CeramTec

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Subject: ***Adaption to scientific and technical progress under directive 2002/95/EC***

Stakeholder comments made in support of **continued** Exemption 7(c) Lead in electronic ceramic parts (e.g. piezoelectronic devices)

Dear Mrs. Zangl,

CeramTec Ag is a renowned producer of technical Ceramics, based in Plochingen, Germany.
The production of piezoceramics based on PZT is located in Lauf/ Germany. No Production takes place outside of germany. The Company is certified according to ISO 14001. based on Lead Zirconate Titanate (PZT) piezo ceramic compounds (lead in ceramic).

The process includes the fabrication of PZT from its raw materials lead oxide, titanium oxide and zirconium oxide. When calcinated to PZT the result is a chemically highly stable piezo material, which is used in a manifold of applications, like ultrasonics, sensors, actuators or energy harvesting.
Examples of applications are:

- piezoelectric actuators for use in internal combustion engines
- knock sensors
- level meters

The industries using PZT within the EU are for example:

- automotive applications
- automation for industries
- medical applications
- Chemical processing,

PZT is often required to operate in applications where; (1) low power consumption is required; (2) safety or environmental aspects have to be taken into account.

It is necessary to point out, that the lead in PZT based piezoceramics is chemically bound into a stable perovskite structure and furthermore sintered to produce ceramic parts with low surface exposed to environment. Therefore it is of minimal risk to the environment after the parts are withdrawn from use.

If persons from the Öko-Institute and Fraunhofer IZM wish to know more about production and application of PZT or to discuss the comments of CeramTec Ag in support of continued exemption further, please contact Hans-Jürgen Schreiner

Yours sincerely,

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Please find enclosed in the appendix

Answers to Specific Questions Section 7C.

Response document to General Questionaire

APPENDIX A:
Roadmap of DKG

APPENDIX B:
Alternative piezo materials
Prof. Dr. M.J. Hoffmann University of Karlsruhe

Adaptation to scientific and technical progress under Directive 2002/95/EC Stakeholder consultation

Specific Questions Section 7C.

1. **What are the different applications of Lead in electronic ceramic parts ?**

   The applications involved are applications of piezoelectric ceramics, for example ultrasonic and sonar applications, automotive applications (e.g. knock sensors, multilayer-actuators), medical applications, non destructive materials testing and aviation. Sensors and actuators as well as energy harvesting are also used in a wide variety of other applications for vibration damping or fine positioning devices for example.

2. **What is the amount of lead per application, the lead content in the homogeneous material, the annual production volume as well as the number of applications related to exemption 7(C) put on the market annually ?**

   The content of Pb^{2+} in PZT based piezoceramics is normally 50-70 weight%. CeramTec is a supplier for piezoceramic components and supplies no systems, so this is the content of leadoxide (bound as Pb2+ in the Perivskite lattice) in the parts sold by CeramTec. The volume of PZT by weight put on the market is around 700 tons per year in a variety of applications with a share of about 60% of the market volume going into automotive applications (e.g. knock sensors, actuators, level sensors, oil sensors, air mass measuring devices). CeramTec delivers a volume of about 35 Mio Euro of piezoceramic products into automotive industries in Europe. The detailed number of applications is hardly to count, because customers use the same piezoceramics for different applications.

3. **Please explain whether and how lead can be substituted in the different applications in ceramics**

   CeramTec frequently reviews the possibility of using other piezoelectric materials. Other piezoelectric materials are known, but none can be considered as a suitable substitute for PZT. Some materials are already used for a few applications (e.g. BaTiO3 or BiTiO3), but they can not substitute PZT by far in the most applications. A ban on PZT would also hinder technical developments towards safety applications or to reduce fuel consumption in cars. Piezoceramic actuators for example are used as well in diesel as in gasoline engines and reduce the consumption to our knowledge by 15-20% which will reduce the CO2 amount in the exhaust.

4. **Please provide a roadmap or similar evidence with activities, milestones and timelines towards a replacement of lead in these applications.**

   Many commercially available lead free piezo ceramic materials and also lead free materials which are under development have been reviewed for current and future applications. Currently none are suitable substitutes. Therefore a roadmap can hardly be given. In appendix A, there is a tentative roadmap of DKG and DGM. An overview over current developments is given in appendix B by an independent renown specialist.
   CeramTec offers to its customers to take back used ceramics and to recycle them in a controlled process.

5. **Do you consider thick film applications to be covered by the current wording of exemption 7(c)? This not applicable to the comments made in support of continued exemption for piezo devices**

   Yes, for certain applications thick film piezoceramics based on PZT are considered as a part of the exemption.

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General questionnaire

- **For which substance(s) or compound(s) should the requested exemption be valid?**

  Lead in electronic ceramic parts (e.g. piezoelectronic devices)

- **What is the application in which the substance/compound is used for and what is its specific technical function?**

  Piezoceramics are used in a multitude of applications, such as sound and vibration transducers, smart structures, sensors and actuators. Its specific function is, to convert an electrical signal into a mechanical movement (actuating or so called indirect piezoelectric effect) or to convert a mechanical signal into an electrical signal (sensing or energy harvesting, so called direct piezoelectric effect)

- **What is the specific (technical) function of the substance/compound in this application?**

  Polarized piezo-ceramic parts exhibit the characteristic of
  a) sensing mechanical deformation stress and convert it into a electrical signal (knock sensors, vibration sensors) for sensor or energy harvesting applications
  b) vibration or elongation or force generation when a voltage is applied (actuators, sonar- and ultrasonic applications.
  c) both effects for sonar or adaptive applications (smart structures).

- **Please justify why this application falls under the scope of the RoHS Directive (e.g. is it a finished product? is it a fixed installation? What category of the WEEE Directive does it belong to?).**

  Piezoelectronic devices are ceramic components. Such components are not finished products and when placed on the market as individual items, they are outside the scope of the WEEE Regulations. These components will be placed into systems, and their mass compared to the mass of the system might be very small. When a finished product containing components which include restricted chemicals are placed on the market, or when discarded as WEEE, the components will contribute to the reported weight of EEE or WEEE. Since CeramTec is not producing systems but only the ceramic components, this can not be answered by CeramTec directly, as CeramTec is only able to report about the ceramic part itself.

- **What is the amount (in absolute number and in percentage by weight) of the substance / compound in: i) the homogeneous material, ii) the application and iii) total EU annually for RoHS relevant applications?**

  The content of Pb^{2+} in PZT based piezoceramics is normally 50-70% by weight. Since Ceramtec usually supplies only the piezoelectrical component and no systems, this is the content of the parts sold by CeramTec. The percentage for the different applications can not be easily given by CeramTec.

- **Please check and justify why the application you request an exemption for does not overlap with already existing exemptions respectively does not overlap with exemption requests covered by previous consultations.**

  To our information there are no overlapping exemption requests for the category “Lead in electronic ceramic parts (e.g. piezoelectronic devices).”

- **Please provide an unambiguous wording for the (requested) exemption. Documentation provided by stakeholders including replies to the questions above should take the following points into consideration:**

  Lead in electronic ceramic parts (e.g. piezoelectronic devices)

- **Please justify your contribution according to Article 5 (1) (b) RoHS Directive whereas:**

  - **Substitution of concerned hazardous substances via materials and components not containing these is technically or scientifically either practicable or impracticable;**

    Substituting PZT is currently not possible. All Materials known up to now, as well as in literature and commercially available, exhibit significantly lower piezoelectric activity by at least a factor of two ($BaTiO_3$, $BiTiO_3$, $(KNa)NbO_3$ or $LiNbO_3$ based materials). This would at least double the amount of material used. Some of these materials are already used for special applications (e.g. very high temperature applications), but they all lack the universal applicability of PZT. Please see appendix A for a detailed discussion. Furthermore, Bismuth for example is very close to Lead from an environmental point of view. Banning PZT and use of only those materials would be a severe drawback to technical and environmental progress. Therefore this is technically impractible.

  - **Elimination or substitution of concerned hazardous substances via design changes is technically or scientifically either practicable or impracticable;**

    For by far the most applications, the piezoelectric effects need to be high to get satisfying results. So, to our knowledge, a substitution of PZT via design changes is impracticable.

  - **Negative environmental, health and/or consumer safety impacts caused by substitution are either likely or unlikely to outweigh environmental, health and/or consumer safety benefits thereof (If existing, please refer to relevant studies on negative or positive impacts caused by substitution).**

    The impact of PZT on the environment, as shown for example in a study about leaching by the University of Erlangen Nürnberg in 1981 (Forschungsbericht 81-10301326), is very small, as the lead is chemically bound inside the stable crystal-lattice.

    The EINECS (European INventory of Existing Commercial chemical Substances) database, recognises PZT by its CAS number. The collection of further data for CAS Number 12626-81-2 was placed by the bureau on its lowest priority category. For this chemical the web site stated “This substance is not listed in a priority list (as foreseen under Council Regulation (EEC) No 793/93 on the evaluation and control of the risks of existing substances.).”
    (please see for example http://ecb.jrc.it/esis/)

    PZT is the most efficient piezoelectric material, and so the use of it reduces the amount of material necessary to obtain a certain performance (which would be by far bigger, if one uses for example $BiTiO_3$). It also reduces the amounts of voltage and current required and so reduces significantly energy consumption or, on the other hand, energy produced in energy harvesting applications is quite high.

So the use of PZT and the progress which has been made in safety and environmental aspects (e.g. crash detection, fuel consumption, flow measurements and so on) outweighs the environmental impact by far.

- **Please provide sound data/evidence on why substitution / elimination is either practicable or impracticable (e.g. what research has been done, what was the outcome, is there a timeline for possible substitutes, why is the substance and its function in the application indispensable or not, is there available economic data on the possible substitutes, where relevant, etc.).**

  Lead Zirconate Titanate (PZT) has by far the highest piezoelectric effect of the commercially available or known piezoelectric substances.

  There are numerous academic papers reviewing the possibilities of alternative lead-free compounds. Despite the research of more than 20 years none of the described systems has entered into production which has, to our knowledge, mainly two reasons:

  - the compositions with interesting piezoelectric coefficients mostly have other problems (e.g. high electrical conductivity, strong temperature dependency)

  - the reproducibility of the reported piezoelectric values is not clear.

- **Please also indicate if feasible substitutes currently exist in an industrial and/or commercial scale for similar use.**

  For some commercial and industrial applications other compounds are known to have piezo properties, These include but are not limited to Barium Titanate, Bismuth Titanate, organic substances such as PVDF.
  CeramTec also produces low lead materials such as $BaTiO_3$ based materials with highly reduced content of lead. Those are currently used by very few customers, which have a very limited necessity of high piezoelectric coefficients, or special other implications apply (e.g. acoustical reasons, historical reasons)

- **Please indicate the possibilities and/or the status for the development of substitutes and indicate if these substitutes were available by 1 July 2006 or at a later stage.**

  To our knowledge, today there is no substitute known, which has the multitude of advantages PZT offers for piezoelectric components. All known materials may show in one aspect or another reasonable values, but none of them is able to replace PZT. This is only possible in some very defined applications (where they are already applied as the example $BaTiO_3$ shows).

- **Please indicate if any current restrictions apply to such substitutes. If yes, please quote the exact title of the appropriate legislation/regulation.**

  Currently we have no knowledge of any restriction applying.

- **Please indicate benefits / advantages and disadvantages of such substitutes**.

  - Barium Titanate, Limitations in piezoelectric coefficient and max. operation temperature, Curie Temperature around 120-180°C.

  - Bismuth Titanate, Disadvantages in stability, higher electrical conductivities and lower piezoelectric coefficients

  - $(KNa)NbO_3$ currently under investigation, not available yet

- PVDF — Used for pyrosensors, not a substitute for PZT based applications

- **Please state whether there are overlapping issues with other relevant legislation such as e.g. the ELV Directive that should be taken into account.**

  The End of Life Vehicles Directive Annex II Materials and components exempt from Article 4 (2)(a), and this includes “Electrical components which contain lead in a glass or ceramic matrix compound except glass in bulbs and glaze of spark plugs”.

- **If a transition period between the publication of an amended Annex is needed or seems appropriate, please state how long this period should be for the specific application concerned**

  This is difficult to answer, because substitutions are mainly in fundamental research (e.g governmental founded projects) and it is not clear if those materials have really the possibility to replace PZT one day. The German ceramical society (DKG) for example has recently published a roadmap, that components and devices based on lead free piezo ceramics might enter the market by around 2020
  (Hochleistungskeramik 2025- Strategieinitiative für die Keramikforschung in Deutschland des Koordinierungsausschusses Hochleistungskeramik der DKG und DGM, 2008 Werkstoffinformationsgesellschaft mbH Frankfurt ISBN 978-3-88355-364-1)

If you have further questions, please feel free to contact us. The contact person is:

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best regards

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Adaptation to scientific and technical progress under Directive 2002/95/EC
Stakeholder consultation
APPENDIX A
Roadmap of DKG

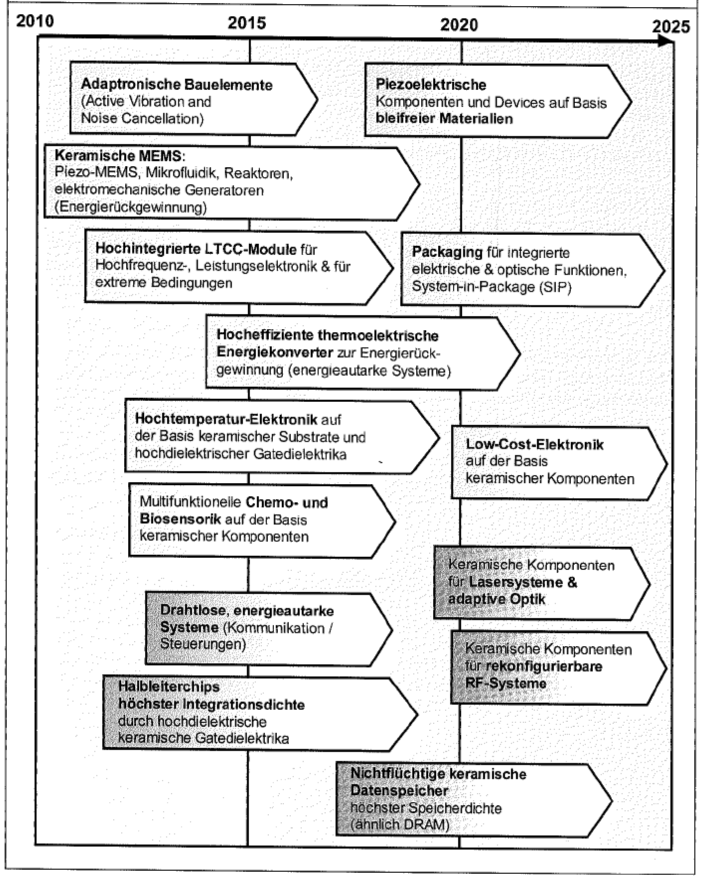

Abb. 5(1): Roadmap für die Bereiche „Elektronik, Information & Kommunikation"

Erkenntnisbedarf

Neuartige und verbesserte Funktionen:
- Bleifreie Piezokeramiken für industrielle Hochleistungsanwendungen
- Hochtemperaturfähige (T> 600° C) Funktions- (Elektro-) Keramiken und thermisch angepasste Substrate
- Materialien für Datenspeichermedien und Mikroelektronik
- Magnetisch und elektrisch (in weiten Bereichen) steuerbare Funktionswerkstoffe
- Neue Funktionalitäten und Leistungsniveaus durch Nanostrukturen
- Nutzung biologischer Konzepte für Funktionskomponenten (z.B. Biomimetik)

Integration, Miniaturisierung und Prozesstechnik:
- Verbesserte Materialkompatibilität für Vielschichtsysteme und MEMS
- Senkung der Prozess- (Sinter-) Temperaturen für kostengünstigere Herstellung (z.B. Substitution von Edelmetallelektroden)
- Feinere Strukturierung für keramische Mikrosysteme (<2 µm)
- Low-Cost-Technologien: Freeforming, Drucktechniken, µ-PIM
- Kostengünstige Dünnschichttechnologien (z.B. CSD) mit industrieller Fertigungsqualität
- Halbleiter-kompatible Prozesstechniken und Workflows
- Biologisch basierte Herstellverfahren für Keramiken (z.B. Biomineralisation)

Simulation und Modellierung:
- Durchgängige Modellierungstools für die Funktionssimulation von der Werkstoffebene bis zur Systemintegration
- Modelle und Tools zur Vorhersage von Zuverlässigkeit und Lebensdauer
- Qualitätsbezogene Modellierung von Prozesstechnologien und Herstellungsprozessen

Abb. 5(2): Erkenntnisbedarf für die Bereiche „Elektronik, Information & Kommunikation"

Adaptation to scientific and technical progress under Directive 2002/95/EC
Stakeholder consultation
APPENDIX B

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Current status of lead-free piezoelectric ceramics as alternatives for PZT

Piezoelectric ceramics based on lead zirconate titanate (PZT) have been investigated for many decades. The most striking feature of PZT is the complete solid solution between lead titanate (PT) and lead zirconate (PZ) with a structural change from a tetragonal modification to a rhombohedral modification at the so-called morphotropic phase boundary (MPB). The MPB is nearly temperature independent up to the Curie-temperature which gives a relatively stable electromechanical behaviour from PZT ceramics over a wide temperature regime. Due to the well-known phenomena at the MPB in PZT, investigations on lead-free piezoelectrics are focused to systems exhibiting also a MPB. The most promising material systems identified today are perovskites based on solid solutions between $(Na_{0,5}Bi_{0,5})TiO_3$ (BNT) and $BaTiO_3$ (BT) and between $NaNbO_3$ and $KNbO_3$ (KNN).

The electromechanical properties of KNN do not show a pronounced maximum at the MPB, as it is the case for PZT. The piezoelectric coefficient d_{33} is approximately 100-200 pC/N [1-3] compared to values of 400-600 pC/N for soft PZT. Recent investigations indicate that the d_{33} could be significantly increased when Na and K is partially substituted by Li and Nb by Sb and Ta [4]. The performance increase is probably caused by a shift of another, more effective, but temperature dependent MPB between an orthorhombic and a tetragonal structure, from above 200°C to room temperature [5]. The more complex KNN with Li, Sb, and Ta exhibit piezoelectric coefficients of 300-450 pC/N similar to PZT, but only in a narrow temperature regime near room temperature. An increase or decrease in service temperature will then reduce strain and polarisation. Up to now, there is no strategy for enhancement of the

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temperature stability. Another critical issue of KNN-based systems is the process stability during up-scaling from a laboratory scale to mass production. Raw materials used are usually the corresponding oxides and carbonates. The carbonates are strongly hygroscopic and cannot be processed in water. Small changes in stoichiometry (ratio of Na+K / Nb) have a significant effect on sintering and grain growth which makes it difficult to keep the microstructure constant [6]. It is not worthwhile to mention here that processing issues related to a co-firing process with internal electrodes (necessary for the production of multilayer actuators) has not yet even started to be under investigation.

BNT-BT is also a lead-free system with a MPB, but the MPB is much more temperature dependent compared to PZT [7,8]. Compositions at the MPB exhibit also a pronounced maximum of the electromechanical properties (d_{33}, ε_r), similar to PZT, but the maximum d_{33}-values are in the range of 100-140 pC/N [9]. Curie-temperature for morphotropic compositions is around 300°C, but there is a phase transition from the ferroelectric state to a non-ferroelectric state already at 100-120°C (depolarisation temperature). Applications are therefore restricted to a limited temperature regime. BNT-BT solid solution were modified by a substitution of Na with K (BKT) [10, 11] or a replacement of Ba by Sr or Ca [12-14]. The consequence of all the modifications is a shift of the MPB and a decrease of the depolarisation temperature. The most extreme case has been reported by Zhang et al. who found a giant strain at high fields (0.45% at 8 kV/mm) when the samples undergo a field induced phase transition from the ferroelectric to the antiferroelectric state [15]. These materials are again very sensitive to temperature changes and it is questionable if the effect can be used without significant degradation of the material. Processing of ferroelectric ceramics based on BNT-BT seems to be more robust compared to KNN-based systems, but processing of multilayer actuators with internal electrodes has also not yet been explored.

Summary: Major efforts have been made in the last years to develop lead-free ferroelectric ceramics. The two systems KNN and BNT-BT are identified as the most promising ones, but they are still far away from applications where high strains over a wider temperature regime (-40-150°C) are required. Furthermore one has to consider that PZT has unique properties in terms of tuning the material properties by using dopants at different levels to create the soft- and hard- type PZTs [5]. Neither KNN nor BNT-BT exhibits this feature at the moment and there are only a few hints indicating that doping directly affects the performances [16, 17].

Karlsruhe, March 25, 2008

(Prof. M.J. Hoffmann)

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