3. Results

3.1. Selection of processing route

Fig. 4 shows the dielectric constants for PNN-PZT materials sintered at temperatures between 1200 and

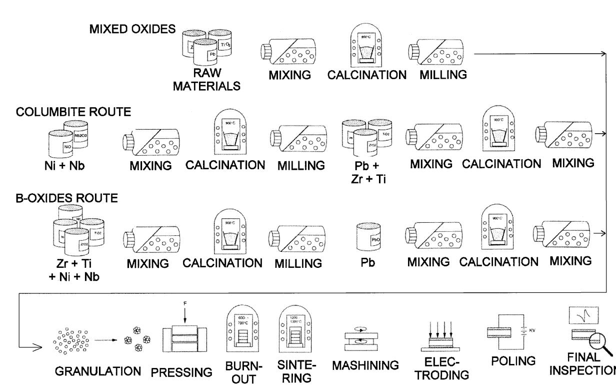

Fig. 3. Schematic presentation of the three different processes.

1280°C for 2 h. It can be seen that the mixed oxides and columbite routes gives significantly lower dielectric constants than materials manufactured by the new B-oxide method. This result, in combination with similar data for piezoelectric properties, therefore clearly indicates that the new B-oxide route should be preferred. Further experimental work was therefore only made for materials processed by this method.

3.2. Microstructural characterisation

A characterisation of the microstructure as a function of calcination and sintering temperature was performed by SEM in order to further determine the optimum sintering conditions and investigate the processing stability of the new composition. An example of the microstructure is given in Fig. 5, where a very fine-grained and pore-free structure without any over-sized grains or inclusions from foreign phases can be seen. Similar analysis on materials sintered at different temperatures showed that the grain size and porosity stays relatively unaffected within sintering temperatures between 1200 and 1280°C.

The results from the microstructural characterisation were compared to the mechanical, dielectric and piezoelectric characteristics. These studies could be used to fix the optimum processing conditions, taking both electrical characteristics and stability of parameters into account.

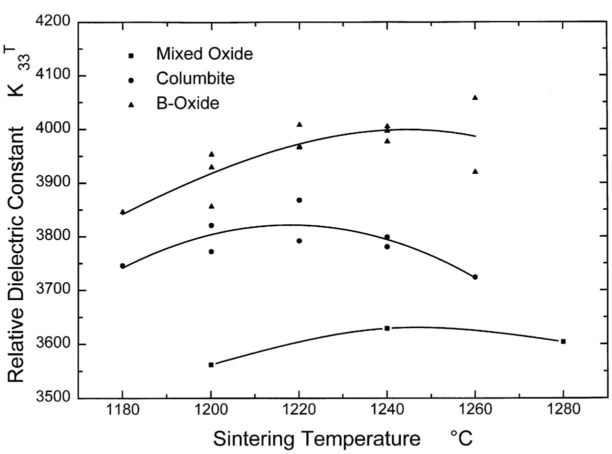

Fig. 4. Dielectric constant for PNN–PZT materials sintered for 2 h at temperatures between 1200 and 1280°C for 2 h.

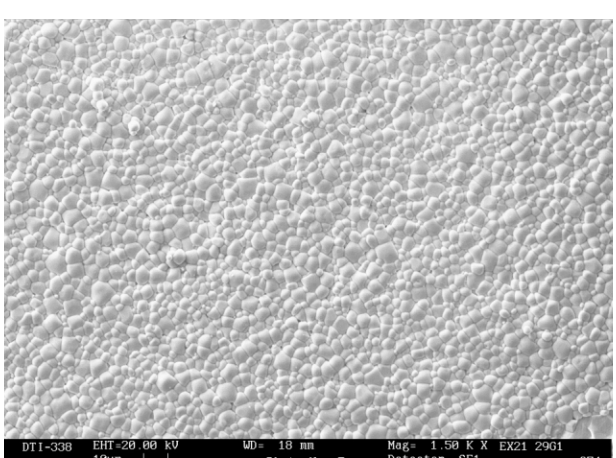

Fig. 5. Microstructure of Pz21 sintered at 1240°C. A pore-free structure with uni-modal grain size distribution is observed.

3.3. Dielectric and piezoelectric properties of Pz21

Detailed poling studies were performed in order to find the optimum conditions for the manufacturing process. Fig. 6 shows an example of the variation in the dielectric constant as a function of poling temperature and time. It can generally be seen, that the dielectric constant increases with poling temperature, while piezoelectric coupling constants unfortunately decreases. A certain compromise must thus be established by the materials supplier as well as the end-users who perform a re-poling of the materials after assembly of the transducer.

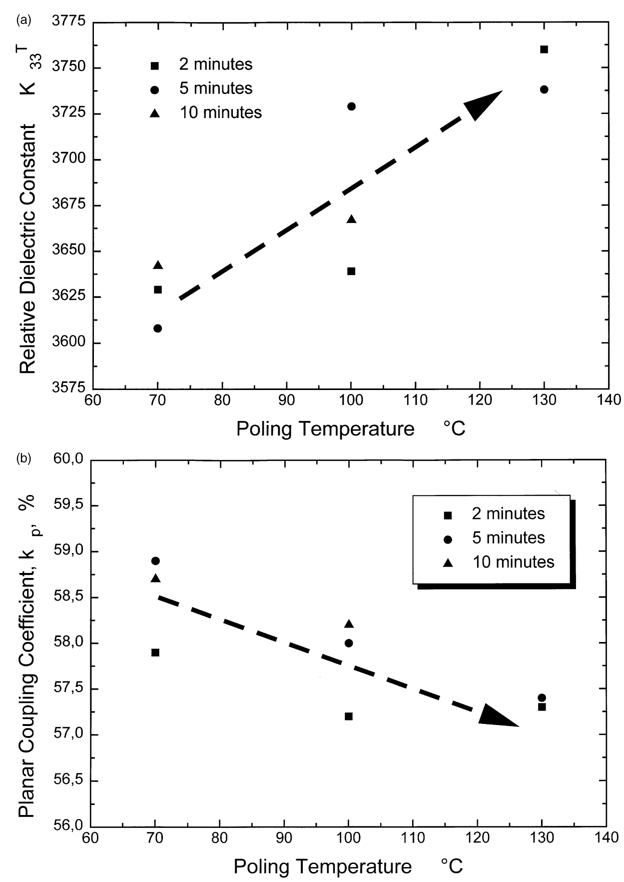

Fig. 6. Example of the variation in dielectric constants and coupling factors as a function of poling temperature and time: (a) dielectric constant; (b) planar coupling constant.

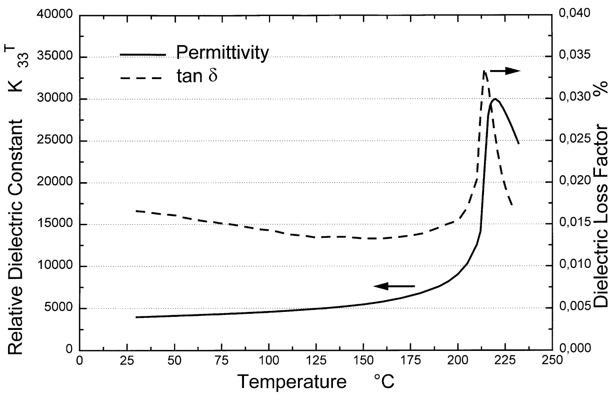

Fig. 7. Dielectric properties of Pz21 as a function of temperature.

Table 1
General specifications for Ferroperm Pz21

Parameter	Symbol	Unit	Value
Relative dielectric permittivity	K_{33}^{T}		3800
Dielectric dissipation factor	tanδ	10^{-3}	17
Curie temperature	T_c	°C	≈ 220
Recommended working range	<	°C	≈ 130
Planar coupling factor	k_p		0.60
Thickness coupling factor	k_t		0.47
Piezoelectric charge coefficient	d_{33}	10^{-12} C/N	640
Mechanical quality factor	$Q_{m,p}$		65
Density	δ	g/cm^3	7.8

A characterisation of the dielectric and piezoelectric parameters as a function of temperature was performed to investigate the stability of the new Pz21 material at elevated temperatures. Fig. 7 shows the permittivity and tanδ from room temperature to a temperature above the Curie point of 220°C. It can be noted that the Curie temperature is significantly higher than stated in Section 1, which of course contributes to the general stability of the material characteristics during any mode of transducer operation. The increase in permittivity as a function of temperature is furthermore very low, and a temperature coefficient of only 0.26% per Kelvin is for example found in the temperature range between 20 and 130°C. This is significantly lower than comparable soft PZT materials, which typically have temperature coefficients of 0.5% per Kelvin or more. The general characteristics of Ferroperm Pz21 are summarised in Table 1.

4. Conclusions

This work has demonstrated the development of a new piezoceramic material, Ferroperm Pz21, optimised for medical imaging applications. The composition of this material was selected from the PZT–$Pb(Ni_{1/3}Nb_{2/3})O_3$ solid solution system, which gives high piezoelectric activity, reproducibility, and corrosion resistance in comparison with conventional PLZT-based compositions.

It was concluded that the required performance, e.g. very high sensitivity and dense structure, could be obtained by use of a new solid state processing route without any use of sintering additives or post-sinter treatments. The main characteristics were a dielectric constant of 3800, planar coupling coefficients of 60%, and a Curie temperature of 220°C. The piezoelectric performance at elevated operation temperatures was furthermore found to be very good, and temperature coefficients in the working ranges were typically 2–3 times lower than in conventional soft PZT materials. The material was thus concluded not only to be suitable for medical diagnostics applications but also as a more general sensor/actuator material.

Acknowledgements

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