



Lead Free Piezoelectric Materials

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Abstract. Lead oxide based ferroelectrics, represented by lead zirconate titanate ($\text{Pb}(\text{Zr,Ti})\text{O}_3$) or PZT) are the most widely used materials for piezoelectric actuators, sensors and transducers due to their excellent piezoelectric properties. Considering lead toxicity, there is interest in developing piezoelectric materials that are biocompatible and environmentally friendlier. The low density of non-lead based materials can also be an advantage in transducers for underwater and medical imaging due to expected lower acoustical impedance. Another impetus for seeking alternative to lead based compositions is the need for piezoelectric materials for operation at high temperatures. Several classes of materials are now being reconsidered as potentially attractive alternatives to PZT for special applications. The potassium niobate family, KNbO_3 , exhibits low dielectric constants, large thickness coupling coefficient along certain non-polar directions, and low density, all of which have advantages for high frequency transducer applications. Several compositions belonging to bismuth titanate family, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, such as $\text{SrTi}_4\text{Bi}_4\text{O}_{15}$, are promising candidates for high temperature applications. Lead free materials alone (eg. $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$) or in solution with PT ($\text{BiScO}_3 - \text{PbTiO}_3$) are also potentially interesting as they combine high piezoelectric activity and, in some cases, relatively high T_c . For these families of piezoelectric materials, the processing and piezoelectric response under different conditions of pressure, frequency, and temperature are presently much less understood than for the classical lead containing systems. In this presentation we review and discuss piezoelectric properties of selected lead free compositions (principally for members of the potassium niobate family and bismuth titanate layered compounds) in relation to structural and microstructural features as well as extrinsic contributions (domain walls displacement, conductivity) to their electromechanical properties. It is shown that it is possible to obtain remarkably stable piezoelectric response in some compositions, while others exhibit strong dependence of piezoelectric properties on driving field and frequency. Origins of these different behaviours are discussed.

Keywords: lead free, piezoelectric, potassium niobate, bismuth titanate

Introduction

Lead oxide based ferroelectrics, represented by lead zirconate titanate ($\text{Pb}(\text{Zr,Ti})\text{O}_3$) or PZT) are the most widely used materials for piezoelectric actuators, sensors and transducers due to their excellent piezoelectric properties [1, 2]. A noticeable feature of these materials is the occurrence of a morphotropic phase boundary (MPB). The compositions close to this boundary show excellent electromechanical properties. Because of lead oxide toxicity, however, there is a raising concern about recycling and disposal of devices containing PZT, especially those used in consumer products such as cars, various kinds of smart systems and sound

generators. The fact that lead oxide vaporizes during processing, that lead stays for long times in the environment and that it accumulates in the organisms, causing damage to the brain and nervous system leads to a hardening of the legislations in many countries. However, the advantages resulting from the high piezoelectric properties of PZTs are obvious. In medical imaging, for instance, use of PZT allows a good signal resolution that is essential for a precise diagnosis, thus saving many lives. On the other hand, there is a trend for developing piezoelectric materials that are biocompatible and for use as sensors and actuators implanted directly into living tissue, including human body. How PZT materials behave in a body fluid environment is not clearly

established yet. Some tests of pyroelectric PLZT sensors implanted in rabbit eyes for up to six weeks have shown no obvious damage to the surrounding living tissues [3]. PZT itself does not seem to be toxic to cells but the question arises if it dissolves/corrodes in presence of body fluids releasing lead ions. For example, some tests on PZT ceramics submerged into water have shown subsequent presence of lead in the water [4]. The strong psychological reluctance to introduce lead containing products in the human body should also be taken into account. Thus, there is an increasing tendency to look for alternative materials. The low density of non-lead based materials can also be an advantage in transducers for underwater and medical imaging due to expected lower acoustical impedance.

Moreover, there is a strong interest in finding materials for a number of applications at high temperatures for which none of the presently available lead based materials are suitable. These materials include materials based on the bismuth titanate layered compounds, the langasite family, GaPO_4 , the well known LiNbO_3 and number of other compositions (for more details see for example. Ref. [5, 6]).

In the search for new complex systems with potentially good electromechanical properties, the presence of MPBs is desirable and it has to be taken into account that the stability of the properties versus time, temperature or pressure is also connected with the phase transition(s) temperature(s) of the material. For example BaTiO_3 based materials, in spite of potentially good electromechanical properties show a Curie temperature that is too low for most applications.

In this paper we review selected piezoelectric and related properties of ceramics compositions based on potassium niobate (KNbO_3) and bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$).

Alkaline Niobates

The KNbO_3 exhibits the same sequence of phase transitions [7] as BaTiO_3 , transforming from the cubic paraelectric to the tetragonal phase at 435°C , from the tetragonal to the orthorhombic phase at 225°C and from the orthorhombic to the rhombohedral phase at -10°C . The tetragonal, orthorhombic and rhombohedral phases are all ferroelectric. Potassium niobate ceramics exhibit weak piezoelectric properties [1]. Until recently, the interest in the piezoelectric properties of KNbO_3 was limited to their large surface acoustic

waves coupling factors [8]. Its bulk piezoelectric coefficients are low. In 1999, however, Nakamura et al. [9, 10] have shown that KNbO_3 exhibits nearly 3 times higher longitudinal piezoelectric coefficients along certain non polar crystallographic directions than along the polar axis. Similar effect has been observed in the thickness coupling coefficient, k_t , which reaches a value of 70%, one of the highest ever reported for this coefficient [11] in any material. Combined with a low permittivity and low density, these properties are of a considerable interest for single element thickness-mode high frequency transducers. As recently calculated by Damjanovic et al. [12] for tetragonal BaTiO_3 crystals, the longitudinal piezoelectric coefficient may exhibit a maximum along a non polar direction when a ratio between the shear and longitudinal piezoelectric coefficients (or respective permittivities) is larger than a certain critical value. In tetragonal BaTiO_3 , this condition is fulfilled only over a narrow temperature range near the tetragonal-orthorhombic phase transition. For orthorhombic KNbO_3 , the anisotropy in the permittivity ($\varepsilon_{11}/\varepsilon_{33}$ and $\varepsilon_{22}/\varepsilon_{33}$) is relatively large over the whole phase region. Our calculations of the critical values of permittivities in KNbO_3 , based on data from Wiesendanger [13], indicate that $d_{33}^*(\theta, \phi)$ (the longitudinal piezoelectric coefficient in an arbitrary direction) probably exhibits a maximum along non polar directions over a large, if not the whole, temperature range where the orthorhombic phase is stable. High quality and large size monocrystals of KNbO_3 are now readily available and are of interest for their excellent optical properties. On the other hand, ceramics are still difficult to obtain by conventional methods.

Solid solutions of KNbO_3 with NaNbO_3 leads to a system with many MPBs, showing ferroelectricity up to about 90% NaNbO_3 . Over most of the phase diagram the phase transition sequence is the same as in pure KNbO_3 and, except for the orthorhombic-rhombohedral, the phase transition temperatures vary little over the whole composition range (T_c around 420°C).

There is a morphotropic phase boundary near the 50/50 composition separating two orthorhombic phases. This composition shows a rather high piezoelectric longitudinal response, a transverse coupling coefficient between those in modified lead titanate and hard PZT (d_{33} reported to be as high as 160 pC/N for $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN)), and a relatively low dielectric constant (around 400 at room temperature). They could therefore be considered as a viable alternative to

those materials for selected applications. In addition, this material in a form of fully dense ceramics appears to be compatible with animal and human tissue.

Potassium niobate and potassium sodium niobate ceramics are difficult to process to full densities by natural sintering for several reasons [1, 14, 15]. One is that the phase stability is limited to 1040°C for potassium niobate and 1140°C for potassium sodium niobate. High temperatures of sintering are therefore not possible. In addition, slight changes in stoichiometry (both on the niobium rich and the potassium rich side) lead to the formation of extra phases [16]. Potassium excess might provide some densification helping liquid phase but some of the formed extra phases are highly hygroscopic and lead to a quick disintegration of the final sample once exposed to humidity. Sintering temperatures for KNbO_3 are between 950 and 1030°C and 1090 to 1120°C for $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$. The best densities reported for undoped KNbO_3 are 90–95% of the theoretical density (taken as 4.62 g/cm³) and the same for $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (theoretical density 4.51 g/cm³). Up to now, only hot pressing techniques have been employed successfully to get very dense ceramics [17, 18]. The piezoelectric d_{33} coefficient as high as 160 pC/N has been reported for a hot pressed ceramic [17] while d_{33} of naturally sintered ceramics are closer to 80 10⁻¹² C/N. Table 1 shows our data for Sr or Ba doped KNN compared with lead metaniobate.

Some concern has been raised about high dielectric losses in these materials. Interestingly, the data available in the literature do not appear to be consistent. For example Kari et al. [19] have reported large losses in single crystals of KNbO_3 whereas Wiesendanger [13] observed nearly order of magnitude lower losses in single crystals. Our data also seem to suggest that it is possible to reduce losses in ceramics, at least at room temperature, to a nearly acceptable level with a proper

treatment. It is significant that both our results on ceramics and those of Wiesendanger on single crystals indicate that a high temperature annealing may reduce losses. The question remains whether this reduction is stable with time, or reappears as sample's surface reacts with the atmosphere. However, our ceramic samples with good properties have shown stability (dielectric losses under 0.04—constant d_{31} , k_t) for over 2 months in humid or water containing atmosphere.

Another difficulty that has been observed is the presence of a second resonance harmonic which origin is not clear yet. This feature has been shown to disappear after an appropriate treatment of low temperature annealing and re-poling (cf. Fig. 1).

The stability of the piezoelectric response of KNN and Sr doped KNN under different driving fields is comparable to rhombohedral PZT close to MPB as shown in Fig. 2. This indicates a strong contribution of the domain walls motions to the piezoelectric response, most probably originating from the 12 polar directions of the orthorhombic structure.

It seems that KNN is one of the most serious lead free candidate for high frequency transducers, with its low density, high T_c and relatively high coupling coefficients. Recent Toyota patents on KNN doped with CuO, Li, Ta and Sc_2O_3 as sintering aids, also claim low dielectric losses and stability with time coupled with good electromechanical properties.

Bismuth Titanate Based Layered Compounds

The crystal structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) and related compositions, first described by Aurivillius [20], is characterized by pseudo-perovskite layers ($\text{A}_{m-1}\text{BO}_{3m+1}$) stacked between $(\text{Bi}_2\text{O}_2)^{2+}$ layers [21]. A is a mono, divalent or trivalent cation and B a quadri, penta or hexavalent metal. m represents the number of perovskite layers. Due to the layer structure, the compositions exhibit a very high anisotropy of properties [22–29]. With the known exception of monoclinic BIT, in most Aurivillius phases the structure can be described as orthorhombic below the paraelectric-ferroelectric phase transition temperature, while the polarization takes place in the ab plane [30]. The piezoelectric effect is the highest in this plane. In the ceramics, the microstructure of such materials consists of plate-like shaped grains [23]. For these crystallites, the smallest dimension of the grain corresponds to the crystallographic c -axis so that the polarization lies in the plane of the grains

Table 1. Properties of some undoped and doped KNN compared to lead metaniobate.

	KNN undoped	KNN 0.5% Sr added	KNN 1% Sr substituted	KNN 1% Ba substituted	PbNb ₂ O ₆ Ferroperm Pz35
diel. perm.	400	330	500	580	220
diel. losses	0.02	0.04	0.05	0.035	0.006
d_{31} pC/N	31	30	43	43	
d_{33} pC/N	70	90	110		100
k_{31}	0.15	0.15	0.2	0.18	
k_p	0.25	0.27	0.35	0.32	
k_t	0.38	0.4	0.39	0.39	0.34

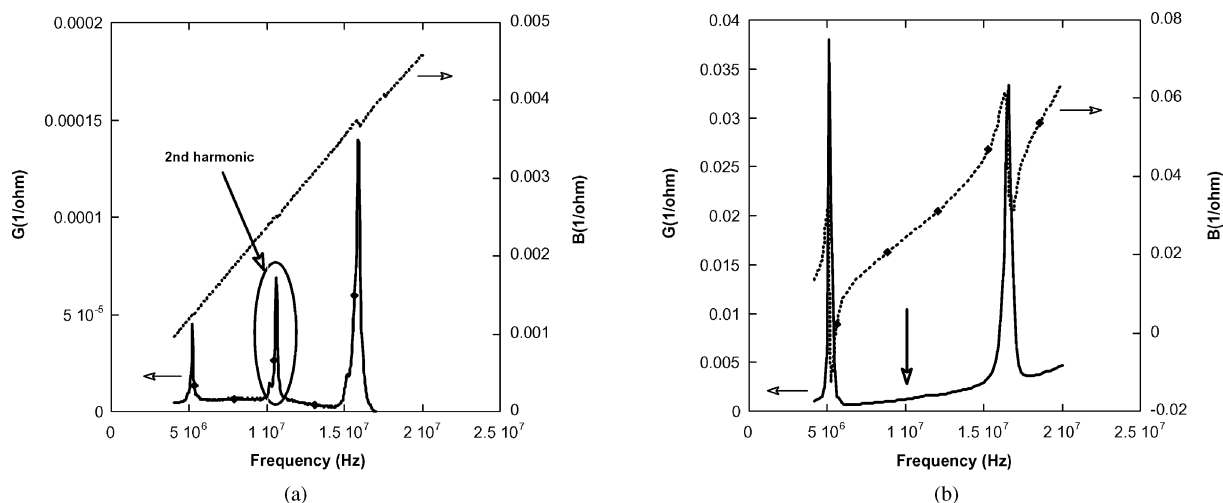


Fig. 1. (a) Presence of a second resonance harmonic that (b) disappears upon annealing 1 h at 250°C and re-poling.

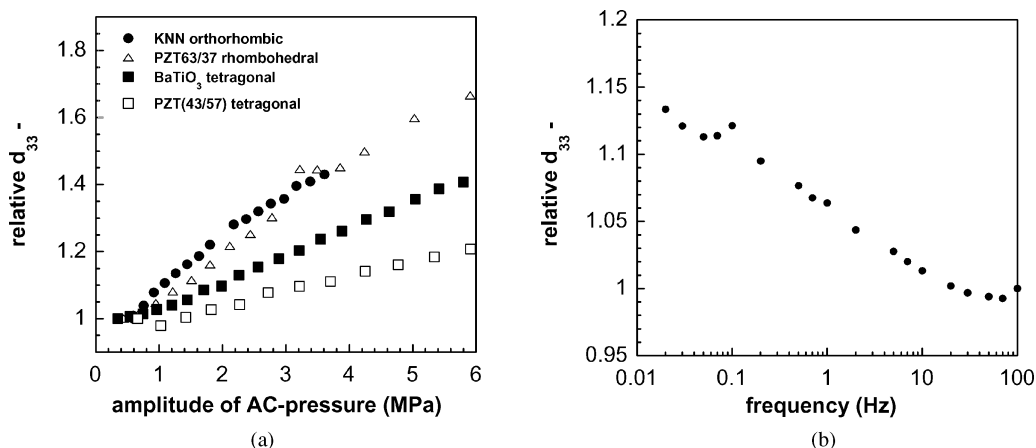


Fig. 2. Longitudinal piezoelectric response (a) versus AC-pressure. KNN compared to PZT and BaTiO₃ and (b) versus frequency for KNN.

(*ab*-plane). Incidentally, the electrical conductivity is also highest in this plane, seriously limiting applicability of materials at elevated temperatures (roughly above 300–400°C).

The conductivity type in pure BTO12 has been reported as being *p*-type [31]. Early studies on doped BTO12 [32] reported a decrease of conductivity with the addition of donors such as Nb, Ta and Sb. Further work [33] showed that, with addition of Nb, the conductivity decreased until a minimum of conductivity is reached for the composition Bi₄Ti_{2.96}Nb_{0.04}O₁₂ (three orders of magnitude lower than for undoped BTO12). It was suggested that the hole compensation is complete

for this composition and with higher levels of dopants, the material could become *n*-type [34]. Nb or Ta doped BTO12 therefore can be polarized, have a *d*₃₃ between 18 and 20 pC/N and can show good stability with time and temperature [35].

As previously noted, many compounds in the family of Aurivillius phases exhibit a high Curie temperature (up to 980°C) and have been proposed for high temperature piezoelectric applications [5, 6, 22–29]. However, it has been noted that different members of the family do not exhibit the same stability of properties with respect to amplitude and frequency of the driving field. Some compositions, such as SrBi₄Ti₄O₁₅ (SBTO15)

exhibit a remarkably constant response over a wide range of driving conditions, whereas the properties of others compositions are non-linear, hysteretic and frequency dependent [36–39]. Moreover, the piezoelectric properties can be strongly influenced by the processing conditions and dopants. Therefore, a better understanding of different processes that affect piezoelectric properties in this group of compositions is of a wide interest. A complete discussion has been published elsewhere and here we summarize the main features of selected bismuth titanate based compositions, which well illustrate richness of different phenomena that can affect the piezoelectric response in ferroelectric materials.

The following figures, (Figs. 3–5(a) and (b)) illustrate two extreme piezoelectric behaviours with respect to driving pressure amplitude. SBTO15 shows, at room temperature and under usual weak to moderate driving pressures, practically ideal longitudinal piezoelectric response, which is free of hysteresis and quasi independent of the amplitude and frequency of the dynamic pressure [39]. Bismuth titanate doped with a small amount of niobium, $\text{Bi}_4\text{Ti}_{2.95}\text{Nb}_{0.04}\text{O}_{12}$ (written BTO12-Nb), exhibits, on the other hand, properties that are typical to those of PZT ceramics. The piezoelectric d_{33} coefficient is non-linear and shows frequency dependence, while the charge density exhibits a large hysteresis with respect to the driving pressure [39]. Non-linearity and hysteresis are typical consequence of irreversible non-180° domain wall displacements.

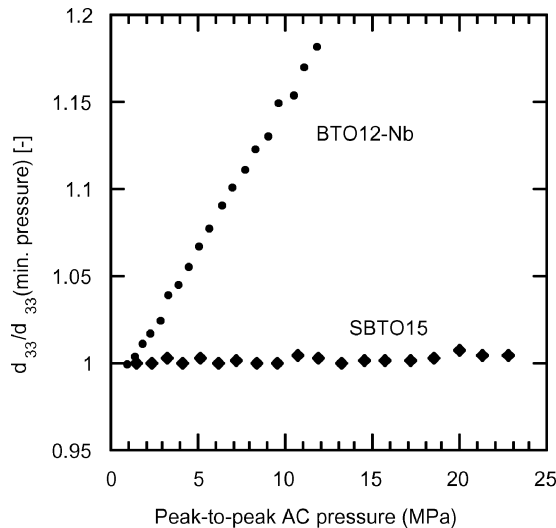


Fig. 3. Field dependence of the relative longitudinal piezoelectric coefficient d_{33} for BTO12-Nb and SBTO15.

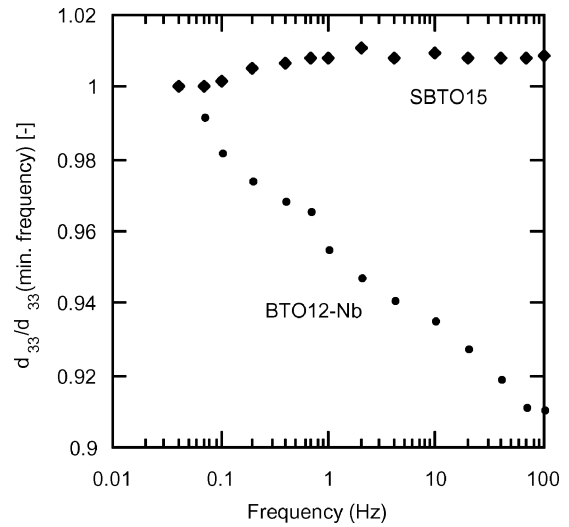


Fig. 4. Frequency dependence of the relative longitudinal piezoelectric coefficient d_{33} for BTO12-Nb and SBTO15.

It is evident from Figs. 3–5, that in BTO12-Nb domain walls move irreversibly even at relatively low pressure.

This difference in piezoelectric behaviour has been related to structural features. Early studies in undoped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BTO12) showed that the phase transformation from the tetragonal paraelectric phase into the monoclinic ferroelectric phase in this material results in a number of different non-180° walls [40] which could, in principle, contribute to the piezoelectric effect when displaced by an external field. It is reasonable that this composition displays the hysteresis and field dependence of the piezoelectric coefficient as shown in Figs. 3–5.

The quasi linear and non-hysteretic response of SBTO15 suggests that non-180° domain walls in this composition are either (1) strongly clamped, (2) move only reversibly over the investigated pressure range or (3) do not exist in this composition. This problem has been discussed using crystallographic arguments by Reaney and Damjanovic [39]. They presented evidence that the ferroelastic and ferroelectric phase transitions in SBTO15 do not occur at the same temperature, as in BaTiO_3 and PbTiO_3 . The decoupling of ferroelastic and ferroelectric transitions leads to an apparition of ferroelectric non-180° domains in a pre-existing ferroelastic domain structure. The movement of the domain walls must be accompanied with a change in polarization. This may be energetically more difficult in SBTO15 than in other ferroelectrics where

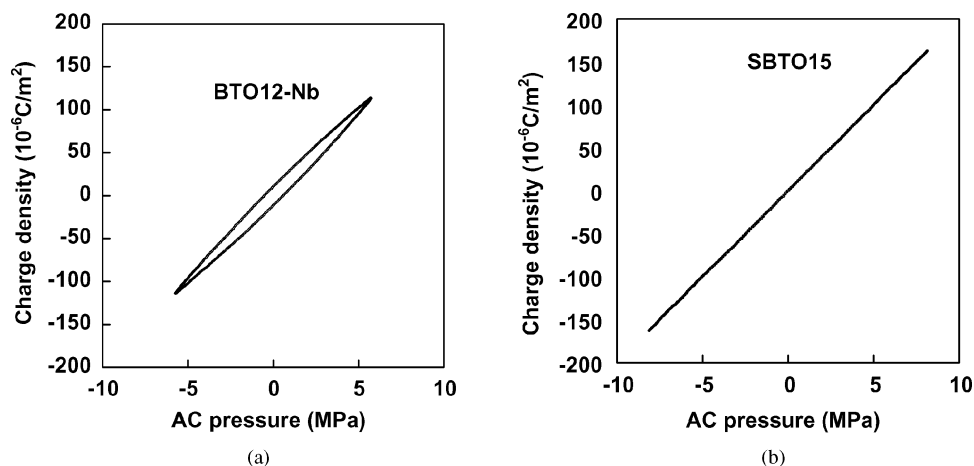


Fig. 5. (a) Hysteretic piezoelectric behaviour of BTO12–Nb and (b) stable piezoelectric behaviour of SBTO15.

ferroelastic and ferroelectric phase transformations occur simultaneously.

Another type of instabilities that can be observed in some materials with bismuth layered structure is linked to their microstructure. In SBTO15, in some cases, a frequency dependence that can be positive or negative (relaxation or retardation) occurs (Fig. 6(a) and (b)), while some other samples with the same nominal composition do not show any dependence (not shown).

We have proposed a simple model based on the anisotropy of electro-mechanical properties and the plate-like morphology of the grains [41] (cf. Fig. 7) to explain this behaviour. The material, composed of colonies of grains with different orientation, behaves like a composite of two piezoelectrics with different

dielectric and piezoelectric properties. In that case, one can easily expect to see Maxwell–Wagner relaxation as in dielectric properties.

An experimental verification of the model has been made by artificially forming a composite made of a piece of hot forged BTO12 poled along the *ab*-plane $d_{33} = 27.6$ pC/N and a piece of hot forged BTO12 poled along the *c*-plane $d_{33} = 7.8$ pC/N. The individual pieces alone do not show frequency dependence while the two pieces placed in series show a relaxation that can be positive or negative as shown in Fig. 8. The frequency dependence is therefore not due to domain walls motions but to piezoelectric Maxwell-Wagner effect. This effect is microstructure dependant, varying with the aspect ratio of the grains and the local texture

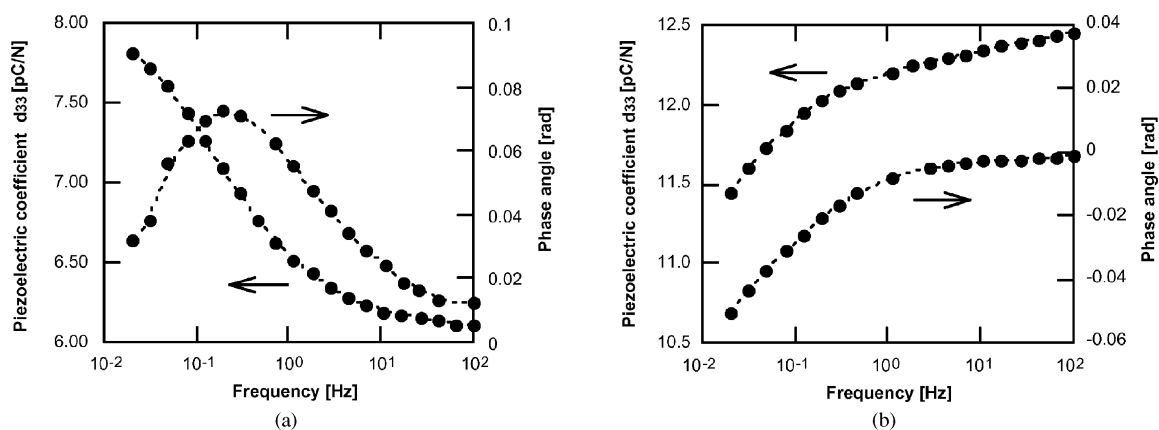


Fig. 6. Relative piezoelectric coefficient and phase angle showing (a) retardation (positive phase angle) and (b) relaxation (negative phase angle).

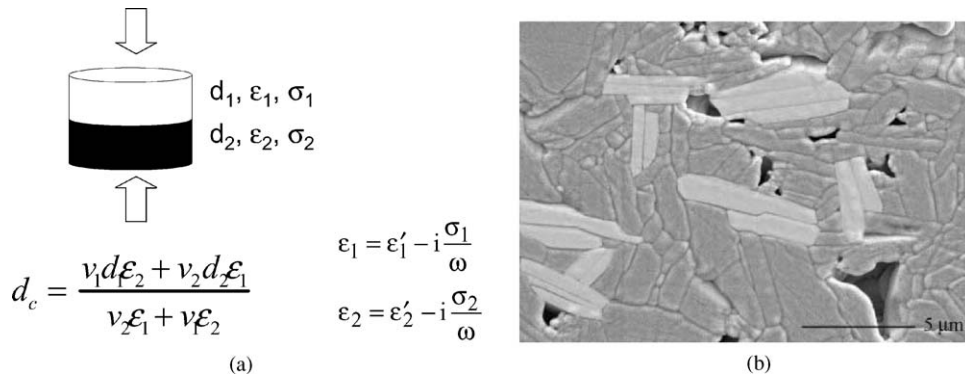


Fig. 7. (a) Model of a composite of two piezoelectric materials with different properties placed in serie. d_i represents the piezoelectric longitudinal coefficient, ϵ_i the dielectric permittivity and σ_i the conductivity of the different phases. (b) Typical microstructure of a sample sintered just below the temperature of the liquid phase onset. The highlighted areas show the selected grain colonies creating a local texture.

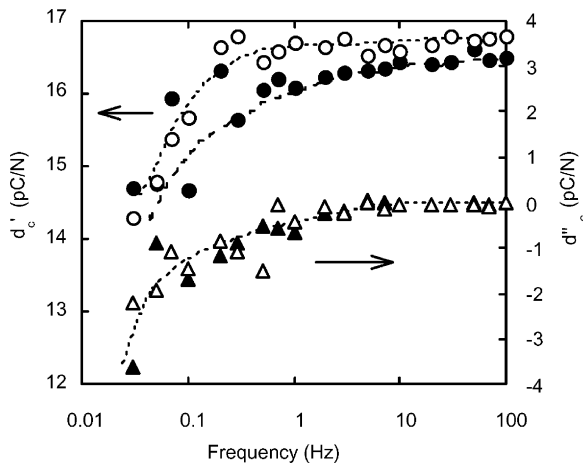


Fig. 8. Real (circles) and imaginary (triangles) part of the piezoelectric coefficient of the SBTO15 hot forged composite at 190°C. The open symbols represent measured values on the composite and the full symbols calculated values. The dashed lines are guides for eye.

formed. Smaller more isotropic grains lead to a stable behaviour.

Those examples show how the stability of the properties depends upon structural and microstructural features and how important it is to understand them in order to get the best properties for high temperature operation.

Recently there is a trend to use the anisotropy of the properties of the compounds of this family to get higher piezoelectric activity. The piezoelectric coefficient is much higher in the *ab*-plane but the conductivity is also increased. Appropriate dopants have to be added to increase the resistivity. Moreover the material has to

be polarized and used in the *ab*-plane of the plate-like grains. Practically, hot forging gives highly oriented materials but it has been observed that annealing at high temperature leads to a loss of the texture (orientation) at the surface. For example, we observed that the Lotgerin factor of 0.80 of a hot forged BTO12 drops to 0.50 after 1 hour annealing at 1100°C. The operating temperature of this material is much lower but the material should be stable with time at those temperature and such effects should be excluded.

The method called reactive templated grain growth (RTGG) has been developed for those materials, starting with BTO12 platelets that react with the other components in appropriate quantities to get the compound with the right orientation. Interesting properties have been reported for $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ (Tc 820°C) [42, 43] and $(\text{NaBi})_{(1-x)/2}\text{Ca}_x\text{Bi}_4\text{Ti}_4\text{O}_{15}$ (Tc 665°C) prepared by RTGG, showing a longitudinal piezoelectric coefficient d_{33} around 45 pC/N and ak_t around 0.50.

Conclusions

While none of the presently available non-lead based materials can match overall performance of PZT, several classes of materials are now being reconsidered as potentially attractive alternatives to PZT for special applications. The families of potassium sodium niobate, bismuth sodium titanate have the advantages of low density, low dielectric constants, high coupling coefficient k_t , higher mechanical strength in general than lead containing ceramics that make them suitable for applications as high frequency transducers. Moreover

their lower acoustical impedance and the fact that they are non toxic are advantages for in water and medical imaging. However their processing has to be carefully controlled in order to get stable properties.

For operation at temperatures higher than 600°C, lead containing compounds are not suitable. Some bismuth layered compounds show a good stability of properties at these elevated temperatures. Their behaviour under different driving conditions depends upon structural and microstructural features that have to be carefully controlled.

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