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Lead-free piezoceramics based on alkali niobates

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Abstract

The market for piezoceramic components is dominated by lead-based PZT materials containing more than 60 wt.% lead. Since lead is a toxic heavy metal, it has become a great concern how to eliminate the use of PZT by replacing it with non-harmful materials while maintaining comparable piezoelectric properties. This was the objective of the European LEAF project within the GROWTH programme, ending in February 2004. In this project, alkali niobates were proposed as alternative piezoceramic materials, and special emphasis was given to potassium sodium niobate, (K, Na)NbO_3. The partners of the project have developed lead-free ceramics that can be a competitive alternative to PZT for certain applications. Considerations on powder synthesis and ceramic processing, obtained properties and examples of industrial applications will be presented.

Keywords: Piezoelectric properties; Niobates; Lead-free piezoceramics

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1. Introduction

The market for piezoceramic components is dominated by lead-based PZT materials containing more than 60 wt.% lead. Lead is a heavy metal, and its toxicity is well known. Some of the symptoms of lead poisoning are headaches, constipation, nausea, anaemia and reduced fertility. Continuous uncontrolled exposure could cause more serious symptoms such as nerve, brain and kidney damage.[1] Some other commercial piezoceramics are based on bismuth and/or barium, which are also heavy metals with expected problems of toxicity. Even if the production is well managed environmentally, the whole lifecycle of the material needs to be considered, including the end-of-life stage where PZT-containing waste might end up in corrosive conditions. This must be taken seriously, especially in the case of large-volume consumer applications such as parts for the automotive industry. Because of the environmental problems with lead, a great effort has already been done in order to eliminate lead in various products, for example, paints and solders. In terms of legislation on the EU level, two recent directives put severe restrictions on the use of hazardous substances in electronic equipment. According to these, lead and other heavy metals should be phased out by 1 July 2006.[2,3] However, those materials are exempted where there use of these elements is unavoidable (the list includes electroceramics).

In view of the above, it is highly relevant to try to find alternatives or replacements for the conventional lead-based materials and several lead-free and “low-lead” systems have been suggested.[4–6] This was also the overall objective of the European LEAF project[7] within the GROWTH programme, running from March 2001 to February 2004. In this project, alkali niobates of the general form $ANbO_3$ (A: alkali metal) were proposed as alternative piezoceramic materials, rather than compositions based on heavy metals. Several ferroelectric perovskites of this family were discovered in the 1950s and 1960s,[8] but research on alkali niobates in ceramic form has not been intensive since the 1970s ($LiNbO_3$ and $KNbO_3$ are both industrially important as single crystals, however). In LEAF, both (Li, Na)NbO_3 (LNN) and (K, Na)NbO_3 (KNN) were considered, but since LNN is mainly relevant for high-temperature applications and these played a minor role in the project, most of the work was focused on KNN. Accordingly, this will also be the main topic of the present contribution.

In comparison with PZT, which has been studied intensively for many years and optimised both in terms of processing and dopants, the KNN system is rather complicated, as Fig. 1 shows. One of the main obstacles for the development of KNN as a commercial piezoceramic material seems

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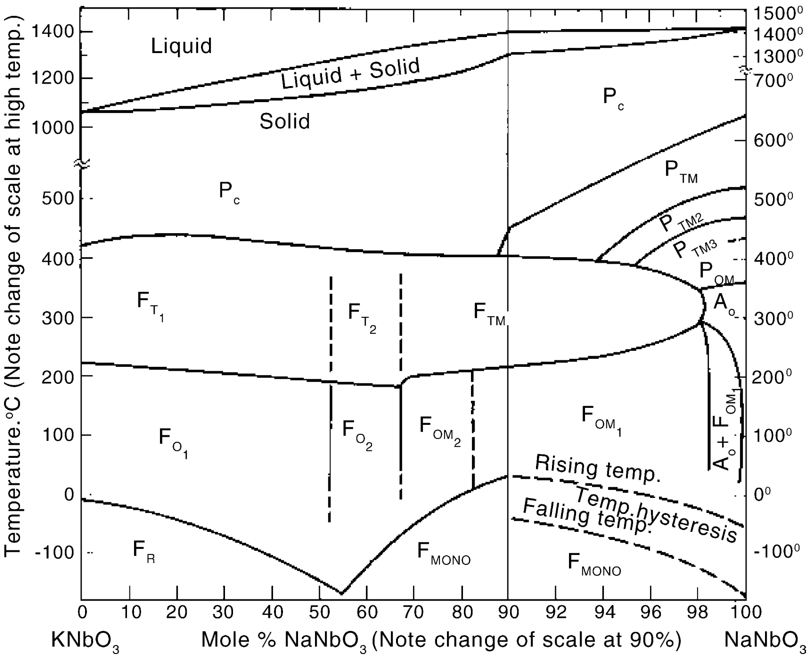

Fig. 1. Phase diagram for KNN, the system $KNbO_3$–$KNaO_3$.[8] This system shows a relatively high degree of complexity, e.g. in comparison with the well-known PZT system.

to have been the difficulties of processing, especially densification. The main objectives of the LEAF project were to investigate the possibilities of doping KNN, develop commercial compositions and to optimise the processing in order to obtain reproducible properties. A consortium with nine partners from eight different European countries was put together, comprising five universities and research centres and four private companies (Table 1). Apart from applications where doped PZT is currently in use, also applications commonly associated with lead metaniobate were targeted. The main reason for this was the low theoretical density of KNN ($\approx 4.5 \times 10^3$ kg/m^3 for a K/Na ratio of 1), giving an acoustic impedance in the same range as lead metaniobate.

2. Synthesis and processing of KNN

The solid-state synthesis of (K, Na)NbO_3 involves several problems, which are less common in PZT and other lead-based systems. One of these is the choice of sufficiently stable precursors, in this case for the alkali elements. A typical choice is carbonates, but especially K_2CO_3 is quite moisture-sensitive. A number of other K and Na precursors have been tried within the LEAF project, and one of the successful solutions has been to use sodium potassium tartrate tetrahydrate (Rochelle salt) as the source of both alkali elements.[9] This is a double salt of K and Na and with respect to the $K_{0.5}Na_{0.5}NbO_3$ composition it has the advantage that the correct K/Na ratio is inherent.

Also the development of compositions has been an important subject in the project. Unlike in PZT, where the ratio between the *B* ions of the perovskite structure is the primary composition parameter, the two end members of the system, $KNbO_3$ and $NaNbO_3$, differ by the *A* ion. In an early study,[10] nine different K/Na ratios have been examined and the highest planar coupling was found for the $K_{0.5}Na_{0.5}NbO_3$ composition. The 1:1 ratio of K and Na has been the preferred choice for most of the work on the system since then, also for the

Table 1
Consortium for the LEAF project

Partner name	Nat.	Main role in project
Ferroperm Piezoceramics A/S	DK	Manufacturer of piezoceramics
Institut “Jožef Stefan”, Electronic Ceramics Department	SI	Development of compositions and processing
École Polytechnique Fédérale de Lausanne, Lab. de Céramique	CH	Dielectric and piezoelectric characterisation
Instituto de Ciencia de Materiales de Madrid—CSIC	E	Mechanochemical activation, characterisation
Forschungszentrum Jülich GmbH, IFF, Electroceramic Materials	D	Sinter forging, characterisation
G.I.P. Ultrasons	F	Development of transducers
Simrad AS	N	End-user, underwater acoustics
Ceram AB	S	End-user, level detection
Karl Deutsch Prüf- und Messgerätebau GmbH & Co. KG	D	End-user, non-destructive testing

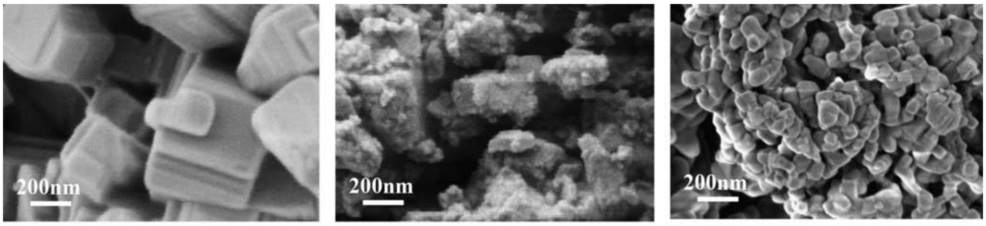
(a) D_{BET}: 0.8 μm (b) D_{BET}: 130 nm (c) D_{BET}: 30 nm

Fig. 2. Morphology and equivalent grain sizes (calculated from BET specific surface area) of various $(K_{0.5}Na_{0.5})NbO_3$ powders prepared within the project: (a) ordinary ball milling; (b) intensive milling; (c) micro-emulsion process.

studies with experiments on dopants. The primary purpose of the additives in earlier studies has been to promote the otherwise difficult densification of KNN, for example, Ba^{2+} and B^{3+},[11] Mg^{2+}[12] and Ba^{2+}[13]. A recent publication reports some of the LEAF activities on doping, namely a comparison of the alkaline-earth dopants Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}.[9]

Another important process parameter is the milling stage. Fig. 2 shows two examples of powder morphology and grain size, obtained by solid-state synthesis with two different milling methods employed after calcination. After ordinary ball milling (Fig. 2a), a characteristic quasi-cubic morphology is apparent and the equivalent grain size is relatively high, $D_{\mathrm{BET}} \approx 0.8\ \mu\mathrm{m}$. More intensive milling yields a powder with a less regular morphology and the equivalent grain size is reduced by a factor of 6. For comparison, an example of KNN nanopowder with $D_{\mathrm{BET}} \approx 30$ nm is included (see Fig. 2c), a powder that has been synthesised by one of the LEAF partners using the microemulsion route. This process is outside the scope of this contribution, but it should be mentioned that XRD and Raman work point to an interesting size effect in terms of crystal structure.[14]

As an alternative to enhancement of densification by doping, several studies have been made on pressure-assisted sintering of KNN. As early as 1962, undoped KNN with various K/Na ratios was prepared by hot pressing and the relative density was increased from 94.2% for air-sintered to 98.9%[15] (cf. Table 2). Also hot isostatic pressing (HIP) has been applied to KNN, and relative densities above 99.5% have been obtained.[16] However, HIP is a rather expensive process, which will hardly become industrially feasible. Within LEAF, sinter forging has been used as a reference method for obtaining very dense ceramics. Relative densities from 99.1% to 99.4% have been obtained by this method, depending on the starting powder.[17] Sinter-forged KNN could be a relevant choice for demanding applications where a very high density is required.

3. Characterisation results

Apart from problems of densification, KNN ceramics also show dielectric and piezoelectric properties that are quite sensitive to processing. In Fig. 3 (top), the dielectric properties of KNN with 0.5 mol% excess Nb_2O_5 are shown as a function of temperature and a significant frequency dispersion is apparent. A similar, though less consistent, behaviour has been observed for poorly processed KNN with a nominally stoichiometric composition. Fig. 3 also shows (bottom) the dielectric properties of well-processed, stoichiometric KNN where the frequency dispersion is almost absent. The Curie point is seen to be close to 400 °C and the permittivity peak at approximately 190 °C shows a ferroelectric ↔ ferroelectric transition.

A rather intriguing phenomenon seen for certain doped and undoped KNN samples is the presence of even harmonic resonances in the impedance spectrum, as seen in Fig. 4. According to common knowledge, these modes cannot be excited electrically due to symmetry and are thus forbidden. However, when a gradient in certain properties is introduced into the classical KLM model, simulations show that these modes will appear,[18] but the exact explanation for the phenomenon is still under investigation. It has been observed that

Table 2
Comparison of the properties of KNN ceramics

Source	Air-sintered, Jaeger and Egerton[15]	Air-sintered, LEAF	Air-sintered, LEAF	Hot-pressed, Jaeger and Egerton[15]
Composition	$K_{0.5}Na_{0.5}NbO_3$	$K_{0.5}Na_{0.5}NbO_3$	Doped KNN	$K_{0.5}Na_{0.5}NbO_3$
ρ_{rel} (%)	94.2	94–95	94–97	98.9
$\varepsilon_{33,\mathrm{r}}{}^{T}$	$290^{(100\ \mathrm{kHz})}$	400	330	$420^{(100\ \mathrm{kHz})}$
$\tan\delta$	$0.02^{(100\ \mathrm{kHz})}$	0.025	0.04	$0.014^{(100\ \mathrm{kHz})}$
d_{33} (pC/N)	80	70–90	90–140	160
d_{31} (pC/N)	32	45	30	49
k_{p}	0.36	0.39	0.27	0.45
k_{t}		0.40 (to 0.5)	0.40 (to 0.5)	

For the relative densities, the value 4.51×10^3 kg/m^3 for the theoretical density of $K_{0.5}Na_{0.5}NbO_3$ has been used. Unless specified, dielectric properties are measured at 1 kHz.

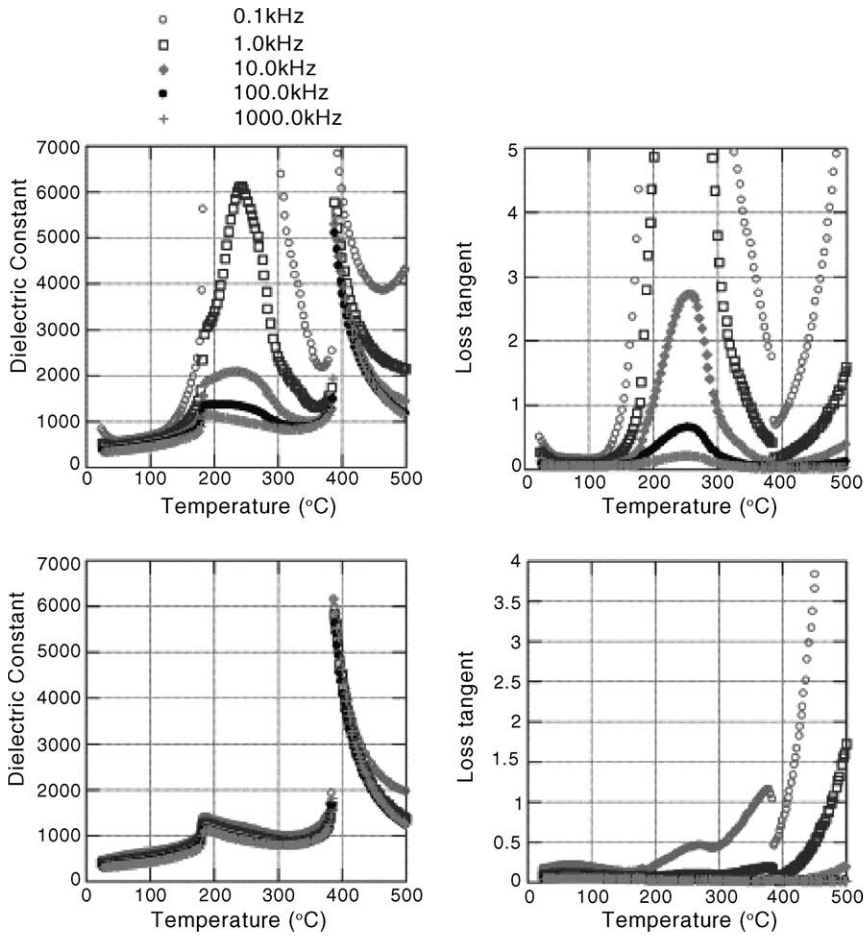

Fig. 3. Relative permittivity and dielectric loss tangent in KNN samples. Top row: KNN with 0.5 mol% excess Nb_2O_5 (K/Na ratio 1). Note the significant dispersion above 200 °C. Bottom row: nominally stoichiometric $K_{0.5}Na_{0.5}NbO_3$ sample.

the presence of even harmonics has a negative influence on the fundamental resonance and d_{33} and it has been found that they can be removed by the correct treatment.

Table 2 gives an overview of some results obtained in the LEAF project in comparison with results from the literature. It can be seen that the properties obtained for air-sintered KNN are generally superior to those reported in the literature (please note that dielectric properties are measured at different frequencies). The doped KNN composition does not show a significantly higher piezoelectric sensitivity than the best results obtained with pure $K_{0.5}Na_{0.5}NbO_3$, but it gives more consistent electrical properties and density. The observation that this composition has a lower k_p than the latter is considered as an advantage for the majority of applications ex-

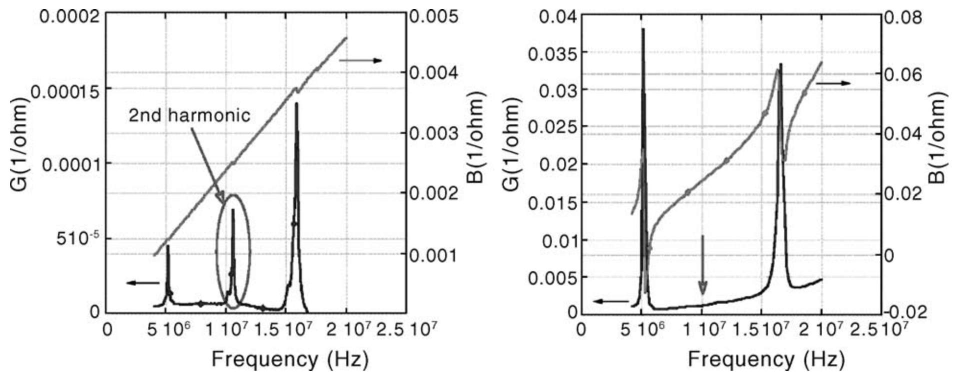

Fig. 4. Elimination of undesired second harmonic in a KNN sample. A KNN sample on the left exhibits $d_{33} = 50$ pC/N, $k_t = 0.16$ and a strong second harmonic (marked by the arrow). After temperature cycling and repoling, the relative intensity of the second harmonic is strongly reduced (on the right) and k_t increases to over 0.4.

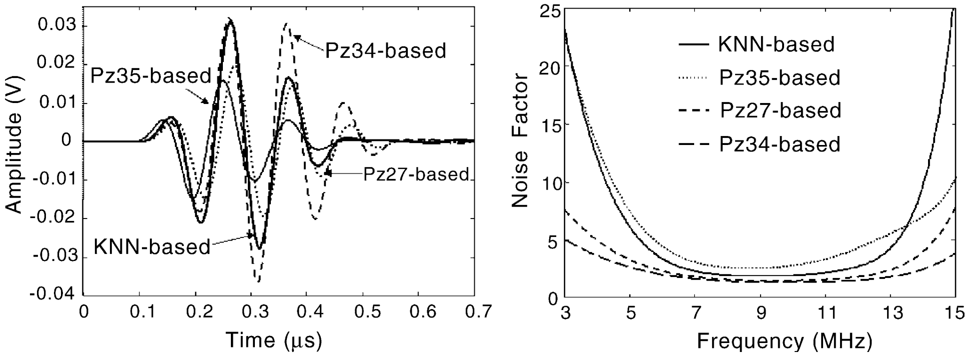

Fig. 5. Simulated noise factors of transducers (left) and simulation of the pulse–echo response of transducers for 10 MHz (right)[19].

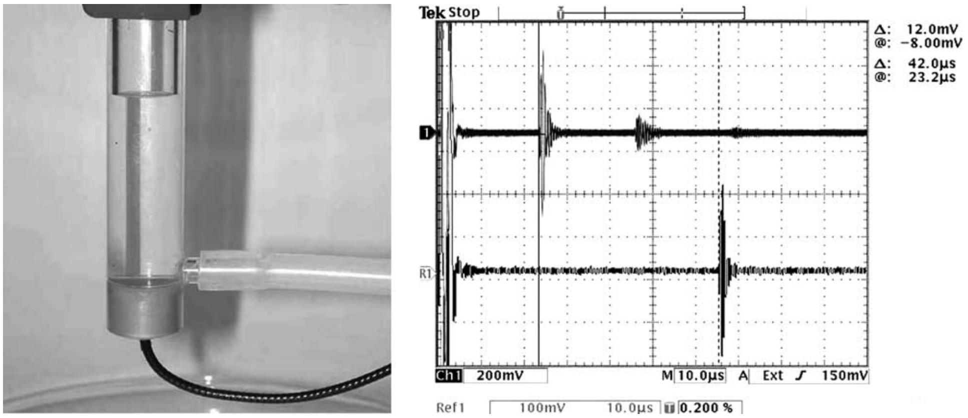

Fig. 6. Measurement set-up and measurement results for liquid-level measurement (Ceram application). The received echo-pulses are shown and in both cases the pulses are transmitted when the trace is in position zero (to the left in the figure). The upper trace (blue) shows the result of a low liquid level (18 mm) and the lower trace (black) a higher liquid level (48 mm).

ploiting the thickness resonance mode. Also the density of the sinter-forged ceramics of this project compare well with literature. The rather low permittivity of KNN may give problems of electrical impedance matching for certain applications, e.g. composite transducers, and a future objective would be to develop doped compositions with higher permittivity.

4. Examples of applications

In order to examine the feasibility of KNN as a piezoceramic material for ultrasonic transducers, a comparative study[19] has been made with three commercial lead-based materials from Ferroperm Piezoceramics:[20] Pz27 (a typical Type 200 soft-doped PZT), Pz34 (a modified lead titanate) and Pz35 (a lead metaniobate). Transducers for 10 MHz were simulated using measured material properties and noise factors were calculated. As seen in Fig. 5a, KNN is characterised by a relatively high loss, only exceeded by the lead metaniobate ceramic. The simulation of the pulse–echo response (50 Ω environment, 1 V excitation pulse) shows that the KNN material is promising for this application (Fig. 5b). A 6 dB bandwidth of 57% is calculated and the sensitivity is seen to be significantly higher than Pz35 and almost as high as Pz34.

One of the KNN-based transducers manufactured by the end-user Ceram AB has been tested in a set-up for liquid-level measurement (Fig. 6). The transducer is mounted in the bottom of the cylinder and the transmitted ultrasound pulse is reflected by the liquid surface. The time delay between the transmitted and received pulse can be used to calculate the liquid level. Fig. 6 also shows the results of two liquid-level measurements. A comparison with a commercial Type 200 PZT material (Ferroperm Pz27) shows that the echo signal amplitude of the KNN sample is only 6–10 dB lower. The example shows that the KNN material coming out of the LEAF project is fully functional for this application.

5. Conclusion

Due to the well-known toxicity of lead, it is a highly relevant task to find environmentally sound alternatives to PZT and other lead-based piezoceramic materials. The LEAF project has shown that KNN is a good candidate for selected applications.

Some of the important aspects of synthesis and processing have been outlined, including choice of precursors and milling route. Within the project, densification has been improved by either doping or pressure-assisted sintering. Dielectric characterisation has showed significant frequency dispersion for unstoichiometric samples, which underlines the need of careful process control. In certain samples, the presence of even harmonic resonances has been observed in the frequency spectrum, but it has proved possible to remove these by the correct treatment. The example of pulse–echo measurement shows that KNN can indeed be an alternative to PZT and lead metaniobate for certain industrial applications.

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