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Feature Article

# Transferring lead-free piezoelectric ceramics into application

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**Abstract**

After twenty years of partly quiet and ten years of partly enthusiastic research into lead-free piezoceramics there are now clear prospects for transfer into applications in some areas. This mimics prior research into eliminating lead from other technologies that resulted in restricted lead use in batteries and dwindling use in other applications. A figure of merit analysis for key devices is presented and used to contrast lead-containing and lead-free piezoceramics. A number of existing applications emerge, where the usage of lead-free piezoceramics may be envisaged in the near future. A sufficient transition period to ensure reliability, however, is required. The use of lead-free piezoceramics for demanding applications with high reliability, displacements and frequency as well as a wide temperature range appears to remain in the distant future. New devices are outlined, where the figure of merit suggests skipping lead-containing piezoceramics altogether. Suggestions for the next pertinent research requirements are provided.


*Keywords:* Lead-free ferroelectrics; Piezoelectrics; Piezoelectric transducer; Piezoelectric actuator; Ferroelectricity

## 1. Introduction

About ten years ago, a publication by Saito et al.,[1] fueled excitement and spurned wide-spread scientific activity in the quest to replace lead-containing piezoceramics represented by $Pb(Zr,Ti)O_3$ (PZT) with non-toxic alternatives. This publication came as a response to legislative activity by the European Union[2–4] geared to eliminate toxic substances from electrical and electronic equipment to reduce their impact on the environment and health. In the following years the number of annual refereed publications increased from about 60 in 2004 to about 400 in 2011.[5] The precursor of these more recent activities is probably a publication by Takenaka and colleagues in 1991.[6] The work of Saito et al.[1] got attention for identifying a mixture of morphotropic and polymorphic phase transition region in a $(K,Na)NbO_3$-based system (KNN) with PZT-like values of piezoelectric coefficients in textured ceramics.

We should mention here briefly that "lead-free piezoelectric materials" is a generic term that encompasses two general groups: one competes for the same applications as PZT and another excels in properties that are outside the range where PZT can be used. To the first group (in competition with PZT) belong KNN, $(Bi_{0.5}Na_{0.5})TiO_3$-$BaTiO_3$ (BNT-BT), and $(Ba,Ca)(Zr,Ti)O_3$ (BCZT) based materials. The second group includes materials with properties with which PZT cannot compete. These materials are "inferior" to PZT in some sense but are superior in another. Examples include: $SiO_2$, AlN, $LiNbO_3$ (single crystals), Aurivillius structures (Bi-based layered structure), and other high temperature piezoelectrics.[7]

Piezoceramics not only command a huge market (piezoactuators alone have in excess of 20 billion $[5]), but also act as an enabling technology for other areas, such as microelectronics through positioning elements in photolithography, medical diagnostics through ultrasound imaging, sensors and actuators

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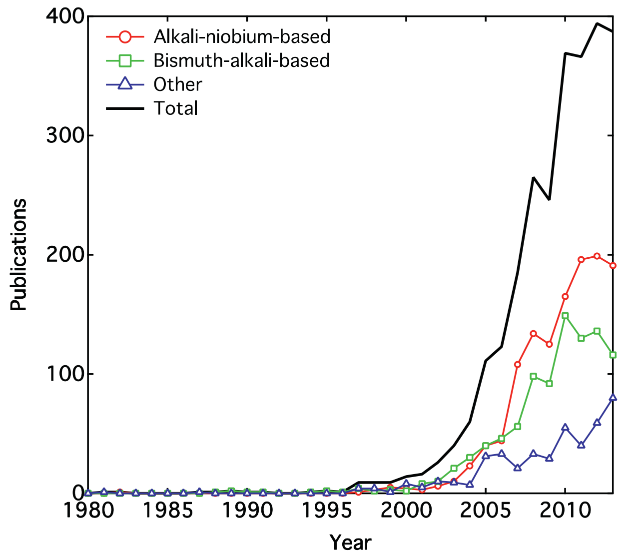


Fig. 1. Increase of the annual refereed publications during the last 34 years, divided into alkali-niobium-based and bismuth-alkali-based ceramics as well as others (mainly BCZT).

in automobile industry, and many others. Consequently, a series of review articles have appeared to aid in the international effort to develop new lead-free piezoelectric ceramics. These articles have typically attempted to survey the composition development process and, in addition, focused on various property issues that have arisen: the review by Damjanovic[8] was one of the first in the field and touched some specific domain wall-(micro)structure-properties relations, the paper by Shrout and Zhang[9] concentrated on a comparison to PZT, Takenaka et al.[10] considered mostly compositions based on BNT, while Li et al.[11] summarized the progress on KNN-based materials. Guidelines in terms of electronic structure, useful elements, and phase diagrams were the focus of the paper by Rödel et al.[12] five years ago. Other review efforts focused on the effects of dopants on electrical properties using a large number of tables to classify property changes,[13] while Aksel and Jones discussed crystallographic aspects.[14] The review by Coondoo et al.[15] provides an extensive dataset on lead-free piezoceramics, including bismuth layer structured ferroelectrics and langasites as well as a chapter on energy harvesting. Subgroups of lead-free piezoceramics are considered by Jo et al.,[5] in a description of incipient piezoelectrics and by Shvartsman and Lupascu with consideration of lead-free relaxors.[16] Recently, fatigue of lead-free ferroelectrics has been specifically addressed by Glaum and Hoffman.[17] Finally, a book on lead-free piezoceramics is currently available.[18] We, therefore, feel that the latest reviews have surveyed the field very effectively and see no need for a further assessment of scientific concepts or extensive discussion of the complete literature.

The latest literature survey, however, suggests that the scientific activity in this field has reached its peak, with about 400 refereed publications in 2010–2013 each (Fig. 1), indicating that the science in the field of lead-free piezoceramics has now reached a certain degree of maturity. In detail, research in KNN-based materials and BNT-based materials has saturated, while new developments in BCZT bring up a third material opportunity. In the meantime, the computational community has developed high-throughput density functional theory, which could facilitate the prediction of experimentally discovered lead-free families that can compete with PZT.[19] Strong progress has been made with many compositions tested and an advanced, although still far from complete, understanding has now also been reached. The in-phase and out-of phase oxygen tilting, for example in the case of BNT may only serve as one example to illustrate the rich materials' complexity in lead-free piezoceramics.[20] With a certain degree of scientific maturity, more advanced methodologies like piezoforce microscopy,[21] in-situ transmission electron microscopy,[22] and in-situ diffraction techniques are considered.[23,24] In order to facilitate salient collaborations, research groups are expected to extend their level of international collaborations, to both academia and industry. With the fundamental understanding nearing, and in some cases even surpassing, the mechanistic understanding of lead-based ferroelectrics and ferroelectric relaxors, a societal responsibility toward application-oriented properties demands due attention. Hence, we have transgressed from an efficient, wide-spread scanning of a broad chemical parameter field toward both a detailed atomistic-based mechanistic understanding and a real-world demand-driven consideration of effects of temperature, frequency, stress, cycle number, processing issues, etc.

We suggest that the scientific and technological progress in the development of lead-free piezoceramics follows a generic picture with a peak of inflated expectations and a trough of disillusionment leading into a slope of enlightenment[25] (see Section 4). Given this assessment, let us, therefore, focus in this work on the transfer of our joint achievements into applications. In the main section we provide a classification of salient applications with respective figures of merit and contrast lead-containing piezoceramics with lead-free piezoceramics (Section 5). To illustrate our prospective path, we follow with select examples of already existing or expected industrial transfer into specific applications (Section 6). In the final sections we then suggest the next steps to take for fundamental as well as applied research (Section 7) and conclude with Section 8. We set the scene by reviewing issues of toxicity and ongoing legal matters (Section 2) and compare our activities to analogous strategies previously employed in different applications, where a replacement of lead has been achieved already (Section 3).

## 2. Toxicity of lead and legal issues

In the discussion about the toxicity of lead-containing ceramics such as PZT, it is important to differentiate the hazards involved in metallic lead, the precursor lead oxide and the final ceramic. The toxic effect of metallic lead is well known.[26–28] Due to the absorption from the lungs, skin, or the gastro-intestinal system, lead can be easily accumulated within the human body where it is stored in bone and soft tissue such as organs or muscles. The most immediate consequence is acute lead poisoning with severe damage to the blood as well as the gastro-intestinal and neurological systems.[29] The median lethal dose LD50, which is the dose sufficient to kill half of a tested