# Exemption Request Form RoHS 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”

Date of submission: XX.XX.XXXX

## 1. Name and contact details

### 1) Name and contact details of applicant:

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|---|---|
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On behalf of the Company/Business organisations/Business associations listed below participants in the **RoHS Umbrella Industry Project (“the Umbrella Project”)**:

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| We will be inserting in this table endorsing Associations: (i) names, (ii) EU Transparency Register IDs (where applicable) and (iii) Logos. | | | |
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## 2. Reason for application:

Please indicate where relevant:

☐ Request for new exemption in:

☐ Request for amendment of existing exemption in

☒ Request for extension of existing exemption in

☐ Request for deletion of existing exemption in:

☐ Provision of information referring to an existing specific exemption in:

☒ Annex III ☐ Annex IV

No. of exemption in Annex III or IV where applicable: 7(c)-I

Proposed or existing wording: existing wording

“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”

Duration where applicable:

We apply for renewal of this exemption for the categories marked in section 4 further below for the respective maximum validity periods foreseen in the RoHS2 Directive, as amended. For these categories, the validity of this exemption may be required beyond those timeframes. With regard to Category 11, we request that this application is not processed earlier than the applicable latest application date foreseen in RoHS2, as amended (i.e. 18 months before the respective maximum validity periods foreseen in RoHS2).

☐ Other: _____

## 3. Summary of the exemption request / revocation request

We apply for extension of the exemption 7(c)-I for electrical and electronic components containing lead in a glass and/or ceramic other than dielectric ceramic in capacitors, e.g. piezoelectronic devices, or in a glass or ceramic matrix compound.

Industry has investigated the substitution of lead in glass and/or ceramic and/or matrix compounds of these materials used in electrical and electronic components before the last review in 2015 and we have continued these investigations after 2015. Nevertheless substitution technology has not been found up to the present day and there are no prospects of finding substitutes at least until the time of the next review. The reasons for the exemption presented by the stakeholders in 2015 are still valid. Consequently, it is necessary to extend the exemption 7(c)-I for the maximum validity period.

Numerous potential compositions have been investigated for ceramic applications in the last 20 years and the main task is still the development of reliable technical solutions on an industrial scale. However up to the present time, substitution technology has not been found and there is no prospect of finding it at least until the next review.

Alternative technologies for glass have also been evaluated but so far no substitution technology is available which ensures the required properties such as integrity of the layer, step coverage, delamination resistance, hermetic sealing and charge balance etc., as well as the reliability to ensure public safety.

Society in the EU requires that electrical equipment is safe to use and protects the health of citizens. Many types of electronic components containing lead in a glass and/or ceramic matrix compounds provide safety features in equipment that prevent failures that can lead to injuries or fires, for example, overcurrent or over-temperature protection. Currently there are no substitutes.

Electrical and electronic components containing lead in a glass or ceramic other than dielectric ceramic in capacitors are used in countless high and low power applications. Piezoelectric components containing Lead Zirconate Titanate (PZT), which are merely one example of many different applications of this exemption, are used in different Biomedical/Medical Applications. Their use allows innovative and special high-power, compact medical device technologies such as ultrasonic surgical devices. Furthermore, PZT is used for sensors and actuators in devices where low power consumption and high performance are key (e.g. in drug delivery systems).

There are no alternative substances which would meet the performance, quality, stability, and reliability requirements which are based on the complex operating environment of ultrasonic surgical devices and implantable devices. To comply with the 2017/745 Medical Devices Regulation (MDR) such devices have to meet these safety relevant requirements.

## 4.Technical description of the exemption request / revocation request

### (A) Description of the concerned application:

1. To which EEE is the exemption request/information relevant?

Name of applications or products:

All types of electrical and electronic equipment (EEE) (Large and small household appliances; IT and telecommunications equipment; consumer equipment; lighting equipment; electrical and electronic tools; toys, leisure and sports equipment; medical devices; monitoring and control instruments (including industrial monitoring and control instruments); automatic dispensers and other EEE categories not covered by any of the categories above.)

List of relevant categories: (mark more than one where applicable)

| | |
|---|---|
| ☒ 1 | ☒ 7 |
| ☒ 2 | ☒ 8 |
| ☒ 3 | ☒ 9 |
| ☒ 4 | ☒ 10 |
| ☒ 5 | ☒ 11 |
| ☒ 6 | |

a. Please specify if application is in use in other categories to which the exemption request does not refer:
   To our knowledge this exemption is used for all categories of electrical and electronic equipment. With regard to Category 11, we request that this application is not processed earlier than the applicable latest application date foreseen in RoHS2, as amended (i.e. 18 months before the respective maximum validity periods foreseen in RoHS2).

b. Please specify for equipment of category 8 and 9:
   The requested exemption will be applied in
   ☒ monitoring and control instruments in industry
   ☒ in-vitro diagnostics
   ☒ other medical devices or other monitoring and control instruments than those in industry

2. Which of the six substances is in use in the application/product?
   (Indicate more than one where applicable)
   ☒ Pb ☐ Cd ☐ Hg ☐ Cr-VI ☐ PBB ☐ PBDE

3. Function of the substance:

Lead is used to obtain appropriate physical characteristics in glass and/or ceramic. As there are extremely numerous applications of utilizing lead-containing ceramic and/or glass, it is impossible to list all of them. Representative cases and examples are listed in question 4(C) as well as Appendix I. Please note that these do not constitute a comprehensive list.

Many example uses were listed in our previous exemption renewal request submitted in 2015 and all of these still require this exemption.

4. Content of substance in homogeneous material (%weight):

Up to 93 wt%

5. Amount of substance entering the EU market annually through application for which the exemption is requested:

   Lead consumption in Europe in 2018 for industrial applications:
   550t ~ 750t

   [Disclaimer]
   Electrical and electronic components are used in a wide range of final products and markets, it is impossible to provide a precise figure of the amount of lead included in glass and ceramic components in the EU for Electrical and Electronic Equipment [EEE].
   The electronic equipment industry is engaged in the reduction of lead and environmental burdens within its powers, although it is impossible to completely cease the use of lead under the scope of 7(c)-I.
   We present the results of an estimate based on above survey.
   It should be noticed that there are likely to be components with lead-containing ceramic and companies which are not included.
   For this reason, although the estimates were done in good faith with the data resources available, the values shown here are provided strictly for reference purposes.

6. Please supply information and calculations to support stated figure.
   Survey performed by ZVEI on member companies. 14 companies provided data on lead use in industrial application. For some of the companies it was challenging to find out what the share of industrial application is and therefore provided a range of quantities. Therefore, the total amount is a variable.

7. Name of material/component:

   Electrical and electronic components containing lead in a glass or ceramic other than dielectric ceramic in discrete capacitor components, e.g. piezoelectronic devices, or in a glass or ceramic matrix compound.

8. Environmental Assessment:
   LCA: ☒Yes
   ☐ No

Refer to answer in question 6(A).

**(B) In which material and/or component is the RoHS-regulated substance used, for which you request the exemption or its revocation? What is the function of this material or component?**

Lead is used in a wide variety of types of Electric and Electronic Components that are incorporated into EEE. The number of applications using Pb in glass and/or ceramic are so numerous it is impossible to list them all. For some representative examples please refer to the cases in Question 4(C) as well as Appendix I. Please note that these do not constitute a comprehensive list.

**(C)** Many example uses were listed in our previous exemption renewal request submitted in 2015 and all of these still require this exemption.**What are the particular characteristics and functions of the RoHS-regulated substance that require its use in this material or component?**

<u>**Introduction**</u>

<u>**Efforts for Substitution of Lead in the Scope of Exemption 7(c)-I**</u>

Even before the adoption of the RoHS Directive in 2003, industry has endeavoured to find substitutes for lead in glass, ceramic, or glass or ceramic matrix compounds for over 20 years. Industry (as well as academia) has proactively promoted these efforts for the following reasons:

1) Corporate Social Responsibility of businesses to accomplish the stated goal of the RoHS Directive of “contributing to the protection of human health and the environment”,

2) Businesses which develop substitutes can, through their scientific and technological innovation, gain strong support from the market and earn commercial profits as first-movers to supply products compliant to the revision of the RoHS Directive exemption triggered by them.

It was through such efforts that industry managed to substitute “lead in dielectric ceramic in capacitors for a rated voltage of less than 125 V AC or 250 V DC”.

This was a significant achievement concerning adaptation to scientific and technical progress, mirrored by the expiration of exemption 7(c)-III as set up by Commission Decision 2010/571/EU.

However, ever since that achievement took place, further substitution of lead in glass or electronic ceramics (in this renewal request, “electronic ceramics” is used as a general term to indicate ceramics whose electrical functions are used in equipment and devices) of electrical and electronic components (hereinafter, E&E components) could not be accomplished in the scope of exemption 7(c)-I. Substitution of lead is not easy on a practical level since the intended properties of lead-containing glass and ceramics in E&E components are closely linked to the physical and electronic structural properties of elemental lead.

Although limited to cases of lead-free piezoelectric ceramics, an assessment of the substitution situation from a perspective external to industry, is presented in "MRS Bulletin, 43 (8). pp. 581-587, A. J. Bell and O. Deubzer".

As described in the above paper, scientifically and pure technically possible lead-free piezoelectric material exists. However physical properties such as dielectric properties and elasticity as well as their temperature dependence will be significantly different to those of lead-containing material, and since this creates major differences in important derivative properties such as sonic or acoustic impedance, industry still has to find applicable substitutes with suitable combinations of performance properties which can be used in practice.

Given the above, it was concluded in the last renewal request, submitted in 2015, that exemption 7(c)-I, which includes piezoelectric ceramics, should be renewed. The situation has not changed since then.

Efforts have been made by industry to identify lead-free substitutes to PZT and that remains the most studied (and published) area for lead substitution in the scope of exemption 7(c)-I: "*The total number of papers on the topic published since 1997 is approaching 4000, and lead-free materials are currently the subject of one-half of all new papers on piezoelectric ceramics.*"[1]

Nevertheless, this recent publication states; "*few of these publications describe materials in terms of the full electromechanical property matrix, the aging characteristics, electrode compatibility, machinability, and process cost that would enable device engineers to judge the suitability of a material to replace PZT in a given application*"[2].As a result, substitutes have stayed merely at a research/ experimental level and devices with lead-free piezoelectric functions with practical applicability have not been achieved.

Moreover, considering the fact that piezoelectric device engineers will not utilize lead-free material without practical applicability for the evaluation of their devices, the outcome is that no viable substitution efforts will be implemented. A similar situation exists for the technical scope beyond piezoelectric devices.

It was against this backdrop that industry conducted its search on study cases concerning substitutes, focusing on information from publicly available papers, and as a consequence very few examples could be identified since the last renewal request.[3]

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[1]Web of Science, Clarivate Analytics, http://apps.webofknowledge.com, accessed January 2018, as cited in "MRS Bulletin, 43 (8). pp. 581-587, A. J. Bell and O. Deubzer".

[2] J. Koruza, A.J. Bell, T. Frömling, K.G. Webber, K. Wang, J. Rödel, J. Materiomics 4,13 (2018)

[3] Web of Science, Clarivate Analytics, http://apps.webofknowledge.com, accessed January 2018, as cited in "MRS Bulletin, 43 (8). pp. 612-616, A. J. Bell and O. Deubzer".

Although a great number of unsuccessful research/development cases exist within businesses (e.g. component manufacturers etc.), they seldom become publicly available and also are usually handled as confidential information of that business, since those cases cannot become Intellectual Property (IP) of the businesses by the issuing of patents, and so if the information is disclosed it will end up as knowledge to competitors. Each manufacturer, quite reasonably, does not want to assist its competitors in case this gives them a competitive advantage (such as obtaining data without effort or cost). In face of what has been explained, it can be said that when seen from an external perspective the investment and efforts put forth by industry for substitution of lead in the scope of exemption 7(c)-I is underestimated due to the fact that only a few successful cases are presented, Whereas in fact, a very significant effort has been expended by industry[4].

**Illustrative Cases of Lead-Free Substitution Research by Industry in the Scope of 7(c)-I**

As described in the introduction, in light of the fact that the investments and efforts carried out by industry regarding the research of lead-free substitution solutions has not been well understood, in this exemption renewal request industry is providing information concerning illustrative cases on substitution research of lead-containing glass and ceramics.*1

Industry is also ready to provide confidential information directly to the consultant concerning details not disclosed in this renewal request.*2

- *1. Please note that confidential information cannot be disclosed in this renewal request form (as it would be necessary to reach a consensus among the relevant stakeholders as well as process IP information).
- *2. If necessary, please indicate for which cases confidential information should be provided. Please be aware that an estimated period of about 1 month should be necessary for processing an information request.

As lead-containing glass and electronic ceramics are used in all categories of electrical and electronic equipment (hereinafter, “EEE”) it is impossible in practice to exhaustively present all applications and cases. In order to describe the current status of substitution research of lead-free glass and electronic ceramics, we introduce below some selected illustrative cases. (It must be noticed that the examples shown below do not constitute an exhaustive list of the whole substitution research of lead-containing glass and electronic ceramics, but merely a selected small part thereof.)

**Case 1**

[4] Springer Science+Business Media, LLC, part of Springer Nature 2019, Balancing hyperbole and impact in research communications related to lead-free piezoelectric materials, Andrew J. Bell and Dragan Damjanovic

In E&E components, bonds between the same or different types of materials such as metal and metal, ceramics and ceramics, ceramics and metal, etc. are formed with glass.

When forming a glass bond, the glass must be melted once. Lead-containing glasses have melting temperatures of about 300 to 340°C, however when compared with lead-containing glasses the melting temperatures of lead-free glasses are about 120-160°C higher. For this reason, if lead-free glass is used as the bonding material, many problems will occur due to higher temperature and increased heat in E&E components during the production process.

For example, since lead-free glasses have higher melting temperatures, the bonding temperature in the glass bonding process will inevitably increase. When bonding different types of materials with different coefficients of thermal expansion, such as ceramics and metal, with lead-free glass the bonding temperature will be higher in contrast to bonding with lead-containing glass and so a larger stress is caused by the larger difference in the extent of thermal expansion that will be generated. The higher the temperature, the more materials expand, however metals expand more than ceramics.

Since this stress causes micro cracks in the internal part of the lead-free glass, it becomes difficult to maintain the sealing/bonding and electrical insulation that are expected as functions of the glass, and the risk of the E&E component not to maintain its functions increases from a long-term perspective.

Another example is the degradation/deterioration of metal surfaces in E&E components. Since an increase in the glass bonding temperature degrades/deteriorates (e.g. oxidises) the metal surface, for example wettability of the glass on the metal surface in the glass bond portion deteriorates resulting in bonding strength degradation.

Furthermore, degradation/deterioration of metal surfaces hinders the wettability of solder on the metal surface in the solder joint portions of the electronic component, also resulting in solder bonding failures.

As described above, for devices incorporating E&E components using lead-free glass as bonding material, mechanical strength and electrical connections cannot be maintained due to deterioration of the bonding portion, and this causes a decrease in reliability. Consequently, at present it is impossible to design practical products that can ensure the reliability of the equipment to withstand usage conditions in the various markets as this would lead to initial failure of the equipment or a decrease in reliability.

**Case 2**

Chip resistors are widely used in all types of EEE for current control, current detection, voltage division, amplification ratio determination, termination, dumping, pull-up and discharge applications in E&E devices. The resistor elements of these chip resistors consist of mixed sintered bodies of conductive particles ($RuO_2$ and $Pb_2Ru2O_7$) and glass (Pb-Si-Al-B-O system), and so contain lead. Chip resistor manufacturers, as well as resistor element material manufacturers, have tried for many years to research and develop lead-free resistor element materials composed of lead-free conductive particles ($RuO_2$) and lead-free glass (Bi-Si-Al-B-Ca-O system), of which only a very few applications have been commercialized. Research has found that lead-free resistor element materials have the following disadvantages when compared with lead-containing resistor element materials:

- Low moisture resistance during load heating.
- Low mechanical strength during overload heating.

If chip resistors are produced using the lead-free resistor element materials that have the above disadvantages they will cause very inferior reliability. Resistance value variations largely exceeding those of the present lead-containing resistors will occur over time or in sudden outbreaks and this depends on the resistance value range for the EEE, usage conditions such as uses in which power is applied in a general high-temperature / high-humidity environment or uses where pulse overloads are applied such as in switching power supplies which are widely used in EEE.

If the large resistance value variations described above occur over time or in sudden outbreaks in chip resistors that are used in many types of electrical devices and in circuits of all types of EEE, various types of failure will occur.

For example, for LED current control applications, if the resistance value decreases, the current will proportionally increase, so that the service life of the LED will be reduced. Conversely, if the resistance value increases and the current decreases, the LED illumination may become dark.

For motor current detection applications, if the resistance value decreases, the applied current would be underestimated so that the control device that receives the information then tries to send an excessive current to the motor, resulting in heat damage to the motor or complete failure. Conversely, if the resistance value increases the current will be overestimated and the current flow that the control device supplies to the motor is suppressed and the motor may not work at all.

For applications when a bias (voltage or current) is applied to a transistor, if the resistance value increases the prescribed current may not flow through the transistor and the circuit may not operate.

For applications of voltage division ratio determination of input voltages to ICs or amplification ratio determination, if the resistance value varies and the voltage ratio or the amplification ratio varies, it may cause the IC to malfunction or stop operating.

As described above, the performance of many types of EEE may be deteriorated over time or suddenly, resulting in a decrease in service life, malfunction and stoppage, and consequently, it will be impossible to ensure reliability of the equipment to withstand market usage conditions. In order to avoid these problems, it would be necessary to take complete moisture prevention measures for the EEE (e.g. hermetic sealing) to compensate for the degraded moisture resistance characteristics of the resistance element material and to increase the size of chip resistors and devices to compensate for mechanical strength during overload heating. However, it is practically impossible to implement these measures for (trans)portable equipment due to the increase in size and complexity of the EEE. One reason why hermetic sealing is not possible is in circuits where air cooling is needed to prevent overheating of circuits that generate heat. Moreover, this will also bring about an increase in the consumption amount of energy and resources at each stage of production, use and disposal, resulting into a significant increase of environmental load.

**Case 3**

A typical example of lead-free piezoelectric ceramics is $(K,Na)NbO_3$ (KNN) ceramics, composed of potassium and sodium niobates. Many of the papers mentioned in the previous section have also described lead-free piezoelectric ceramics of this composition type, and industry has conducted research and development several times that of the publicly known papers in its attempts to develop lead-free piezoelectric actuators, piezoelectric buzzers, etc.

However, currently available $(K, Na)NbO_3$ lead-free piezoelectric ceramics have the following disadvantages compared to PZT that do not enable the achievement of lead-free E&E components in practice at present:

- Low piezoelectric performance (piezoelectric constant), so in order to achieve equivalent electrical performance it is necessary to increase the element size several times.

- Inferior thermal properties, so operating condition temperatures must be lowered in order to achieve the required electrical functions.

- Inferior fatigue properties and mechanical strength, resulting in the reduction of the present service life of the product being reduced within a range from several tens to several hundreds of times.

Assuming that E&E components such as piezoelectric actuators and piezoelectric buzzers are produced from materials with these disadvantages and applied to EEE, it would be necessary to significantly increase the size of the components, add cooling mechanisms, etc. to make them applicable in practice, which would cause the increase in the size of the equipment (not possible for most portable products).

Furthermore, core modules of the equipment as well as the equipment main body itself, which currently operate for more than 10 years, is likely to need to be disposed or replaced within a few months of operation due to the decrease in the E&E components reliability. This is directly linked to massive consumption of energy and resources and is contrary to the EU’s intention to move towards material efficiency and circular economy.

The sintering reaction of $(K, Na) NbO_3$ ceramics is more difficult to progress when compared to PZT, as alkali metal elements (K, Na) have high volatilization (higher vapour pressure) and produce alkali metal vapours during the firing process making it difficult to control the firing atmosphere. This is described in a publication on the preparation, characterisation, and electrical properties of $(K_{0.5}Na_{0.5})NbO_3$ lead-free piezoelectric ceramics[5].

For this reason, firing stability is not possible, and the process yield cannot be ensured as material with an incorrect composition cannot be used.

So, when trying mass production in order to meet the demand for piezoelectric ceramics, a large amount of by-product waste is generated, causing an increase in environmental load due to the massive consumption of energy and resources.

In addition, as it is described later, niobium also presents resource supply risks.

**Case 4**

Transducers used in ultrasonic sensor applications in which devices emit and receive ultrasonic waves are another typical example of the present use of PZT piezoelectric devices.

Ultrasonic sensors are indispensable devices to modern society, used in a variety of applications such as distance measurement to objects, crack detection in concrete and metal, detection of foreign bodies inside food as well as every type of life-saving medical diagnosis.

In view of this variety of applications it is necessary that they can be utilized in broad operating ranges. In order to meet such social demands, PZT devices with outstanding piezoelectric performance, heat resistance and durability characteristics must be applied for transducers in ultrasonic applications.

Industry has attempted the research and development of (Na, Bi, Ba)$TiO_3$-type ceramic materials as lead-free alternatives for transducers used in ultrasonic sensor applications. However, compared with PZT devices, the currently available (Na, Bi, Ba)$TiO_3$-type ceramic materials show the following disadvantages, which preclude their application in practice.

- Inferior piezoelectric performance: in order to deliver equivalent electrical performance the size of the device must be increased several times.
- Low depolarization temperature: in order to ensure the functionality of the device, operation temperatures must be lowered. However, even at lower operation temperature conditions, depolarization progresses along with temperature changes that occur during operation so that the service life of the product is largely reduced when compared with the current lead-based materials.

Objectively speaking, if the above lead-free substitute is used, the piezoelectric device will inevitably have to be increased in size in order to achieve the same piezoelectric characteristics as the existing product. This leads to the increase in the size of the

[5] Preparation, characterisation, and electrical properties of (K0.5Na0.5)NbO3 lead-free piezoelectric ceramics, Journal of Electroceramics, May 2014, Volume 32, Issue 2–3, pp 255–259, abstract downloaded from https://link.springer.com/article/10.1007/s10832-013-9883-z

ultrasonic sensor itself, and, as an example, image resolution of equipment in the medical field would be very significantly and unacceptably degraded. Insertion of the product into the body might become impossible in some cases and high precision examination as performed until now might become impracticable. Precision is also important in most other uses, such as crack detection and foreign body detection, so inferior performance is also unacceptable for these applications.

Moreover, since reliability and durability of the piezoelectric elements would be degraded, problems concerning short-term replacement of components or device failures might occur, causing significant decrease in the service life of the equipment itself. As this directly results into massive consumption of energy and resources as well as into the increase of waste amounts, it is contrary to the EU's intention to move towards material efficiency and circular economy.

Additionally, likewise to the case of (K, Na) $NbO_3$ type ceramics, mass production under stable process control conditions becomes difficult since alkali metals easily vaporize during the firing process of ceramics.

**Case 5**

PTC (Positive Temperature Coefficient) thermistors make use of semiconductor ceramics having the property that their electrical resistance increases as temperature rises.

PTC thermistors have the electrical function of a rapid increase of their resistive values when a certain temperature is exceeded, and they are used for temperature/current control and protection of circuits from abnormal heating and overcurrent.

In PTC thermistors, materials become semiconductive by the addition of rare earth elements, etc. to barium titanate, however in order to ensure the thermal characteristics and resistive value stability it is necessary to add lead.

In order to achieve lead-free semiconductor ceramics for PTC thermistors, industry conducted research and development activities of materials using alkali metals, alkali earth metals and bismuth as additive elements in substitution of lead.

Nevertheless, it was clarified through this research that, for this type of additive element composition, under actual operation conditions part of the alkali metals will precipitate in the crystal grain boundary over time and electrical resistance will vary, and with that long-term stability of the electrical functions cannot be attained and reliability cannot be ensured.

Service life of the E&E components whose material was substituted by these lead-free ones is reduced to about one tenth of the original lifespan.

Since PTC thermistors are used for temperature control and circuit protection of large-sized equipment that use high electrical current, substitution to lead-free material will drastically reduce the service life of the equipment and may cause failures if they do not provide the intended protection when needed.

Supposing that lead-free semiconductor ceramics, lacking long-term stability, is applied to EEE (expected to operate continually for around 10 years with the present technology), desired temperature/current control and circuit protection as set in the equipment specification becomes unattainable in about one year and life service is largely reduced.

Reduction of the service life of large-sized equipment is directly related with the increase of mass consumption of resources and waste amounts, which is contrary to the EU's intention to move towards material efficiency and circular economy.

In addition, examples collected by industry concerning research on substitution to lead-free materials are shown in the Appendix I. Based on these examples of substitution research and their results, industry has concluded that lead-free materials have not achieved a level to comprehensively substitute the lead-containing materials in the range of applications that rely on exemption 7(c)-I.

It is not currently possible for device manufacturer businesses to obtain E&E components using lead-free materials that have sufficient functionality, good reliability and are environmental friendly. This is also discussed in MRS Bulletin.[6]

*"For all but the simplest devices, the replacement exercise would demand a complete redesign of the device and associated electronics, involving both modeling and experimental iterations, and requiring amendments to manufacturing processes. For a relatively simple device, a conservative estimate of the effort to redesign around a new piezoelectric material is one to two person-years, whereas for more complex devices, the redesign process may employ tens of person-years of effort and expense. The cost of developing the current "world catalog" of PZT-based devices has been spread over the last 60 years. Lifting the RoHS exemption on piezoceramics would mean that the PZT replacement costs would need to be swallowed by industry and their customers over a relatively short time scale. Despite the progress made over the last 20 years in piezoelectric materials research, the industry is not much closer to the goal of eliminating lead now than it was 20 years ago. Even if industry accepted the materials that have been proposed to date, the effort required to convert the whole device industry to lead-free would be many times that already spent on materials research."*

Industry considers that the content above can be said not only of piezoelectric ceramics: it is common to almost all businesses of devices that incorporate E&E components containing lead in glass or ceramics in the range of 7(c)-I. Moreover, as demonstrated by the above illustrative cases and in Appendix I, since lead-free materials generally have insufficient performance or unsuitable properties when compared with lead-containing materials, it is difficult to ensure reliability data for the devices that use them. Also, there is a high risk that the negative impact caused by substitute materials to the environment, health and safety of consumers may exceed

[6] MRS Bulleting 43 (8). pp. 581-587, A. J. Bell and O. Deubzer.

the overall benefits brought to the environment, health and safety of consumers of not using lead.

Required properties of EEE that are brought up by the use of lead-containing materials are described next.

**Specific Properties of Lead in Glass or Glass Matrix Compounds**

Glass is a non-crystalline (amorphous) solid obtained when viscosity increases by the supercooling of a liquid. A glass combines properties that are different from those of common crystalline substances.

Lead-containing glass is used in EEE with the purpose to electrically/physically form, preserve and protect E&E components and is an indispensable constituent material of EEE.

“Binding/adhesion”, “weather resistance/corrosion resistance”, “breakdown voltage” and “mechanical strength” can be mentioned as representative properties required of lead-containing glass in E&E components.

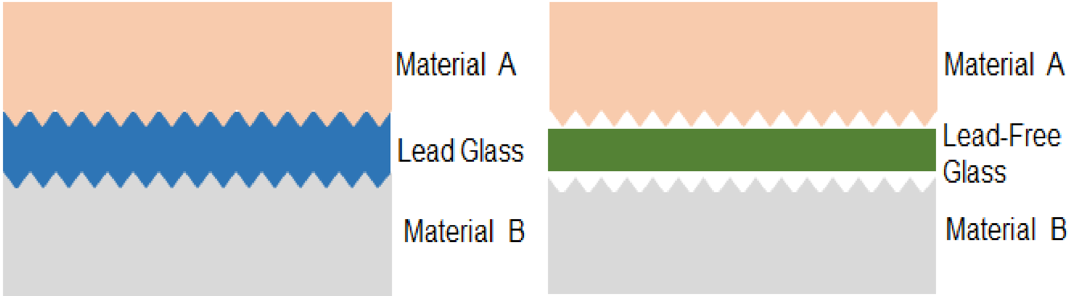
These various properties are comprehensively used and the glass is combined with materials such as metals and ceramics to form E&E devices of EEE.

Glass-constituting elements such as phosphorus, calcium, zinc, niobium, ruthenium, bismuth, etc. have been investigated as substitutes for lead, however lead-free glass in which lead was substituted by these elements could not achieve the intended properties of lead-containing glass in E&E components. As these properties are commonly required for all types of EEE, lead-containing glass is required for almost all EEE and currently substitution of lead is impossible.

**Binding/Adhesion**

Lead-containing glass has excellent wettability (affinity) with metals and ceramics, and can improve binding/adhesion in bonds between the different materials that constitute E&E components.

This schematic diagram shows images at a microscopic scale of typical examples of glass and material bonds often used in electrical and electronic components.




| | | | | |
|---|---|---|---|---|
| Material A | Ceramics | Ceramics | Metal | Glass |
| Material B | Ceramics | Metal | Metal | Ceramics |

*The above table is illustrative and not exhaustive.

In contrast, lead-free glass has poor wettability (affinity) with metals and ceramics, and binding/adhesion in bonds between the materials that constitute E&E components deteriorate.

This can cause breakdown between the bond parts of the materials that constitute E&E components incorporated in EEE if changes occur in the usage environment that they are placed or under long-term use and this may lead to quality problems.

For example, EEE used in outdoor environments is subjected to heating-cooling cycling depending on the operational environment conditions.

In order to protect E&E components of EEE from this temperature cycling, lead-containing glass that has excellent binding/adhesion is used for the bonds between different materials, improving resistance and reliability of the components.

If this glass is substituted by a lead-free glass, the heating-cooling cycling can cause cracks and delamination in the bond due to stress generated by the difference in thermal expansion coefficients between the different materials resulting in failure of the equipment due to breakdown of the E&E components.

If a short circuit happens in the E&E circuit in such a situation it may cause an electrical fire.

Lead-containing glass having excellent binding/adhesion is also used for bonding different materials in E&E components subject to vibration or sliding during operation since large stresses are applied. If, on the other hand, that glass is substituted by lead-free glass, stress accumulates over normal conditions of use, causing breakdowns in the bond and EEE incorporating those components lose their functionality over a short period of time.

As seen above, if electronic components that use lead-free glass are utilized in applications that require the binding/adhesion properties of lead-containing glass, reliability will be deficient and sufficient service life of the product will not be ensured. Thus, product design applicable in practice is not possible under the current realm of knowledge of E&E device businesses.

**Weather Resistance/Corrosion Resistance**

Lead-containing glass has excellent chemical stability and is not easily degraded even when exposed to moisture or acidity from the environment (e.g. high humidity, rain etc.). It has good weather resistance/corrosion resistance, such as good moisture and acid resistance and possesses indispensable properties for the reliability of EEE used in a broad range of environments. In contrast, lead-free glass has low chemical stability when compared with lead-containing glass, showing inferior weather resistance/corrosion resistance, such as moisture and acid resistance characteristics.

Household EEE used in kitchens, bathrooms, etc. use large amounts of water in their periphery during operation, so they must necessarily be resistant to high humidity operating conditions. In addition, EEE exposed to outdoor weather, including acid rain, as well as industrial EEE used in harsh weather or factory conditions must withstand highly reactive atmospheres such as high humidity and acidity. If glass used in the E&E components of this EEE is substituted by lead-free glass, long-term stability under humid or highly-reactive atmospheres will not be preserved, E&E components will deteriorate or break down and the EEE will lose its functionality.

Thus, lead-free product design applicable in practice is not possible under the current knowledge of EEE businesses.

**Breakdown Voltage**

Due to its high chemical stability, lead-containing glass is less susceptible to dielectric breakdowns even if high electric loads are applied and has excellent breakdown voltage characteristics.

In contrast, lead-free glass has inferior voltage breakdown characteristics when compared with lead-containing glass. Therefore, if glass used in E&E components which are subjected to high voltage is substituted to lead-free glass, the glass in the E&E components will suffer dielectric breakdown, functions required for the E&E component will be lost and in the worst case short circuits in the E&E circuits may occur as a result of that dielectric breakdown.

For example, lead-containing glass is used for power supply devices to withstand high input/output voltages.

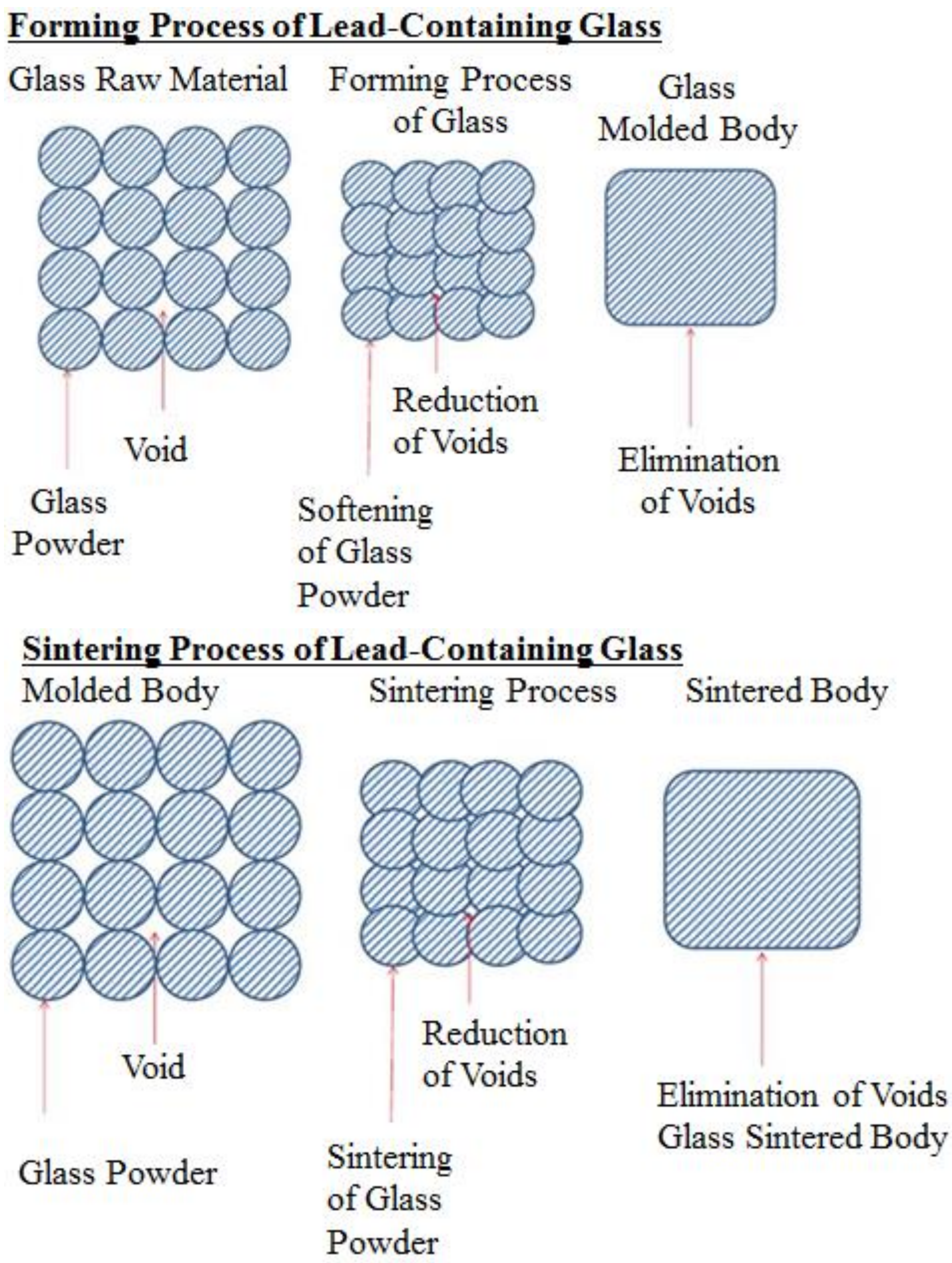
When substituted by lead-free glass, the power supply device cannot withstand high voltages, the supply voltages cannot be maintained, and the EEE will not operate normally.

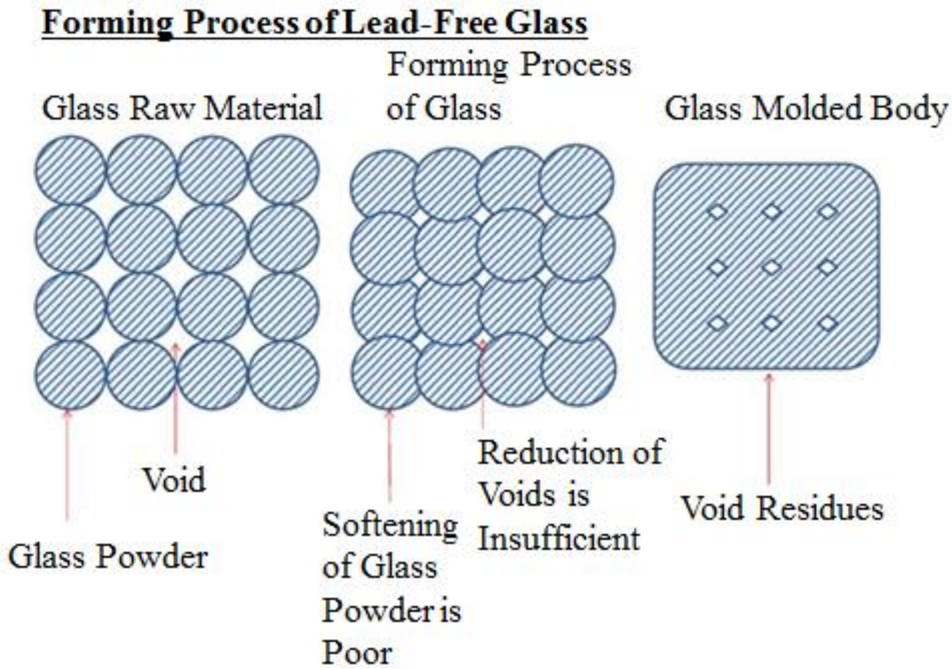
Thus, lead-free product design applicable in practice is not possible under the current knowledge of EEE businesses.

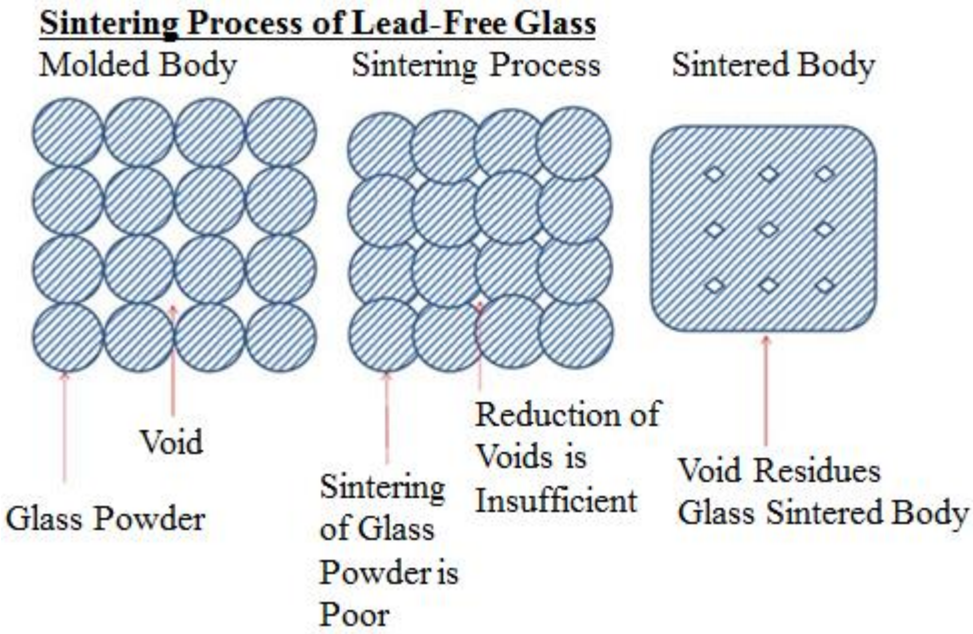
**Mechanical Strength**

Since lead-containing glass has relatively small thermal expansion coefficients while keeping chemical stability, it has excellent crack resistance characteristics. In addition, voids are difficult to form within the component elements during manufacturing process, so it can keep its high mechanical strength.

In contrast, lead-free glass is more susceptible to the occurrence of cracks than lead-containing glass and has many remaining internal voids from the formation processes that result in insufficient mechanical strength.






*It should be noted that voids may not be round (round holes may reduce cracking tendency, but real voids can be in any shape and do promote cracks.)

If the mechanical strength of a glass used to form or protect E&E components is insufficient, it will be easier for that glass to break down in usages at high or low temperatures, by thermal shock caused by rapid temperature changes, vibration or shock (collision or being dropped), etc.

For example, if glasses of EEE with parts exposed to processes such as heating/cooling, etc. (e.g. temperature sensors, pressure valves, etc.) or glasses of E&E components for EEE used outdoors in various temperature conditions are substituted by lead-free glasses with insufficient mechanical strength, it becomes easier for the glass to break down due to thermal shock, which will cause deterioration of the equipments' reliability.

Hand-held EEE that is assumed to be dropped by the user, may be subjected to a strong physical impact due to falling onto hard surfaces.

If the E&E components of this hand-held EEE are substituted by E&E components using lead-free glass which have poor mechanical strength, the EEE is prone to fail even by slight drop accidents.

Also, for EEE subjected to strong heating or vibration during normal operation, insufficient mechanical strength of E&E components is directly connected to equipment failure and loss of functionality in the course of operation, thus the use of lead-containing glass which has high mechanical strength is indispensable for the formation and protection of the components.

Since such EEE has functions and outputs that can cause serious injury to humans, there are many cases in which safety devices are installed inside EEE, however if the E&E components incorporated in those safety devices malfunction, this can impair the safety of the EEE itself.

Consequently, substitution to lead-free glass with insufficient mechanical strength is not a realistic option.

In EEE that requires large current/high voltage for start-up strong stress is applied due to thermal shock derived from the Joule heat generated at the start-up which may cause damage upon repeated use of the equipment.

For this reason, a glass coating is applied for protection to the parts of the E&E components that are subjected to strong thermal shock, and lead-containing glass, having mechanical strength to withstand the thermal shock is used for that purpose.

If this glass is substituted by lead-free glass, the required mechanical strength to withstand thermal shock cannot be ensured, and cracks will occur due to thermal shock over repeated use, making it impossible to protect the E&E components. This type of EEE will fail or lose its functionality in a short period of time.

As seen above, the mechanical strength of lead-containing glass is essential for E&E components used in various parts of EEE. Therefore, with the currently available technology and knowledge it is not possible to design practical EEE with E&E components using lead-free glass.

In other words, it is impossible to design practical EEE by comprehensively eliminating lead from glass and/or glass matrix compounds of E&E components incorporated in EEE and there is no technical prospect for achieving that presently.

**<u>Specific Properties of Lead in Ceramics or Ceramic Matrix Compounds</u>**

As explained in our previous renewal request, lead-containing electronic ceramics constituted by oxides of tetravalent cations of Group 4 elements (elements corresponding to the 4th column of the periodic table such as Ti, Zr, etc. which have the characteristics of easily becoming tetravalent or divalent cations) and divalent cations of lead (Pb) can be formed with particular crystal structures such as the perovskite structure, etc. over a broad range of use conditions.

Lead-containing electronic ceramics not only stabilize electrical functions (dielectric properties, piezoelectric properties, pyroelectric properties, ferroelectric properties, semiconductor properties, magnetic properties, etc.) achieving outstanding characteristics with high efficiency, they are also used as important additive constituents to control and expand the applicable usage condition range (temperature, voltage) of other ceramics.

As lead-containing electronic ceramics can be sintered to reach high density over a broad range of firing conditions, E&E components obtained by the sintering process have high electrical and mechanical durability.

In short, lead-containing electronic ceramics have properties such as “thermal properties”, “low energy loss properties”, and “fatigue resistance/mechanical strength properties” (referred to as “intended properties” altogether in this document) which are essential to the normal operation of EEE with high reliability in the various types of use conditions. In addition, the properties of these lead-containing electronic ceramics can contribute to energy saving and effective use of resources along the entire life-cycle of the product.

Looking at it from another perspective, the properties of electronic ceramics strongly depend on the crystal structure and its distortion, and the crystal structure is determined by the presence of lead. In other words, since properties such as valence and ionic radius are different for elements other than lead, the crystal structure and distortion obtained are also different and the required properties for EEE cannot be intentionally achieved.

So far, EEE industry has investigated various elements and compositions of lead-free electronic ceramic materials, but only a tiny amount of materials that satisfy some of the required properties has been obtained at laboratory level.

These properties are necessary to all EEE, and in almost all of the cases several of these properties are required simultaneously for correct function and operation. As it has just been demonstrated above, lead-containing electronic ceramics are indispensable for almost all EEE and at present their substitution is impossible.

The “intended properties” introduced in this section will be explained in details below.

In addition, industry’s attempts to achieve both the properties necessary for ensuring electrical functionality of the EEE as well as the “intended properties” described below are presented in detail in the section “Illustrative Cases of Lead-Free Substitution Research by Industry in the Scope of 7(c)-I” above.

## Description of “Intended Properties”

### Thermal Properties

With the high sophistication of functionality and expansion of the range of use of EEE in recent years, E&E components are required to withstand use in temperature conditions of a hundred and several tens of degrees and have stable operation over a broad range of temperature conditions.

In response to such demands, lead-containing electronic ceramics can achieve excellent electrical functions over a broad temperature range. Lead-containing materials are the only electronic ceramics found so far that can achieve both such stable thermal properties and excellent electrical functions.

Electronic ceramics lose their electrical functions above a certain temperature (Curie temperature), however lead-containing electronic ceramics have high Curie temperatures and can perform at high temperatures.

In electronic ceramics using substitute lead-free materials, electrical functions and properties vary greatly with temperature changes. For example, it has been reported that (K, Na) $NbO_3$-type ceramics composed of potassium, sodium and niobium can be used to achieve electrical functions [7] (and (Bi, Na, K) $TiO_3$-based ceramics composed of potassium, sodium and bismuth can be used to achieve electrical functions at high temperatures [8] , but in all of these cases, product design is impossible due to large electrical function variations that occur with temperature changes.

Specific examples of EEE are shown below:

As EEE used in social infrastructure applications[*9]require high accuracy and reliability, the required functionality can be stably achieved regardless of the operational condition temperatures and their changes by the use of E&E components having lead-containing electronic ceramics.

In contrast, functionality of lead-free electronic ceramics will become unstable with changes in operational temperature conditions.

There are also cases when some E&E components for social infrastructure applications will require large power outputs and the temperature of the operating part will rise up to 150°C or above due to Joule heat during operation.

When lead-free electronic ceramics are used, the output becomes unstable, and in the worst case, electrical functions will be lost due to temperatures exceeding the Curie temperature.

For this reason, when E&E components with lead-free electronic ceramics are used, product design of EEE for social infrastructure applications cannot be achieved, at least with the current technology and knowledge by industry, in face of the problems presented above.

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[7] J. Am. Ceram. Soc., Vol. 96, pp 3677-3696 (2013) and Acta Materialia, Vol122, pp344-351 (2017)

[8] Ceramics International, Volume 44, Issue 7, pp7378-7383 (2018)

[9] EEE for social infrastructure: medical equipment (equipment used for medical practice such as clinical, diagnostic, inspection, analysis, monitoring, etc.) and industrial and other types of monitoring, control, analysis and measurement equipment corresponding to categories 8 &9, information telecommunication equipment and IT equipment that supports information infrastructures, power receiving and transmission equipment that supports energy infrastructures, and security and disaster prevention equipment that supports security and safety infrastructures.

Since portable EEE is used within a broad range of environmental conditions, it must be able to maintain stable performance from the low-temperature conditions when the equipment is started up to the internal temperature of the equipment during normal operation (generally 100°C or higher inside some components). Portable EEE with substitution to lead-free electronic ceramics cannot have stable performance because its electrical function varies greatly depending on the temperature conditions of the usage environment. Therefore, it is impossible to design lead-free portable EEE maintaining the current size.

EEE with imaging functions that have undergone rapid progress towards downsizing and high-functionality in recent years need to incorporate functions that operate with high outputs and high accuracy in a limited space, so E&E components using lead-containing electronic ceramics are applied. As these functions are based on the premise of stability of the lead-containing electronic ceramics against changes in the operational conditions, in case of substitution to lead-free electronic ceramics, either the E&E component will not operate or the substitution will lead to increased power consumption or reduced speed due to performance deficiency. Therefore, achievement of imaging equipment with downsizing and/or high functionality will not be possible.

**Low Energy Loss Properties**

By using lead-containing electronic ceramics in E&E components, energy loss can be suppressed when high voltage and/or high frequency is applied. By comparison, if lead-free electronic ceramics is used, heat generation due to energy loss is high when high voltage and/or high frequency is applied, the EEE becomes unstable because of the heat and in the worst case it will malfunction.

For this reason, substitution to lead-free electronic ceramics is impossible for devices where high voltage and/or high frequency are applied.

In a rectification / detection module of a high-frequency signal device incorporated in communication / broadcasting equipment using a high frequency band, the signal is attenuated and cannot be correctly transmitted if the electrical energy loss is large. Hence, it is common to suppress energy loss by using E&E components with lead-containing electronics.

Substituting these E&E components by lead-free electronic ceramics makes it impossible to design communication / broadcasting equipment that can achieve high-speed, high-density communication (high resolution video services with large amounts of data, etc.) using high-frequency bands.

EEE with imaging functions is equipped with a large number of sensor components for detecting the posture and movement of the EEE and accurately correcting the image. These sensor components use high-frequency signals for detection and transmission, and if the loss of electrical energy is large, the signals are attenuated and the sensors no longer correctly detect the posture and movement of the equipment. For this reason, E&E

components using lead-containing electronic ceramics must be incorporated in the equipment.

If such E&E components are substituted by lead-free electronic ceramics, it becomes impossible to design the image correction function.

**Fatigue Resistance/Mechanical Strength**

General EEE is treated as durable consumer goods and is expected to stably function over a long period of time. EEE is generally expected to have a durability of at least one year or more.

Assuming the expected useful life of a certain EEE to be one year, it is said that the installed E&E components must be able to perform their functions for at least 1 million times. Therefore, it is expected that actual E&E components will perform their functions for a further several million times during longer than one year lifetimes.

Lead-containing electronic ceramics have stable crystal structures and can be densely sintered, so that besides keeping the reliability of EEE they have sufficient mechanical strength, and even after going through a few million times of operation, function deterioration is small. Moreover, as the crystal structures are less dependent on temperature changes and electrical energy, mechanical strength remains stable over a broad use-condition range.

In contrast, there are reports of lead-free electronic ceramics, for example (K, Na)$NbO_3$-type ceramics, for which the cycling stability of the electrical functions is deteriorated over long-term use[10].

Furthermore, phase boundaries (i.e. one crystal form can change to another) exist near room temperature, and if these boundaries are crossed change of crystal structure (phase transition) occurs.

The impact of this phase transition on mechanical strength still needs to be clarified and lead-free materials such as (K, Na)$NbO_3$-type ceramics have not reached a practical application level and research has not progressed. When E&E components using such materials undergo large variations in their electrical functions within their useful life, operation of EEE incorporating these components become unstable and reliability cannot be ensured in practice, so currently these products cannot be applicable for practical utilization.

Functional stability to maintain long-term high accuracy and reliability is indispensable to EEE for social infrastructure applications[*3] used in 24-hour continual operation or in applications involving human lives, etc. For this reason, E&E components with lead-containing electronic ceramics are incorporated as the most crucial components.

[10] J. Appl. Phys., Vol.118, p.134102 (2015)

In case of substitution to lead-free electronic ceramics, long-term reliability cannot be ensured and practical product design that fulfils the required specifications cannot be achieved.

As shown in the above examples, if E&E components made of lead-containing electronic ceramics applicable to exemption 7(c)-I are substituted by E&E components that use lead-free electronic ceramics, it will no longer be possible to achieve the properties of electronic ceramics required for the operation of EEE, and since product design will not be possible at least with the existing technology and knowledge, there is no technical perspective at all to comprehensively eliminate lead.

**Reduction of Resource/Energy Consumption in the Product Lifecycle**

Advantages of lead-containing glass and ceramics include not only achieving the properties required for the operation of EEE, but also saving of energy and resources along the entire product lifecycle.

**Saving of Energy in the Production Process**

Lead-containing glasses have a broad “vitrification range”, which makes it easy to lower the melting temperature, and as viscosity (fluidity) changes gradually with temperature, it is easy to produce high-quality products in a stable manner. In contrast to this, in order to lower the melting temperature of lead-free glasses it is necessary to use components with inferior chemical stability. As already explained, it is not realistic to use components with inferior chemical stability from the viewpoint of weather resistance and breakdown voltage.

Similarly, lead-containing electronic ceramics can also be sintered at low temperatures, so that energy required for production can be reduced by decreasing the temperature of the sintering furnace.

While the sintering temperature of lead-free electronic ceramics is generally well above one thousand degrees, lead-containing electronic ceramics can be sintered at around 1000°C. This greatly reduces energy consumption in production, both inside and outside the EU, and contributes to reduction of $CO_2$ emissions on an international level.

A comparison of the production energy of lead-containing electronic ceramics in Europe/ the World and the production energy assuming that they are substituted by lead-free electronic ceramics is shown below.

Total Production Energy Amount EU/World ➔ Conversion to $CO_2$ Emission Amounts

Table1. Comparison of Production Energy when Assuming Substitution to Lead-free Electronic Ceramics

| | Lead/Lead-free Process | Power Consumption Amount/GWh | | |
|---|---|---|---|---|
| | | Per kt | World | Europe |
| Exemption 7(c)-I | Lead-containing ceramics process | 82 | 220 | 48 |
| | Lead-free ceramics process | 96 | 255 | 56 |

Power consumption amounts in the production process (sintering process) were estimated based on the raw material production volume of raw material suppliers in 2018 and the production figures of E&E component manufacturers that use lead-containing electronic ceramic raw materials.

At present there is no technical prospect of comprehensively eliminating lead from E&E components using lead-containing glass or ceramics, so the above table is only a hypothetical estimate.

**Efficient Utilization of Resources**

E&E components using lead-containing electronic ceramics can bring out functions/properties with high efficiency even if they are reduced in size and thickness or if surface mounted; moreover this can be done while achieving both long service life and high reliability. EEE incorporating such E&E components can be easily reduced in size and resources required for manufacturing can be minimised. In addition, since the disposal amount of equipment due to failures caused by E&E components can be reduced, they can greatly contribute to the efficient use of resources.

On the other hand, lead-free substitute materials have low efficiency to bring out functions/properties, so E&E components that are reduced in size and thickness or surface-mounted bring out insufficient functions/properties, and thus material reduction by downsizing of EEE becomes no longer possible. Even if, those insufficient functions/properties can be overcome by technological development, promoting the reduction of size or thickness and surface mounting of E&E components using lead-free substitute materials, as shown in the above section on “Fatigue Resistance/Mechanical Strength”, reliability cannot be ensured, probability and frequency of failures increase and the service life of the E&E component is reduced. If surface mounted components which cannot be reused or individually repaired present failures, the main IC board has to be replaced as a whole, and in the end disposal amounts of EEE will increase.

In recent years, downsizing on the premise of high efficiency to bring out functions/properties by E&E components using lead-containing electronic ceramics has advanced for all types of EEE regardless of whether they are for household and personal or professional use.

In contrast, unreasonable substitution to E&E components using lead-free substitute materials is directly connected to reduction of the service life of the EEE incorporating them, leading to further resource consumption due to the increase of disposal amounts and increasing costs for the entire society.

In addition, as it is possible to reduce the size of production equipment and reduce the required amount of electric power in the production processes of E&E components using lead-containing electronic ceramics, production facilities such as clean rooms, etc. are smaller than those that would be needed for lead-free components (if these could be made with suitable performance) and, as a result, it can significantly contribute to saving of energy and prevention of global warming.

**<u>Supply of Resources</u>**

Lead exists abundantly in the outer layers of the earth's crust as sulfide ores such as galena, etc. Considering that a recycle system centered on lead batteries for automobiles has already been established, the risk of resource depletion is relatively low, and it is possible to procure lead at low cost. In addition, as there is no uneven distribution of resource ores by geographical areas, the risk of supply of resources being disrupted due to political instability in certain countries is low.

In comparison, niobium and bismuth can be mentioned as examples of potential substitute elements for lead-free glass and lead-free electronic ceramics. However, when compared to lead, risks concerning supplies of resources are higher.

The production amount of niobium resources has a strongly uneven distribution with 90% in Brazil and 9% in Canada, so it is classified as a critical raw material by the EU[11].

Since bismuth is obtained as a by-product in the production mainly of lead from ores, substitution to bismuth-type materials does not lead to a reduction in the extraction amounts of lead. Moreover, differently from lead there is no established recycling system, so producing bismuth in amounts just enough for production of E&E components will rather increase the amount of lead extraction and smelting[12].

Also, similarly to niobium, bismuth resources are unevenly distributed between China (75% of the world's reserves), Mexico, Bolivia and Peru, and so it is classified as a critical raw material by the EU.[13]

In the event that the supply of niobium or bismuth is stopped or restricted, it is expected to have a significant impact to the EU industry.

[11] https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_en

[12] http://mric.jogmec.go.jp/public/report/2012-05/34.Bi_20120619.pdf

[13] https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_en

As shown in the cases above, when E&E components using lead-free electronic ceramics are compared with those using lead-containing electronic ceramics, energy and resource consumption during the product lifecycle is large, and the risk of depletion is also significant.

From this perspective, elimination of lead from E&E components incorporated in EEE is not appropriate as it rather increases environmental load than decreases it.

**Conclusion: Necessity of Lead of Exemption 7(c)-I**

Several of the properties of lead-containing glass and ceramics are used simultaneously as indispensable elements of EEE. For this reason, lead in the technical scope of 7(c)-I is used in a wide variety of E&E components in all types of EEE and so it is not possible to specify categories and items of EEE. As shown in the section “Illustrative Cases of Lead-Free Substitution Research by Industry in the Scope of 7(c)-I”, even if industry succeeds in the substitution of a specific E&E component in a device to a lead-free one, the negative impacts of the substitution are estimated to exceed the benefits. That is to say that if the exempted applications in the technical scope of 7(c)-I are revoked it will not be possible to maintain the performance and reliability of all EEE and resource and energy consumption and waste amounts will increase.

Moreover, the negative impact caused to the environment by the elements investigated as candidates for substitution, niobium and bismuth, have high possibility to exceed the benefits brought by the substitution of lead.

According to what has been described above, lead of exemption 7(c)-I is indispensable to product design of EEE, and its elimination or substitution is not scientifically and/or technically feasible, and there is no actual perspective to realize it at least until the next review.

## 5. Information on Possible preparation for reuse or recycling of waste from EEE and on provisions for appropriate treatment of waste

**1) Please indicate if a closed loop system exist for EEE waste of application exists and provide information of its characteristics (method of collection to ensure closed loop, method of treatment, etc.)**

Components in the scope of 7c-I exemption are incorporated into EEEs and at the end of life, such WEEEs are collected and treated according to the WEEE directive. In general there is no closed loop system exclusively for such components, due to the very large variety of final applications, just in some cases on customer basis related to specific sectors.

**2) Please indicate where relevant:**

☒ Article is collected and sent without dismantling for recycling
☒ Article is collected and completely refurbished for reuse:
☒ Article is collected and dismantled:
 ☐ The following parts are refurbished for use as spare parts: _____
 ☐ The following parts are subsequently recycled: _____
☒ Article cannot be recycled and is therefore:
 ☒ Sent for energy return
 ☒ Landfilled

Note: In general, electrical and electronic equipment using components in the scope of the 7c-I exemption is not separately collected or recycled from other types of electrical and electronic equipment and so recycled using the same procedures as other WEEE.

**3) Please provide information concerning the amount (weight) of RoHS substance present in EEE waste accumulates per annum:**

☐ In articles which are refurbished _____
☐ In articles which are recycled: _____
☐ In articles which are sent for energy return _____
☐ In articles which are landfilled _____

Note:

EU industry complies with all applicable waste legislation.

The industry refurbishes EEE where this is practical, recycles materials where possible and uses landfill only as a last resort. No data is available on the quantities of components in the scope of the 7(c)-I exemption separately from all EEE, which are refurbished, recycled or landfilled.

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## 6. Analysis of possible alternative substances

**(A) Please provide information if possible alternative applications or alternatives for use of RoHS substances in application exist. Please elaborate analysis on a life-cycle basis, including where available information about independent research, peer-review studies development activities undertaken**

In addition to the lead zirconate titanate (PZT), there are 2 prominent lead-free piezo materials: Potassium Sodium Niobate (KNN) and Bismuth Sodium Titanate (BNT) / Sodium Bismuth Titanate (NBT).

Since the last exemption renewal request submitted in 2015, an independently researched Life Cycle Assessment (LCA) of lead-free piezoelectrics has been published by Ibn-Mohammed et

al. from the University of Sheffield [4], as part of the research programme Substitution and Sustainability in Functional Materials and Devices.
With the help of this LCA, the theses about the environmental compatibility of lead-free alternatives can be supported with reliable information. It is important to keep in mind that in the LCA, due to the lack of established industrial-scale processes, the production of lead-free alternatives on a laboratory scale was compared with mass production in the PZT. Thus, the process steps are compared in general, but not comparable to a real production.

This lifecycle assessment considers PZT ceramics for piezoelectric and pyroelectric materials which are typical examples of glasses or ceramics other than dielectric ceramics of capacitors, or glass or ceramic matrix compounds.

Impact of LCA results
Assessing the sustainability of a material is a complex issue as it overlaps with different and sometimes competing factors such as energy consumption, financial costs, environmental impact, health and safety, strategic applications and the impact of national authorities on regulations

***Especially for KNN:*** There is no evidence that niobium and its oxides cause harm, but the environmental impact of extraction and utilization is extremely high for all indicators. Harmful impacts occur before the use phase. After extraction, refining and manufacture, no problems occur in the use phase.

***Especially for BNT / NBT:*** Bismuth (Bi) is a by-product of Pb refining (2-3%). The impact of Bi extraction without the Pb refining process is not reflected in all existing balances.
For Bi there is currently no reliable recycling process.

***Especially for PZT:*** Lead and its oxide are classified as being hazardous. Negative environmental impacts occur during the production and disposal phases, but it is well known that this has been steadily minimized in recent years by industry and manufacturers.

As indicated in the exemption renewal request submitted in 2015, possible elements for PZT substitutes are: niobium, tantalum, antimony, lithium and rare earths.
Last but not least, note that niobium is contained in coltan and this is a conflict mineral (as it also contains tantalum).

The environmental impact of Pb in ceramics is low because the water solubility of lead in ceramics and thus the leakage into the environment are extremely low.
Tsurumi has also concluded that PZT ceramics are not harmful to health and the environment, and that the amount of lead elution can be controlled by modifying the PZT composition. **[5]**

For a life cycle analysis (LCA), detailed information on the relevant material and energy flows is taken into account. For the sake of brevity, only main components and environmental indicators will be shown. The following 5 environmental indicators are finally evaluated:

- greenhouse gas emissions (GHG emission),
- material use,
- land use,
- toxicity (5 variants),
- pollution.

For details see Figure 1.

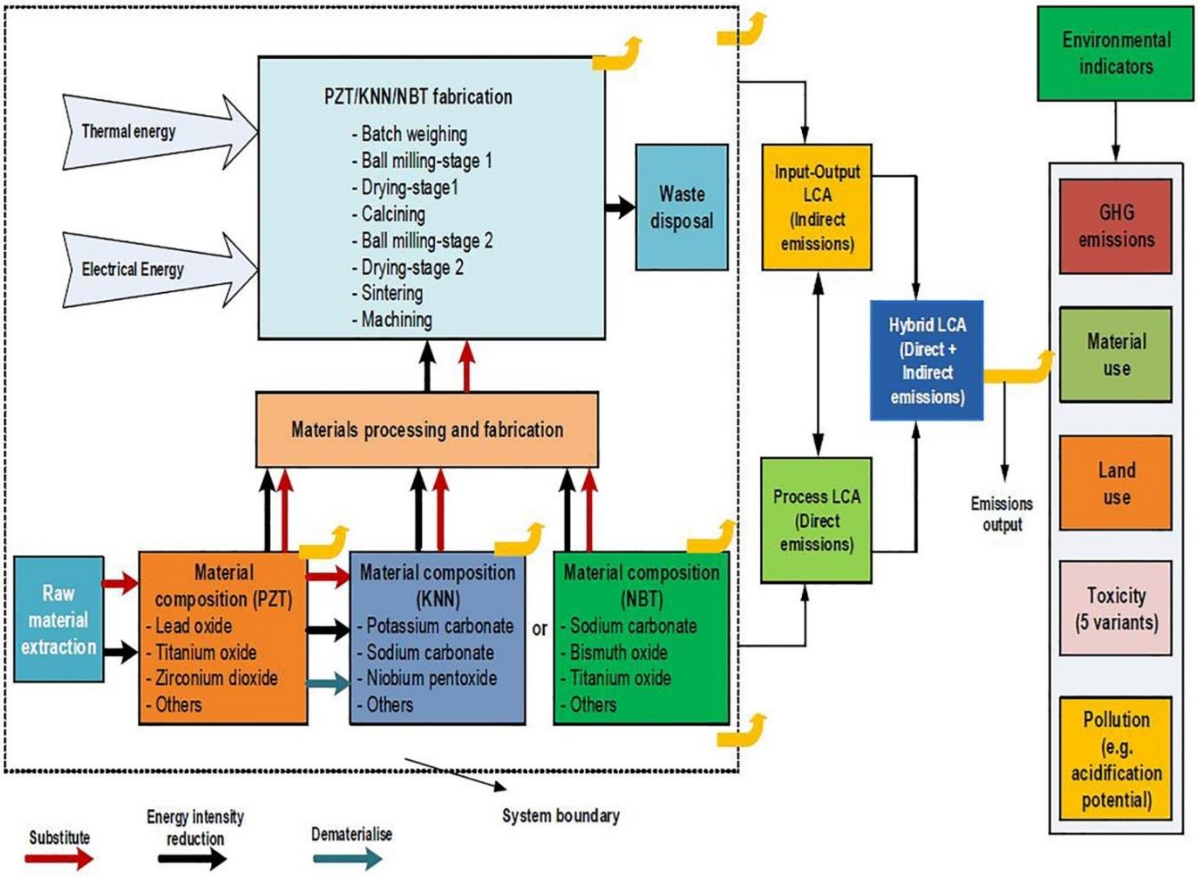



Figure 1 Process-based LCA modelling **[4]**

For the manufacturing path of the lead-free piezoelectric material typical laboratory related times and temperatures are given for comparison. However, it can be assumed that it will be modified for production by different manufacturers.

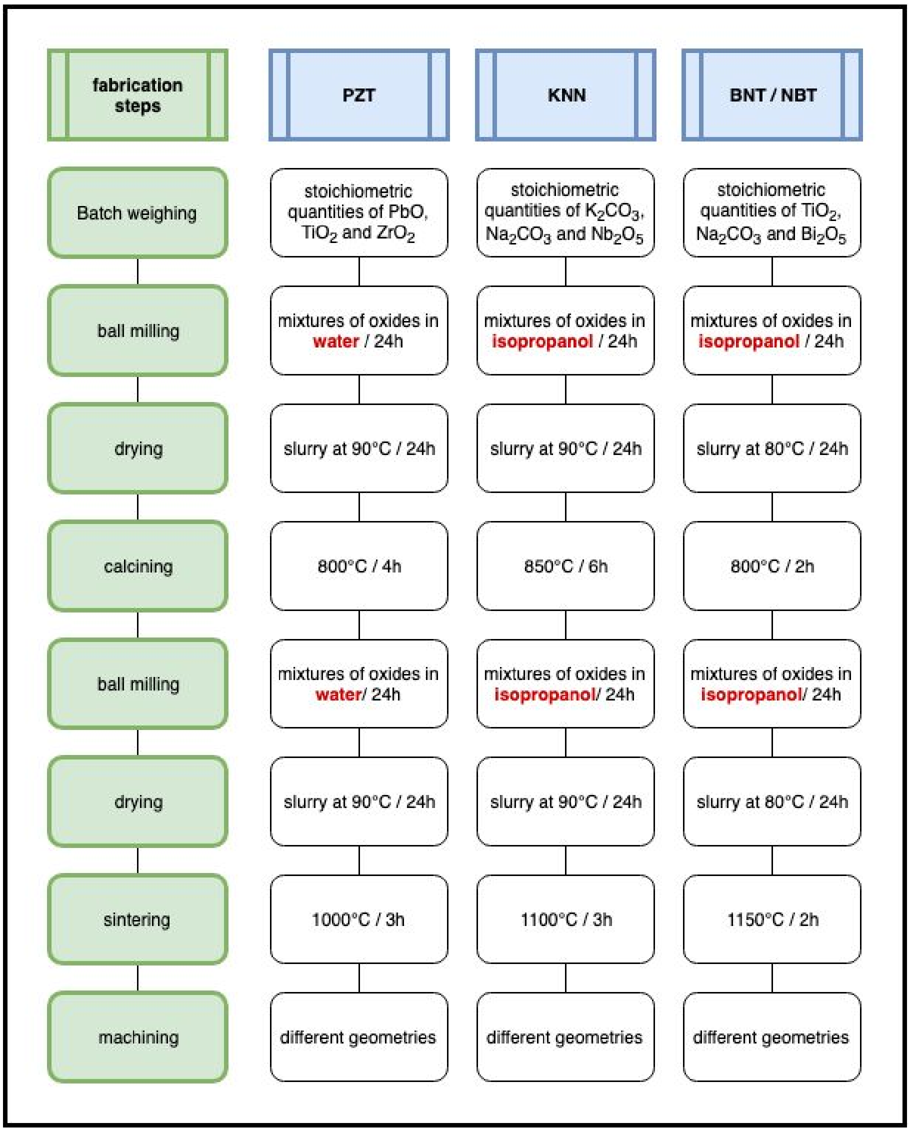



Figure 2 Comparison of the production steps of BNT / NBT **[4]**, PZT and KNN piezoelectric materials **[3]** in accordance with those in the existing literature. In the literature, isopropanol was also specified for PZT as a medium for ball milling, this does not correspond in series production to reality. It is used for ball milling water.

When comparing the manufacturing steps, it quickly becomes clear that all three materials are produced in the same process. In detail, the manufacturing processes differ in temperatures and times. It should be noted once again that a laboratory-scale production for KNN and NBT / BNT is compared with a series production for PZT.
For the production process described in the literature, the PZT ball milling step is an industrial standard using water and thus no explosion protection is necessary, unlike the lead-free materials which use flammable isopropanol. Due to this fact, the process step of producing slurry is much more environmentally friendly and less hazardous to health than the lead-free materials as shown in figure 2. Moreover, substitution materials are most challenging in terms of synthesis due to the use of organic solvents with an impact on production safety and because the PZT raw materials are not water soluble.

The safe mass production of PZT materials based on conventional ceramic processes, including water based mixing and milling processes as well as a sintering in normal atmosphere, is well established. In contrast, for BNT based materials as well as for KNN based materials new processes must be developed to bring out the properties obtained in the laboratory to mass production. All process steps starting with the highly hygroscopic raw materials up to the final machining of the piezo ceramic elements must be considered.

**Primary energy consumption**

The primary energy consumption takes into account the electrical and thermal energy consumption and material used per material composition (i.e., cumulative energy demand) for the manufacture of the ceramic from raw materials. It does not include the energy consumption from activities related to raw material production (e.g. mining, extraction, purification …). At this point the note that the LCA on the one hand compares the production basing on isopropanol instead of water for PZT and the other laboratory scale with series production.

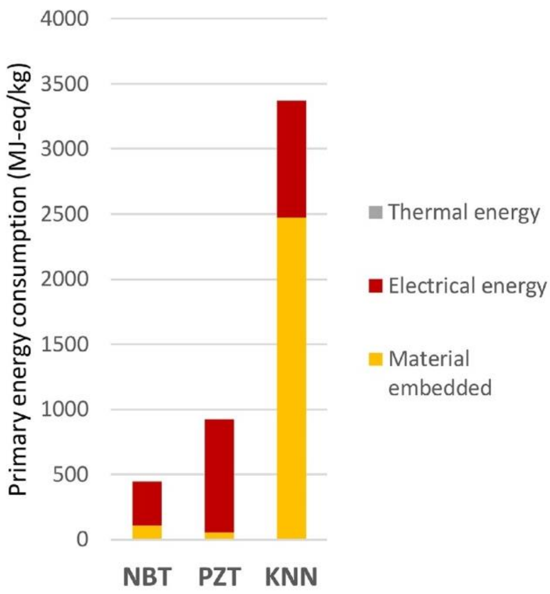



Figure 3 Comparison of overall environmental profile of lead-based (PZT) and lead-free (KNN and NBT) piezoelectric functional ceramics - Primary energy demand **[4]**

As shown in Figure 3, "*NBT is responsible for the least primary energy consumption in comparison to PZT and KNN. This pertains to the fact that NBT's specific heat capacity (~101 J/kg K) is notably lower than that of PZT (350 J/kg K) and KNN (420 J/kg K). This drives down NBT's primary energy demand as it consumes lower thermal energy and by extension electrical energy, during the heating cycles involved in its fabrication. As such, its environmental impact at the fabrication stage is therefore lower, although the impact of materials embedded in Bi2O3 (74.56 MJ-eq) within NBT is higher than that of PbO (32.07 MJ-eq) within PZT.*" **[4]**

**Eco indicator 99**

The Eco-Indicator 99 is a methodology for the damage-oriented impact assessment of environmental influences over the entire life cycle (cradle-to-grave) of a product. The Eco-Indicator 99 expresses the environmental relevance of a product or system in a score in the form of an aggregated measure. The smaller the key figure, the more environmentally friendly the product or the product component can be considered. The Eco-Indicator 99 meets the requirements of the ISO-14042 standard.

The damage (negative impact) is assessed in three impact categories: Ecosystem Quality, Human Health and Resources. In each category, a main impact measurement is used, which is then normalized to be comparable with the others, adding up to the final score.
Human Health: The impact on human health is modelled by the toxic effects of emissions associated with the product system. It is shown as a factor of the estimated amount of years of life lost or disabilities incurred according to the DALY system from WHO, and considers health damage like infectious, respiratory and cardiovascular diseases, cancer and many more.
Ecosystem Quality: The damage on the ecosystem is modelled by the loss of species diversity. It is shown as a factor of the percentage of species endangered or lost in a certain area during a certain period of time.
Resources: The impact on resources is modelled by the depletion of mineral and fossil fuel resources. It is shown as a factor of the energy needed to extract a kg of a mineral in the future, which increases with lowering resource quality. **[6]**

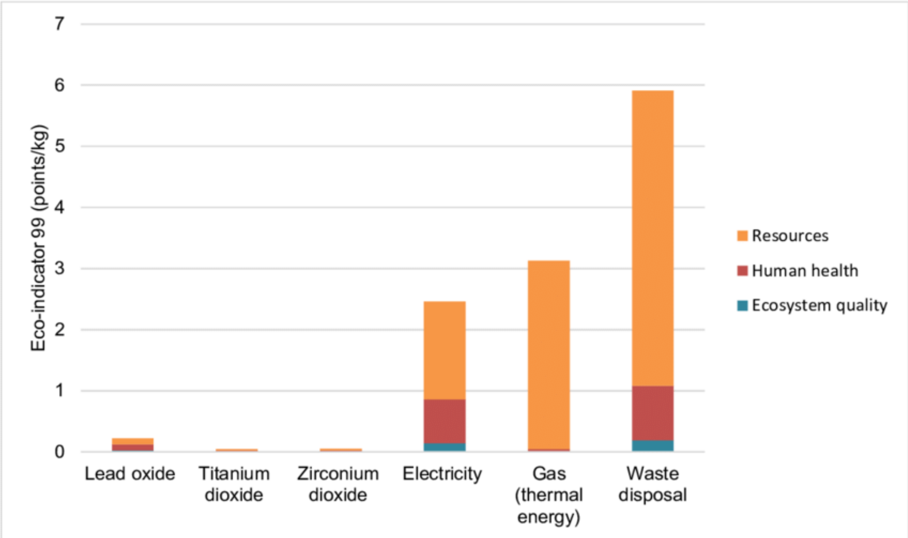



Figure 4 Eco indicator 99 results for 1 kg of PZT ceramic [3]

In Figure 4 you can see that, for PZT, the predominant damaging influence is by far the impact on resource depletion, rather than human health or the ecosystem.

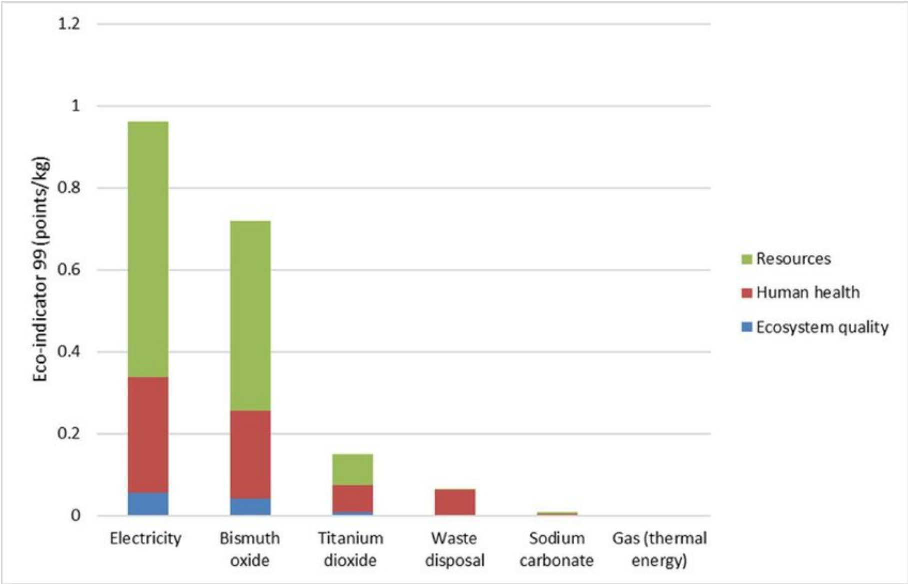
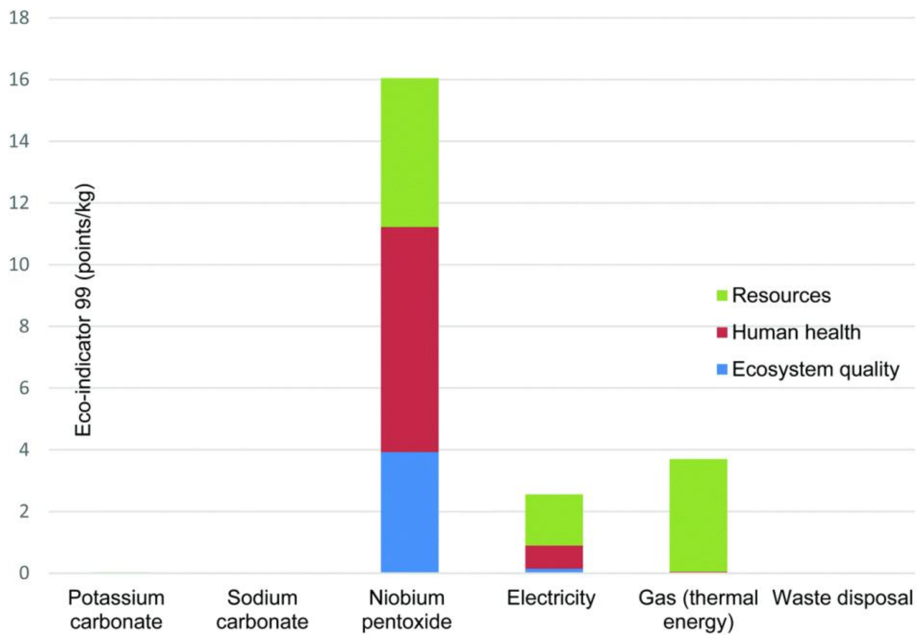



Figure 5 Eco indicator 99 results based on functional unit of 1 kg of NBT ceramic fabricated in the laboratory **[4]**

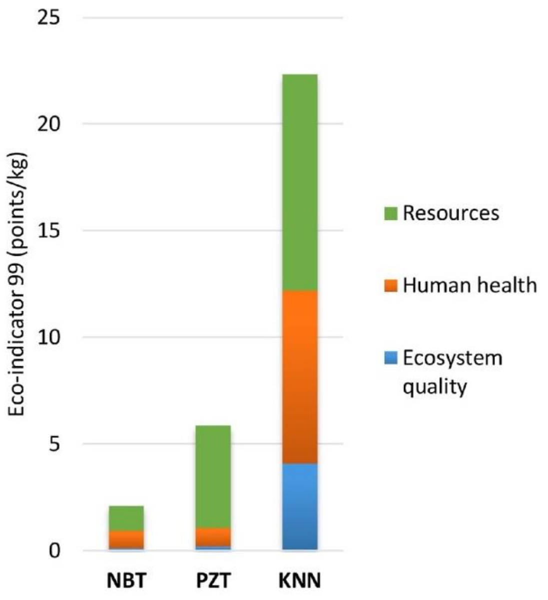
In Figure 5, the Eco-Indicator 99 for NBT has a detrimental effect on the resources attributable to the raw materials Bismuth Oxide and Titanium Dioxide. The impact on the category of damage to human health is comparable to the influence of PZT.




Firgure 6 Eco indicator 99 results for KNN **[3]**

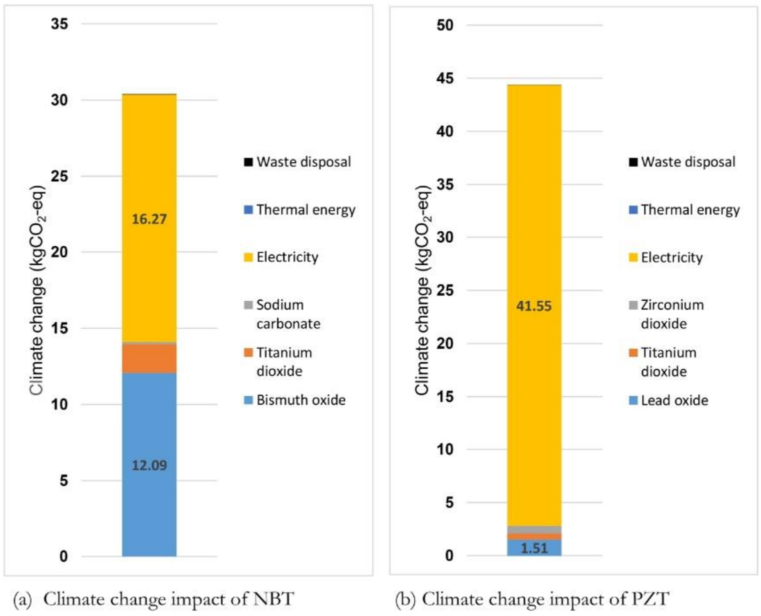
KNN in Figure 6 is clearly more damaging, especially considering the raw material Niobium Pentoxide.

Figure 7 shows that PZT has about 6 points and BNT 3 points per kilogram. This comparison is a series product with a production on a laboratory scale and therefore cannot be easily compared. KNN falls away as an alternative due to the bad environmental performance. In terms of health, PZT performs even better than the BNT. The greater environmental impact of PZT is the resources.




Firgure 7 comparision of the Eco indicator 99 **[4]**

**Climate change impact ($CO_2$- footprint)**




**[4]**

Figure 8 Climate change impact of NBT / BNT (left) and PZT (right)

Given that lead is the most immediate economic and environmental competitor to bismuth, it is important to examine the details of the environmental impact of $Bi_2O_3$ and PbO within NBT and PZT and to compare the overall environmental profile of lead and bismuth. As shown in Fig. 8, it is interesting that the influence of NBT (30.4 kg $CO_2$-eq.) under the environmental indicator climate change is lower than that of PZT (44.4 kg $CO_2$-eq.). This is mainly due to the higher power consumption in the production of PZT compared to NBT (see Fig. 2).

In summary, it should be noted that the greatest influence on the $CO_2$ footprint of PZT is the energy requirement. This means that the power mix has the biggest leverage on the $CO_2$. The current trend towards an increasing share of renewable energies contributes to more $CO_2$ savings on the part of PZT and at the same time reduces the climate change impact of PZT.

However, a closer look at Fig. 8 shows that the material constituents of both ceramics, the carbon footprint of $Bi_2O_3$, exceed that of PbO due to the added burden of processing and purifying bismuth and its oxide compared to PbO. If PZT manufacturing techniques, such as the use of sintering aids, are fully optimized, thereby reducing electrical energy consumption, the environmental profile of NBT may be worsened compared to PZT. **[4]**

There are process steps such as casting, extruding, roughing, metal powder forming, wire drawing, vaporizing, machining and grinding processes, for which the eco-audit data for bismuth and lead are similar (typically <5% deviation) [84]. In the processes for converting lead into metal powder, a larger amount of energy is consumed than for bismuth. On the other hand, evaporation processes are more energy-intensive and accordingly higher for bismuth $CO_2$ footprint than lead [84]. This explains why an enormous amount of energy is invested in the production of bismuth and its oxides and thus a high carbon footprint. For this reason, the evaporation of bismuth during sintering may present a greater problem than the evaporation of lead, leading to reliability problems in piezoelectric applications. **[4]**

The main difference between lead and bismuth is found in the actual extraction from the earth's crust, where the total energy of primary lead production (between 25 and 29 MJ / kg) is lower than that of bismuth (between 139 and 154 MJ / kg). [60, 84]. The extraction of bismuth leads to a three- to four-fold increase in the acidification and eutrophication potential compared to lead [84]. In bismuth production, water consumption is one order of magnitude higher than with lead [60, 61, 84]. In terms of re-use criteria - bismuth is unfavourable compared to lead due to its energy recycling costs, which are almost quadruple compared to lead [84]. Bismuth currently has an average recycled content of 9-10% compared to lead recycling, which is an average of 68 to 76%. The uneconomic approach of recovering bismuth from ever smaller electronic components makes it a material for one-shot applications [84]. **[4]** With this scientific proof, our statement from 2014 confirms: Substitutions based on niobium and bismuth have a higher impact on the environment than lead during extraction and purification, since lead already has a very high level of recycling and is relatively abundant in nature (10- to 70-fold amount of Bi and 3-fold amount of Nb).

The material with the third largest environmental impact is titanium dioxide ($TiO_2$), which contributes 6% to climate change, 13% to acidification, 9% to eutrophication, 4% to land use and 7% to material use. $TiO_2$ also contributes to the aquatic ecotoxicity of freshwater, the ecotoxicity of freshwater sediment, human toxicity, aquatic ecotoxicity of the marine environment, ecotoxicity of marine sediment and terrestrial ecotoxicity. Titanium dioxide also contributes to ionizing radiation and airborne odors. $TiO_2$ is a harmless mineral particle in the form of a white powder with high opacity and brilliant white, therefore its application in the areas of cosmetics, food, pharmaceuticals, paints and inks, plastic and rubber products and many more [85,86]. Most environmental impacts of $TiO_2$ occur in production processes and in waste management. $TiO_2$ pigments are produced by two common methods, the sulphate and the chloride method [87]. The sulphate process produces $TiO_2$ by treating titanium ores with concentrated sulfuric acid. The resulting titanium compound is selectively extracted and processed to pure $TiO_2$. This process generates large quantities of dilute sulfuric acid and other harmful by-products, resulting in the largest amount of environmentally hazardous waste per unit of $TiO_2$ produced. In the chloride process, natural rutile, a rare high quality titanium ore, is treated with chlorine gas to produce titanium tetrachloride. It is then mechanically separated from the other chlorides, distilled and oxidized to $TiO_2$ [87]. Compared to sulphate, the chloride is 15 times cleaner but more expensive and requires high quality ores. Around two-thirds of EU production of $TiO_2$ is based on the sulphate process [88]. **[4]**

$TiO_2$ itself is essentially a useful, non-toxic and non-carcinogenic [89-94] inorganic compound. However, the waste associated with $TiO_2$ is extremely acidic and its manufacturing methods and final disposal pose numerous environmental problems. For example, a number of coastal production facilities based on the sulphate approach introduce large amounts of sulfuric acid into rivers and interconnecting waterways. Although the alkaline seawater buffers and neutralizes the dilute acidic waste, the discharge of sulfuric acid causes a sudden drop in pH at the point of introduction and decreases the oxygen content of the water, thereby depleting marine life. The impact on the land and the air from odor is due to the fact that sulfuric acid also gets into the ground and emissions to the atmosphere are released. Inland water-based $TiO_2$ production plants neutralize the acidic waste by mixing it with chalk and disposing of the resulting solid in landfills [87, 88]. However, these systems release dust and gas emissions. **[4]**

**References:**

[1] M.M. Lencka, M. Oledzka, R.E. Riman: Hydrothermal synthesis of sodium and potassium bismuth titanates (Chem. Mater., 12 (2000), pp. 1323-1330)

[2] C.-S. Chou, C.-Y. Wu, R.-Y. Yang, C.-Y. Ho: Preparation and characterization of the bismuth sodium titanate (Na0.5 Bi0.5 TiO3) ceramic doped with ZnO (Adv. Powder Technol., 23 (2012), pp. 358-365)

[3] T. Ibn-Mohammed, S. Koh, I. Reaney, A. Acquaye, D. Wang, S. Taylor, et al.: Integrated hybrid life cycle assessment and supply chain environmental profile evaluations of lead-based (lead zirconate titanate) versus lead-free (potassium sodium niobate) piezoelectric ceramics (Energy Environ. Sci., 9 (2016), pp. 3495-3520)

[4] T. Ibn-Mohammed, I.M. Reaney, S.C.L. Koh, A. Acquaye, D.C. Sinclair, C.A. Randalle, F.H. Abubakar, L. Smith, G. Schileo, L. Ozawa-Meida: Life cycle assessment and environmental profile evaluation of lead-free piezoelectrics in comparison with lead zirconate titanate

[5] Takaaki Tsurumi*, Shuhei Takezawa, Takuya Hoshina, and Hiroaki Takeda: Elution of lead from lead zirconate titanate ceramics to acid rain

[6] M. Goedkoop, R. Spriensma, PRé Consultants B.V., „The Eco-Indicator 99: A Damage Oriented Method for Life Cycle Impact Assessment – Methodology Report", June 2001, Third Edition

### (B) Please provide information and data to establish reliability of possible substitutes of application and of RoHS materials in application

As stated previously there is no suitable substance for substituting lead. Please refer to answer in question 4C and Appendix I.

## 7. Proposed actions to develop possible substitutes

### (A) Please provide information if actions have been taken to develop further possible alternatives for the application or alternatives for RoHS substances in the application.

Boron, phosphorus, zinc, tin, bismuth, etc. have been investigated as elements for substituting lead as a constituent element of glass. However, when compared with lead-containing glasses, chemical stability and mechanical strength of the glasses are insufficient (to meet the required functionality).

As a result, there are concerns of accidents originating from crucial failures in EEE incorporating electrical and electronic components composed of glass with lead substituted by these elements due to their insufficient reliability and quick deterioration.

Niobium, Tantalum, Antimony, Lithium, Rare Earth, etc. have been investigated as elements for substituting lead as a constituent element of ceramic.

However, those electrical and mechanical properties are inferior when compared with lead-containing ceramic and cannot be stably achieved throughout a wide temperature range. Moreover, the properties obtained in the laboratory cannot generally be stably achieved in a mass production scale. There are still many remaining issues needing to be solved in order to achieve mass production of practical products. Adding to that, even in the case that mass production technology is achieved, the required properties for substituting almost all of the applications cannot be obtained.

### (B) Please elaborate what stages are necessary for establishment of possible substitute and respective timeframe needed for completion of such stages.

There are no prospects concerning the technical scope of exemption 7(c)-I for a comprehensive substitution to “lead-free” glass and/or ceramic at least until the next revision.

## 8. Justification according to Article 5(1)(a):

**(A) Links to REACH: (substance + substitute)**

1) Do any of the following provisions apply to the application described under (A) and (C)?

☐ Authorisation

☐ SVHC
☐ Candidate list
☐ Proposal inclusion Annex XIV
☐ Annex XIV

☐ Restriction

☐ Annex XVII
☐ Registry of intentions

☐ Registration

2) Provide REACH-relevant information received through the supply chain.
Name of document:

Based on the current status of Annexes XIV and XVII of the REACH Regulation, the requested exemption would not weaken the environmental and health protection afforded by the REACH Regulation. The requested exemption is therefore justified as other criteria of Art. 5(1)(a) apply

**(B) Elimination/substitution:**

1. Can the substance named under 4.(A)1 be eliminated?

☐ Yes. Consequences?

☒ No. Justification: Please see answers in questions 4(C), 7(A) and 7(B)

2. Can the substance named under 4.(A)1 be substituted?

☐ Yes.

☐ Design changes:
☐ Other materials:
☐ Other substance:

☒ No.

Justification: Please see answers in questions 4(C), 7(A) and 7(B)

3. Give details on the reliability of substitutes (technical data + information): see 6(A)
4. Describe environmental assessment of substance from 4.(A)1 and possible substitutes with regard to

1) Environmental impacts: see 6(A)
2) Health impacts: see 6(A)
3) Consumer safety impacts: see 6(A)

⇨ Do impacts of substitution outweigh benefits thereof?
Please provide third-party verified assessment on this: Not applicable

**(C) Availability of substitutes:**

a) Describe supply sources for substitutes: None
b) Have you encountered problems with the availability? Describe: Not applicable
c) Do you consider the price of the substitute to be a problem for the availability?
☐ Yes ☒ No
d) What conditions need to be fulfilled to ensure the availability? see 6(A)

**(D) Socio-economic impact of substitution:**

⇨ What kind of economic effects do you consider related to substitution?
Not applicable

☐ Increase in direct production costs

☐ Increase in fixed costs

☐ Increase in overhead

☐ Possible social impacts:

☐ Possible social impacts external to the EU

☐ Other: ______

⇨ Provide sufficient evidence (third-party verified) to support your statement:

## 9. Other relevant information

**Please provide additional relevant information to further establish the necessity of your request:**

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## 10. Information that should be regarded as proprietary

**Please state clearly whether any of the above information should be regarded to as proprietary information. If so, please provide verifiable justification:**

There is no information which should be regarded as proprietary information.

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## Appendix I

In order to describe the current status of substitution research of lead-free glass and electronic ceramics, we introduce below some selected illustrative examples. However, as lead-containing glass and electronic ceramics are used in all categories of electrical and electronic equipment (hereinafter, “EEE”) it is impossible in practice to exhaustively present all applications and cases. Therefore, it must be noticed that the examples shown below do not cover an exhaustive list of the whole substitution research of lead-containing glass and electronic ceramics, but it is merely a selected small part thereof.

### Examples for Lead-free vs Lead-containing Materials Tests in practical Applications:

### Lead in Glass:

Example 1:

In this example, Lead-free glass was tested against a glass-metal-ceramic system containing lead that is unique to this company [1]. The glass is used in a pressure sensor. During manufacturing, the glass needs to cool down without cracks within the metal and ceramic components. While lead-containing glass showed 0% cracking, the lead-free alternative cracked 50-100% of the time, making the device inoperable. In order to eliminate cracking, the lead content was then substituted with additional silicate and other mixed alkalis and alkaline earth materials. However, the resulting glass did not show the required stable electrical and geometrical properties over the product operating temperature range. With shifting temperatures, as anelastic effect occurred and the sensor error increased by 1.5 times. As a result, no lead-free glass alternatives were found suitable for the application.

Sources:

[1] Internal Study. Confidential Material can be provided to the Consultant upon request.

Example 2:

In this example, lead-free glass was tested for chip fuses used for electronic circuit protection. For this application, the fuse needs to show a stable resistance over a long period of use. For reliability testing of the new material, the fuse was subjected to aging through humidity, and then tested for its function. While chip fuses with lead in glass were within the requested specification, the chip fuses made with lead-free glass insulation layers showed too-high resistance shifts upon aging [1]. These shifts in resistance made the fuses unreliable, rendering them useless for circuit protection.

Sources:

[1] Internal Study. Confidential Material can be provided to the Consultant upon request.

Example 3:

In this example, lead-free glass was used as a material component (conducting and resistive elements) in chip resistors in electronic circuits. For this application, the resistance value of the component needs to remain stable over a long period of use. To simulate this, the resistors were subjected to an Operational Life Test. While the chip resistors with lead-containing glass remained within the specification limits during the test, the components using lead-free glass showed resistance shifts outside of the desired specification limits [1].This made them unfit for the desired application.

Sources:

[1] Internal Study. Confidential Material can be provided to the Consultant upon request.

Example 4:

In this example, we examined the application of Si-(B, Ba, Zn)-Li based lead-free glass as a bonding glass for bonding ceramic elements to metal electrodes for electrical and electronic components for temperature control applications. The electrical and electronic components for this application must have thermal shock resistance against repeated thermal shocks, but this lead-free glass has insufficient thermal shock resistance compared to lead-containing glass. Therefore, the life of the electrical and electronic components will be shortened to one-hundredth, practical application could not be achieved.

Sources:

[1] Internal Study. Confidential Material can be provided to the Consultant upon request.

**Examples for Lead-free vs Lead-containing Material Tests in practical Applications:**

**Lead in Ceramics:**

Example 5:

In this example, the lead-free piezoelectric ceramic Aluminium Scandium Nitride (AlScN) was to be tested as a thin film for its actuation properties, to be used optical elements. For this application, the material needs to show a large elongation at moderate voltages. It was found that only PZT thin films yield the piezoelectric coefficient values necessary [1], while AlScN [2] and other lead-free piezoelectric ceramics showed piezoelectric coefficient values of only 8% or lower compared to PZT. These properties are not sufficient for application purposes.

Sources:

[1] ACS Appl. Mater. Interfaces 2017, 9, 9849−9861, DOI 10.1021/acsami.6b16470

[2] Microsyst. Technol. (2016) 22:1613–1617, DOI 10.1007/s00542-015-2787

Example 6:

In this example, lead-free piezoelectric ceramics from the potassium sodium niobate ((K, Na)NbO3) family were tested as an alternative to PZT for piezoelectric sensors to be used in accelerometers. For this application, the material needs to show piezoelectric properties that remain stable within a wide temperature range, and up to 200°C. This calls for a material with a small sensitivity variation within this temperature range. While KNN is operable within a large temperature range, it also showed five times higher sensitivity variation compared to PZT. These properties were not sufficient for the application purposes [1]. Furthermore it may be mentioned that ceramics based on solid solutions of sodium bismuth titanate and barium titanate (NaBi(TiO3)2)–BaTiO3), another intensely studied family of lead-free piezoelectric ceramics, are also unsuited in this case, since they can only be used for operating temperatures well below 200°C [2].

Sources:


[1] Study conducted by Meggitt, presented at. Piezo 2019, Špindlerův Mlýn (CZ)

[2] Rödel, Jürgen ; Li, Jing-Feng (2018): Lead-free piezoceramics: Status and perspectives. MRS Bulletin, 43 576-580.


Example 7:

In this example, a material showing piezoelectric activity at temperatures beyond those available by PZT was sought. It was to be used in an ultrasonic transducer for industrial structural health monitoring at high temperatures, up to 500°C. Such transducers employing piezoceramics are now deployed in safety critical systems in oil refineries, chemical processing plants and nuclear power plants to enable continuous monitoring for corrosion and cracking of plant assets, e.g. pipes. Continuous monitoring at temperatures from 300°C to 500°C is necessary for these applications, while the materials also need to provide sufficient spatial resolution. This means that both the Curie temperature and the piezoelectric coefficient need to be sufficiently high. Several lead-containing and lead-free piezoelectric materials were evaluated for this purpose. It was found that no lead-free materials satisfy the requirement of high dielectric coefficients at high temperatures [1]. Finally, a proprietary lead-containing piezoceramic based on Bismuth Ferrite and Lead Titanate (BiFeO3-PbTiO3) was able to meet the required specification [2].

Sources:


[1] Stevenson T; Martin DG; Cowin PI; Blumfield A; Bell AJ; Comyn TP; Weaver PM (2015) Piezoelectric materials for high temperature transducers and actuators. Journal of Materials Science: Materials in Electronics, 26 (12), pp. 9256-9267

[2] Bennett J; Bell AJ; Stevenson TJ; Comyn TP (2013) Tailoring the structure and piezoelectric properties of BiFeO3-(K0.5Bi0.5)TiO3-PbTiO3 ceramics for high temperature applications. APPLIED PHYSICS LETTERS, 103, 152901


Example 8:

In this example, several lead-free pyroelectric materials were tested as an alternative to PZT for their use in infrared sensors for motion detection, burglar alarms and automatic light switches. For these applications, good human movement detection and low false alarm occurrence are needed. A high pyroelectric coefficient and high Curie temperature are essential to ensure high responsivity, good signal-to-noise ratio and appropriate operating temperatures. Compared to PZT, Potassium Sodium Niobate ((K, Na)NbO3) showed a signal-to-noise ratio three times lower than PZT [1, 2]. As a result, both detectivity and detection range were too low for application purposes. Lithium Tantalate (LiTaO3) experienced spike discharges due to its too-high electrical resistivity, leading to false alarms. Some formulations of Sodium Bismuth Titanate (NaBi(TiO3)2), showed a pyroelectric coefficient comparable to PZT, but had to be discarded due to their too-low responsivity [2]. Strontium Barium Niobate ((Sr,Ba)Nb2O6) also showed promise, but still remains at 30-50% of performance vs PZT depending on the dopant [2]. Calcium Barium Niobate ((CaBa) Nb2O6) only achieved 10% of the responsivity of PZT [2]. . Finally, Triglycine Sulfate crystals, which are a material of choice for scientific IR-detectors, are too fragile and are not temperature-stable, making them unsuitable for typical consumer applications [3]. Among the many available lead-free pyroelectric materials, PZT still shows the best characteristics for sensitive, stable and durable infrared detectors in consumer applications [3].

Sources:

[1] Cranfield University, MSc THESIS Clément DENIS, Academic year: 2011-2012, DEVELOPMENT OF LEAD FREE PYROELECTRIC MATERIAL

[2] Research Collaboration Agreement with National University of Singapore: Research for Academic year 2017-2020, “Development of Pyroelectric Ceramics for Infrared Sensors”, by He HongYing, Puloma Dwibedi, Emil Hanc, Zheng HongJuan in the Research Group of Prof. Lu Li

[3] Aggarwal, Batra, Guggilla, Edwards, Penn, Currie, “Pyroelectric Materials for Uncooled Infrared Detectors: Processing, Properties, and Applications”, NASA, 2010

Example 9:

In this example, a lead-free piezoelectric ceramic ((Ag, Li) (Nb, Ta) O3) was tested for use in a resonator that provides a reference clock for the operation of electrical and electronic equipment. The reference clock for electrical and electronic equipment needs to be supplied stably for a long period of time. However, since this lead-free piezoelectric ceramic has a composition containing silver, it easily causes silver migration and loses its function in a short period of time (electromigration causes short circuits). Therefore, resonator using this lead-free piezoelectric ceramic was only a prototype in the laboratory and is too unreliable to be usable.

Sources:

[1] Internal Study. Confidential Material can be provided to the Consultant upon request.