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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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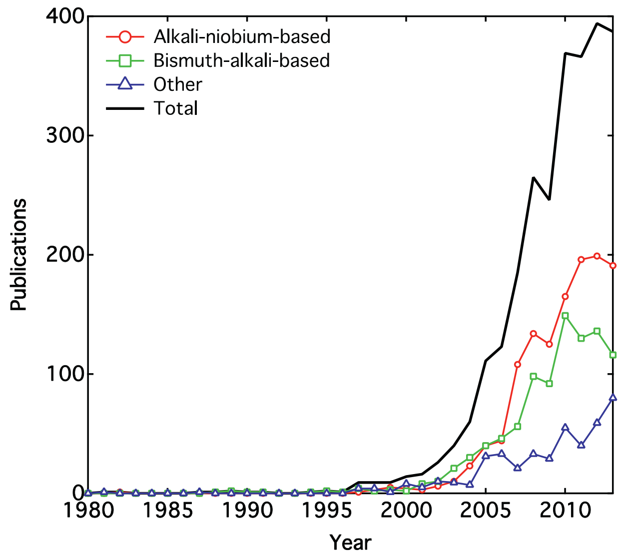

Fig. 1. Increase of the annual refereed publications during the last 34 years, divided into alkali-niobium-based and bismuth-alkali-based ceramics as well as others (mainly BCZT).

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 gastrointestinal 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 population, is reported to be 450 mg/kg, which is equivalent to 36 g of lead for a person with a mass of 80 kg.[30] Chronic lead exposure may result in hypertension, nephropathy, and, furthermore, affects the physical and mental development, especially of children.[31,32] Lead also impairs fertility, resulting in an increased probability of miscarriage, stillbirth, and neonatal deaths.[33,34]

In the production of lead-containing electroceramics, however, metallic lead is not used; only lead oxide PbO, which is less hazardous than Pb. The actual threshold limit value (TLV), which determines the highest air concentration of a hazardous substance that is not expected to result in acute or chronic damage, is 0.1 mg/cm^3 for PbO compared to 0.05 mg/cm^3 for Pb.[35] The LD50 then is 4300 mg/kg.[36] The toxicity of PbO is of particular concern as it has a high vapor pressure[37] and is fired at high temperatures.

It was demonstrated by Kosec et al.[38] that the final PZT ceramic may not be stable in an aqueous environment. Not only do electromechanical properties degrade in water but lead may also be dissolved and can be detected by means of ICP (induced coupled plasma) spectroscopy. This finding is especially alarming as a car may contain up to 100 g of PZT in small devices such as knock sensors, resistors, or piezoceramic injectors.[39] This is of particular concern because it may not be feasible to recycle all lead-containing components. In addition, due to the good etchability of PZT, acid rain also poses a serious concern in terms of lead leaching into the environment, e.g., groundwater. According to a publication by the United Nations Environment Programme, electronic waste generation volumes in developing countries exhibited an exponential growth in the past years.[40] The wide distribution of rather small components is critical for end-of-life vehicles as proper disposal or recycling is more complex than, for example, a lead acid battery. On a side note, some researchers see a similar issue with the heavy metal bismuth, which is used in many lead-free alternative piezoceramics. Its toxicity has been discussed in one of the review papers before,[12] but its use as the active ingredient bismuth subsalicylate in pepto-bismol,[41] an over-the-counter drug in the USA, may suffice as a further argument for its well-proven usage. A related issue concerns antimony, which is employed in a number of very promising lead-free piezoceramics. Here, one may note that antimony is also toxic and not suited to be part of a non-toxic replacement for PZT.

Consequently, legislation increasingly restricts the use of lead and lead-containing materials in order to reduce their impact on health and environment. With numerous regulations, the European Union (EU) is at the forefront of this movement, with others following.[12] For example, China has implemented a set of legislations by the Ministry of Industry and Information Technology of the People's Republic of China[42] with the following temporal evolution:

I. Measures for Pollution Prevention and Management of Electronic Information Products Manufacturing, was issued in 2006 by Ministry of Industry and Information Technology of the People's Republic of China, and validated from March 1, 2007. Hazardous components, such as Pb, Cd, Cr^{6+}, are restricted in electronic products.
II. Regulations on Pollution Control of Electronic Information Products (draft for comment), was issued in June 2012 by Ministry of Industry and Information Technology of the People's Republic of China, National Development and Reform Commission, and Ministry of Environmental Protection of the People's Republic of China. Comments could be provided until July 10, 2012.

One of the most comprehensive set of rules by the EU is the REACH (Registration, Evaluation, Authorisation and Restriction of Chemical Substances) Regulation, which regulates the import and production of chemicals within the EU.[43] According to REACH, the fabrication, use, import, or sale of those hazardous substances, designated as substances of very high concern (SVHC), may eventually require authorization by the European Chemicals Agency (ECHA). As of June 2014, there are 155 SVHCs with PZT added in December 2012 due to its 'toxic for reproduction' classification.[44] SVHCs added to the Candidate List may subsequently be included in the Authorisation List (Annex XIV) of REACH, with the result that they are given a 'sunset date'. After this date, the substance must not be used or manufactured unless an exemption applies or authorization is provided for a specific use.

Another important regulation is the directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment, abbreviated as RoHS, which was adopted in the European Union in 2003.[45] The most recent version of the regulation is the directive 2011/65/EU, which took effect on 2 January, 2013.[46] Consequently, the use of certain hazardous materials in electronic devices and electrical equipment is restricted within the EU. According to Annex 2 of the directive, this comprises lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyl, and polybrominated diphenyl ethers. The regulation applies, among others, to consumer equipment, toys, medical devices, IT equipment, lighting equipment, and sports equipment. For example, lead in piezoceramics (appendix 7(c)-I) as well as in certain capacitors (7(c)-II and 7(c)-IV) is exempted because a substitution is currently technically impracticable. The validity of these exemptions expires after five years, that is, in July 2016, unless it is renewed.

However, the regulation does not apply to applications such as, for example, military equipment, spacebound devices, active implantable devices, photovoltaics, or R&D equipment. For a non-exempted application each homogeneous material within a certain device must contain less than 0.1% of the above-mentioned six substances. Then again, for certain cases exemptions are defined when a substitution is not possible for scientific and technical reasons, when reliability is not ensured, or when safety and health concerns and benefits from using a compound outweigh the benefit of a substitution (see Fig. 2). Environmental and health benefits of PZT-based devices can be significant in specific applications. Examples include less consumption of gasoline and cleaner air, enabled in part by piezoelectric fuel-injection actuators; noninvasive medical

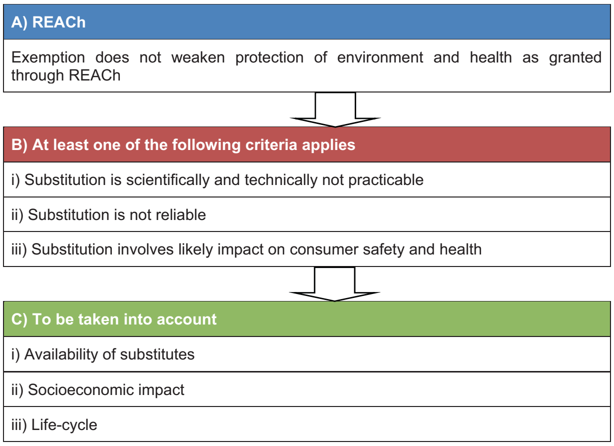

Fig. 2. Criteria for exemptions within RoHS.[46]

Table 1
List of exemptions in annex II of the directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment as of November 2013. It is important to note that all cases are reviewed after the expiration date and a new expiration date may be established.

	Exemption	Scope and Dates of Applicability
7(c)-I	Electrical and electronic components containing lead in a glass or ceramic other than dielectric ceramic in capacitors, e.g. piezoelectronic devices, or in a glass or ceramic matrix compound	After 5 years (21 July 2016)
7(c)-II	Lead in dielectric ceramic in capacitors for a rated voltage of 125 V AC or 250 V DC or higher	After 5 years (21 July 2016)
7(c)-III	Lead in dielectric ceramic in capacitors for a rated voltage of less than 125 V AC or 250 V DC	Expires on 1 January 2013 and after that date may be used in spare parts for EEE placed on the market before January 2013
7(c)-IV	Lead in PZT based dielectric ceramic materials for capacitors which are part of integrated circuits or discrete semiconductors	Expires on 21 July 2016

imaging and diagnosis, enabled by ultrasonic piezoelectric transducers; safety in transport, enabled by ultrasonic distance sensors; and structural health monitoring, enabled by piezoelectrically driven ultrasonic nondestructive testing. Specifically, health benefits from using PZT in ultrasonic medical imaging treatment and diagnosis far outweighs health hazard from unlikely uncontrolled disposal of a medical device in the environment at the end-of-life. The message is clearly that as long as an adequate alternative is not available, replacement of lead-based piezoelectrics used in critical applications such those listed should not be forced (Table 1).

Another regulation is the Directive on End-of-Life Vehicle 2000/53/EC, to be referred to as ELV in the following.[47] This directive aims at reducing the amount of waste stemming from passenger cars and light commercial vehicles within the European Union. One of the main elements of ELV is pollution prevention by reducing the amount of hazardous substances in vehicles such as lead, mercury, cadmium, and hexavalent chromium. Again, certain exemptions are listed in the annex of the directive with revisions taking place regularly; the sixth revision amended the annex in May 2013.[2] Here, exemptions 10 (a–d) deal with lead in electric and electronic components as listed in Table 2.

Table 2
List of exemptions in annex II of the Direction on End-of-Live Vehicles as of November 2013.

	Exemption	Expiration date
10(a)	Electrical and electronic components which contain lead in a glass or ceramic, in a glass or ceramic matrix compound, in a glass-ceramic material, or in a glass-ceramic matrix compound.	
10(b)	Lead in PZT based dielectric ceramic materials of capacitors being part of integrated circuits or discrete semiconductors	
10(c)	Lead in dielectric ceramic materials of capacitors with a rated voltage of less than 125 V AC or 250 V DC	Vehicle type approved before 1 January 2016 and spare parts for these vehicles
10(d)	Lead in the dielectric ceramic materials of capacitors compensating the temperature-related deviations of sensors in ultrasonic sonar systems	2014

Much of the worldwide R&D on lead-free piezoelectric materials in the last 10–15 years was triggered by the European legislations. Considering the number of applications that employ piezoelectric materials in industry, transport, and medicine, one would expect that the European Commission would follow its legislative actions by a concentrated support of the industrial, national, and academic research institutes working on developing new lead-free piezoelectric materials through its framework programs and now Horizon 2020. This has not happened. We could identify barely half a dozen projects financed by the Commission over the last 15 years with some activities on materials aspects of lead free piezoelectrics,[48] and only half of those were fully dedicated to materials research. In Japan, on the other hand, strong and sustained activities in development of new lead free piezoceramics were funded in the form of seven large research projects running over several years (2–5 years) and focusing on numerous materials, e.g., Ref. 49. In Korea, in 2013 two large projects started with a total financing of 13 million $, which involves several companies, national laboratories, and universities. Besides the above team projects, based on search results using a database in National Science and Technology Information Service (http://www.ntis.go.kr/), 100 small sized projects on

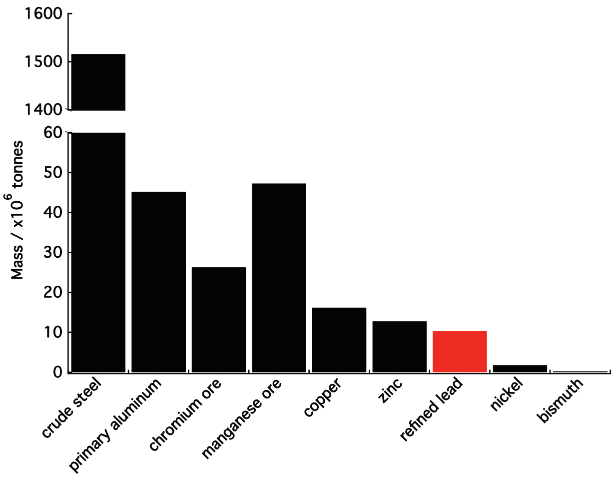

Fig. 3. World production of lead compared to other metals in 2011.[50]

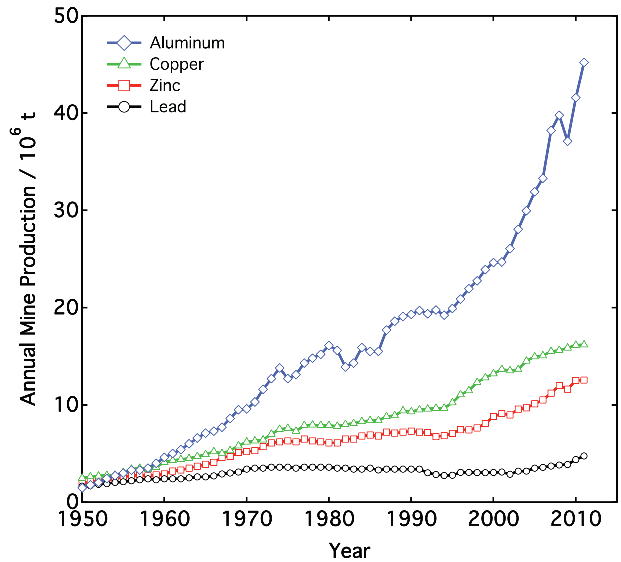

Fig. 4. Annual production of lead in megatons, compared to aluminum, copper, and zinc (according to Ref. 50).

lead-free piezoelectrics that have been carried out by individual researchers for the last decade were found that had funding in the range of US$ 10–150 K per year. In China, however, the government-based funding agencies are the primary sponsors. There have been, for example, three key projects funded in 2014 by the National Natural Science Foundation (NSFC) on lead-free ferroelectrics.

3. World production of lead and its elimination outside of the battery world

According to the British Geological Survey,[50] the annual global production of refined metallic lead was 10.4 million tons in 2011, with 4.7 million tons stemming from actual mine production; the remainder came from recycling. By far the biggest producer is China with more than 4.6 million tons, followed by the USA (1.25 million tons), Germany (0.43 million tons), India (0.43 million tons), and South Korea (0.42 million tons). Therefore, lead is one of the most produced metals in the world with respect to weight as illustrated by Fig. 3.

Compared to 1970, the annual world production of refined lead has increased by 120% from 4.7 million tons, whereas mine production went up by almost 60% from 3.0 million tons.[51] Even in recent years the production of lead has significantly increased. From 2007 to 2011 the annual production of refined metallic lead has increased by 2.2 million tons or 27%, whereas the mine production went up by 1.0 million tons or 27%.[50] Compared to other metals such as aluminum, copper, or zinc, this evolution may appear like a comparably small increase (see Fig. 4). However, it appears astounding that the world production of lead is of comparable level to zinc and copper!

An increase of 27% is surprising when one considers that lead has been banished and replaced in a number of different applications. One of the most prominent examples for a replacement is the substitution of lead-containing additives in fuel. Used since the 1920s, tetraethyllead was a highly effective antiknock agent, increasing the efficiency and the peak power in engines. In 1972 the U.S. Environmental Protection Agency initiated the phasing out of leaded fuel, which began in 1975 and was fully accomplished in 1996.[52,53] In the European Union, restrictions on leaded fuel started in 1981 until it was eventually banned in 2000.[4,54] Similar regulations took effect almost everywhere in the world. It is most important to note that the economic benefits exceed the cost for the replacement of lead in fuels by a factor of ten. According to Tsai and Hatfield[55] the global annual benefit due to decreased morbidity and mortality adds up to more than 2 trillion US-$. According to the United Nations, the only remaining countries in the world not selling unleaded fuel are Afghanistan, North-Korea, and Myanmar.[56]

Lead-free alternatives have also been developed for solders.[57,58] According to the U.S. Environmental Protection Agency about 80 thousand tons of lead-tin solder had been used worldwide in 2002.[59] However, owing to legislation lead-containing solders have been replaced to a great extent. A major driving force for that evolution has been RoHS, which effectively enforced lead-free solders within the European Union as of 1st of July 2006.[45] Furthermore, Japanese companies had been encouraged to use lead-free solders and China adopted its own regulations.[60,61] Moreover, the development of lead-free solders also became necessary as new applications like the hybrid electric car demanded higher working temperatures beyond 150 °C.[62] Conventional lead-containing solders such as Sn/37Pb, Sn62/Pb36/Ag2, or Sn63/Pb37 are not suited for temperatures that high.[63] Today, one of the most widely used solder is the ternary eutectic Sn/Ag/Cu, while other systems in use are mainly alloys of tin with copper, silver, or bismuth.[57]

Lead paint had been used since the days of the Roman Empire and the ancient Greeks owing to the good quality of white, yellow, and red pigments.[64] France, Belgium, and Austria banned white-lead interior paint as early as 1909,[65] but the worldwide movement of prohibiting lead paint only gained momentum in 1978 when the U.S. Consumer Product Safety Commission banned the use of lead paint in housing.[66] The consumption of lead in lead paints in the United States has consequently dropped from a peak value of more than 150 thousand tons per year to

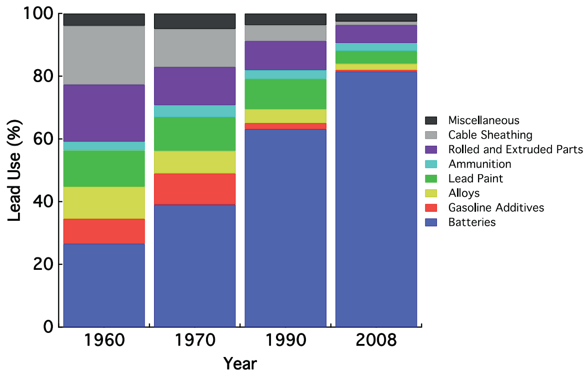

Fig. 5. End use of lead (after Refs. 76, 77).

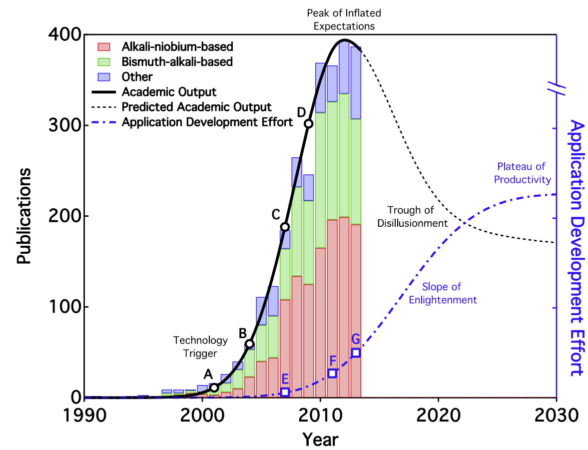

Fig. 6. Evolution of research (black) and transfer into application (blue) are contrasted in the time period from 1990 to 2030 with the evolution in research until 2013 stemming from the number of publications per year and the other curves predicted. Points indicate the following milestones: (A) Adoption of RoHS European Regulations, (B) Publication of Saito et al.,[3] (C) Publication of Zhang et al.,[78] (D) Publication of Liu and Ren,[79] (E) development of first commercial ultrasonic cleaner using lead-free piezoelectrics (Honda Electronics, BLT-type vibrator using BNT-BT), (F) development of lead-free multilayer actuator on water basis, and (G) medium-scale quantities (50 kg batches) for transducer applications such as flow meters.[80]

nearly zero.[67] Furthermore, the European Union forbade the sale of lead paint beginning 1992.[3] While many more countries such as China, Brazil, and India adopted laws to restrict the use of lead paint, tests performed by NGOs indicate that the enforcement of these laws especially in developing countries is not always as comprehensive as desired.[68]

Other applications where lead has been replaced include ceramic glazes,[69] fishing sinkers,[70,71] food-processing equipment,[72] plumbing,[73,74] and lubricating greases.[75] As a consequence of these substitutions, the worldwide use of lead has largely changed since the 1960s. Today, more than 80% of all lead is used for the production of car batteries (Fig. 5). Thus, the increasing use of lead in the last 40 years has been due to an increased use of lead batteries. This knowledge should provide encouragement for the field of lead-free piezoceramics.

4. Evolution of research

Let us first assess the achievements in research in a very broad manner by inspecting Fig. 1. EU legislation in combination with the 2004 paper by Saito et al.,[1] triggered research, leading to the steep rise in annual publications for the duration of time (to the year 2007) approximately needed for one Ph.D. thesis. These initial two triggers were followed by the investigations of Zhang et al.,[78] on BNT-BT-KNN and Liu and Ren[79] on BCZT. About two Ph.D. durations after the initial triggers (in 2011), a certain saturation has set in. From here on, the number of refereed publications per year has been nearly constant. Progress has been so rapid, that it has become difficult for new researchers to enter the field. The "obvious" innovations have been put forward, and from now on advancement requires deeper understanding, advanced methodology, and complementary expertise. Novel ideas can be imported by bringing researchers in from the consolidated field of lead-containing piezoceramics. If this does not happen, the research output in numbers of publications will go down. We have extended, therefore, the thick line (backed up by real data until 2013) by predictions using a dotted line from 2014 to 2030 (Fig. 6). To generalize the trend, we plot products (publications, parts, and devices) versus time in Fig. 6. The maximum in research productivity is often termed "peak of inflated expectations" with the following minimum being termed "trough of disillusionment".[25]

Academic arrogance may assume that solid research progress lures companies into the field, which may be driven to protect their pre-existing business based on lead-containing piezoceramics or because excellent, transferable expertise may enable new product lines challenging existing state-of-the-art technologies. In this latter case, however, several companies, like Toyota and Murata, e.g., Ref. 81, have been active in this field since the late 90s. Their expertise, in combination with new research funding in dynamic geographic areas and a newly created human potential eager to work in a field made attractive by its inherent nature of social responsibility, will determine the "slope of enlightenment". If this picture holds true a plateau of productivity may be reached (in our prediction) between 2020 and 2025. Then, finally, the last sentence in the paper by Cross[82] may come true: "As the results (referring to Ref. 1) are brought to the market place, all producers may be forced to explore this option". We need to critically examine in the next sections if this promise has potential to hold true and which applications are concerned as well as which applications are not ready and should not be currently required to go lead-free.

The decline in research output may seem as dreadful as the increase in applications seems unsubstantiated. As we are currently progressing from "peak of inflation" to "trough of disillusionment" it is timely to inquire how we can contribute to the technological "slope of enlightenment" and how we can substantiate our predictions for an increase in the number of applications.

We continue in the next section by classifying applications, defining figures of merit, and providing a direct comparison of the most advanced lead-free piezoceramics to lead-containing piezoceramics.

5. Competition between PZT and lead-free piezoceramics

5.1. Material parameters of concern

Piezoelectric materials are characterized by several physical parameters that bridge their electrical and mechanical properties. Due to the inherent crystallographic anisotropy of piezoelectric materials[83] as well as various types of available vibrational modes, the piezoelectric coefficient tensor is of the third rank and relates second rank mechanical and first rank electrical variables. During operation one of these variables denotes the input signal and the other denotes the output signal. The key examples of these properties include piezoelectric charge or strain coefficients (d_{ij}), piezoelectric voltage or strain coefficients (g_{ij}), electromechanical coupling coefficients (k_{ij}), and mechanical quality factor (Q_m), which are shown here in reduced notation or Voigt notation.[83] Tables 3 and 4 outline a number of applications and their respective figures or merit.

As the term 'piezoelectricity' suggests, one of the most important physical properties is the piezoelectric charge coefficient that correlates mechanical and electrical signals. When a small mechanical stress is applied to piezoelectric materials, an electrical displacement that is linearly proportional to the input mechanical force is generated and *vice versa, an electric field generates strain*. Since the electrical displacement requires charge accumulation at the electrodes, this proportionality is referred to as the piezoelectric charge coefficient or simply as piezoelectric coefficient. The same coefficient, now called strain coefficient, describes the converse effect. This piezoelectric charge or strain coefficient is known to be a consequence of the intrinsic piezoelectric effect and extrinsic reversible domain wall motion (also irreversible domain wall motion if the ac field is not small enough) in the case of ferroelectric-based piezoceramics,[84] and commonly called a small signal piezoelectric coefficient ($d_{ij} = [pC/N] = [pm/V]$). When the input signal is large enough, e.g., larger than the local coercive field for domain walls, irreversible domain wall motion and partial switching contributions play a significant role, causing the piezoelectric coefficient to vary nonlinearly with the amplitude of the applied mechanical or electrical field. This dependence of piezoelectric coefficient on electric field and mechanical stress defines another useful parameter, the so-called large signal piezoelectric coefficient (d^*_{ij}), which is especially useful in characterizing the actuating performance of piezoelectric materials. The large signal piezoelectric coefficient is simply given by the maximum achievable strain ($S_{\max}$) normalized by a given maximum electric field (S_{max}/E_{max}), where E is usually unipolar. While in PZT small and large signal piezoelectric coefficient are empirically related, for example through a factor of 0.5,[85] the community working on lead-free piezoceramics has developed materials which exhibit a high large signal piezoelectric coefficient by purposely reducing the remanent polarization, which in turn diminishes the small signal piezoelectric coefficient.[86] This approach, however, can lead to a reduction in the usable temperature range and until recently, suffered from the requirement of high maximum electric fields in excess of 4 kV/mm.[87]

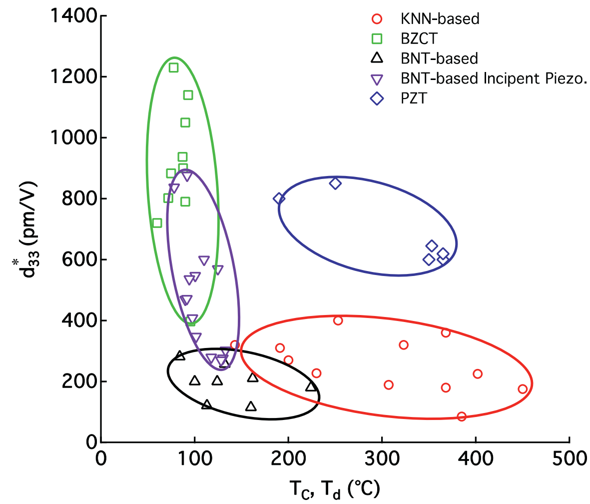

Fig. 7. The large signal piezoelectric coefficient (at room temperature) as a function of depolarization temperature for KNN-based,[1,9,88–90] BCZT,[79,91–94] BNT-based,[9,95–98] BNT-based Incipient piezoelectrics,[99–105] and PZT.[9,106,107] It is important to note that the maximum applied electric field is not that same for each data point.

There are a number of key material parameters to be considered. In the following section we will outline the main figures of merit for some of the key applications and compare lead-free and lead-containing materials for each of these. In order to gain an overview of the various material systems, we have chosen to graphically represent two figures of merit as a function of Curie point or depolarization temperature: the large signal piezoelectric coefficient, important for actuator applications, and the small signal $d \cdot g$ properties, used to evaluate materials for non-resonance sensing and energy harvesting applications. Key properties for actuator and sensor applications are large signal piezoelectric coefficient, d^*_{33}, and small signal piezoelectric coefficient, d_{33}, respectively. It has been shown before[9,12] that these are a strong function of the depolarization temperature (T_d). Representative data of the large signal piezoelectric coefficient for lead-free and lead-containing piezoceramics are presented in Fig. 7. If several classes of piezoceramics are plotted, including lead-containing relaxors and barium titanate, a strong function of depolarization temperature is obtained. From Fig. 7 several features are apparent. High temperature applications with lead-free piezoceramics should be addressed with KNN-type materials. For actuators with usage temperatures below 100 °C, both (Ba,Ca),(Ti,Zr)O_3 and incipient piezoelectrics appear feasible candidates for transfer into application. In detail, one may note, that very soft lead-containing materials with very low depolarization temperature need to be considered as competitor for these low temperatures.

When the piezoelectric charge coefficient is divided by dielectric permittivity, ($\varepsilon_r\varepsilon_0$, where ε_r and ε_0 are denoted as relative dielectric permittivity and permittivity of free space, respectively), another useful material parameter is derived. Given that charge divided by capacitance represents voltage, this parameter is called piezoelectric voltage coefficient (g_{ij}), which measures the achievable voltage output for a given mechanical input signal, and alternatively, a mechanical

Table 3
Current and future piezoelectric applications and their critical figures of merit (FOM).

Temperature range	Resonant or non-resonant	Applications		FOM	Other
		Well-established	Impending		
Special use $T > 500°C$	Resonant		Aerospace, Aircraft, nuclear power plant or geothermal power plant sensors[127]	$k^2 \cdot Q_m$	
	Non-resonant			$d \cdot g$	
SMD $T > 250\,°C$	Resonant	Filter		k	$F_r - TC$
		Oscillator		Q_m	$F_r - TC$
		Gyro sensor		$k^2 \cdot Q_m$	
	Non-resonant	Acceleration sensor, HDD shock sensor		$d \cdot g$	
Automotive $T = 40$ to $180\,°C$	Resonant	Knocking sensor, Back sonar	Energy harvesting(TPMS)[128,129]	$k^2 \cdot Q_m$	
	Non-resonant	Knocking sensor	Energy harvesting(TPMS)[128,129]	$d \cdot g$	
		Fuel injection		S_{max}/E_{max}	
Consumer $T = -20$ to $80\,°C$	Resonant	Fish sonar, Flow meter, Medical probe	Energy harvesting (Burglar alarm), Ultrasonic transducer (data entry device), Non destructive testing	$k^2 \cdot Q_m$	
		Ultrasonic cleaner, Ultrasonic machining tool,[a] Camera lens autofocus (motor), Power window (motor), Backlight inverter, High-voltage supply transformer	Wind blower, Air ionizer,	$k^2 \cdot Q_m$	v_{max}
			Micro-mass sensor[130]	Q_m	
	Non-resonant	Microphone	Energy harvesting (Burglar alarm)	$d \cdot g$	
		Stove burner, Lighter, Buzzer, Vibration damping (sports equipment)[131]		d	
		Ink jet, Loud speaker, Camera lens module	HDD tracking, Pump,	S_{max}/E_{max}	

[a] High power Langevin transducers are often used for ultrasonic machining tools. In this case large d_{33} values under a pre-stress are important.

displacement in response to accumulated charge density (also called strain coefficient). This parameter is especially useful in characterizing the sensitivity of sensors and the functionality of piezoelectric igniters. The piezoelectric strain coefficient d multiplied by the piezoelectric voltage coefficient g ($d \cdot g$) is an important figure of merit for a number of non-resonant transduction applications, such as microphones and energy harvesting. Lead-free and lead-containing piezoceramics are contrasted with representative materials in Fig. 8. It is deduced that KNN becomes competitive for high-temperature applications and (Ba,Ca),(Ti,Zr)O_3 deserves attention for room temperature usage.

The square of the electromechanical coupling coefficient (k_{ij}) represents the energy stored in a piezoelectric material when an electric field is applied while the mechanical distortion is constrained (note that it is a small signal property). This means that the electromechanical coupling coefficient is an indicator for conversion efficiency between electrical and mechanical energy. Ideally, the remaining (non-converted) applied energy is not lost. Thus the word efficiency is not appropriate to describe coupling coefficients. It is also important to note that the electromechanical coupling factor only concerns the ratio between input and stored energy; thus, it does not represent the actual working efficiency of the material when utilized in transducer applications. Simply put, not all of the energy stored can be transferred to the mechanical output signal due to mechanical and electrical losses.[123,124] The normally quoted electromechanical coupling coefficients are the theoretical maximum values usually determined at the resonance frequency. When a piezoelectric material is exposed to an AC electric field with increasing frequency it starts to vibrate, and this vibration peaks at the mechanical resonance frequency with the absolute value of its impedance being the minimum (short circuit condition). This mechanical resonance frequency is determined by the geometry of the specimen along the observed vibration axis. This mechanical vibration dies away with further increasing driving frequency due to another resonance with electrical capacitance, which is commonly called ‘antiresonance’ (open circuit condition). The larger the distance

Table 4
Piezoelectric properties of lead-containing and lead free materials.

T_C ºC	Application	Material	T_C/T_d ºC	k_{33}	d_{33} pC/N or pm/V	g_{33} 10^{-3} Vm/N	S_{max}/E_{max} pm/V	Q_m	$k^2 \cdot Q_m$	$d \cdot g$ pm^3/J	$F_r - TC$ ppm/ºC	v_{max}	Ref
>500	Aerospace, Aircraft and Nuclear sensor, etc.	$BiInO_3$-$PbTiO_3$	542	0.38(k_t)	60								132
		$La_2Ti_2O_7$ (textured)	1461		2.6								133
		$CaBi_4Ti_4O_{15}$ (textured)	800	0.53(k_t)	45	36.5				1.6			134
		$Na_{0.5}Bi_{4.5}Ti_4O_{15}$ based	663	0.34(k_t)	30			3800	440				135
>300	Resonator	$PbTiO_3$ based	310	0.35(k_{15})	70(d_{15})	24		3000	368	1.7	50		
		AT cut Quartz	576	0.11(k_t)	2	50		>50000	>600		0.1		
		$SrBi_2Nb_2O_9$ based (textured)	350	0.21 (k_{15})	30 (d_{15})			2850	126		0.4		136
	Ultrasonic sensor[a], motor	Hard Pb(Zr,Ti)O_3	360	0.54 0.50(k_{15})	220 290(d_{15})			2000	583				
		(K,Na,Li)NbO_3 based	410	0.25(k_{31}) 0.72 (k_{15})	93 207(d_{15})			1400	726				137
		(K,Na)(Nb,Ta)O_3 based	400(est.)	0.41(k_p)				1400					138
		$SrBi_2Nb_2O_9$ based (textured)	350	0.33	27			2320	253				139
	Automotive sensor, SMD sensor, FI actuator	Soft Pb(Zr,Ti)O_3	300	0.71	410	22	600	80	40	9.0			
		Soft Pb(Zr,Ti)O_3 (FI)	330				900						
		(K,Na)NbO_3 based	373	0.46(k_p)	262								140
		(K,Na)NbO_3 based (textured)	323		373		672(est.)						1
>100	Ultrasonic sensor Ultrasonic cleaner, Motor, Transformer	Hard Pb(Zr,Ti)O_3	360	0.54 0.50(k_{15})	220 290(d_{15})			2000 2000	583 500			1	
		(K,Na,Li)NbO_3 based	410	0.25(k_{31}) 0.72 (k_{15})	93 207(d_{15})			1400	726				137

Table 4 (*Continued*)

		(K,Na)(Nb,Ta)O_3 based	400(est.)	0.41(k_p)				1400					138
		(K,Na)NbO_3 – Bi(Na,K)ZrO_3	227		490								141
		(Bi,Na)TiO_3 based	260	0.41(k_t)	110			500	84			2	142
		$Sr_2NaNb_5O_{15}$ based (textured)		0.072	210	13	260	3193	16.6			1.84	143, 144
	Microphone, Buzzer, Actuator	Soft Pb(Zr,Ti)O_3	250	0.68(k_p)	600	20	900	50	23	12.0			
		(K,Na,Li)NbO_3 based	278	0.46(k_p)	295		466	84					145
		(K,Na)NbO_3 based	243	0.54(k_p)	420								146
		(K,Na)NbO_3 based (textured)	253	0.61(k_p)	416	29.9	750						140
		PVDF	170	0.20(k_t)	18	340		8	0.32	6.12			
<100	Sensor	Ba(Zr,Ca)TiO_3	94	0.65	546	15.3	1140			8.4			79, 110
	Actuator	BNT-BKT-ST	14				600						147
		BNT-BT-KNN			30		570						102
		(Ba,Ca)(Zr,Ti)O_3	94	0.65	546	15.3	1140			8.4			79, 110

[a]High planar coupling coefficients (actuator mode) and a high piezoelectric performance (sensor mode) are required as well as a low temperature coefficient of permittivity for the sensor systems.

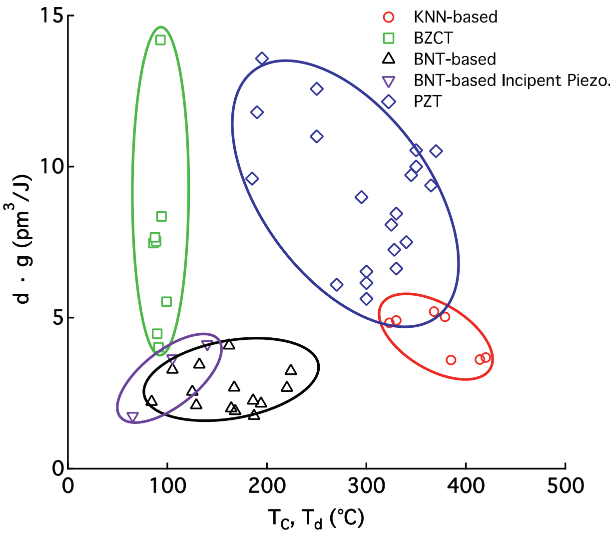

Fig. 8. $d \cdot g$ as a function of depolarization temperature for KNN-based,[9,108,109] BCZT,[79,110,111] BNT-based,[9,112–118] BNT-based Incipient Piezoelectrics,[119,120] and PZT.[9,121,122].

between the resonance and antiresonance frequencies is, the larger the electromechanical coupling factor.

The energy loss during the operation of an electromechanical system is of great concern in device fabrication, as the loss brings about reliability issues due to self-heating of the material.[125] Generally, both dielectric and mechanical dissipation must be considered. The former is important when the device operates at off-resonance frequencies, while the latter is critical when the material is driven in resonance modes. The mechanical quality factor is inversely proportional to the difference between antiresonance and resonance frequencies. Hence, it is commonly considered that the enhancement of this property is achieved at the expense of the electromechanical coupling factor. Quartz thus exhibits a coupling coefficient of about 0.1 and Q_m up to 10^6 while donor doped PZT exhibits a coupling coefficient of 0.5–0.7 and a Q_m on the order of 10^2.[126]

5.2. Figures of merit for applications

For real-world applications, temperature stability of the functional properties is as important as all the other physical properties. In this regard, piezoelectric applications are firstly classified in terms of required temperature regime and summarized in Table 3. Next, each category is sub-divided into resonance and non-resonance applications. It is noted that a piezoelectric device is a translator between mechanical and electrical energy. Thus, the electromechanical coupling coefficient is essential for the assessment of piezoelectric materials, especially when driven in resonance modes. Simultaneously, mechanical displacements and electric charge are also proportional to the mechanical quality factor for a piezoelectric device driven in resonance state. Therefore, the product of mechanical quality factor (Q_m) and square of electromechanical coupling coefficient (k^2) is usually taken as the key evaluation factor for applications in resonance modes. In this table v_{max} stands for maximum vibration velocity without loss in piezoelectric properties due to heat generation. In high power transducer applications, the performance often depends on the v_{max} value.

The energy density in non-resonant sensors under the application of stress is proportional to both the piezoelectric charge (d_{ij}) and voltage (g_{ij}) coefficient, and the figure of merit is defined as being proportional to the product of these piezoelectric coefficients ($d \cdot g$). Piezoelectric strain of non-resonant actuators is proportional to the piezoelectric d coefficient. However, the strain for actuators driven by high electric field is not proportional to the intrinsic d_{ij} coefficient because it strongly depends on the ferroelectric domain motion; in this case the strain is a nonlinear function of the field and is usually described by $S_{\max}/E_{\max}$. In the case of frequency control devices, such as piezoelectric filters, oscillators, or micro-mass sensors, the electromechanical coupling coefficient or mechanical quality factor is used as the main indicator for the suitability of the materials. Although characteristics of piezoelectric materials should be optimized for the device shape or peripheral circuits in actual use, electromechanical coupling coefficient, piezoelectric constants, mechanical quality factor, and their products are fundamentally set as figures of merit for many piezoelectric applications.

Piezoelectric characteristics of lead-containing and lead free materials are compared in Table 4 on the basis of the classification in Table 3. The characteristics denoted in blue cells were proposed as a figure of merit or important properties for these applications in Table 4. Some observations can be drawn from Table 4. In the intermediate and low temperature regime ultrasonic applications of KNN materials may become competitive with PZT-type materials. In the temperature regime with $T < 100\,^{\circ}C$, (Ba,Ca),(Ti,Zr)O_3 may become competitive for sensors and actuators, while incipient piezoelectrics based on BNT are attractive as actuators only, due to the relatively weak small signal piezoelectric coefficient.

Note, that the discussion above relies on only a subset of materials and properties identified as representative. In addition, there are a number of secondary properties that are essential for reliable and cost-effective manufacture (in addition to the financial cost of base materials) as well as for device operation, which are not directly related to electro-mechanical inter-conversion coefficients. We will consider these in turn.

5.2.1. Temperature dependence

During operation the temperature of a piezoelectric pressure sensor may change. A piezoelectric material that belongs to one of ten polar symmetries (which includes all piezoelectric ceramics) develops pyroelectric charge due to temperature sensitivity of the polarization.[148] In the case of ferroelectric materials, non-piezoelectric charge may also originate from thermally induced motion of domain walls. The generated noise may substantially degrade the performance of the sensor. Furthermore, elastic, dielectric and piezoelectric coefficients of piezoelectric materials are functions of temperature and may change appreciably in the vicinity of phase transitions. On the other hand, the higher Curie temperature of KNN (especially Li-doped KNN) may be turned into an advantage when compared to PZT.[11] Here, however, the phase transitions between ferroelectric phases may be of more concern than the Curie temperature. This is true for KNN and BCZT based materials in which a so-called morphotropic phase boundary has a strong polymorphic character. This degree of the polymorphic character has recently been reduced and opened a new opportunity for tailoring KNN.[141,149] One of the notable advantages of quartz over PZT for sensor applications is exactly the remarkable thermal stability of its elastic constants.

5.2.2. Cycle dependence

Actuators may be subjected to 10^9 or more electrical cycles and need to remain in a narrow performance window. Cycling is usually done under unipolar driving fields, but can be required at different temperatures and under mechanical preload.[17] Thermal cycling during operation is also an important consideration that has received limited attention. Cyclic reliability is particularly important for certain applications, where replacing electroactive components is not possible or requires considerable effort, such as trailing edge flaps on large wind turbines or biomedical devices that are implanted within the body.

5.2.3. Dielectric permittivity

The piezoelectric voltage coefficient g is in part determined by the permittivity. If multiplied with the piezoelectric strain coefficient d, the resulting product ($d \cdot g$) is an important figure of merit for non-resonant applications like parking pilots and energy harvesting systems (see Table 3). The large dielectric permittivity is undesired for operation at high frequencies, because it may lead to a low electrical impedance $\propto 1/\omega C$, where C is capacitance) and poor electrical impedance matching of the transducer with other electrical devices.[150]

5.2.4. Blocking force

In many actuator applications, strain needs to be provided against a certain mechanical load. This is, for example, the case in multilayer actuators that are preloaded to avoid cracking at the edges of the partial electrodes or that operate against a spring load. In these situations, a critical figure of merit is the blocking force, defined as the maximum force that can be generated in the fully clamped state, i.e., displacement held at zero during electrical activation.[151] Here, the conversion efficiency, namely the amount of strain that can be effectively converted into force,[94] is highly important and is controlled by the elastic properties and the particular mechanism responsible for strain generation, i.e., domain wall motion, field-induced phase transition.

5.2.5. Density

In underwater and medical applications the acoustic impedance of the transducer ($\propto \sqrt{\rho c}$, where ρ is the density and c speed of sound) should be close to that of the object under investigation (acoustic impedance matching). This favors materials with a lower density and ceramic-polymer composites are materials of choice.[152] The resonant frequency (f_r) is related to the size of the sample (l), the density (ρ), and the mechanical compliance (s), so that ($f_r \propto 1/l\sqrt{\rho s}$). All other parameters being the same, a material with a lower density is advantageous for high frequency (>20 MHz) transducers because for a given frequency it is easier to fabricate thicker elements. In such cases lead-free materials have an advantage over lead-based materials. For example, KNN has a density of 4.5 g/cm^3 and BNT has a density of 5.3 g/cm^3, compared to PZT with a density of 8.0 g/cm^3 (see Section 6).

5.2.6. Reliability and processing window

Evaporation of alkali elements and/or of bismuth during processing, e.g., sintering, may pose a more significant problem than the evaporation of lead. Therefore, the processing windows, especially in KNN-derived materials[11,148] have been described to be very narrow and may entail reliability issues in cases where select properties are reported on few samples. Scaling production to the required batch sizes for industrial applications but may be difficult to achieve. If large-scale production of lead-free piezoceramics is considered, availability of raw powders with controlled purity and morphology needs to be ascertained. Especially, carbonates with high sensitivity to humidity warrant special precautions. Furthermore, the long-term interplay between piezoelectric, electrode, and passivation requires further study.

5.2.7. Cost

Tantalum and niobium, which are considerably more expensive than the raw materials in PZT, are often, or in the case of niobium always, used in typical KNN compositions. This will not appeal to potential customers or manufacturers. An advantage for KNN may lie in the opportunity to use low-cost nickel as an electrode material, which is not possible for PZT.[153] In comparison, only copper electrodes are available for PZT multilayer actuators.

We will reconsider some of the primary and secondary issues stated above in terms of action items in Section 7.

6. Case Studies on examples where lead-free piezoceramics have specific merit and have entered or are about to enter the marketplace

It is useful to start this section by mentioning that the first practically used piezoelectric materials were lead-free: quartz (silicon dioxide – SiO_2), Rochelle salt (sodium potassium tartrate tetrahydrate – $KNaC_4H_4O_6{\cdot}4H_2O$), KDP (potassium dihydrogen phosphate – KH_2PO_4), and BT.[154] Lead-based piezoelectrics, for the most part PZT, have become widely used since the 1960s. However, even during this subsequent half a century of dominance of PZT, lead-free piezoelectric materials were employed in many applications where properties of PZT were not adequate. Examples of these lead-free materials (grouped by usage) include quartz or $GaPO_4$ (which is isomorphic to SiO_2), bismuth titanate based layer structures (Aurivillius phases), the langasite family, $LiNbO_3$, AlN, and polyvinylidene fluoride (PVDF). Quartz is commonly used as an oscillator in watches and in filters because the elastic properties (which define resonance frequency) of PZT are strong functions of temperature. Furthermore, quartz and gallium phosphate are also employed in pressure sensors. In this case, PZT easily depolarizes at high pressures, has high conductivity at low frequencies and elevated temperatures, and exhibits strong charge-force hysteresis.[155–159] Bismuth titanate-based layered structures are used for high temperature applications since PZT exhibits a low T_C (350 °C at morphotropic phase boundary), depolarizes easily at elevated temperatures, and exhibits charge drifts associated with pyroelectric effect and domain wall motion.[7,155,160,161] Next, the langasite family, $LiNbO_3$ and AlN are found in applications requiring high temperature and high frequencies, where PZT is at a disadvantage due to a low T_C, easy depolarization, and a low mechanical quality factor.[127] Polyvinylidene fluoride, $(–(C_2H_2F_2)_n–$ or PVDF) is employed in sensor applications where its enhanced impedance matching with gases, liquids and biological systems, mechanical flexibility, and possibility to produce large thin layers over large areas give a large benefit as compared to PZT.[162]

In this section, however, we are more interested in cases where lead-free materials are meant to *replace* PZT, that is, in the large number of situations where PZT exhibits excellent properties and needs to be replaced not for technical but for environmental reasons as controlled through future legislation. It turns out that developing materials that are competitive with PZT presents considerable scientific and engineering challenges.

Currently, there are many reports in the literature on prototypes of lead-free piezoelectric devices and materials being developed for specific applications. Here we discuss two recent examples: an ultrasonic imaging probe developed by a transducer company and a ceramic material for a broad range of applications that is now commercially available.

A high frequency transducer – Merits of potassium niobate, $KNbO_3$ (KN), for high frequency transducers have been already discussed in the literature.[163,164] Briefly, among the most attractive features of KN for high frequency transducer applications are: the high thickness electro-mechanical coupling coefficient ($k_t \approx 69\%$) along directions close to pseudo-cubic $[0\,0\,1]_C$ off-polar axis, high ferroelectric-ferroelectric transition temperature (≈220 °C), good temperature stability of k_t, and low density (4.6 g/cm^3 in KN versus ≈8.0 g/cm^3 in PZT).[165] As the resonance frequency is inversely proportional to the density and the thickness of the resonator, a low density means that a high frequency transducer may be fabricated with a significantly larger thickness than a PZT transducer operating at the same frequency, or may operate at a higher frequency for the same thickness. This is a significant advantage for transducers operating above 20 MHz where thickness is well below 100 μm. Recently, a French consortium lead by Vermon (Tours, France) reported a high-frequency linear-array transducer (30 MHz) for *in vivo* skin imaging, Fig. 9.[166]

The array is fabricated from a 1–3 composite consisting of a domain engineered $[0\,0\,1]_C$-oriented KN single crystal and a polymer. The performance of the probe is reported to be comparable to that of a device fabricated from PZT ceramic and operating under the same conditions at 20 MHz, but with a better image resolution and penetration depth than achieved with the PZT probe.

Availability of lead-free materials – An important aspect in the wider application of lead-free piezoelectric materials is their commercial availability. Development of a lead-free composition with excellent properties in a university laboratory or even

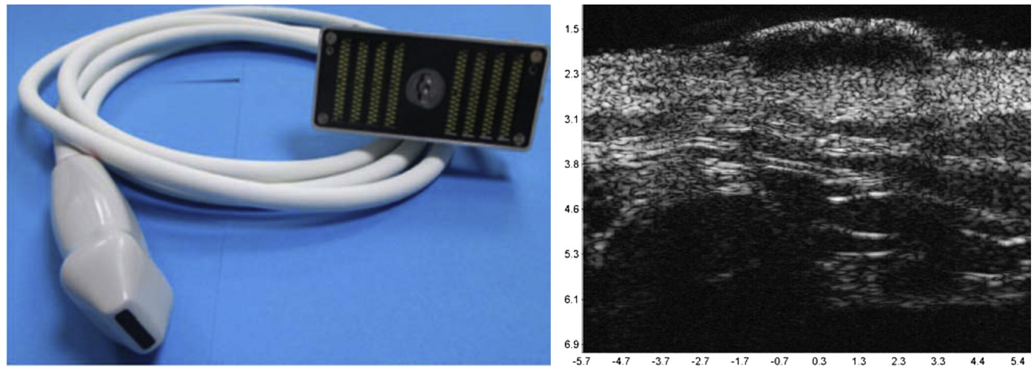

Fig. 9. Picture of a high-frequency linear-array transducer, which was used to image in vivo skin tissue. (Permission obtained from Vermon).

in an industrial research center does not bring much benefit to a wider community if that material cannot be produced reliably, in industrial quantities, and, most importantly, if it is not readily available to other users. This situation is now changing as shown by several material producers that offer various lead-free piezoelectric materials and devices, including lead-free based single crystals (KN and others by FEE[167]), lead-free tranducers by PI[80] and ceramics (e.g., BNT-BT based by Honda Electronics[168]). The latter are advertised with the brand name "Lead Off" and are proposed for high power applications due to their excellent high mechanical quality factor up to high vibration velocity.

7. Steps to take for applied and basic research

We recall that PZT cannot be replaced by just one material.[12] Therefore, different applications are expected to see different material solutions that come with different challenges. The predicted line for technology transfer into applications in Fig. 6 then would be more accurately represented as a family of curves reaching the plateau of productivity in different years. As we are specifically interested in the first year of application of a specific product, it is expedient to transform Fig. 6 into Fig. 10 with the *x*-axis in years to realization.

Table 4 may now be utilized to extract different product realization timelines in an exemplary manner. We propose to use the following classification:

(A) Lead-free piezoceramics with better properties than lead-containing piezoceramics.
(B) Lead-containing piezoceramics can be replaced in ten years.
(C) Lead-containing piezoceramics cannot be replaced in ten years.
(D) New applications call for direct development of lead-free piezoceramics.

In the following, archetypical examples will be provided for each of the categories:

A: High power applications for ultrasonic motors feature a strongly decreasing mechanical quality factor with increasing vibration velocity if manufactured from PZT. In contrast, both textured $(Sr,Ca)_2NaNb_5O_{15}$ as well as BNT-BT based materials maintain a high mechanical quality factor up to high vibration velocity and thereby can generate high output power density.[169–171] These are currently material solutions but not converted into device solutions as of yet. The aforementioned stringent reliability issues may necessitate a further development step of up to five years from now.

B: Ultrasonic cleaners are according to Table 3 in the category of consumer products with moderate temperature requirement. The figure of merit (k^2Q_m) for lead-free piezoceramics is comparable to that for hard PZT. It is, therefore, not surprising that BNT-based piezoceramics have already been marketed for this application by Honda Electronics with relevant literature published several years ago.[142]

C: Actuators for fuel injection in automobiles require very high reliability, low cost, and need to provide high temperature stability and cycling stability with good normalized strain and

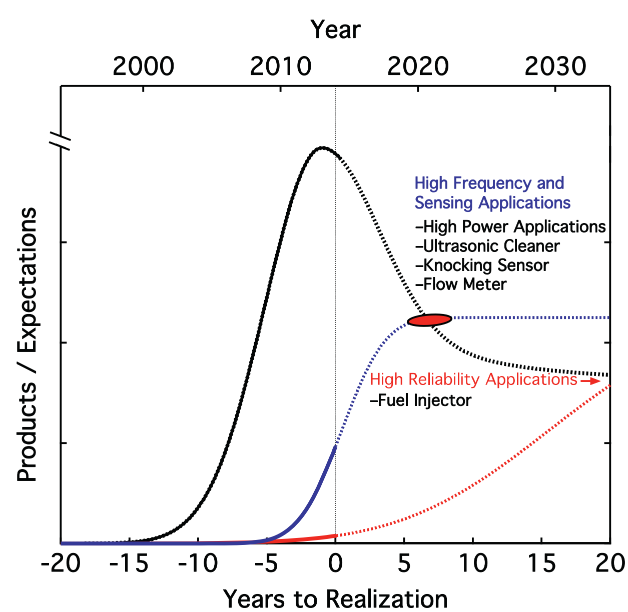

Fig. 10. Evolution of research and application transfer as a function of years to realization with some proposed applications earmarked and a time frame to realization predicted. (For interpretation of the references to color in the text, the reader is referred to the web version of the article.)

blocking force at high frequency.[172] This is, therefore, a component in a very competitive market, which sees very stringent multifold requirements and faces strict reliability requirements. The overall length of the piezo-injector is restricted as the free space under the engine hood is a safety requirement for crashes with pedestrians. The stringent reliability requirements are demonstrated by the fact that Continental Automotive GmbH had reached a total production of 50 million units in 2012. Hence, it is not suggested to replace this PZT component in the next ten years, as it also helps to provide energy-efficient engines with low emissions.

D: Some kinds of energy harvesting devices demanding a figure of merit of $d \cdot g$ are competitive when manufactured in lead-free piezoceramics. In use, they are prone to be spread around the environment with little chance of being collected and recycled afterwards. These devices should go into production only in lead-free varieties. New applications with wide distribution of non-recyclable components that should go lead-free right from the start. A similar issue concerns flow and heat meters.

These products then can be positioned in Fig. 10. Materials in category A, B and D offer, therefore, feasible solutions if the necessary reliability requirements are met. These form a small percentage of all lead-free piezoceramic materials but offer a feasible start into the commercialization of these materials. They are on an advanced technology track and could offer product lines in about five to eight years from now (Points A, B, and D, elongated red dot). The overall development of these high frequency and sensing applications is schematically represented by the blue dotted line in Fig. 10. In contrast, several other applications, as exemplified by the piezoelectric fuel injector, do not yet offer a viable materials solution and do not provide a feasible date for transfer into application (red dotted line). It is expected that the development and, therefore, the number of years until commercialization will be longer than for smaller, less complex components, e.g., parking pilots that do not operate under high temperatures. This will result in a more gradual, adoption and product development slope, shown as the red dotted line in Fig. 10.

Next to the materials solution, there is also the issue of market pull in very dynamic and competitive market segments. Our inquiries resulted in the following predictions: In 2017, multilayer ceramic actuators for haptic applications may be used in mobile phones and in 2018, thick film piezoelectric speakers using lead-free ceramics for mobile phones. These, are, however, select opinions and not placed in our chart. Nevertheless they suffice to demonstrate the uncertainties related not only to materials but also to markets, scale, and competition.

Let us now discuss what remains to be done to move our worldwide scientific achievements into fruitful environmentally safe products. For the devices that can be marketed on a rather short-term basis, applied research recommendations are in due order. At the same time a number of fundamental research issues need to be addressed. We will consider both topics in turn. As we are concerned with a timely transfer of scientific achievements into application, we begin here with strongly warranted applied research topics and then add few issues in the field of basic research.

7.1. Applied research

7.1.1. Temperature dependence

Structural issues determine the temperature dependence of lead-free piezoceramics. In KNN, optimum properties are obtained around the tetragonal to orthorhombic transition temperature,[1,173–175] where reduced properties are observed with an increasing temperature difference to the T-O phase transition temperature. For large piezoelectric coefficients, however, texturing can lead to good temperature insensitivity[1] as does decoupling the small signal and the large signal piezoelectric coefficients accomplished through tailoring the free energy barrier between two ferroelectric phases.[88] Similarly, for small-signal properties, like the coupling factor and the piezoelectric coefficient, good thermal stability has also been achieved using texturing, which naturally raises the question of financial viability.[176] As mentioned before, the development of KNN materials with MPB may provide a significant breakthrough. For BNT-based piezoceramics, this level of temperature insensitivity has not been reached and may, fundamentally, not be accessible due to the strong influence of the depolarization temperature on the remanent polarization and the large-signal piezoelectric coefficient.[147] BCZT, with its low Curie temperature, has a very limited temperature stability for piezoelectric properties.[177]

7.1.2. Frequency dependence

Frequency dependence of actuating strain in soft PZT is well described and provides a minor reduction of performance with increasing frequency.[178] Limited studies in KNN-based materials suggest that there is a strong compositional dependence with opportunities to obtain similar frequency dependence as in soft PZT.[179] In contrast, BNT-based materials can provide a very high strain through field-assisted phase change, but this mechanism suffers from a significant frequency dependence.[180]

7.1.3. Cycle dependence

The field has witnessed significant advancement in the understanding of electric fatigue for lead-free piezoceramics.[17] Salient application-oriented investigations are, however, still rare. In particular, influences of temperature[181] and uniaxial stress[182] are only available for PZT. Studies on the electric fatigue behavior of lead-free multilayer actuators are only now being performed and preferably would include issues of self-heating during electric loading.[183]

7.1.4. Blocking force

There are very limited studies available that directly characterize the blocking force of bulk ferroelectrics,[151,184] particularly in lead-free compositions.[94,185] Most previous studies focused on the displacement and force generation capabilities of a specific device that contain piezoelectric and non-piezoelectric components, such as bending actuators,[186,187] or functionally graded actuators with varying material properties.[188] These applications often expose the electroactive material to a complex stress state that typically varies spatially.[189] Due to this, the obtained free displacement and blocking force values are not material parameters, but rather geometry-dependent values specific to a particular application. Recent work on bulk ferroelectrics has indicated that lead-free compositions are able to produce comparable, or even greater, blocking force values than commercial PZT, in some cases with 50% less free strain. The origin of the observations is not currently understood, although it is expected that the differences in displacement generation, i.e., piezoelectricity, ferroelectric domain wall motion, field-induced phase transitions, play an important role.

7.1.5. Hardening and softening mechanisms:

Hardening through acceptor doping provides reduced dielectric losses and increased mechanical quality factor in PZT.[126] Although the effect has been known for a long time, there are still two competing models. These describe the orientation of an acceptor-oxygen vacancy complex or dimer,[190] in one case. In the other case, the charge drift of oxygen vacancies is considered.[191] Although applications for hard lead-free piezoceramics may require less stringent property requirements than for soft lead-free piezoceramics and appear to show great promise, this field has not yet attracted as many scientists as expected. However, doping with manganese in BNT-BT based materials[192] and in BNT-BKT-based materials[193] have yielded materials with increased mechanical quality factor Q_m. Enhanced mechanical quality factors have likewise been achieved in KNN-derived materials. This field is expected to grow strongly in the next years.[194] Similarly, softening mechanisms as described in soft PZT have not yet been detailed in lead-free piezoceramics.

7.1.6. Mechanical properties

The fracture toughness of PZT is very close to the fracture toughness of window glass and thus very low.[12] An inherent toughening mechanism is provided through ferroelastic toughening,[195] while the most attractive composite toughening mechanism is transformation toughening.[107] The low fracture toughness is a very serious hindrance to device integration as multilayer actuators entail areas with severe strain incompatibility.[196] In particular, the interface to the electrode is prone to cracking[197] and will suffer from thermal expansion mismatch and electric field singularities.[198] Therefore, it is surprising that only very few studies are reported on lead-free piezoceramics. These include determinations of fracture toughness[199] and subcritical crack growth[200] in KNN-based materials, and fracture toughness in BNT.[201]

7.1.7. Reproducibility

Poor reproducibility of the final functional properties remains among the major problems of lead-free compositions, preventing their wide use in practical applications.[12,18,202] The origins of the observed batch-to-batch variations can be in general ascribed to the following factors: hygroscopicity of the starting materials and/or some intermediate reaction products,[203] different diffusion rates resulting in local compositional inhomogeneities,[204] high-temperature stability and volatilization,[205,206] specific sintering mechanisms,[207] and grain/domain-size dependence of the final properties.[208,209] Although these issues are repeatedly reported throughout the literature, only few systematic studies of processing conditions and mechanisms can be found. In order to assure reproducibility further knowledge of relevant chemical processes is needed, such as reliable phase diagrams, reaction kinetics, diffusion studies, detailed microstructural analyses, and others. At the same time, the adaptability of the synthesis processes to large-scale industrial production should be considered. This includes, among others, the use of inexpensive starting compounds of sufficient purity, aqueous processing routes, industrial-scale equipment, and optimized calcination and sintering conditions.

7.1.8. Cost

Although RoHS considers the scientific and technological and socio-economic aspects, the price is not officially a criterion. However, replacing PZT is a tremendous endeavor and requires the careful consideration of companies' concerns, which naturally includes the overall production costs as well as competing technologies such as, e.g., magnetic fuel injection systems. For BNT-based materials, a phase evolution with Ag/Pd electrodes has been studied[210] and successful multilayers with these electrodes have been obtained via a water-based processing route.[211] Similarly, acceptable actuator performance has been obtained for KNN with Ag/Pd electrodes.[212] A breakthrough, which is estimated to be very important for the future, was obtained by manufacturing KNN with nickel inner electrodes.[153] The nickel inner electrodes in KNN have been shown by TEM to be structurally sharp without secondary phases.[213] The nickel is expected to provide low electro-migration and strong interfaces. As cofiring has to be performed under reducing atmosphere, electrical resistivity and dc degradation become an issue. Note, that the development of low cost solutions in this area has begun to attract the attention of large corporations (Murata, Taiyo Yuden) dominating the market of multilayer capacitors.[153,213]

7.1.9. Electrical resistivity

In the development of base-metal capacitors, the conductivity as a function of oxygen partial pressure for doped barium titanate resulted in seminal studies by the group of D.M. Smyth in the early eighties.[214] This approach was adopted by numerous research groups, resulting in detailed electrical impedance studies of many materials.[215] Similarly, it is expected that the development of actuator materials with base-metal electrodes will require fundamental studies using impedance spectroscopy as a function of oxygen partial pressure. These investigations have only now begun for different gas atmospheres, for example in the case of BNT-BT materials.[216]

As befitting to the focus of this review, we propose some items for basic research. These are given less room here, but it is nevertheless clear, that focused fundamental research into lead-free piezoceramics will continue for many years and will be fueled by the next successful transfers of non-toxic piezoceramics into applications, giving further emphasis to this research work. Before we conclude, we provide some suggestions for basic research topics.

7.2. Basic research

7.2.1. Atomistic structure

It appears that in particular the local structure in lead-free piezoceramics has remained somewhat elusive. This concerns the limited understanding to tailor lead-free piezoceramics using acceptor- and donor-doping and the relaxor character of BNT-based materials in particular. The interpretation and correlation to specific acceptor defect complexes in lead-containing ferroelectrics has reached now a mature level[217] if electron paramagnetic resonance (EPR) is contemplated. It has also benefitted strongly by the advances in density functional theory.[218] In contrast, however, the analysis of the EPR signal in acceptor-doped lead-free piezoceramics has just begun.[219] A very similar situation is observed if we consider nuclear magnetic resonance (NMR), which has been recently used to help elucidate the role of the local structure of lead-containing relaxors.[220] In contrast, application to lead-free piezoceramics has only rendered the very first results.[221] Funded coordinated programs with a combination of expertise in EPR, NMR, ab-initio computation, and possibly Raman spectroscopy[222] would, therefore, be highly beneficial.

7.2.2. ab-initio computations[19]

Atomistic computer simulations based on ab-initio methods such as density functional theory (DFT)[223,224] have been employed for a long time in the study of ferroelectric materials, especially since the introduction of the modern theory of polarization,[225–227] whose implementation into DFT programs allows calculation of spontaneous polarization and piezoelectric properties of any kind of material without input from experiment. Most studies focus on single-phase lead-free materials, such as KNN,[228–230] BNT,[231–233] or other Bi-based perovskites,[234] but also attempts to predict the morphotropic phase boundaries in lead-free solid solutions exist.[231,235] Another approach enabling prediction of so-far unknown materials allows the technique of high-throughput screening, which was applied to different perovskites[19,236] and other structures from crystallographic data bases[237,238] testing different elemental compositions in order to find new candidates with desirable physical properties and thermodynamic stability. The drawback of DFT calculation is their restriction to small system sizes up to 1000 atoms. It can be overcome by using DFT methods to develop effective Hamiltonians, which can be used in Monte Carlo simulations.[239] This allows the prediction of phase stabilities as a function of different variables such as composition, pressure, anisotropic strain, and temperature on larger length scales.[240,241]

7.2.3. Field dependent structure

Highest piezoelectric properties are obtained in the vicinity of phase transitions. These depend not only on temperature and composition, but also on electrical and mechanical fields, particularly in the case of relaxor ferroelectrics.[242] This challenging field, particularly in the case of lead-free piezoelectrics, has initiated a wealth of innovative experimental techniques and may have surpassed the work on lead-containing piezoceramics with respect to novel in-depth understanding. BNT-based piezoceramics benefitted particularly from in-situ structural characterization, using synchrotron techniques[243] or a combination of synchrotron and neutron diffraction.[244] This material class was also deemed particularly intriguing to apply the very challenging in-situ transmission electron microscopy to render advanced understanding during increasing and decreasing electric fields.[245,246] More recently, very high strain BCZT materials were investigated using in-situ synchrotron diffraction.[247]

8. Conclusions

To summarize our findings in a few succinct bullet points:

- While legislation is not predictable, it is apparent that many other fields have successfully developed routes to lead-free solutions already. The predominant usage of lead is now restricted to lead-containing batteries, which can be easily recycled.
- Contrasting lead-free piezoceramics with lead-containing piezoceramics using salient figures of merit allows identification of different material classes
  - A: current applications, which are ready to go lead-free in the near future if critical issues of reliability are solved. This concerns, for example, some kinds of high power applications.
  - B: current applications, which can go lead-free in the foreseeable future (<10 years) if critical issues of reliability are solved. These are, for example, some kinds of ultrasonic transducers.
  - C: with applications, where a switch to lead-free piezoceramics may lie in the distant future (>10 years), for example piezo-injectors.
  - D: with new applications with wide distribution of non-recyclable components that should go lead-free right from the start. This could be materials for some kinds of flow meters and energy harvesting. The important caveat is that the needed piezoelectric materials are only partly commercially available.
- Application-oriented topics for the near future have be identified:

  A: temperature-, field-, and cycle dependence.
  B: blocking force and mechanical properties.
  C: hardening, softening, and electrical resistivity.
  D: most importantly: cost and reliability.
- Basics science issues are:

  A: Atomistic structure in experiment and ab-initio computation
  B: field-dependent investigations

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