Exemption Renewal Form
Exemption 7c-I, Annex III

Date of submission: **02 January 2020**

1. Name and contact details

1) Name and contact details of applicant

Company:	**COCIR**	Tel.:	**00327068966**
Name:	**Riccardo Corridori**	E-Mail:	**corridori@cocir.org**
Function:	**EHS Policy Senior Manager**	Address:	**Blvd A. Reyers 80, 1030 Bruxelles**

2) Name and contact details of responsible person for this application (if different from above):

Company:	_____	Tel.:	_____
Name:	_____	E-Mail:	_____
Function:	_____	Address:	_____

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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 Annex III

☐ 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: 7c-I

Proposed or 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: **Maximum validity period**

☐ Other: _____

3. Summary of the exemption request / revocation request

This exemption is utilised by the medical sector for medical ultrasound transducers that contain polycrystalline ceramic materials and it is also used for electronic components that contain glass and ceramics that contain lead. Extensive research, described in this renewal request has been carried into lead-free piezoelectric materials, but so far all lead-free substitutes give very inferior performance compared with lead-based materials.

This exemption covers polycrystalline medical ultrasound transducers, whereas single crystal ultrasound transducers are covered by exemption 14 of Annex IV. It may be possible to combine these two similar exemptions.

Medical device manufacturers use many other types of electronic components that also rely on exemption 7c-I. This renewal request describes medical ultrasound transducers only as COCIR expect that component manufacturers will request renewal for other applications.

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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: Ultrasound scanners and electronic components are used in all other types of electrical medical device

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

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

   b. Please specify if application is in use in other categories to which the exemption request does not refer: Categories 1-7, 9-11, IVD Medical devices

   c. 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:

Constituent of polycrystalline piezoelectric material used for medical ultrasound transducers. Lead is used as lead zirconium titanate (PZT) which gives superior image quality to any lead-free piezoelectric material.

Lead is also used in glass and ceramics of many types of electronic components, such as resistors, capacitors, inductors, sensors, semiconductors, etc., to provide specific physical and electronic properties that are required for the components to function correctly in electronic circuits of medical devices.

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

Medical ultrasound piezoelectric dielectric: ca. 64wt% lead

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

Medical ultrasound transducers: 4.2kg

Please supply information and calculations to support stated figure.

Medical ultrasound transducers; Estimated by an ultrasound probe manufacturer based on numbers sold in the EU, average mass of lead per probe and their market share

6. Name of material/component:

Lead zirconium titanate ($PbZr_{0.5}Ti_{0.5}O_3$) in medical ultrasound transducers

7. Environmental Assessment: _____
   LCA: ☐ Yes
   ☒ No

(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?

Medical ultrasound applications

Medical ultrasound imaging is used to generate images of the interior of the human body, such as to examine unborn babies, to examine internal organs to look for tumours or abnormalities, etc. muscles, tendons, blood vessels, etc. It is also used for minor surgery for example to guide hypodermic needles to the required locations.

Medical imaging uses a driver circuit to impose a broad range of AC frequencies onto the piezoelectric material which causes it to generate a broad range of frequency vibrations akin to sound waves. These waves travel from the transducer to an interface, such as the surface of an organ, within the patient where these waves are reflected back to the transducer. The force from the reflected waves striking the piezoelectric material generates an electric field that is used to generate an image.

Different imaging frequencies are used depending on what is being viewed, for example higher frequencies give better image quality but lower frequencies are needed to view deeper inside the body (higher penetration). As a result, the transducer should generate a wide range of frequencies, referred to as a large bandwidth.

The ultrasound transducer obtains an image by using one or more piezoelectric elements (often as an array) which are connected to the control system which also has a display and digital recorder. Modern medical ultrasound imaging uses polycrystalline lead zirconium titanate (PZT) based ceramic materials as well as single crystal materials that give superior performance, but are more difficult to fabricate and so are more expensive than ceramic PZT transducers and so are used only when the higher performance is required for medical diagnostics and treatment.

(C) What are the particular characteristics and functions of the RoHS-regulated substance that require its use in this material or component?

While there are many properties of piezoelectric materials that have a bearing on the quality of the ultrasound image that they provide, only one property continuously improves the output as it is increased, which is the coupling factor. Coupling factor is the efficiency of the material's ability to convert mechanical energy from vibrations into an output electrical charge and vice-versa. It should be noted that this is not the same as the ratio of force applied to charge generated; because the same crystal is used as the receiver and transmitter, so any change in this property would either make it easier to transmit or receive, but the overall effect cancels out.

Two main properties are desired in medical ultrasonic transducers:

- High imaging resolution
- High depth of penetration

To achieve these, the following are needed:

1. High bandwidth – this improves axial resolution and contrast resolution; and
2. High sensitivity - high frequency at greater depth = higher centre frequency= better lateral resolution

Both a large bandwidth and high sensitivity are required to get the best resolution of ultrasound images.

The properties of ultrasound materials are defined by the following five piezoelectric parameters:

1. Coupling factor
2. Piezoelectric constants
3. Dielectric constant
4. Insertion and other losses
5. Depoling and Curie temperatures
6. Velocity

Coupling Factor

The coupling factor is the most fundamental property.

$$coupling\ factor = \sqrt{\frac{energy\ that\ can\ be\ converted}{between\ mechanical\ and\ electrical\ energy}}$$

If ultrasound energy is not efficiently converted from electrical to mechanical energy or vice versa, then there is a reduction in sensitivity. Oakley and Zipparo state in their paper that:

> "*A failure to convert a large fraction of energy in a single cycle must result in either a loss of sensitivity (if the energy is not converted in a later cycle) or a loss of bandwidth (if the energy is converted in later cycle, thus spreading the response in time). A loss of coupling cannot be compensated for by any known design strategies to maintain bandwidth and sensitivity simultaneously*".

A high coupling factor is therefore essential as it is impossible to compensate for inferior coupling factors by design change, etc[1]. It may be possible to compensate to some extent for other characteristics by design change, but this is not possible for the coupling factor. Most other properties can be altered with alterations to the circuit of the device or the way that the material is cut or produced, although these will have limitations that can affect performance. The coupling factor is an indicator of the effectiveness with which a piezoelectric material converts electrical energy into mechanical energy or converts mechanical energy into electrical energy and so is closely related to and dependent on the piezoelectric constants of the material.

Piezoelectric Constants

These define the properties of the material. Properties include the piezoelectric charge constant and the piezoelectric voltage constant, both of which define the performance of the material. The piezoelectric charge constant is the mechanical strain experienced by a piezoelectric material per unit of electric field applied and piezoelectric voltage constant is the

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[1] 'Single Crystal Piezoelectrics: A Revolutionary Development for Transducers' by CG Oakley and MJ Zipparo, Ultrasonics Symposium, 2000 IEEE.

mechanical strain experienced by a piezoelectric material per unit of electric displacement applied.

Dielectric Constant

This is a primary parameter that affects the impedance of a transducer element. It is possible to compensate to some extent for low values such as by changing the electrical control circuit design and using multilayer piezoelectric materials, but this increasing circuit complexity and difficulties with fabrication. Dielectric constant therefore has some importance and the best single crystal materials have relatively higher values.

Losses

Insertion loss is proportional to the material's sensitivity and so can be an important parameter for image quality. Ultrasound materials can also suffer from a loss of energy. A loss in performance can be dealt with by increasing power (applied current), but this heats the crystal which if the temperature becomes too hot can cause loss of performance (sometimes due to a phase change) or even exceed the Curie temperature, resulting in depoling. Cooling is an option but is impractical with medical ultrasound transducers. Losses cannot be zero, but should not be greater than 10%.

Depoling/phase transition temperatures:

Piezoelectric materials undergo a series of phase transitions with increasing temperature. For example, above the Curie temperature, they lose their ferroelectric properties due to the depoling process which makes them not usable for ultrasound transducer applications. Each phase transition is accompanied by a corresponding strain within the piezoelectric material structure. This internal strain can either result in cracking the material or changing its properties. Therefore, piezoelectric materials with low phase transition temperatures show unstable performance during the operation of an ultrasound transducer which normally runs at temperatures higher than room temperatures (due to internally generated heat). In addition, low Curie temperature materials can partially depole during shipping or storage in areas with a hot environment. This partial depoling will have an adverse effect on the performance of ultrasound transducer.

Velocity

Low ultrasound velocity requires a thinner transducer, but thinner materials have higher capacitance, which is good for smaller piezolectric elements - but fabrication is more difficult.

Curie temperature should be sufficiently high so that solder bonding, use and storage do not degrade performance. Piezoelectric properties degrade if the material is heated to temperatures close to and above this temperature

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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.)

Ultrasound transducers

Although the majority of ultrasound transducers are returned to the manufacturer, a significant proportion, due to the small size, reach disposal and recycling via other routes (i.e. the WEEE Directive) so a closed loop does not exist for this application

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

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 No data is available
☐ In articles which are sent for energy return _____
☐ In articles which are 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

Research into substitute piezoelectric materials for medical ultrasound imaging has been carried out in recent years. A wide variety of dielectric materials have been produced and tested and some are commercially available. However, as shown below, none of the lead-free materials can achieve the same high performance of the best performing lead zirconium titanate (PZT) compounds.

A summary of published data of piezoelectric materials from various data sources are as follows:

Table 1. Published performance characteristics of piezoelectric materials[2]

Material	**Dielectric constant $\varepsilon_{33}/\varepsilon_0$**	**Piezoelectric constant D_{33}**	**Coupling coefficients**		**Comments**
			K_{33}	**K_t**	
Lead zirconium titanate (PZT)[3]	4000 to 7000	650 - 820	0.75 to 0.77	0.52	Curie temperature is typically 145 - 210°C
Lead zirconium titanate (PZT), grade recommended for medical ultrasound	4200	600			Curie temperature is 185°C
Barium sodium titanate – barium potassium titanate – barium titanate BNT–BKT–BT	1000	181	0.56		Typical values for barium titanate based piezo-materials
Unusual Barium zirconium titanate – barium calcium titanate ceramic (BZT–BCT)	2820	Up to 560–620			Has too low a Curie temperature of ca. 93°C
Potassium sodium niobate – lithium titanate – lithium antimonite (KNN-LT-LS)	506 - 1865	175 - 315		0.39	
Potassium Sodium	890	245		0.42	

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[2] Most data is from "Lead-free piezoelectric materials and ultrasonic transducers for medical imaging", Taghaddos et. al., Journal of Advanced Dielectrics, Vol. 5, No. 2 (2015)

[3] PZT data from http://www.tayca.co.jp/english/products/electro_ceramic/spec.html

Material	**Dielectric constant $\varepsilon_{33}/\varepsilon_0$**	**Piezoelectric constant D_{33}**	**Coupling coefficients**		**Comments**
			K_{33}	**K_t**	
Niobate – Lithium Titanate (KNN-LT)					
Barium niobium titanate – barium titanate (BNT-BT)	730	125	0.55		
Bismuth sodium titanate[4]	700	120	-	0.40	Commercially available ceramic piezoelectric material
Potassium, sodium niobate antimonate – Bismuth sodium potassium zirconate KNNS-BNKZ		490			Highest D_{33} value for lead-free material listed in review by Hong[5].
Potassium Sodium Niobate (KNN) thick film	90			0.34	Coupling coefficient is too low
Lithium niobate (single crystal)		35		0.49	Very high curie temperature but too low D_{33} and K_t. Used for non-destructive testing of industrial equipment.

The review by Taghaddos[2] includes many other lead-free materials as well as transducers made using various lead-free piezo materials, but all materials and devices are very inferior to PZT. Other publications provide similar values of piezoelectric properties for lead-free materials. Hong et al, for example quotes a highest value for piezoelectric constant D_{33} of 490 for the complex material KNNS-BNKZ[5] and states that lead-free materials are not yet (as of

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[4] Physik Instrumente GmbH & Co. KG. Material PIC700. http://www.piezo.ws/pdf/Piezo_Materials_Piezo_Technology_Piezo_Components.pdf

[5] „Lead-free piezoceramics - Where to move on?“, Hong et. al. J Materiomics Vol 2, issue 1 (March 2016) https://www.sciencedirect.com/science/article/pii/S2352847815300083

2016) equivalent to lead-based materials such as polycrystalline ceramic PZT (lead zirconium titanate).

In the past two decades, lead-free piezoelectric materials have been extensively studied for various applications such as electronics, sensors, actuators, capacitors, sonars, ultrasound transducers, and so forth. Promising lead-free composition have been developed for some electronics and high power device applications.

Lead-based piezoelectric ceramics and single crystals which are commercially used in fabricating ultrasound transducers for medical imaging possess a unique combination of electromechanical properties such as high dielectric constant, high piezoelectric constant, high coupling coefficient, and relatively high depolarization or curie temperature. These properties have been optimized for specific medical imaging applications to enhance the performance of the transducers and hence the image quality. As a result, there are different grades of Pb-based piezoelectrics with wide range of electromechanical properties which cover a wide range of medical imaging applications performed at different frequencies. Pb-based single crystals, for example, offer a remarkably high dielectric constant and coupling coefficient. This resulted in a revolution in medical imaging industry by introduction of Matrix arrays for high quality 3D imaging. Pb-based piezoelectrics are also thermally stable across the working temperature range in which the ultrasound transducers operate.

Pb-free piezoelectrics, on the other hand, have much lower electromechanical properties due to their intrinsic chemistry. Despite the remarkable progress made in improvement of properties of lead-free materials in the last two decades, there is still an appreciable deficit compared to Pb-based materials used in medical imaging applications. The majority of research done on lead-free materials has been focused on so-called Morphotropic Phase Boundary (MPB) compositions where the material offers the highest electromechanical properties compared to other compositions. However, MPB compositions have very low thermal stability which is not desirable for medical imaging applications. Even in the vicinity of MPB region, lead-free materials still have much lower piezoelectric and dielectric properties compared to lead-based materials. Pb-based piezoelectric ceramics and single crystals with rhombohedral structure offer a more stable performance compared to MPB compositions. These rhombohedral compositions are widely used in the medical ultrasound market. A few lead-free compositions with rhombohedral structure have been developed recently. They all suffer from low electromechanical properties or high coercive field requiring very high voltages for operating the ultrasound transducers which would not be practical. Another prohibitive factor in using lead-free piezoelectrics in medical imaging transducers is that the manufacturing process of these materials is not mature and very well understood yet. Lead-free materials have complex chemistry containing elements such as potassium (K), sodium (Na), and lithium (Li) which are relatively volatile therefore are difficult to control during the synthesis process. The data available in the literature mostly relate to the materials prepared on the laboratory scale as opposed to commercially available materials. There is no viable lead-free composition commercialized for medical imaging applications. Below is a brief summary of some of the mostly studied lead-free piezoelectric materials in the literature:

Barium Titanate (BT): BT ceramic has relatively high electromechanical properties, high dielectric constant, and low Curie temperature (T_C ~ 120 ^{O}C). BT-based ceramics have been mainly used for capacitor applications. Their low Curie temperature restricts the working temperature range in which these materials can be used. The highest electromechanical properties were achieved at BZT–50BCT composition around the morphotropic phase boundary (MPB). A piezoelectric coefficient d_{33} of 560–620 pC/N was attained for this composition which was noticeably higher than that of other BT-based ceramics. However, due to low Curie temperature of about 90^{o}C, this composition is thermally unstable and not suitable for medical imaging applications.

Bismuth Sodium Titanate (BNT): Pure BNT ceramics, however, suffer from high conductivity and a large coercive (73 kV/cm) field which makes the poling process difficult. Therefore they are not usable for making ultrasound transducers. In order to enhance the electromechanical properties and decrease the coercive field, binary or ternary solid solutions in the vicinity of MPB have been developed. BT, $Bi_{0.5}K_{0.5}TiO_3$ (BKT), $Bi_{0.5}Li_{0.5}TiO_3$ (BLT) are the most widely used materials which have been added to BNT ceramics to improve their electromechanical properties. As mentioned above, MPB compositions are not attractive for medical imaging application due to their thermal instability. Rhombohedral BNT based ceramics have been used in high power devices due to their high coercive field and thermal stability. However, they are not suitable for medical transducers because if their very low dielectric constant and high operating voltage.

Potassium Sodium Niobate (KNN): KNN has the most complex chemistry among the lead free piezoelectrics. This makes it difficult to process high density ceramics or single crystals with stoichiometric composition. A dielectric constant of 1255, d_{33} of 230 pC/N, and kp of 0.5 was reported for $(K_{0.5}Na_{0.5})_{0.07}Li_{0.03}(Nb_{0.8}Ta_{0.2})O_3$ ceramics reported by Saito et al. The simultaneous addition of Li and Sb via LiSbO3 decreased the tetragonal–orthorhombic phase transition temperature while not significantly affecting the Curie temperature. Shifting the transition temperature down to room temperature considerably improved the electromechanical properties. However, this results in a highly unstable thermal properties which is not acceptable for medical imaging transducers.

Overall lead-based polycrystalline ceramic piezoelectric materials have higher dielectric constant and piezoelectric constants that lead-free piezoelectric materials as show below in Figure 1. The data points for PZT are for commercially available materials and the data for lead-free materials are from Table 1.

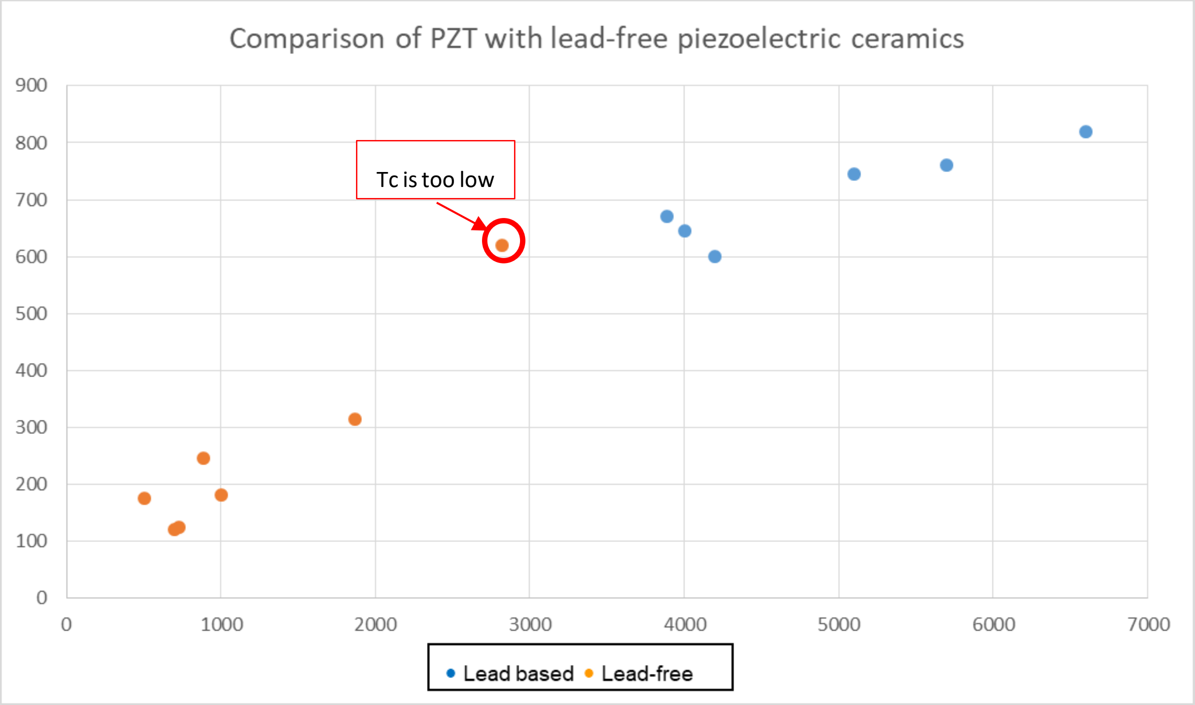

Figure 1. Comparison of dielectric constants (horizontal axis) versus piezoelectric constants (vertical axis) of published values for commercial PZT ceramic piezo materials with lead-free piezo materials (published literature values and one commercial material)

A selection of applicable peer reviewed publications on lead-based and lead-free piezoelectric materials are listed in the appendix to this exemption renewal request.

Summary of lead vs lead-free materials

Lead-free piezoelectrics have lower electromechanical properties and inferior thermal stability compared to their lead-based counterparts. As a result, a medical imaging transducer made with lead-free piezoelectrics would have lower performance and image quality compared to commercially available lead-based materials. The manufacturing of lead-free materials is not mature yet and there is still great amount of work need to be done before lead-free medical ultrasound materials can be commercialized. The risk of medical misdiagnosis using lead-free transducers would very high, and therefore, their use for medical applications is not possible at present as EU Notified Body approval for the Medical Devices Directive would not be granted.

Substitute transducer design

An alternative technology that has been developed is capacitive Micromachined Ultrasonic Transducers (cMUT)[6], which do not contain lead. These function in a completely different way to piezoelectric ultrasound transducers and so it is not possible to compare the technical characteristics of cMUT with those of single crystal piezoelectric materials, such as piezoelectric coupling constants, piezoelectric constants, etc.

cMUTs have the potential to be a lead free alternative for ultrasound imaging with potentially wider bandwidths and smaller feature size. However cMUT technology has yet to overcome significant technical limitations necessary to be a clinically viable alternative to lead based single crystals and PZT ceramics for medical imaging. These limitations include output pressure, reliability and linearity.

Engholm et al.[7] gives a recent comparison with PZT. They report a deficit in insertion loss (this includes both transmit and receive losses) of ~15dB compared to PZT which would result in an unacceptable loss in penetration (depth of imaging inside the patient) and flow sensitivity (e.g. ability to image and measure blood flow) for core clinical applications. This comparison did not use harmonic imaging mode which is today's standard for difficult to image patients. Harmonic imaging insertion loss would double the transmit loss since tissue generated transmit pressure is proportional to the square of the transmit pressure. Losses compared with PZT for harmonic modes would then be an additional 5dB for this transducer.

Zhao et al[8] report what is perhaps the best cMUT reliability results found in the published literature (published in 2017), but of only a 2 year lifetime achieved for low duty cycle modes (therefore even shorter for high duty cycle modes). This is well-short of the desired 5 to 10 year lifetime of a clinical transducer that may also use high duty cycle modes such as shear wave imaging[9]. Lifetimes significantly degrade as pressures are increased in an attempt to achieve pressures that are routinely achieved with PZT and single crystal materials. Some desirable configurations such as 2D arrays for 3D imaging use a common bias for all elements.

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[6] https://www.innovationservices.philips.com/looking-expertise/mems-micro-devices/mems-applications/capacitive-micromachined-ultrasonic-transducers-cmut/

[7] Mathias Engholm, Hamed Bouzari, Thomas Lehrmann Christiansen, Christopher Beers, Jan Peter Bagge, Lars Nordahl Moesner, Søren Elmin Diederichsen, Matthias Bo Stuart, Jørgen Arendt Jensen, Erik Vilain Thomsen, "Probe development of CMUT and PZT row–column-addressed 2-D arrays", Sensors and Actuators A: Physical, Volume 273, 2018, Pages 121-133

[8] Zhao, Danhua, Simopoulos, Costas & Zhuang, Steve. (2017). Long term reliability test results of CMUT *Ultrasonics Symposium (IUS), 2017 IEEE International*, 1-3. doi:10.1109/ULTSYM.2017.8092902

[9] A relatively new technique used for detecting viscosity abnormalities, which can be caused by serious internal injuries, such as internal bleeding, brain injury, and concussive organ damage

However, if an individual cMUT element fails in such a way as to short the bias, the whole array will no longer function.

cMUTs are fundamentally non-linear devices since their pressure (force of transmitted wave) is proportional to the square of the applied voltage (signal + bias). This presents difficulty with harmonic imaging since it is important not to transmit 2nd harmonic energy (as this will distort images or make them illegible). Solutions to this issue have been presented[10] but require the substantially added complexity of a high voltage arbitrary waveform transmit generator. This complexity presents technical and design challenges for handheld devices (the device will be too large and heavy) and matrix devices which use an array of transducers, with each transducer element requiring its own control circuitry.

Recognizing these limitations, researchers have focused their investigations on applications that play to the strengths of cMUTs, namely their ability to produce small feature sizes and wide bandwidths. These applications include catheters[11], endoscopic probes[12], high frequency linear arrays[13] and probes with wide clinical coverage[14]. Transducers for these applications cannot be fabricated easily using PZT or single crystal technology and therefor accept the reduced acoustic output performance associated with cMUTs. Also, single use catheter devices can accept limited lifetimes as they are disposed of after one use.

Due to the current limitations of cMUT technology, lead base sensor technology is necessary to achieve the adequate clinical performance in core imaging modes. Given it took 20 years to mature cMUTS to their current performance, it is unlikely that sufficient performance will be obtained for at least another 5-10 years.

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[10] Savoia, Alessandro Stuart, Caliano, Giosue, Matrone, Giulia, Ramalli, Alessandro, Boni, Enrico & Tortoli, Piero. (2016). Nonlinear ultrasound imaging experiments using a CMUT probe *Ultrasonics Symposium (IUS), 2016 IEEE International*, 1-4. doi:10.1109/ULTSYM.2016.7728699

[11] Pekař, Martin, Mihajlović, Nenad, Belt, Harm, Kolen, Alexander F, van Rens, Jeannet, Budzelaar, Frank, Jacobs, Bas, Bosch, Johan G, Vos, Hendrik J, Rem-Bronneberg, Debbie, van Soest, Gijs & van der Steen, Antonius F W. (2017). Quantitative imaging performance of frequency-tunable capacitive micromachined ultrasonic transducer array designed for intracardiac application: Phantom study *Ultrasonics*, *84*, 421-429. doi:10.1016/j.ultras.2017.11.021

[12] Moini, Azadeh, Nikoozadeh, Amin, Choe, Jung Woo, Chang, Chienliu, Stephens, Douglas N., Sahn, David J. & Khuri-Yakub, Pierre T.. (2016). Fully integrated 2D CMUT ring arrays for endoscopic ultrasound *Ultrasonics Symposium (IUS), 2016 IEEE International*, 1-4. doi:10.1109/ULTSYM.2016.7728542

[13] Danhua Zhao, Steve Zhuang & Lee Weng. (2016). One-probe solution in medical ultrasound imaging with CMUT technology *Ultrasonics Symposium (IUS), 2016 IEEE International*, 1-3. doi:10.1109/ULTSYM.2016.7728443

[14] Probes available form Hitachi and Kolo Medical

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

Reliability of alternative piezoelectric materials is not the reason why lead-based materials have to be used. However the shorter lifetime of cMUT devices, as explained in section 6, is a significant limitation for long lifetime applications.

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.

Please see section 6 for past work done to identify substitute materials and designs.

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

Medical ultrasound transducers

At present, there are no lead-free materials available that can replace PZT for medical ultrasound transducers. Although substitute materials do not at present appear to be likely to be available for many years, if one does become available, it will need to be thoroughly tested, prototype transducers designed and built for testing and is suitable also for clinical trials. If performance and reliability are at least as good as PZT, the approval from an EU Notified Body and also from medical authorities globally would be sought. The timescale between a material becoming available and global approval for use typically takes about 8 years.

Other electronic components

Medical device manufacturers rely on component manufacturers to develop substitute components. If a substitute component does become available, medical device manufacturers need to assess its characteristics and if these appear suitable, test these in medical devices to ensure that performance and reliability are unaffected. If the components prove to be identical to the leaded versions, then re-approval under the medical device directive may be required as well as in non-EU jurisdictions before they can be used in medical devices. The total elapsed time can be as long as 8 years if redesign is required.

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 – Lead titanium zirconium oxide (PZT) is an SVHC
☒ Candidate list – PZT is an SVHC
☐ Proposal inclusion Annex XIV
☐ Annex XIV

☐ Restriction

☐ Annex XVII
☐ Registry of intentions

☒ Registration – PZT is registered in the EU

2) Provide REACH-relevant information received through the supply chain. Name of document: Registration dossier for PZT https://echa.europa.eu/registration-dossier/-/registered-dossier/14607

(B) Elimination/substitution:

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

☐ Yes. Consequences? _____

☒ No. Justification: Technically impractical

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

☐ Yes.

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

☒ No.

Justification: Technically impractical

3. Give details on the reliability of substitutes (technical data + information): See section 6 (B)
4. Describe environmental assessment of substance from 4.(A)1 and possible substitutes with regard to
   1) Environmental impacts: None
   2) Health impacts: None, unless this exemption is not renewed when no alternatives exist that have been fully evaluated and tested and medical devices with alternative components are approved
   3) Consumer safety impacts: None

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

(C) Availability of substitutes:

a) Describe supply sources for substitutes: See section 6 (A)

b) Have you encountered problems with the availability? Describe: Suitable performance alternatives do not exist

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? Alternatives must first be developed. This has so far not been possible and is likely to take many years

(D) Socio-economic impact of substitution:

⇨ What kind of economic effects do you consider related to substitution?

☐ Increase in direct production costs

☐ Increase in fixed costs

☒ Increase in overhead Without this exemption, hospitals may be forced to use different imaging techniques of which MRI is sometimes one option, although this is often less suitable or is not suitable. MRI typically cost €2 million each compared to less that €20,000 for ultrasound. One EU hospital may typically have more than 5 ultrasound imaging equipment (of different types for different applications) but most hospitals can afford only one MRI (many have none). Smaller clinics and doctors' practices could not afford or have space for an MRI, but do have ultrasound equipment. The running costs of MRI are also much more than for ultrasound imaging. These extra costs would have a very serious negative impact on hospitals budgets which EU Member State governments will not compensate.

☒ Possible social impacts within the EU Without this exemption, hospitals and clinics will not be able to buy ultrasound imaging equipment as no alternative lead-free transducers with sufficient performance exist (except in the few applications where CMUT can be used as explained above). This means that millions of EU patients will suffer as diagnosis and treatment will be much more difficult or impossible. Ultrasound imaging is the most effective and safe way of viewing babies before they are born to ensure that they are healthy. It is also the quickest and easiest method for imaging for tumours (MRI is much more costly for hospitals and so has longer waiting times, which would delay cancer treatment). It is not possible to estimate the number of EU citizens who would die or their illness would become worse but numbers are likely to be significant.

☐ 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:

_____

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:

_____

Appendix

Peer reviewed published literature on lead-free piezoelectric materials

[1] E. Aksel, J. S. Forrester, J. L. Jones, P. A. Thomas, K. Page, and M. R. Suchomel, "Monoclinic crystal structure of polycrystalline Na0.5Bi0.5TiO3," Applied Physics Letters, vol. 98,p. 152901, Apr 11 2011.

[2] H. Nagata, M. Yoshida, Y. Makiuchi, and T. Takenaka, "Large piezoelectric constant and high Curie temperature of lead-free piezoelectric ceramic ternary system based on bismuth sodium titanate-bismuth potassium titanate-barium titanate near the morphotropic phase boundary," Japanese Journal of Applied Physics Part 1, vol. 42, pp. 7401-7403, Dec 2003.

[3] D. Q. Xiao, D. M. Lin, J. G. Zhu, and P. Yu, "Investigation on the design and synthesis of new systems of BNT-based lead-free piezoelectric ceramics," Journal of Electroceramics, vol. 16, pp. 271-275, Jul 2006.

[4] H. Choy, X. X. Wang, H. L. W. Chan, and C. L. Choy, "Electromechanical and ferroelectric properties of (Bi1/2Na1/2)TiO3-(Bi1/2K1/2)TiO3-(Bi1/2Li1/2)TiO3-BaTiO3 lead-free piezoelectric ceramics for accelerometer application," Applied Physics a-Materials Science & Processing, vol. 89, pp. 775-781, Nov 2007.

[5] T. Takenaka, K. Maruyama, and K. Sakata, "(Bi1/2Na1/2)TiO3-BaTiO3 System for Lead-Free Piezoelectric Ceramics," Japanese Journal of Applied Physics Part 1-Regular Papers Short Notes & Review Papers, vol. 30, pp. 2236-2239, Sep 1991.

[6] M. Groting, S. Hayn, and K. Albe, "Chemical order and local structure of the lead-free relaxor ferroelectric Na1/2Bi1/2TiO3," Journal of Solid State Chemistry, vol. 184, pp. 2041-2046,
Aug 2011.

[7] N. Lei, M. K. Zhu, P. Yang, L. L. Wang, L. F. Wang, Y. D. Hou, and H. Yan, "Effect of lattice occupation behavior of Li+ cations on microstructure and electrical properties of Na1/2Bi1/2TiO3-based lead-free piezoceramics," Journal of Applied Physics, vol. 109, p. 054102, Mar 1 2011.

[8] R. B. Sun, X. Y. Zhao, Q. H. Zhang, B. J. Fang, H. W. Zhang, X. B. Li, D. Lin, S. Wang, and H. S. Luo, "Growth and orientation dependence of electrical properties of 0.92(Bi1/2Na1/2)TiO3-0.08(Bi1/2K1/2)TiO3 lead-free piezoelectric single crystal," Journal of Applied Physics, vol. 109, p. 124113. Jun 15 2011.

[9] J. Kreisel, A. M. Glazer, P. Bouvier, and G. Lucazeau, "High-pressure Raman study of a relaxor ferroelectric: The (Bi1/2Na1/2)TiO3 perovskite," Physical Review B, vol. 63, p. 174106, May 1 2001.

[10] Y. P. Guo, M. Y. Gu, H. S. Luo, Y. Liu, and R. L. Withers, "Composition-induced antiferroelectric phase and giant strain in lead-free (Nay,Biz)Ti1-xO3(1-x)-xBaTiO(3) ceramics," Physical Review B, vol. 83, p. 054118, Feb 28 2011.

[11] M. Davies, E. Aksel, and J. L. Jones, "Enhanced High-Temperature Piezoelectric Coefficients and Thermal Stability of Fe- and Mn-Substituted (Bi1/2Na1/2)TiO3 Ceramics," Journal of the American Ceramic Society, vol. 94, pp. 1314-1316, May 2011.

[12] Y Hiruma, K. Yoshii, H. Nagata, and T. Takenaka, "Phase transition temperature and electrical properties of (Bi(1/2)Na(1/2))TiO(3)-(Bi(1/2)A(1/2))TiO(3) (A=Li and K) lead-free

ferroelectric ceramics," Journal of Applied Physics, vol. 103, P. 084121, Apr 15 2008.

[13] T. Takenaka, H. Nagata, and Y. Hiruma, "Phase Transition Temperatures and Piezoelectric Properties of (Bi1/2Na1/2)TiO3- and (Bi1/2K1/2)TiO3-Based Bismuth Perovskite Lead- Free Ferroelectric Ceramics," IEEE Transactions on Ultrasonics Ferroelectrics and Frequency Control, vol. 56, pp. 1595-1612, Aug 2009.

[14] Y. Hiruma, H. Nagata, and T. Takenaka, "Phase-transition temperatures and piezoelectric properties of (Bi1/2Na1/2)TiO3-(Bi1/2Li1/2)TiO3-(Bi1/2K1/2)TiO3 lead-free ferroelectric ceramics," IEEE Transactions on Ultrasonics Ferroelectrics and Frequency Control, vol. 54, pp. 2493- 2499, Dec 2007.

[15] T. Takenaka and H. Nagata, "Current status and prospects of lead-free piezoelectric ceramics," Journal of the European Ceramic Society, vol. 25, pp. 2693-2700, 2005.

[16] Y. J. Dai, X. W. Zhang, and K. P. Chen, "An Approach to Improve the Piezoelectric Property of (Bi1/2Na1/2)TiO3-(Bi1/2K1/2)TiO3-BaTiO3 Lead-Free Ceramics," International Journal of Applied Ceramic Technology, vol. 8, pp. 423-429, 2011.

[17] Y. Hiruma, H. Nagata, and T. Takenaka, "Depolarization temperature and piezoelectric properties of (Bi1/2Na1/2)TiO3-(Bi1/2Li1/2)TiO3-(Bi1/2K1/2)TiO3 lead-free piezoelectric ceramics," Ceramics International, vol. 35, pp. 117-120, Jan 2009.

[18] "IRE Standards on Piezoelectric Crystals: Measurements of Piezoelectric Ceramics," Proceeding of the IRE, pp. 1161-1169, 1961.

[19] T. R. Meeker, "Publication and proposed revision of ANSI/IEEE standard 176-1987 "ANSI/IEEE standard on piezoelectricity"," IEEE Transactions on Ultrasonics Ferroelectrics and Frequency Control, vol. 43, pp. 717-718, Sep 1996.

[20] P. K. Panda, Review: environmental friendly lead-free piezoelectric materials. J Mater Sci (2009) 44:5049–5062.

[21] M. Hejazi. ACOUSTIC AND ELECTRICAL PROPERTIES OF BISMUTH SODIUM TITANATE –BASED MATERIALS, PhD Thesis, Rutgers Univeristy, 2013.

[22] E. Taghaddos, M. Hejazi, A. Safari, “Lead-free piezoelectric materials and ultrasonic transducers for medical imaging. JOURNAL OF ADVANCED DIELECTRICS, Vol. 5, No. 2 (2015) 1530002

[23] E Taghaddos, M Hejazi, A Safari, Electromechanical Properties of Acceptor-Doped Lead-Free Piezoelectric Ceramics, Journal of the American Ceramic Society 97 (6), 1756-1762.

[24] MM Hejazi, B Jadidian, A Safari, Fabrication and evaluation of a single-element Bi0.5Na0.5TiO3-based ultrasonic transducer, IEEE transactions on ultrasonics, ferroelectrics, and frequency control 59 (8)

[25] M Hejazi, E Taghaddos, E Gurdal, K Uchino, A Safari, High Power Performance of Manganese-Doped BNT-Based Pb-Free Piezoelectric Ceramics, Journal of the American Ceramic Society 97 (10), 3192-3196

[26] A Safari, M Hejazi, Lead-free KNN-based piezoelectric materials, in Lead-Free Piezoelectrics by Springer, 139 175

[27] B. Jaffe, W. Cook, and H. Jaffe, Piezoelectric Ceramics. (Marietta, OH: Academic Press, (1971).

[28] K. Uchino, Ferroelectric Devices. (New York, NY: Marcel Dekker Inc., (2000)

[29] A. Kholkin, N. Perstev, and A. Golstev, "Piezoelectricity and Crystal Symmetry," in Piezoelectric and Acoustic Materials for Transducer Applications, A. Safari and K. Akdogan, Eds., (New York, NY: Springer, 2008).

[30] A. Safari and M. Abazari, "Lead-Free Piezoelectric Ceramics and Thin Films," IEEE Transactions on Ultrasonics Ferroelectrics and Frequency Control, vol. 57, pp. 2165-2176, Oct 2010.

[31] Y. P. Guo, M. Y. Gu, H. S. Luo, Y. Liu, and R. L. Withers, "Composition-induced antiferroelectric phase and giant strain in lead-free (Nay,Biz)Ti1-xO3(1-x)-xBaTiO(3) ceramics," Physical Review B, vol. 83, p. 054118, Feb 28 2011.

[32] H. J. Lee, S. O. Ural, L. Chen, K. Uchino, and S. J. Zhang, "High Power Characteristics of Lead-Free Piezoelectric Ceramics," Journal of the American Ceramic Society, vol. 95, pp. 3383-3386, Nov 2012.

[33] Y. Gao, Y. Chen, J. Ryu, K. Uchino, and D. Viehland, "Eu and Yb Substituent Effects on the Properties of Pb(Zr0.52Ti0.48)O3-Pb(Mg1/3Sb2/3)O3 Ceramics," Japanese Journal of Applied Physics, vol. 40, pp. 687-693, 2001.

[34] J. B. Lim, S. J. Zhang, J. H. Jeon, and T. R. Shrout, "(K,Na)NbO3-Based Ceramics for Piezoelectric "Hard"Lead-Free Materials," Journal of the American Ceramic Society, vol. 93, pp. 1218-1220, May 2010.

[35] E. A. Gurdal, S. O. Ural, H. Y. Park, S. Nahm, and K. Uchino, "High Power (Na0.5K0.5)NbO3-Based Lead-Free Piezoelectric Transformer," Japanese Journal of Applied Physics, vol. 50, p. 027101, Feb 2011.

[36] N. Quan et al, Current Development in Lead-Free Bi0.5(Na,K)0.5TiO3-Based Piezoelectric Materials, Advances in Materials Science and Engineering, 365391, 2014.

[37] J. Wu et al, Potassium–Sodium Niobate Lead-Free Piezoelectric Materials: Past, Present, and Future of Phase Boundaries, Chem. Rev., 115 (7), pp 2559–2595, 2015.

[38] S. Leontsev, R. Eitel, Progress in engineering high strain lead-free piezoelectric ceramics, Sci. Technol. Adv. Mater. 11 044302, 13pp, (2010).

[39] X. Liu, Design and development of high-performance lead-free piezoelectric ceramics, PhD Thesis, Iowa State University, 2015.

[40] Y. Hosono and Y. Yamashita, "Piezoelectric ceramics and single crystals for ultrasonic medical transducers," Journal of Electroceramics, vol. 17, pp. 577-583, Dec 2006.

[41] K. K. Shung, J. M. Cannata, and Q. F. Zhou, "Piezoelectric materials for high frequency medical imaging applications: A review," Journal of Electroceramics, vol. 19, pp. 141-147, Sep 2007.

[42] H. H. Kim, J. M. Cannata, R. B. Liu, J. H. Chang, R. H. Silverman, and K. K. Shung, "20 MHz/40 MHz Dual Element Transducers for High Frequency Harmonic Imaging," IEEE Transactions on Ultrasonics Ferroelectrics and Frequency Control, vol. 55, pp. 2683-2691, Dec 2008.

[43] B. Jadidian, N. M. Hagh, A. A. Winder, and A. Safari, "25 MHz Ultrasonic Transducers with Lead-Free Piezoceramic, 1-3 PZT Fiber-Epoxy Composite, and PVDF Polymer Active Elements," IEEE Transactions on Ultrasonics Ferroelectrics and Frequency Control, vol. 56,

pp. 368-378, Feb 2009.

[44] G. C. Edwards, S. H. Choy, H. L. W. Chan, D. A. Scott, and A. Batten, "Lead-free transducer for non-destructive evaluation," Applied Physics a-Materials Science & Processing, vol. 88, pp. 209-215, Jul 2007.

[45] D. M. Lin and K. W. Kwok, "Piezoelectric Properties of K(0.47)Na(0.47)Li(0.06)NbO(3)-NaSbO(3) Lead-Free Ceramics for Ultrasonic Transducer Applications," International Journal of Applied Ceramic Technology, vol. 8, pp. 684-690, 2011.

[46] S. T. F. Lee, K. H. Lam, X. M. Zhang, and H. L. W. Chan, "High-frequency ultrasonic transducer based on lead-free BSZT piezoceramics," Ultrasonics, vol. 51, pp. 811-814, Oct 2011.

[47] D. W. Wu, R. M. Chen, Q. F. Zhou, K. K. Shung, D. M. Lin, and H. L. W. Chan, "Leadfree KNLNT piezoelectric ceramics for high-frequency ultrasonic transducer," Ultrasonics, vol. 49, pp. 395-398, Dec 3 2009

[48] Y. Chen, X. P. Jiang, H. S. Luo, J. Y. Dai, and H. L. W. Chan, "High-Frequency Ultrasonic Transducer Fabricated With Lead-Free Piezoelectric Single Crystal," IEEE Transactions on Ultrasonics Ferroelectrics and Frequency Control, vol. 57, pp. 2601-2604, Nov 2010.

[49] J. Yang et al., New KNN-based lead-free piezoelectric ceramic for high-frequency ultrasound transducer applications, Volume 118, Issue 4, pp 1177–1181, 2015.