Questionnaire 2 Exemption 14 of RoHS Annex IV

Lead in single crystal piezoelectric materials for ultrasonic transducers

Acronyms and Definitions

US ultrasonic

1. Background

Bio Innovation Service, UNITAR and Fraunhofer IZM have been appointed1 by the European Commission through for the evaluation of applications for the review of requests for new exemptions and the renewal of exemptions currently listed in Annexes III and IV of the RoHS Directive 201ylj1/65/EU.

You submitted information to substantiate your request for the renewal of the above-mentioned exemption. This information was reviewed and as a result, we ask you to kindly answer the below questions for further clarification of your request until 25 January 2021 latest.

2. Questions

1) In your exemption request you speak of important parameters k33, Kt and d33. Could you please define and explain these paramters?

   K33 is an electromechanical coupling coefficient. These are a measure of the efficiency of the material's ability to convert mechanical energy from vibrations into an output electrical charge and vice-versa. It is explained as the most critical property as it is impossible to compensate for inferior coupling factors by design change. K33 refers to induced strain in direction 3 per unit electric field applied in direction 3.

   Kt is the thickness mode coupling coefficient and is a measure of the effect of thickness on the electromechanical coupling coefficient. Kt affects the impedance of a transducer element, where the best single crystal materials have higher values. Low values can only be somewhat compensated by changing the electrical control circuit design and using multilayer piezoelectric materials.

   d33 is the piezoelectric constant. Piezoelectric constants are defined as is the polarization generated per unit of mechanical stress applied to a piezoelectric material or, alternatively, is the mechanical strain experienced by a piezoelectric material per unit of electric field applied. As properties of single crystal materials depend on axes, there are different constants for each axis and d33 is the constant in direction 3. With single crystals usually having higher d33 values than PZT ceramics.

2) You estimate the amount of lead used in the EU under the exemption to be about 500 g per year and state that this has been estimated by one manufacturer using the amount they ship into the EU and their estimated market share. To avoid misunderstandings, these 500 g are the total

[1] It is implemented through the specific contract 070201/2020/832829/ENV.B.3 under the Framework contract ENV.B.3/FRA/2019/0017

mass of lead used under the exemption in the EU, NOT the volume of lead used by this one manufacturer?

That is correct.

3) You say that the properties of lead-free single crystals have been optimized for specific medical imaging applications so that there are different grades of lead-based piezoelectrics with a wide range of electromechancial properties which cover a wide range of medical imaging applications performed at different frequencies.
Could the same be done with lead-free single crystals to make them applicable to specific applications where their current performance suffices the requirements without claiming that the respective materials can be used for all types of medical ultrasonic imaging?

The exemption renewal request states that the properties of lead-based crystals have been optimized and are superior to all other piezomaterials that have been developed including the few single crystal materials that have been developed. Although alternative Pb-free single crystal materials have been heavily researched, at present (January 2021) only lead-piezoelectric materials can achieve the performance required for medical ultrasound imaging.

4) You explain that besides PMN-PT also PIN-PMN-PT is used in medical US imaging. In you application, however, PIN-PMN-PT is not mentioned further. Where is PIN-PMN-PT used, what are indications for its use?

PMT-PT is widely used as the single crystal piezoelectric material in medical ultrasound applications. PIN-PMN-PT was developed relatively recently and has been proposed for industrial manufacturing applications. Its properties are different to PMT-PT so it is not a drop-in replacement for PMT-PT.

PIN-PMN-PT is often targeted for devices that employ a thin layer of active ceramic, such as higher frequency (>10Mhz Fc) transducers. As the Coercive withstand voltage of PIN material (Ec) is higher than PMN ceramic, there is less risk of depoling the transducer under high drive voltages that can be encountered due to the necessity for adequate tissue penetration for good clinical performance. However, there are challenges as if the system drive voltage is reduced to avoid damaging the transducer, clinical performance may be inadequate.

Medical ultrasound transducer manufacturers main aim is to search for lead-free materials whereas use of PIN-PMN-PT still contains lead.

5) In your application, you explain electromechancial properties of most common lead-based and lead-free piezoelectrics. What about less common lead-free piezoelectrics? Are there any promising lead-free materials with promising properties, even though they might have other disadvantages?

All lead-free piezoelectric solutions have been considered including research materials as well as commercially available materials. However, to date the intrinsic lower electromechanical properties and inferior thermal stability of lead-free materials compared to their lead-based counterparts has not allowed for the development of a solution which would offer a comparable performance and image quality. At present, no lead-free material shows sufficiently promising performance as a potential substitute.

6) You mention that MPB compositions having rhombohedral compositions are widely used in the medical ultrasound market and that a few lead-free compositions with rhombohedral structure have been developed recently.

You also state that 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 medical ultrasound market.

Could you please give us some more insights into MPB compositions and rhombohedral compositions? Are MPB compositions and rhombohedral structures linked, or can both also occur separately?

a. Which ones and what are their properties compared to currently used piezomaterials?

MPB materials are discussed in our exemption renewal request on pages 10 and 11, however we state that these are **not** suitable as substitutes for medical ultrasound applications irrespective whether they are lead-based or lead-free.

Morphotropic Phase Boundary is not a composition but refers to the phase transition between the tetragonal and rhombohedral ferroelectric phases as a result of varying the composition, temperature or pressure. Certain solid solution of perovskite-type ferroelectrics (such as lead zirconate titanate - PbZr1−x Ti x O3 (PZT) and Lead Magnesium niobate-lead titanate (1-x)PbMg1/3Nb2/3O3-xPbTiO3), shortly known as PMN-PT) show excellent properties such as giant dielectric and electromechanical coupling constant in the vicinity of MPB.

At the MPB, the rhombohedral and tetragonal phases may coexist, therefore there may be less stability of material properties (sensitive to temperature, stress and composition), resulting in low thermal stability and inferior electromechanical properties. Rhombohedral compositions near MPB are preferred for piezomaterial performance and stability. For further information Figure 1 in the exemption application illustrates the performance difference between lead-based and lead-free materials.

b. Is there improvement potential foreseeable for these or other lead-free rhombohedral piezomaterials?

COCIR does not foresee any big breakthough in developing lead-free piezoelectric materials with rhombohedral structure for medical ultrasound transducers due to their insufficient piezoelectric properties (for example, poor electromechnical coupling coefficients) comparing to lead-based piezomaterials.

7) You say that some lead-free piezomaterials with rhombohedral structures have been developed recently.

a. Which ones and what are their properties compared to currently used piezomaterials?

Barium titanate and Bismuth Sodium Titanate (BNT) are examples of a rhombohedral materials, which are described in our renewal request.

b. Is there improvement potential foreseeable for these or other lead-free rhombohedral piezomaterials?

Not known. COCIR's members do not carry out research into new materials as this is carried out by Universities and by our suppliers of dielectric materials. Extensive research is being carried out[2], which would need to overcome challenges to their piezoelectric properties, but COCIR is not able to predict the future improvement potential.

[2] For example a paper published in 2018 http://ceramics.hfut.edu.cn/_upload/article/files/35/06/57b4646e4615967ac69a5fbed9de/a02b275e-eafd-4e6d-8798-d87293b3a434.pdf

8) You explain that rhombohedral BNT based ceramics have been used in high power devices due to their high coercive field and thermal stability. What are these power applications?

This is stated in reference 3 of COCIR's exemption renewal request. COCIR has no knowledge of these uses, but they may be industrial processes such as for ultrasonic bonding.

9) You mention cMUTs as a mean to potentially eliminate the use of lead in ultrasonic transducers. Could you please explain in more details this technology and its performance capacities, possibly including some graphics illustrating the technology and how it generates (and receives) ultrasonic waves?

This is explained in reference 8 of COCIR's exemption renewal request. cMUT used thin flexible membranes that oscillate under the influence of an electric field to generate ultrasound. An electric signal is generated when the membrane is exposed to the return ultrasound signal.

cMUT consists of a thin metalized membrane (<few µm) suspended over a silicon (Si) substrate separated by an air or vacuum gap. A thin dielectric layer, such as SiO2, is deposited in the membrane. In operation, DC bias and RF signal are applied to the electrodes on the membrane and substrate. The DC bias generates the electrostatic force, which pulls the membrane toward the substrate. In transmit mode, the membrane vibrates by the superimposed RF signal. Similarly, in receive mode, the DC biased membrane is being deformed (or vibrated) under the action of the incoming ultrasound wave.

Using standard silicon IC fabrication, cMUT cells can be fabracated as small capacitors as illustrated in Fig. 1 below and with the connecting circuit shown in Fig 2. During cMUT operation, a direct current voltage is applied between the metallized membrane and substrate. The membrane is attracted to the bulk 'well' by electrostatic force and induced stress within the membrane. Driving the membrane with an alternating voltage generates an ultrasonic wave. Conversely, if the biased membrane is subject to ultrasound waves as a receiver, a current output is generated due to capacitance change in receive.

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, including output pressure, reliability and linearity. Information from studies is provided to allow a comparison between the technologies in relation to insertion loss and reliability results.

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, endoscopic probes, high frequency linear arrays and probes with wide clinical coverage. Transducers for these applications cannot be fabricated easily using PZT or single crystal technology and therefore accept the reduced acoustic output performance associated with cMUTs.

This technology is still in development, but it is considered highly unlikely by COCIR that sufficient performance will be obtained in the next 5-10 years. (from Oko-Institut e.V. pg.10) cMUT devices utilize a thin membrane of Silicon (typically <2um thick) that is situated over a shallow well that moves from a capacitive coupling mechanism. An AC signal is injected to control the frequency. There are typically thousands of these "drumheads" on a transducer. Each transducer element consists of a selected group of the drumheads. Diameter of the drumheads is the main controlling factor in the resonance of the drumheads. Typically each element can have a multitude of different diameters all active in unison, thus generating large bandwidths because of frequency overlaps. A DC bias is necessary for cMUTs as well. cMUTs excel in receive sensitivity, but the main limitation of cMUT devices is the relatively weaker transmit capabilities compared to PZT based devices.

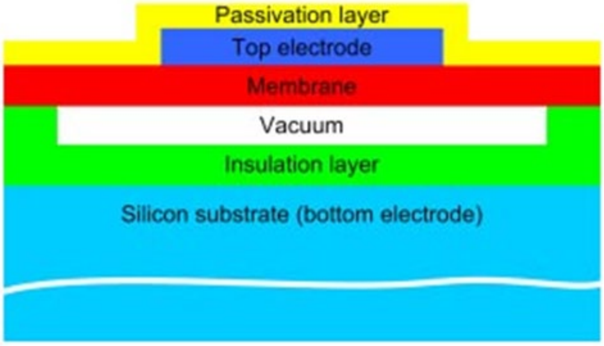


FIGURE 1. Basic CMUT structure.

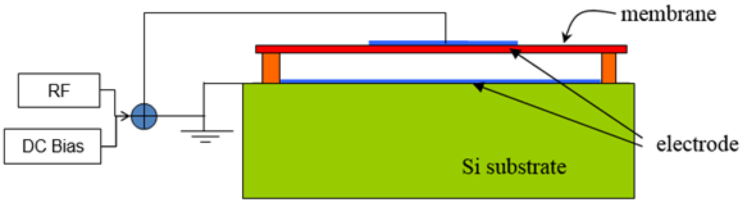


Figure 2 circuit

10) You put forward that lifetimes of cMUTs significantly degrade as pressures are increased towards routinely applied pressures used and achieved with PZT and single crystal materials. What about the sensitivity of CMUTs for ultrasonic signals? If this sensitivity would be higher, the pressulre could be reduced thus increasing the life time of the cMUTs provided they function as sending and receiving element at the same time.

Due to the insertion losses and linearity as described in the exemption request the sensitivity of the cMUTs is not higher than that of PZT or single crystal materials, so pressure cannot be reduced without unacceptable loss of performance.

Specifically in the widely used tissue harmonic imaging (THI) applications, the transmit pressures at low frequencies are more critical than the receive sensitivity senstivity. Low transmit pressure may cause significant Signal to Noise Ratio (SNR) reduction since the tissue harmonics generation is proportional to transmit pressure (by square of amplitude A^2). For instance, 1dB less transmit voltage will result in 2dB lower THI signals. Moreover, the ultrasound wave will be attenuated by the tissue as it is propagating, so it is not easy to overcome poorer SNR by receiver only.

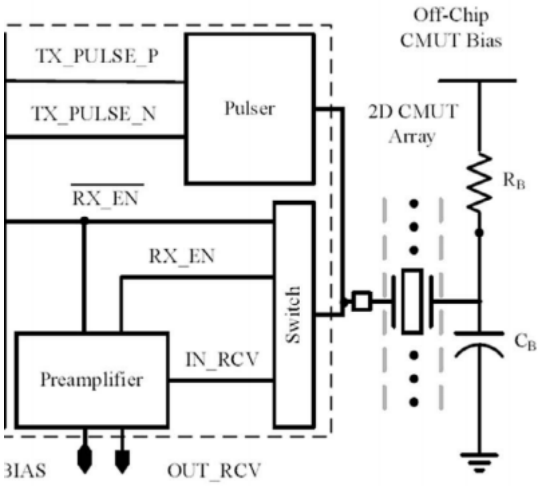
11) You state that some desirable configurations such as 2D arrays for 3D imaging (these use arrays of many elements) use a common bias for all elements. However, if an individual cMUT element fails in such a way as to short the bias, the whole array will no longer function.

a) Could you please explain the meaning of “common bias for all elements”?

Common bias is the applied voltage between the membrane and the substrate. This refers to the DC signal that is necessary to control the Silicon membrane positions relative to the base well and to be able to use capacitive coupling for wave generation.

b) Could you please also explain why a failing individual cMUT element results in failure of the entire array compared to lead-based piezomaterials which seem not to have this problem?

If a failing indiviual cMUT element is due to common DC bias short, then the whole array will not functional. A DC bias voltage is typically applied to common (ground) side of all cMUT elements (e.g. through a capacitor C_B to signal ground as in the figure below). If one element is shorted in such a way (e.g. to ground), the DC bias voltage will drop due to current flow by shorting. The leakage current of shorting also generates extra heating for cMUT. Piezomaterials usually do not need bias to operate, so this failure mode will not occur.



12) We support your argument that exemptions should not overlap with other exemptions and that a clear scope demarcation of exemption 14-IV and exemption 7(c)-I of Annex III is desirable. As long as there is no generally acknowledged definiton of ceramics, the approach to assume or claim single crystal piezomaterials not to be ceramics might not be the most expedient solution to separate the exemption scopes. We think about going the following way:

a) Exclude the scope of exemption 14-IV from the scope of 7(c)-I of Annex III.

   This would be acceptable, but is not necessary if it is accepted that single crystal materials are not ceramics

b) Since we cannot be sure that manufacturers of EEE other than cat. 8 rely on exemption 7(c)-I for leaded single crystal piezomaterials in ultrasonic transducers, we consider shifting exemption 14-IV to Annex III and open it up for all or at least a broader range of ultrasonic applications outside category 8.

   Exemption 14 of Annex IV was originally adopted as a result of the recommendation made by ERA in its report on the inclusion of categories 8 and 9 in scope of the RoHS Directive. Since then, there have not been any requests from industry for exemption 14 to apply to any other RoHS categories. However, COCIR cannot comment on whether this exemption is used in non-medical applications that are in scope of RoHS.

We are aware that this might cause administrative burdens in the transition period, but at the same time deem it necessary to avoid exemptions with overlapping scopes which may also create uncertainties and confusions in the supply chain, which we could actually experience based on questions we received from industry in the past years.

Please let us know your opinion, or which better solutions you might see.

Exemption 14 is for single crystal piezoelectric ultrasound transducers, so it is our understanding that as 7(c)-I is currently worded, it does not include single crystal materials which COCIR believe are not described as "ceramics" creating a demarcation between the scopes. As with the clarification questions posed in 7(c)-I, we are suggesting that the wording of exemption 14 could be changed to:

"Lead in polycrystalline ceramic piezoelectric materials containing PZT, and in single crystal piezoelectric materials made of lead-compounds, used in medical ultrasound transducers", or:

"Lead in polycrystalline ceramic piezoelectric materials and single crystal piezoelectric materials used in medical ultrasound transducers".

COCIR members do not make products in other categories, so cannot comment on other applications.

Please note that answers to these questions may be published as part of the evaluation of this request. If your answers contain confidential information, please provide a version that can be made public along with a confidential version, in which proprietary information is clearly marked.

It would be helpful if you could kindly provide the information in formats that allow copying text, figures and tables to be included into the review report.