Requirements for the transfer of lead-free piezoceramics into application

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ABSTRACT

The recent review for the Restriction of Hazardous Substances Directive (RoHS) by the expert committee, appointed by the European Union, stated that the replacement of PZT "… may be scientifically and technologically practical to a certain degree …", although replacement "… is scientifically and technically still impractical in the majority of applications." Thus, two decades of sustained research and development may be approaching fruition, at first limited to a minority of applications. Therefore, it is of paramount importance to assess the viability of lead-free piezoceramics over a broad range of application-relevant properties. These are identified and discussed in turn: 1. Cost, 2. Reproducibility, 3. Mechanical and Thermal Properties, 4. Electrical Conductivity, and 5. Lifetime. It is suggested that the worldwide efforts into the development of lead-free piezoceramics now require a broader perspective to bring the work to the next stage of development by supporting implementation into real devices. Guidelines about pertinent research requirements into a wide range of secondary properties, measurement techniques, and salient literature are provided.

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1. Introduction

With the functionality of interconverting mechanical and electrical energy, piezoelectric materials have the versatility to address a wide range of applications, including actuators, sensors, and transducer devices. The majority of these employ lead-containing materials, particularly lead zirconate titanate (PZT). Since a large piezoelectric charge coefficient comparable to that of PZT (416 pC/N) was achieved in textured potassium sodium niobate ceramics in 2004 [1], the past two decades have witnessed enthusiastic research into lead-free piezoceramics [2]. Several systems have been considered as potential alternatives for lead-containing counterparts in certain fields, including $(K,Na)NbO_3$ (KNN) [3,4], $Na_{1/2}Bi_{1/2}TiO_3$ (NBT) [4], $BiFeO_3$ [5—7], and $(Ba,Ca)(Ti,Zr)O_3$ (BCTZ) [8,9]. For example, with acceptable piezoelectricity and high Curie temperature, KNN is regarded as a possible alternative for PZT in overall properties. NBT-based piezoceramics show strong promise for high-power applications [10]. BCTZ exhibits similar or even higher piezoelectric performance than PZT, though merely around the room-temperature regime. At temperatures above 250—300 °C, where PZT depolarizes, $BiFeO_3$—based ceramics still maintain considerable piezoelectricity, whilst presenting challenges in terms of processing of single phase material [6]. However, there are indications that in order to alleviate the conduction issues associated with $BiFeO_3$ based materials, some phase separation is actually desirable, as demonstrated in $BiFeO_3$-$BaTiO_3$ solid solutions [7]. In addition to its solid solution with $BaTiO_3$, other potential alloying compounds include the "high T_C" complex perovskites, $Bi(Mg_{1/2}Ti_{1/2})O_3$ and $Bi(Zn_{1/2}Ti_{1/2})O_3$ [5]. However, far fewer steps have been taken towards commercialization of lead-free $BiFeO_3$-based ceramics compared to KNN and NBT and, therefore, less relevant data has been published. Note also that most lead-free piezoceramics have a lower theoretical density than PZT (KNN: 4.51 g/cm^3, $BaTiO_3$: 5.7—6 g/cm^3; 0.94NBT-0.06BT: 5.92 g/cm^3; PZT: 7.5—8.0 g/cm^3; $BiFeO_3$: 8.3—8.5 g/cm^3). This helps, for example, when equipping drones for transport is concerned or when ultrasound into low-density media is considered. This is an issue which is not discussed in the following further, as it does not demand any specific new research.

Regarding the transfer of lead-free piezoelectric ceramics into applications, a range of application-specific properties is required, which must be supported by viable mass-production processing techniques. For the time being, there is still lack of incentive for manufacturers to push lead-free products forward, as lead-containing materials in electric and electronic components retain their exemption status. Nevertheless, there are encouraging achievements from industry, especially from Japan and Europe. NBT-based piezoceramics for ultrasonic transducers and sonar/hydrophone applications have been offered for several years by PI Ceramic GmbH. Other NBT-based compositions have proved very promising for high-power applications by several companies [10—12], with prototype commercial products released [11]. A NBT-based multilayer device with large strain and high temperature

stability was made by a water-based preparation process [13]. Moreover, it is now possible to reproducibly prepare granulated modified-KNN powders in batches of 100 kg using a spray-dryer [14—16].

Progress in both scientific and industrial scenarios is stimulated by the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) directive. A recent review for RoHS by the expert committee in 2016, which regularly assesses the exemptions from the RoHS, recommended a shorter scheduled review period within 3 years, instead of 5 years. Moreover, the review stated that "the replacement of PZT may be scientifically and technologically practical to a certain degree". However, as the exemption was extended for a further five years, until 2021[1], there may be sufficient time to progress some lead-free products to a sufficient readiness level within this period.

In selecting a piezoelectric material for a specified application, an initial assessment is typically made on the basis of achieving a minimum level of performance for a small number of indicators, such as the piezoelectric charge or voltage coefficient, the coupling coefficient, and the upper operating temperature. It is convenient to refer to these properties as the primary criteria. The downselection from a short-list of materials that meet the primary criteria is then made by considering a range of other properties and characteristics, which are both technical and commercial. It is tempting to label these as secondary criteria, which suggests that they are less important than the primary ones. This is certainly not the case; more often than not, failure to meet one of the secondary criteria will eliminate a candidate from the shortlist. These characteristics [17—19] are just as important, and sometimes more critical, to the success of the product as are the primary properties. These are identified in this work and discussed in turn: 1. Cost, 2. Reproducibility, 3. Mechanical and Thermal Properties, 4. Electrical Conductivity, and 5. Lifetime. In order to gather input from the industry, a small survey on these topics was carried out focusing on piezoceramics producers active in the field of lead-free materials. Their answers are incorporated in individual chapters.

Once a selection has been made, it is often the case that the final design requires a finite element model to be constructed to allow optimization of the design. In order to do this, the full matrix of the electromechanical properties (d_{ijk}, ε_{ij} and s_{ijkl}, or equivalent) will be required, entailing a further, more detailed level of characterization to be undertaken.

2. Discussion

2.1. Cost

2.1.1. Chemical elements

In selecting and approving materials for device manufacture,

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[1] A draft version of the new directive is available from the following link: http://ec.europa.eu/info/law/better-regulation/initiatives/ares-2017-4565004_en (September 2017).

assuming that a range of materials meet the technical specification, cost, availability, and, in some circumstances, sustainability then become critical considerations.

2.1.1.1. Availability. Unsurprisingly, of the above characteristics, availability is the highest priority. At the simplest level, if a material is not commercially available, there is no merit in selecting it. However, even when there is commercial availability, many manufacturing organizations apply more selective criteria in approving a material. For example, to ensure long-term viability, some purchasers will not specify a material that has a limited manufacturing history or is only available from small and medium sized enterprises (SMEs). Most manufacturers also require a second source, *i.e.*, an alternative supplier, in case the preferred source becomes unavailable. From the purchaser's viewpoint a second source also maintains downward price pressure on the preferred source.

After technical capability, availability is currently the most significant barrier to the adoption of lead-free piezoelectric materials in new products. There are a vanishingly small number of commercial suppliers of lead-free materials. Correspondingly, there is scant production history and no second sources. Hence, even if the technical specification demands it, buyers are reluctant to rely on the current limited commercial supply. Conversely, this situation is generally interpreted by potential suppliers as a lack of demand for lead-free materials. Hence, the inertia on both sides of the supplier-buyer relationship couples to inhibit the rapid adoption of lead-free materials. For this to change, both materials and device manufacturers need to believe that the adoption of lead-free piezoelectrics is mission critical, *i.e.*, that environmental concerns and legislation with respect to PZT have sufficient weight to restrict their business in the short to medium term, or that early adoption will provide a significant commercial advantage. In both cases, purchasers are more likely to circumvent normal practice by partnering with suppliers to ensure that their demand and availability criteria are eventually met.

2.1.1.2. Cost of raw materials. In any commercial endeavor, cost is a major factor in materials' acceptance. With a notable exception, which will be addressed below, the processing of lead-free piezoelectric materials differs little from that of PZT. For the foreseeable future, where supply and demand are both somewhat limited, there is bound to be a price premium for lead-free materials compared to PZT. However, in the longer term, as volumes increase, prices for lead-free ceramics will equilibrate and become more dependent upon the cost of raw materials.

Fig. 1 displays the cost of relevant reagent grade sources (oxides or carbonates) relative to that of TiO_2 [20]. In general, the cost of industrial grades follows the same trend. On this scale, all the major component oxides of PZT fall within a relative cost of 10 (PbO: 8.9, ZrO_2: 7.4), whilst for lead-free piezoelectrics, most components fall within a relative cost of 12 (Bi_2O_3: 11), the exception being Nb_2O_5, which has a relative cost of 29, making it the most expensive of the commonly used oxides. Whilst Nb_2O_5 is used as a dopant in some soft PZT compositions, this is normally in quantities of around 1 %, with minimal impact on cost. Some "ultra-soft" lead-based compositions contain higher levels of Nb, of the order of 10 %, in the form of $Pb(Ni_{1/3}Nb_{2/3})O_3$ or $Pb(Mg_{1/3}Nb_{2/3})O_3$ solid solution components, which has a marked influence on the price of these grades. In KNN-based lead-free materials, Nb is a major component and is, therefore, a significant factor in the relatively high cost of manufacture of this material. Ta addition is considered to provide enhanced piezoelectric properties, but is even more expensive than Nb and is, therefore, often avoided in the industrial developments [21]. Furthermore, as alluded to above, there are additional reasons for the relatively high manufacturing costs of KNN. The hygroscopic nature of K_2CO_3, the main source of potassium for ceramic manufacture, necessitates that at least the initial milling step in the conventional ceramic process is water-free, meaning that ball milling must be carried out either with the aid of organic liquids, *e.g.*, iso-propanol, or via an alternative drying process. In addition to the cost of alcohol, both processes require additional capital cost and in the case of ball milling, the requirement to handle, dispose of, or recycle solvents according to local health and safety regulations adds markedly to production costs.

2.1.1.3. Sustainability. An increasing number of manufacturing companies are adopting sustainability policies to ensure that their products provide environmental, social, and economic benefits, whilst protecting public health and preserving ecosystems and natural resources for future generations. In addition to their clear ethical message, such policies also make good business sense, simply because they ensure that manufacturing businesses themselves can rely on the long-term availability of resources. In that context, the focus here is on the availability of key raw materials.

Fig. 2 (a) and (b) provide the abundance and annual production of the common constituent cation elements of piezoelectric ceramics. These are grouped as (a) major components and (b) minor components and dopants. Fig. 2 (c) and (d) feature the log of the ratio of these two measures as a sustainability index; the larger the index, the less at threat is the resource. These data reveal some surprising details in comparison to the cost data in Fig. 1. For example, Sc is relatively abundant, but due to the limited annual production, which is reflected in its high cost, its sustainability is the highest amongst the two groups. The annual production of many of the relevant elements is greater than 1 million tonnes. In contrast, the annual production of piezoelectric ceramics is less than 5000 tonnes [22]. Hence, perhaps a more relevant measure of sustainability in the piezoelectric context is to express the quantities used in piezoelectric production as a fraction of the total annual production per element, as shown in Fig. 3.

In order to understand the impact that the production of lead-free piezoelectric materials will have, Fig. 3 assumes that the future production levels of lead-free piezoelectric materials will be similar to the current annual production of PZT (~5000 tonnes). In only a few cases does the piezoelectric requirement exceed 1 % of annual production (niobium, bismuth, scandium, tantalum, and indium), at which level, the piezoelectric usage may start to influence the pricing and availability of the raw materials. Perhaps of most concern is bismuth. It already has one of the lowest
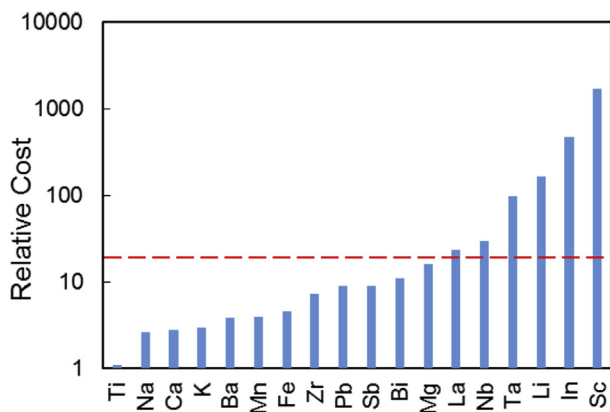

Fig. 1. Cost of reagent grade oxides or carbonates used in piezoelectric ceramic manufacture, relative to that of TiO_2 [20]. An arbitrary boundary has been provided at a relative cost of 20x that of TiO_2 (dashed line).
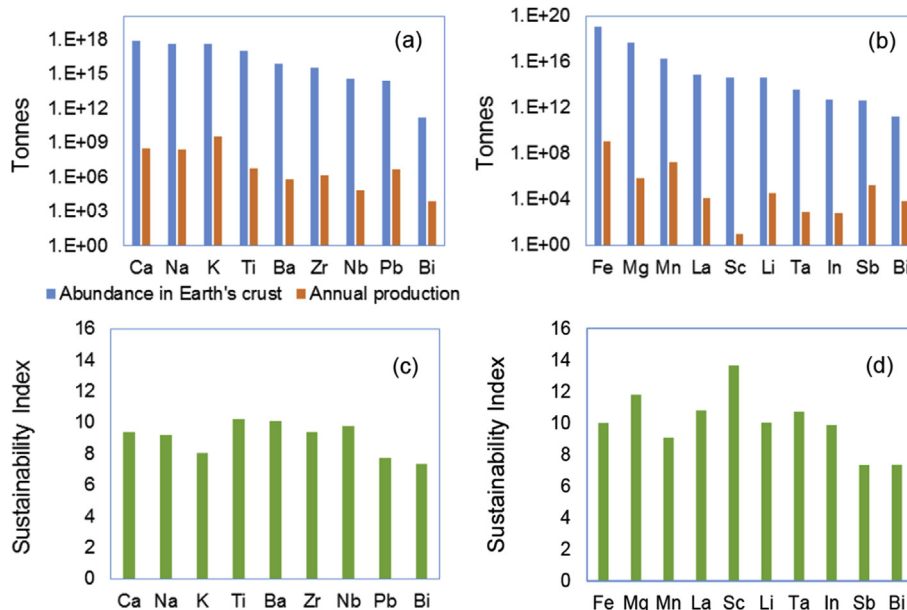
Fig. 2. Abundance and annual production of (a) major component elements and (b) minor component elements; sustainability index for (c) major component elements and (d) minor component elements in piezoelectric ceramics.
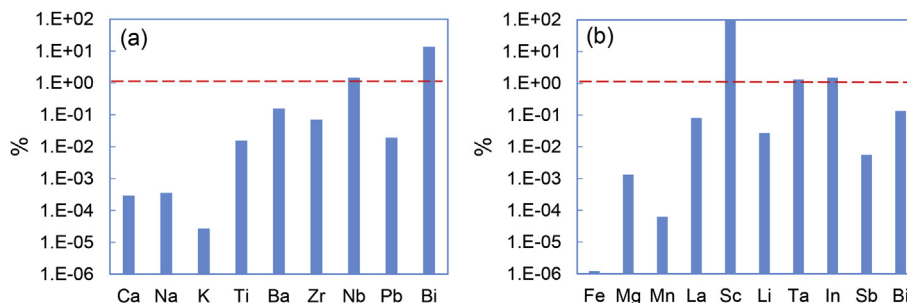

Fig. 3. Estimated annual usage of selected elements in piezoelectric ceramics as a percentage of the total annual production of each element for (a) major components (1000 tonnes estimated annual piezoelectric usage) and (b) minor components and dopants (10 tonnes estimated annual piezoelectric usage). The projected future annual production for lead-free piezoelectrics is assumed to be similar to that of current PZT production.

sustainability indices, but if Bi-based piezoelectrics were to be produced in quantities equivalent to today's production of PZT, they would account for more than 10 % of annual bismuth production. Ironically, perhaps, most bismuth is produced as a by-product of lead smelting [23]. By comparison, current PZT production accounts for less than 0.1 % of global lead production.

Niobium may also be a cause for concern. If KNN production were to reach a similar scale to that of PZT, it would account for just over 1 % of global niobium production. Perhaps more seriously, it has recently been argued that the environmental impact of large scale KNN production would be considerably worse than that of PZT. Using established Life Cycle Assessment (LCA) techniques, Ibn-Mohammed *et al.* suggest that the large scale production of KNN would create far greater negative environmental impact than PZT [24]. The increased impact of KNN occurs in the early stages of its life cycle, during mining and extraction of niobium, hence the environmental damage would occur before its life in a piezoelectric device, rather than at end of life, as is the case for PZT. The authors advocate that the use of the terms such as "environmentally friendly" for the description of alternative piezoelectrics should be avoided until similar LCA studies have demonstrated the veracity of the label.

One further economic factor may influence the viability of alternative piezoelectric materials. Similar in concept to the lack of second sources for manufactured materials, the limited geographical distribution of the occurrence and production of some raw materials can pose risks for security of supply. The Herfindahl-Hirschman index (HHI) attempts to quantify in a single number the extent to which market share is distributed amongst producers of goods [25,26], or in this case, how mineral reserves or production are distributed geographically. Simply, the HHI of a material is equal to $\sum_i^N s_n^2$, where s_n is the percent market share of the nth of the N countries, which mine or produce the material. For example, an HHI of 10000 would indicate that there is a sole producer, whereas HHI = 3333 would indicate 3 producers with equal market shares; HHI = 4400 is obtained for a market with one dominant producer (60 % share) and two minor producers (20 %). In general, the higher the HHI, the higher is the risk to the consumer in terms of security of supply or competitive pricing. Fig. 4 depicts the relevant group of raw materials with data from Ref. [27]. Given the limited distribution of supply indicated by their HHI values, both niobium and bismuth may be cause for concern if lead-free production were to grow to similar volumes as current PZT manufacture.

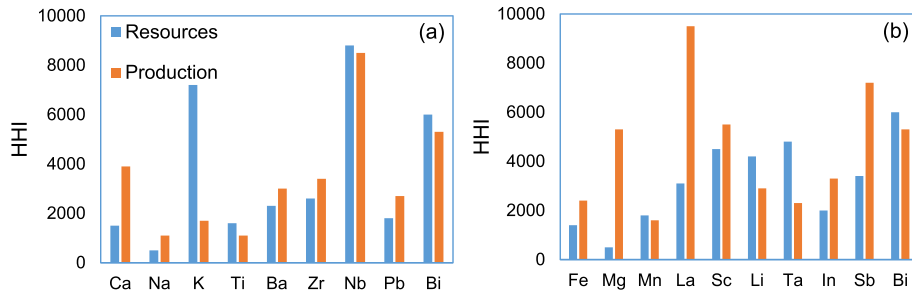In summary, in the short to medium term, the limited supply

Fig. 4. The Herfindahl-Hirschman Index for the geographical distribution of the reserves and production of selected raw materials reserves as (a) major and (b) minor components of piezoelectric ceramics.

and market for lead-free piezoelectrics will impose a cost penalty compared to PZT. If the supply and demand side can partner to overcome the availability issues, the differential will no doubt be eroded in time as more players enter the market. Nevertheless, KNN based ceramics will always demand a price premium due to both higher raw materials and process costs, although this is unlikely to be prohibitive for demanding applications. Risks due to long-term raw material availability are generally low, although both bismuth and niobium based products will be at greater risk in this context. A major unknown is whether legislation based on whole life cycle analysis may be introduced at some point in the future as a more sophisticated form of global environmental protection. If so, the comparison of KNN and PZT indicates that our current understanding of the term "environmentally friendly" would need substantial revision.

2.1.2. Electrodes

Conductive electrodes are an integral component of piezoceramic devices. In most cases, electrodes are applied after the sintering process, using painting or sputtering methods. The most common form of electrode material is metallic Ag, which is frequently integrated with both lead-containing and lead-free piezoceramics. Upon implementation, electrode Ag paste is coated manually or by screen printing, and experiences a sintering process to form electrodes with adherence to the ceramic substrate. Screen printing is commonly adopted in the industrial scenario while manually coating is favored by small-batch production in the laboratory. In the case of multilayer structures, electrodes are co-fired with ceramics during the sintering process. A multilayer structure satisfies an engineering approach to increase the overall displacement in the current state of performance level whilst effectively lowering the driving voltage, rendering lead-free materials promising candidates for multilayer actuators [18]. As inner electrodes are co-fired with ceramics in multilayer structures, technical and cost-effective viability of suitable electrodes should be addressed.

Besides the cost-efficiency and availability of raw materials, the production costs of electrode materials should also be taken into consideration when it comes to device manufacturing, which are neglected in the laboratory-level experimentation. Table 1 summarizes the relative prices of common metals for electrodes in the past ten years. It is noted that the cost of electrodes can be up to 80 % of the total materials cost of the actuator's basic constituents when adopting Ag/Pd electrode [28], which of course is also dependent on the exact electrode compositions. Taking 70/30 Ag/Pd alloy, for example, which is typically used as internal electrodes for actuators, there would be a large reduction in electrode costs if Ag/Pd could be replaced by Ni electrodes, as highlighted in Table 1.

Generally, there are two major commercially available electrode systems: (1) alloyed Ag/Pd electrodes as Ag and Pd form a complete solid solution. By adjusting relative contents, an electrode with broad operating temperature range meets most co-firing demands in air atmosphere; (2) base metal electrodes, represented by Cu and Ni. An additional requirement for base metals is that co-firing should be conducted in a reducing atmosphere.

The Ellingham diagram in Fig. 5 provides the temperature dependence of the stability for compounds and is used to predict the equilibrium temperature between a metal and its oxide. NiO is less stable than PbO and sintering at ambient atmospheres easily oxidizes Ni to NiO. Unfortunately, a reducing atmosphere maintains the metallic state of Ni, while simultaneously reducing PbO in PZT. Thermodynamic incompatibility between metallic Ni and oxide PbO excludes Ni as a feasible electrode to co-fire with PZT. Thus, the piezoelectric industry has been continually under price pressure from the high costs of alloyed Ag/Pd electrodes, especially in the case of increased stacking layers, where the proportion of the electrode cost dominates the overall cost [30]. It is noted that compatibility of Cu electrodes with PZT was already reported

Table 1
Price ratios of common metal electrode materials (after Ref. [18]). The values are based on the price of the investment market in 2016 and are normalized by the factor of mass density due to the actual consumed amount in applications.

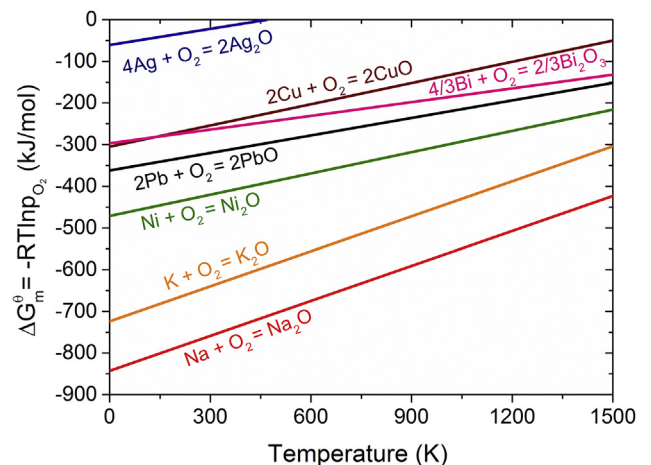| Metals	Firing atmosphere	Price ratio
Cu	Reducing	1
Ni	Reducing	2
Ag	Air	133
Pd	Air	5930
Pt	Air	16390

Fig. 5. Ellingham diagram for selected oxides (standard Gibbs free energy), readapted from the Interactive Ellingham Diagram Tool [29].

[31—33]. As for applications, a Cu co-fired PZT actuator product shows promising cycling performance [34,35]. In contrast, it can be seen from the Ellingham diagram that some lead-free systems are thermodynamically compatible with base metals. For example, KNN- and NBT-based ceramics can be co-fired with Cu electrodes, while KNN systems are also compatible with Ni electrodes. Ni has long been used in multilayer ceramic capacitors (MLCC) based on BaTiO$_3$, stimulating the development in the field of multilayer piezoelectrics. Inspired by this, most companies do not see electrodes for lead-free materials as an issue, compared to PZT.

2.1.2.1. Technical viability. There have been previous successful investigations into implementing base metal electrodes in lead-free systems. Kobayashi *et al.* investigated sintering of KNN ceramics in a reducing atmosphere [36], where the piezoelectric and dielectric properties were not affected, but resistivity was improved. The ceramic-electrode interface is crucial, since the diffusion of Ag from the electrode has been reported to notably influence the piezoelectric performance of KNN multilayer actuators [37]. In another study of Kobayashi *et al.* [38], the KNN/Ni interface was found to be both compositionally and structurally sharp, and no grain boundary or secondary phase associated with the Ni diffusion was observed in the TEM analysis. Kawada *et al.* systematically investigated KNN multilayer ceramics co-fired with Ni electrodes [39—41]. A normalized strain (S_{max}/E_{max}) of 360 pm/V was reported, accompanied by a strong stability at rigorous conditions, *e.g.*, wide temperature range, high humidity, and large thermal shock resistance. The reported samples can reach higher displacement comparable to that of PZT by stacking more ceramic layers with smaller thickness. In particular, Ni electrodes have an intrinsic advantage when combined with lead-free piezoceramics over Ag electrodes. For example, KNN materials have a linear displacement-field relationship up to 4 kV/mm, whereas the displacement in PZT typically saturates above 2 kV/mm. Ni electrodes possess a high electro-migration resistivity [38,40]. On the other hand, Ag ions are found to easily migrate along grain boundaries under humidity and DC voltages, thus seriously deteriorating piezoelectric performance, especially at fields as high as 4 kV/mm [28,42,43]. Therefore, displacement of KNN/Ni multilayer actuators can be enlarged by stacking more layers and using a driving field of up to 4 kV/mm, an option not available for PZT/Ag-Pd multilayers. Compared to co-firing with Ni, co-firing with Cu is more challenging due to the lower melting temperature and oxidation. Prototyped KNN multilayers with Cu electrodes displayed a normalized strain coefficient of 220 pm/V [44]. Importantly, no diffusion or chemical reactions, in the form of alloy formation or Cu oxidation at the internal electrode-ceramic interfaces, were observed.

NBT-based ceramics are endowed with high electric-field-induced strain and large blocking force, which are favored in piezoelectric actuator applications. Since large driving fields are always required, a multilayer structure enables reducing applied voltages while maintaining high strain outputs. NBT-based multi-layer actuators using Pt electrodes were first reported by Nagata *et al.* [45]. Schütz *et al.* demonstrated that NBT-based ceramics do not interact with Pd in the absence of free bismuth oxide [46], and then followed up by using Ag/Pd electrodes, including a prototype sound speaker device [47]. However, diffusion of Ag ions across grain boundaries has a negative impact and thus deteriorates performance [28,43]. An alternative approach is to adopt base metals Ni and Cu, with additional benefits of cost reduction. Unlike the incompatibility of Ni with Bi at reduced atmosphere, co-firing NBT with low-melting Cu is thermodynamically viable, however, at a temperature below 1000 °C [48]. By doping with multiple additives, Yesner *et al.* demonstrated the feasibility of NBT multilayers with Cu inner electrodes [49].

Low-temperature sintering of a (Ba,Ca)(Ti,Zr)O$_3$ ceramic co-fired with Cu electrodes was recently investigated [50], yielding high dielectric constants (~9500) and high relative densities (>98 %).

In summary, lead-free materials have a better compatibility with base metals than lead-containing materials. Cost advantages of lead-free multilayer structures compensate for their inferior performance for the time being, and can be regarded as a driving force to develop lead-free products by industry. From the feedback from the questionnaire, firing in reducing atmosphere is feasible, but could necessitate additional investment for the required equipment. So there would be a foreseeable trade-off between extra capital investment and cost reduction in electrode materials, from the prospective of producers.

2.1.3. Processing

2.1.3.1. Water-based solid-state processing. Solid-state processed lead-free piezoceramic powders are on the laboratory level almost exclusively processed using organic solvents [51,52] due to the inherent hygroscopicity of the starting carbonates. This has largely hindered their direct transfer into industrial production. We note that the use of organic solvents on an industrial scale is very limited, due to economic, environmental, and safety reasons. The introduction of water into processing of lead-free piezoceramics is related to at least three main problems: solubility of the carbonates in water, strong polarity of water compared to organic solvents, and leaching of metal ions from the calcined oxide during final milling. These effects can result in large deviations from the desired stoichiometry, formation of secondary phases, demixing of the slurry, or hydrolysis of the surfaces. Approaches to tackle these issues include adjustment of the pH value [53], use of spray- or freeze-drying [52], or addition of surfactants [54,55]. With the exception of a few promising reports on NBT-based [13] and BCTZ-based [56,57] systems, research on solid-state processing of lead-free piezoceramics using aqueous routes is relatively scarce. Studies of individual synthesis steps and detailed information on solubility limits, stability diagrams, and surface hydrolysis of these powders are desperately needed. Nevertheless, these processing issues seem to have been partially overcome by individual companies, which offer lead-free piezoceramics with different compositions in their product list, for example PI Ceramics, CeramTec, Meggitt Ferroperm, Kyungwon Ferrite, CerPoTech, and NGK Spark Plug. We note that the latter two reported the capability to produce KNN-based piezoceramics in 100 kg batches [14,16].

2.1.3.2. Sintering parameters. Sintering is the most energy-demanding step during piezoceramics production, consuming about 43 % of the total thermal energy [24]. In order to reduce the thermal input and consequently the cost, several approaches for the reduction of the sintering temperature were developed. In addition, reduction of the sintering temperature enables the use of less-expensive electrode materials in multilayer structures, which further decreases the production cost.

Sintering of BT-based compositions requires very high temperatures (1300—1500 °C) [58], while the sintering window is relatively wide (Fig. 6). NBT-based materials exhibit similar sintering behavior as PZT and are easily densified at 1050—1200 °C [59]. Densification of KNN-based solid solutions is considerably more difficult [17] due to the very narrow shrinkage interval, proximity of the liquidus temperature, and particle coarsening [60,61]. NBT-based and KNN-based compositions are additionally affected by
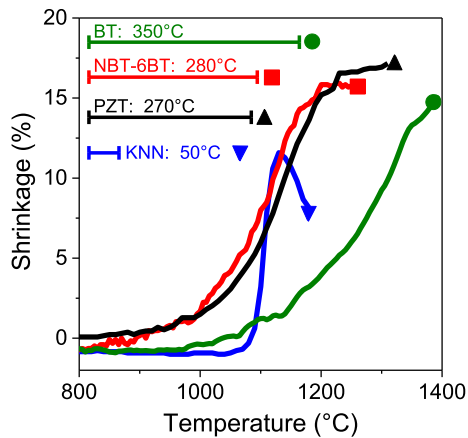
Fig. 6. Sintering curves of various lead-free piezoceramics, as compared to PZT (dynamic measurement of the real shrinkage using optical dilatometry in air; heating rate 5 °C/min). The bars denote the width of the sintering temperature intervals (sintering window) for each material.

evaporation of alkali metal oxides, which seems to be more critical for the former material [62] and can be partially controlled by the use of sacrificial atmospheric powder.

The most cost-effective approach for the reduction of sintering temperature is the enhancement of diffusion by additives, such as dopants introducing A-site vacancies [58] or sintering aids inducing liquid phase sintering [63]. While improved densification is frequently reported, the influence of the additives on the defect chemistry is not always well understood. Densification can also be enhanced by reducing the powder particle size [64], modification of the heating schedule [65], or the use of pressure/field/microwave-assisted sintering techniques [66]. However, these methods require additional equipment, are limited to certain sample sizes, or necessitate the use of reducing atmospheres (carbon dies), which limit their applicability on an industrial scale.

2.2. Reproducibility

The rapid expansion of the research on lead-free piezoceramics over the past decades resulted in the development of numerous novel compositions. However, the exciting new advancements were also accompanied by some drawbacks, one of them being the questionable reproducibility of certain reported properties. It is hard to identify origins unambiguously, but may be related to sensitivity of individual processing steps, poor reporting of experimental conditions, absence of testing large statistically-relevant sample quantities, and also increasing pressure for publishing. Poor reproducibility, which is in fact a critical challenge for the entire scientific community [67], has brought distrust and reduced interest from some industries.

With respect to processing-related reproducibility, initial issues can already arise by the selection of the raw materials. Different particle sizes and size distributions will influence the reaction kinetics, while hygroscopicity may lead to off-stoichiometry [68]. Raw powder impurities often include transition metal ions and should thus be kept as low as possible, as already small amounts influence the defect chemistry and, consequently, the electromechanical properties. Even a different crystallographic structure of the raw material can lead to different results, despite the same composition and impurity level [69]. The processing issues can be identified by carefully analyzing individual steps using X-ray

diffraction, thermal analysis methods (TG, DTA, DSC), particle size analysis, and chemical compositional analysis. In addition, the evaporation during high-temperature processing, described in the previous section, should be considered. The second processing-related reproducibility issue is associated to the microstructural features and their influence on the functional properties, which are only comparable if the sample's relative density, pore distribution, grain size, domain size, and morphology are similar [70]. Despite the challenges, we note that many of the listed processing issues are not unique to lead-free piezoceramics and also appeared in PZT and other commercial ferroelectrics, where they were properly investigated and addressed over a period of more than 60 years of constant development. Similar systematic studies of individual processing parameters for many lead-free compositions are still missing.

Finally, some of the reported experimental observations may be misinterpreted or even false due to the misuse of the measurement techniques or the inappropriate selection of measurement conditions. We note that lead-free piezoceramics may exhibit peculiar behavior, which can preclude the use of measurement parameters from lead-based compositions. Some of these issues, related to microanalytical compositional analysis or electrical measurements, have been discussed in the literature [71—74].

2.3. Mechanical and thermal properties

2.3.1. Elastic modulus

During operation, piezoelectric materials are often exposed to external stresses. For example, internal residual strains can originate from temperature changes, either through self-heating from large-field hysteretic losses or external sources of heat, such as a knock-sensor on a car engine that heats up during the initial engine warm-up phase. As the electro-active elements must be in contact with other components for force transmission, strain incompatibilities can increase the mechanical stress of the piezoelectric component proportional to its elastic modulus. Stresses can also originate from preloads purposefully applied to decrease cracking, by dynamic electrical loading of actuators, or in piezoelectric films due to various phenomena resulting in mismatch strains, *e.g.*, epitaxial, film densification, thermal expansion mismatch, *etc*. The elastic stiffness is an important parameter that helps to determine both the force that can be generated during actuation as well as the resonance frequency of the piezoelectric material. In the case of a clamped film on a substrate, for example, the elastic properties also help determine the effective piezoelectric response. Force generation, an important advantage of piezoelectric systems, is also directly related to the system configuration, *e.g.*, multilayer actuators have a higher effective stiffness than unimorph bending actuators and can, therefore, transmit more force, albeit with a lower displacement. In resonance applications, such as ultrasonic transduction, the elastic properties play a crucial role in determining the emitter efficiency and the receiver sensitivity through the electromechanical coupling factor. An additional consideration is acoustic impedance matching of the piezoelectric to the investigated medium, *e.g.*, body tissue, which allows for a more efficient transduction of acoustic waves. Therefore, changes to the elastic properties during operation are detrimental to efficiency, requiring accurate knowledge of the elastic properties as a function of temperature to account for this.

There are a number of ways to determine the elastic modulus of piezoelectric materials across a spectrum of frequencies from static to dynamic, such as partial unloading [75], nanoindentation [76], dynamical mechanical analysis [77], impulse excitation [78],

resonant ultrasound spectroscopy [79], pulse-echo ultrasonics [80], and Brillouin spectroscopy [81]. There is, however, no single elastic measurement technique that can sweep across many orders of magnitude of frequency, as is routinely done when investigating dielectric behavior with impedance spectroscopy. Static methods, such as partial unloading experiments, have the advantage of allowing determination of the elastic modulus as a function of stress, which is important for transducers with large applied mechanical loads. Fett *et al.* [82], amongst others, have demonstrated a dependence of the observed elastic modulus on the domain state, *i.e.*, electrically poled and mechanically compressed, which is due to the anisotropic elastic properties of ferroelectrics. Although, similar studies are not currently available for lead-free ferroelectrics, it is expected that there is an analogous evolution in the apparent elastic modulus with external stress. In the case of NBT-based materials, these changes could be either due to a stress-induced relaxor-ferroelectric transition or ferroelasticity.

In addition to providing salient data for applications, the characterization of the elastic and anelastic properties of ferroelectrics can provide a wealth of information on the structural and electronic transitions [77,83], oxygen octahedral tilting [83], domain wall motion [84], defect mobility [85], volume content of polar nanoregions (PNRs) [78], and precursor ferroelectric fluctuations [86]. In addition, mechanical spectroscopic techniques can also be directly employed to investigate relaxation phenomena [87,88], which are of particular importance in lead-free relaxor ferroelectrics that feature polar nanoregions. Similar to dielectric permittivity, the elastic response of relaxor ferroelectrics display a strong frequency dispersion with Vogel-Fulcher-like freezing based on the interaction of external stress with strain heterogeneities at the nano-scale, *e.g.*, twin boundaries in polar nanoregions [87]. Such studies are not currently known for lead-free relaxors. Recent investigations of temperature-dependent elastic properties, however, have identified an elastic anomaly at relaxor-ferroelectric transition temperature, consistent with dielectric studies [19], and have been used to determine the volume of PNRs [78]. Importantly, multiple order parameters can be simultaneously active in multiferroics, which can result in an overlap of strain fields and a coupling of the phenomena.

2.3.2. Fracture toughness

Fracture toughness is a particularly critical material property for piezoceramics, as not only an external load can cause crack propagation, but also the strain incompatibility from differently strained volumes, *e.g.*, at electrode edges [89]. Domain switching, therefore, can provide a crack driving force, but also a shielding term through ferroelastic toughening [90], which can double the fracture toughness. In principle, any remanent hysteretic process, such as a metastable phase transformation, can result in a toughening effect during crack growth, assuming that the critical stress can be activated by the crack tip stress field. There is notably very little reliable data available for lead-free piezoceramics, with a recent review summarizing the current findings [19]. The scientific community spent a lot of time and effort in determining the most suitable testing techniques in the 80s and 90s of the last century and conducted several round robin exercises [91], resulting for example in the standards by the American Society for Testing of Materials (ASTM) [92]. One of the recommended techniques is the short crack in flexure (SCF) method, which was recently applied to NBT-xBT materials [93] and demonstrated a higher fracture toughness for NBT-derived materials as compared to PZT.

2.3.3. Subcritical crack growth

Piezoelectric devices experience mechanical stress on several length scales: (i) at the microscopic level, domain switching leads to local strain incompatibility between switching regions; (ii) at a mesoscopic level, internal electrode edges provide field and stress singularities; and (iii) at a macroscopic level, the piezoceramic may be under external stress or bonded to a dissimilar material. These stresses can lead to immediate failure or to subcritical crack growth. Although subcritical crack growth, for example in PZT, leads to a long-term reduction of load-bearing capacity by about 50 % [94], there are no data available for the recently developed lead-free piezoceramics. This topic, therefore, requires additional consideration. The subject of subcritical crack growth including various measurement techniques is in detail described in the textbook by Munz and Fett [95]. Simple approaches yielding valuable data sets rely on loading samples under constant tensile stress until failure occurs, while more elaborate techniques quantify crack propagation at well-defined stress intensity factors [95].

2.3.4. Fracture strength

Fracture strength is linearly related to fracture toughness through the largest critical defect [95]. Hence, it is not an intrinsic material value like fracture toughness but probes the defect distribution of a sample. Efficient sampling dictates that the sample should be processed like the final product in the application and ideally would probe exactly that product or be extracted from that product. Further, the sample volume should be as large as possible to afford efficient extrapolation to large batch sizes. In addition, not only fracture strength, but also Weibull distribution should be determined. In conclusion, tensile strength testing is preferred to bending strength and gives considerably lower values [96]. Recognizing that most laboratories only provide means for bend testing, 4-point bending is preferred to 3-point bending due to the larger volume sampled.

Ferroelastic materials display domain switching, which results in plastic deformation. For cases where the coercive stress lies below the fracture stress, the standard equation for determining the fracture strength from a bend bar test cannot be applied. Hence, special efforts have to be made to arrive at a valid fracture strength value. The recommended procedure in this case has been published by Fett *et al.* [97]. In testing fracture strength of piezoceramics, therefore, the coercive stress of these materials should be known, which is considerably below the fracture strength for soft PZT [97]. Only a few coercive stress values are currently available for lead-free piezoceramics: NBT-xBT [19,98], BCTZ [99], BF-BKT [100], and KNN [101,102].

The literature provides yet few examples of the determination of strength of lead-free piezoceramics materials. An example of both fracture strength and Weibull distribution is provided by Martin and Kakemoto for KNN-based [103] and by Takahashi *et al.* for NBT-based [104] piezoceramics.

2.3.5. Mechanical constitutive behavior

The macroscopic mechanical constitutive behavior of perovskites is largely controlled by nonlinear processes that have order parameters coupled to a local strain field, such as ferroelasticity [58], field induced structural phase transformations [105], and magnetic spin transitions [106]. Ferroelasticity, the primary nonlinear effect observed in ferroelectrics, is caused by the nucleation and growth of ferroelastic domain walls during the application of an external mechanical field. It results in the development of a remanent strain and, in poled samples, a remanent polarization [107], as well as an increase in elastic modulus [82] and a decrease in the piezoelectric coefficient [108]. Ferroelectric and ferroelastic domain wall motion has been suggested to be the primary nonlinear contribution in both KNN [109,110] and BCTZ [111] systems, despite some studies that have revealed the importance of field induced phase transitions, in particular near structural phase transition boundaries [112,113]. Recent investigations have also

demonstrated the influence of external stress on Bi-based lead-free relaxor ferroelectrics [98,114]. In analogy with electric field loading [115,116], a mechanical stress was able to induce a long-range ferroelectric order, resulting in the dielectric anomaly at the ferroelectric-relaxor transition temperature [19]. Although there is presently little data available, these studies indicate that the strain fields in the polar nanoregions can be directly influenced by the application of an external stress.

2.3.6. Blocking force

The primary objective of a piezoelectric actuator is to produce a mechanical displacement upon electrical loading under given system conditions, *e.g.*, operation temperature, frequency and amplitude of electrical signal, *etc.* Of particular importance are the various internal and external stresses that the actuator is exposed to, such as compressive preloads to increase reliability, the large internal residual stresses at partial electrodes edges [117], and dynamic tensile stresses during high frequency operation due to the mass of the actuator system. During actuation, piezoelectric actuators must also do work on the system, such as opening a valve, compressing a spring, *etc.*, meaning that the force-electric field relationship can be of special importance. In the simple case of an actuator acting against a linear spring with spring constant k, the force on the actuator linearly increases with displacement. In the stress-free condition (k = 0), the displacement is referred to as the free displacement. In contrast, the blocking force is defined as the force that an actuator can produce when the displacement is completely blocked, *i.e.*, the actuator acts against an infinitely stiff spring (k = ∞) [118,119]. The blocking force depends significantly on the type of actuator as well as applied stress state [120,121]. The free displacement and the blocking force are common figures of merit that characterize the operational range of the piezoelectric actuator and can be used to impedance match the actuator to the external system and thereby optimize work output [122]. It is important to note that the blocking force depends on the actuator geometry, whereas the blocking stress does not. Previous work has revealed significant material-specific variations in blocking stress [99], although it remains unclear how the electrical and mechanical properties, as well as the individual phenomena responsible for the observed electromechanical properties, *e.g.*, domain wall motion, piezoelectricity, field-induced phase transformations, *etc.*, affect the generated actuation force. Blocking stress values for several

NBT-based and a BCTZ lead-free piezoceramics are depicted in Fig. 7 and compared to commercial soft PZT. Note that no reports could be found for KNN-based piezoceramics.

2.3.7. Machinability

The majority of piezoelectric applications require that the ceramics are of a specific physical shape, size, and tolerance that is not achievable from as-sintered parts. For example, the piezoelectric elements in ultrasound transducers are to exhibit a specified resonant frequency and bandwidth, which are both a function of size and shape. For thickness mode transducers, the element thickness, parallelism, flatness, and surface roughness must all be controlled to high tolerance, typically in the range 0.5−2 μm. Other applications require curved surfaces; for example, the staves in multi-element toroidal transducers or hemispherical sections for therapeutic high intensity focused ultrasound treatments. Such shapes cannot be achieved by net-shape forming within appropriate tolerances. Similarly, MEMS devices relying on micro-actuation are often manufactured by top-down machining from bulk ceramics. In the example of monolithic ink-jet printer heads, the required tolerances are combined with the need for thin (~50 μm) high aspect ratio (1:10) sections [123]. All these devices necessitate that the piezoelectric ceramics undergo post-sintering combinations of cutting, drilling, lapping, and polishing to achieve their functional specification. Although there are instances where electric discharge machining or laser machining are used, the majority of operations on PZT are carried out by machining or grinding, employing tools embedded with suitable abrasives, such as diamond or silicon carbide.

The machinability of a material is an expression of the ease of achieving a high rate of material removal whilst maintaining acceptably low levels of surface damage and tool wear. Such a compromise can only be truly assessed within the context of the overall cost and price of the component being manufactured. Good machinability means that the time required and tool wear experienced to machine a part with acceptably low surface damage do not add prohibitively to its cost.

Understanding the differences in machinability between different materials is a complex issue. It is possible to make comparisons in terms of speed, by measuring the rate of material removal for a given rotational speed and force. In general, the higher the material hardness and fracture toughness, the lower will be the rate of material removal. However, microstructural features, including the porosity size distribution and strength of the grain boundaries, are also a controlling influence [124]. Moreover, the level of surface damage may not correlate simply with the rate of removal. At a macroscopic level, one can assess surface damage by measuring surface roughness, but at the microscopic level the damage is characterized according to a variety of features associated with brittle material removal: grain pull out, trans-granular and inter-granular fracture, plus residual stress. Variations in the density of these microscopic features between materials is strongly correlated with characteristics of the microstructure mentioned above. The most prevalent type of microscopic damage is likely to have a much greater correlation with impairment of functional properties than does a simple roughness measurement. Ductile machining, which avoids the propagation of these flaws, and depends critically on the depth of cut, is difficult to achieve uniformly in piezoelectric materials due to their ferroelastic nature. The complexity of the mechanism of material removal in piezoelectric materials is discussed in Ref. [125].

It should be noted that whilst the consequences of surface damage can often be ameliorated by post-machining annealing, in many applications, for example, those employing piezoelectric shear modes, the geometry demands that machining is carried out
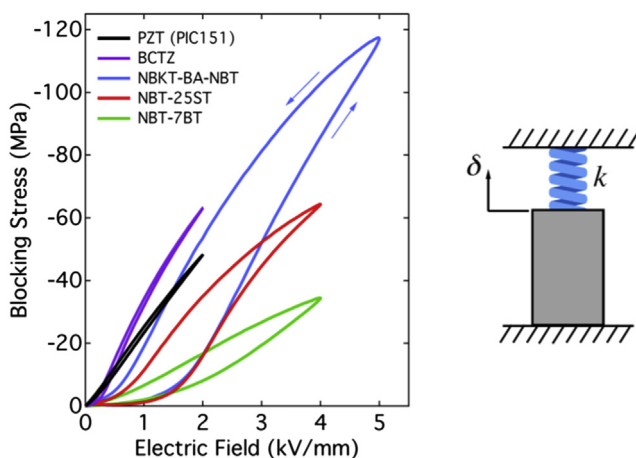

Fig. 7. Blocking stress values for various lead-free piezoelectrics, as compared to commercial PZT. Note the different applied maximum fields. During the blocking force measurement the sample is fully clamped (δ = 0) and acts against an infinitely stiff spring (k = ∞), as specified by the schematics on the right.

after poling, which rules out the possibility of annealing.

Whilst it would be advantageous to develop a simple model from which to predict machinability from bulk properties, this seems to be far from practicable. Hence, when comparing the machinability of different materials, *e.g.*, a lead-free piezoceramic with PZT, the ultimate test is actually a comparison of machining times, surface damage, and tool wear, combined with functional performance, noting that the minimum acceptable value for each of these factors is application dependent.

2.3.8. Thermal conductivity

In the case of high-power applications, hysteretic processes in the material lead to internal heating of the sample, followed by a degradation of salient properties, *e.g.*, the electromechanical quality factor Q_m [126]. A further increase in electrical load leads to further heat dissipation and eventual depolarization [127]. Solutions to this problem are provided by better heat dissipation, large surface to volume ratios, and increased thermal conductivity of the piezoceramic. Better scientific understanding, therefore, demands knowledge of the thermal conductivity of piezoceramics envisaged for high-power applications. This is one of the applications where lead-free piezoceramics were predicted to be competitive in very few years to lead-containing piezoceramics [2]. A related application where heat needs to be extracted efficiently from the sample is electrocaloric cooling [128]. In this application, low thermal conductivity will limit the frequency of the cooling cycle. Investigations into the thermal conductivity of perovskites are unfortunately very rare with few data on only very few systems available. Current knowledge suggests that lead-free piezoceramics have a higher thermal conductivity than PZT [129] and, therefore, may have an edge in high-power applications.

2.4. Electrical conductivity

The contribution of the defect chemistry to leakage current and dielectric loss has not been a major focus in the research of lead free materials. Initially, it was assumed that the defect chemistry of NBT-, KNN-, and BT-related materials has a similar impact on the electrical properties as for lead-based ceramics. However, recent investigations demonstrated that this assumption is not fully valid. Even the primary requirements, like hardening due to acceptor doping, are impacted differently compared to lead-based materials [130].

Considering leakage current and dielectric loss, NBT exhibits unusual and unexpected behavior. With increasing concentration of the acceptor dopant Mg or with Bi_2O_3 evaporation during processing, NBT undergoes a transition from low intrinsic electronic conductivity to high oxygen ionic conductivity [131]. In the case of NBT-BT, the electromechanical properties are extensively modified by a change in *A*-site stoichiometry defect concentration, with only a subsequent minor decrease in resistance [132]. Although the leakage current in KNN-based ceramics is often reported to be "very high" [133], it does not reach the levels of acceptor doped NBT. There is, however, only limited knowledge of the defect chemical origin of the energy loss and means of its prevention. Some studies have revealed that donor doping leads to a reduction of conductivity [134]. A large decrease in leakage current was also obtained by doping with Mn [135,136]. This suggests that the dominant charge carriers in nominally undoped KNN ceramics are electron holes or oxygen vacancies, which are reduced due to the presence of donor cations or mixed valency dopants, such as Mn. Pure BT is the most intensively researched ferroelectric material apart from lead containing ceramics [137]. However, PZT is preferred for piezoelectric applications because of its superior ferroelectric properties and opportunity to modify these properties

extensively by doping. In comparison, donor doping of BT leads to a highly electronically conductive material and is, hence, not suitable for ferroelectric applications [138]. There are, nevertheless, some BT derived solid solutions, like BCTZ [8] or BT with Bi-based oxides [139], which display piezoelectric coefficients that exceed those of PZT or have a temperature stable high permittivity, respectively. However, it has been found that these solid solutions can undergo significant defect chemical changes depending only on small variations of compounds of a solid solution, leading not only to resistance changes but also to a different dominant charge carrier type [140]. This results, *e.g.*, in an entirely different response to a change of sintering atmosphere. As mentioned in the previous chapters, further complexity may be added depending on electrode material, sintering atmosphere, and sintering aids [46]. A careful investigation of conduction properties and their relationship with the defect chemistry of the material therefore requires consideration of all aspects of the synthesis route. Hence, the knowledge on conduction properties and defect chemistry obtained on a laboratory scale produced pellet cannot easily be transferred to, *e.g.*, multilayer structures of the same material. This remains a challenge for lead-based ceramics [141].

2.5. Lifetime

2.5.1. Electrical fatigue

Hysteretic cyclic processes have the potential to lead to fatigue with increasing number of loading cycles [142]. Investigation of fatigue resistance can be conducted using bipolar, unipolar, or sesquipolar cycling. While the former is in general more severe and of interest for ferroelectric memories, unipolar loading results in slower property degradation and is relevant for actuators. However, please note that fatigue of ferroelectric memories is not considered here as we focus on piezoelectric applications. In the case of piezoceramic multilayer actuators, stability up to 10^9 electric cycles at temperatures up to 150 °C may be required. It should also be noted that fatigue resistance was listed as the most important non-piezoelectric property in our survey of piezoceramic producers. Extensive summaries of the current state-of-the-art on electric fatigue of lead-free piezoceramics [143], which compare PZT to KNN-based, BCTZ-based, and NBT-based piezoceramics [130], can be found in the recent literature. Mechanistic considerations for fatigue of PZT included the effects of temperature and maximum electric field and cumulated in a model based on charge carrier migration due to the depolarization field [144]. Later studies found related effects in KNN-based [145] and BCTZ-based [146,147] materials and were able to apply this model successfully. Moreover, fatigue in these two systems was found to be sensitive to vicinity of the phase transitions [147,148]. These determine the extent of the extrinsic domain contributions to the field-induced strain, which are strongly influenced by the agglomerated charge carriers. Acceptor doping was proposed as an approach to improve fatigue resistance in KNN-based materials [145], whereby the exact mechanism is still not clear. NBT-based ergodic relaxors reveal very low cyclic degradation, which was surmised to be due to the disappearance of the domain structure under decreasing electric field and, therefore, the reduced depolarization field [149]. Related materials also featured very low degradation, which was proposed to be related to the very low defect concentrations in the material [150].

While electric fatigue is often described as a degradation mechanism leading to a reduction in piezoelectric performance, a resistance degradation, as typically discussed in dielectrics, can also occur to the degree that the device fails completely. Due to mobile defects like oxygen vacancies, a change in defect chemistry can be induced in electroceramics depending on the applied electric field,

polarity of the field, and type and kinetics of reactions occurring at the electrodes [151–153]. These can eventually cause a complete breakdown in resistance. When it comes to piezoelectric materials, other fatigue mechanisms usually occur prior to resistance degradation. However, if an application is considered that involves unipolar application of field, resistance degradation would mean the ultimate failure of the material. So far, there is little research on the effect of mobile vacancies on properties after long electric field application times in lead-free piezoelectric materials [151]. Thus, extensive highly accelerated life tests should be conducted with subsequent investigations of the defect chemistry.

2.5.2. Mechanical fatigue

Mechanical fatigue is a property commonly probed in structural ceramics. As piezoceramic actuators are subjected to cyclic electric straining, a cyclic mechanical loading is implied if the actuator does work against a force. Cyclic mechanical loading will naturally include subcritical crack growth (see ch. 2.3.3.: Subcritical crack growth), which needs to be subtracted to find the origin of the intrinsic degradation mechanism for mechanical fatigue. Investigation methods into mechanical fatigue can be divided into two approaches [95]. One probes the failure upon mechanical cycling of a sample and, thereby, is of a very applied nature. The other interrogates the actual crack growth per cyclic load and requires fracture mechanical test specimens. Both investigations have been conducted for PZT; Fett *et al.* and Okayasu *et al.* investigated the strength of PZT [154,155], while Salz *et al.* [156] presented work on the cyclic crack growth. Studies into the mechanical fatigue of lead-free piezoceramics are not known to the authors, but were noted of high pertinence by the consulted companies.

3. Conclusions and recommendations

In this paper we have attempted to review the "secondary" properties and characteristics of lead-free piezoceramics. The priority assigned to each of these is, of course, application specific. Whilst some are ubiquitous, *e.g.*, cost, availability, reproducibility, the importance of others depends on how the material will be employed and on the cost structure of the final product. For example, for micro-electromechanical systems or high load actuators, machinability and fracture toughness, respectively, may be paramount. Whilst it is, therefore, impossible to produce a general, prioritized list of properties for the community of academic researchers to address with further research, it is believed that the issues raised here will provide signposts to the broader sets of characteristics that should be addressed and the motivation to understand their interdependence.

Despite its relatively long history, research into lead-free materials can now be said to be successful; it has produced materials with primary properties that match or, in some cases, exceed those of lead-based materials. It is therefore suggested that lead-free piezoelectric research is now entering a second phase, in which the work becomes more application specific and will focus more on what we have referred to as secondary criteria. Each of the commercial PZT producers manufacture between 4 and 20 different grades of PZT, so, clearly, there is not a single ideal specification for a piezoelectric material. Whilst some of these grades may be considered to be generic "hard" or "soft" materials, a large number will have been tailored to particular applications or even single user requirements, differentiated by their secondary properties. Increasingly, we should now also see the targeted development of lead-free materials to meet specific applications or single user requirements. To facilitate this second phase of research, we make the following recommendations:

- Increased collaboration between scientists developing new materials and researchers in application-relevant properties, particularly in the areas of mechanical properties, lifetime, and electrical conductivity,
- National or supranational funding schemes for interdisciplinary and industry/academia collaborations in design and modeling of devices with lead-free materials; and
- Increased lead-free piezoelectric content in relevant educational programs, to prepare a future cohort of piezoelectric engineers to employ these new material classes.

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