

EIA/CB-30

EIA ENGINEERING BULLETIN

Industry Response to Potential Elimination of RoHS Exemption 7(c)-I

EIA/CB-30

February 2015



Electronic Components Industry Association

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(From Project Number 5350, formulated under the cognizance of the P-1 Committee on Resistive Devices Standards).

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Directive 2011/65/EU of the European Parliament and of the Council of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS recast) continued and expanded the restrictions on hazardous substances that have been in place since February 2003. Annex III of the current directive lists various exemptions to these requirements. One of these, exemption 7(c)-I (*“Electrical and electronic components containing LEAD in a glass or ceramic other than dielectric ceramic in capacitors [piezoelectronic devices] or in a glass or ceramic matrix compound”*) applies to certain raw materials required in the manufacture of most resistors that use thick film technology.

Currently, lead (Pb) is one of the necessary components of the glass used in thick film resistor elements and passivation. It is included at a percentage that bonds the lead ions into the silicate glass matrix. As a result, it is bound as part of the glass material and would require extremely high temperatures (800°C) to separate. Any substance that would cause leaching of lead into the environment would have to break down the glass material itself.

There are two critical functions of lead in these materials. The first is to reduce the working temperature of the glass. The component manufacturing process normally subjects these parts to around 500-600°C. Without the lead, a higher temperature is needed, resulting in a higher processing cost. The second function of lead in a lead-borosilicate is to give the glass a better dielectric strength, allowing better protection from high-voltage and high-power conditions. This has been confirmed in testing. The fully lead-free parts (with no RoHS exemption) are not as stable in long-term operation. No acceptable technical substitute for the current lead bearing materials has been developed yet. These are the reasons exemption 7(c)-I is necessary.

The current version of RoHS maintains the 7(c)-I exemption until at least July 2016. The EU can renew it and many industry groups have petitioned for its renewal. It is our expectation that the EU will renew this exemption until at least 2021 because of the economic costs and the technical barriers to its elimination.

Annex -1

Supplementary Information to CB-30

Final application for renewal of RoHS2 (2011/65/EU) Annex III Exemption # 7(c) – I prepared under the umbrella of the cross-industry project submitted Jan 16th, 2015 to the European Commission by the Application for Renewal of RoHS2 Exemptions Cross-Industry Project Strategic Management Team.

Exemption Request Form





Date of submission: January 16, 2015

1. Name and contact details

1) Name and contact details of applicant:

American Chamber of Commerce to the European Union (AmCham EU) ID number: 5265780509-97		European Partnership for Energy and the Environment (EPEE) ID number: 22276738915-67		TechAmerica Europe (TAE) ID number: 2306836892-93	
DIGITALEUROPE ID number: 64270747023-20		European Passive Components Industry Association (EPCIA) ID number: 22092908193-23		Zentralverband Elektrotechnik- und Elektronikindustrie e. V. (ZVEI) ID number: 94770746469-09	
Electronic Components Industry Association (ECIA)		European Semiconductor Industry Association (ESIA) ID Number: 22092908193-23		Avago Technologies Ltd	
European Ceramic Industry Association (Cerame-Unie) ID number: 79465004946-12		Information Technology Industry Council (ITI) ID number: 061601915428-87		Diodes Incorporated	
European Coordination Committee of the Radiological, Electromedical and Healthcare IT Industry (COCIR); ID Number: 05366537746-69		IPC – Association Connecting Electronics Industries		Ferro Corporation	
European Committee of Domestic Equipment Manufacturers (CECED) ID number: 04201463642-88		Japan Business Council in Europe (JBCE) ID number: 68368571120-55		Knowles (UK) Ltd	
European Garden Machinery Industry Federation (EGMF) ID number: 82669082072-33		LIGHTINGEUROPE ID number: 29789243712-03		PI Ceramic	

With support from:

Japan Electronics and Information Technology Industries Association (JEITA) ID number: 519590015267-		Japan Electrical Manufacturers' Association (JEMA)		Japan Business Machine and Information System Industries Association (JBMA) ID number: 246330915180-10		Communications and Information network Association of Japan (CIAJ)	
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**2) Name and contact details of responsible person for this application
(if different from above):**

Lead in Ceramic	
Company: Murata Elektronik GmbH	Tel.: +49 (0) 911 6687 412
Name: Klaus Kelm	E-Mail: kkelm@murata.com
Function: Engineer Environmental Management	Address: Holbeinstr. 23; D-90441 Nuernberg Germany
Lead in Glass	
Company: VISHAY BC components BEYSCHLAG GmbH	Tel.: +49 (0) 481 95-457
Name: Wolfgang Werner	E-Mail: wolfgang.werner@vishay.com
Function: Sr. Mgr. Research & Development Draloric/Beyschlag Resistors Division	Address: Rungholtstr. 8-10, D-25746 Heide, Germany

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:

In the existing wording electronic components expressed as "capacitors" are precisely speaking "discrete capacitor components" which are out of the technical scope applicable to exemption 7(c)-I. Capacitors are covered by exemption 7(c)-II as well as by exemption 7(c)-III (which has already

expired). We propose the underlined additions to the current wording for clarification of the technical scope of 7(c)-I/ 7(c)-II /7(c)-III. Our proposal does not have the intention to enlarge the technical scope of 7(c)-I.

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”

Proposed additions (underlined):

“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”

Note: Our proposal does not have the intention to enlarge the technical scope of 7(c)-I, it has the only intention to revise the current wording into a more precise, unambiguous meaning.

Additional Explanation:

Discrete disk-type ceramic capacitors and multilayer ceramic capacitors¹ were split from this exemption 7(c)-I into 7(c)-II and 7(c)-III. However, with RoHS exemption 7(c)-III having expired on 1 January, 2013, misinterpretations have occurred with “capacitors” being mistaken for “electrostatic capacitance” due to the ambiguity of the expression “capacitors”. That is, since all ceramic components have electric capacitance, there have been misinterpretations that lead in all ceramic components (including ICs and boards) having electric capacitance for a rated voltage of 125 V AC or less, or 250 V DC or less, was included in the technical scope of 7(c)-III and became restricted with the expiry of that exemption. As already mentioned, what was split from exemption 7(c)-I and has expired as exempted application in 7(c)-III is lead in dielectric ceramic of discrete disk-type ceramic capacitors and multilayer capacitors for a rated voltage of 125 V AC or less, or 250 V DC or less. All other lead in ceramic and/or glass of electrical and electronic components is covered by the scope of exemption 7(c)-I. For this reason, it became necessary to revise the existing wording of 7(c)-I to a more precise content.

As a conclusion, in order that anyone can have the correct understanding of the exemption scope without having to refer to exemption 7(c)-III (already expired) or the final report previously mentioned, the technical scope excluded from the exemption should be clarified and rectified to its original meaning, i.e. discrete capacitor components.

Duration where applicable:

We apply for renewal of this exemption for categories 1 to 7, 10 and 11 of Annex I for an additional validity period of 5 years. For these categories, the validity of this exemption may be required beyond this timeframe. Although applications in this exemption renewal request may be relevant to categories 8 & 9, this renewal request does not address these categories. Further, categories 8 & 9 have separate maximum validity periods and time limits for application for renewals.

¹ Technical scope specified on page 188 “Shapes and manufacturing of capacitors ”of “Adaptation to scientific and technical progress of Annex II to Directive 2000/53/EC (ELV) and of the Annex to Directive 2002/95/EC (RoHS) final report”

functionality. In addition, chemical stability and mechanical strength of glass are improved, and excellent reliability can be obtained.

As there are extremely numerous applications of utilizing lead-containing ceramic and/or glass, it is impossible to list all of them. Please refer to examples provided in Annex 2, Annex 3 (Ceramic) and Annex 5 (Glass). These are "illustrative" examples and they do NOT constitute a comprehensive list of the uses of lead in ceramics and in glass used in electronic components.

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

Very varied depending on application, up to 93 wt%.

5. Amount of substance entering the EU market annually through application for which the exemption is requested: ~ 350 tons

Please supply information and calculations to support stated figure.

Estimate based on 2013 data for the quantity of lead used for applications covered by this exemption from the below companies, who represent the major players on the EU market:

Ceram Tec

Emerson

EPCOS

Freescale

Johnson Matthey Piezo ProductsMeggitt DK

Morgan Advanced Materials

Murata

PI Ceramic

[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].

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 company figures.

It should be noticed that there may 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. 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.

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?

Lead is used in Electric and Electronic Components incorporated in EEE. The number of applications and the corresponding materials using Pb in glass and/or ceramic are so numerous it is impossible to list them all. Please refer to examples provided in Annex 1 (Ceramic) and Annex 4 (Glass). These examples are "illustrative" examples and they do not constitute a comprehensive list.

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

Although some progress has been reported in the extremely limited applications, the incorporation of lead into the crystal structure of ceramic is absolutely indispensable to obtain the required effects and functionality, for example a high performance at the application temperatures etc. Without the necessary minimum performance requirements in the respective applications, the ceramic cannot perform according to the standards such as commodity products specification/Minimum performance requirements, etc. Glass containing lead as a constituent element is able to provide the high functionality required for electrical and electronic components. Such glass can fulfil the appropriate characteristics and manage to meet the high reliability requirements over a wide range of applications.

For details please refer to Product Examples in Annex 1 (Ceramic), Annex 2 (Piezoelectric ceramic), Annex 3 (Positive Temperature Coefficient Semiconductor ceramic) and Annex 4 (Glass).

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.)

Currently one third of WEEE in the EU is being reported by compliance schemes as separately collected and appropriately managed (note some of this might be via destinations outside the Member State of origin).

The remaining WEEE is either:

- 1) Collected by unregistered enterprises and properly treated
- 2) Collected by unregistered enterprises and improperly treated or even illegally exported abroad or
- 3) Disposed of as part of residual (e.g. municipal) waste (e.g. to landfills or incinerators).

References:

[1] Eurostat

http://epp.eurostat.ec.europa.eu/portal/page/portal/waste/key_waste_streams/waste_electrical_electronic_equipment_weee

The component manufacturers are not directly involved in EEE Waste - In general there is no closed loop system, just on customer basis related to specific sectors. There are some companies that reprocess recycled PZTs to reuse it, such as re-poling.

Some companies recycle metallic Pb from PZT.

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: Some EE Equipment is recycled and refurbished. Some Equipment is disposed as part of residual waste (e.g. to landfills or incinerators).

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 _____

Electrical equipment containing electronic parts are not collected or recycled separately from other types (if any) of electrical equipment and there are no data on the volume of the lead in the parts refurbished, recycled or landfilled.

However, we provide estimates as follows:

Total Waste (t)	2005	2006	2007	2008	2009	2010
Products put on the market	1.394.785	6.636.645	9.719.550	10.398.205	9.205.514	9.574.734
Reuse	3.147	20.725	26.404	44.001	59.316	69.368
Recovery	334.462	1.391.705	2.297.955	2.874.517	3.071.115	2.785.286
Total recycling and reuse	305.816	1.236.613	2.030.483	2.564.782	2.833.061	2.564.384
Treated in the Member State	251.034	1.280.288	2.119.001	2.554.495	2.790.144	2.775.050
Treated in another Member State of the EU	9.222	82.917	125.786	150.912	141.180	165.717
Treated outside the EU	7	25.932	96.891	95.759	110.988	106.465

Pb content (t) max	2005	2006	2007	2008	2009	2010
Products put on the market	1.395	6.637	9.720	10.398	9.206	9.575
Reuse	3	21	26	44	59	69
Recovery	334	1.392	2.298	2.875	3.071	2.785
Total recycling and reuse	306	1.237	2.030	2.565	2.833	2.564
Treated in the Member State	251	1.280	2.119	2.554	2.790	2.775
Treated in another Member State of the EU	9	83	126	151	141	166
Treated outside the EU	0	26	97	96	111	106

Based on the trend of waste amount during the period 2007 to 2010 an estimated mean value can be calculated for 2013 waste under the worst case assumption that Lead content ratio of the waste is not exceeding the RoHS limit, i.e. less or equal to 0.1 percent.

Estimate 2013:

Maximum lead content for Products on the market: ~ 9.000 t

Reuse: ~ 100 t

Recovery: ~ 3500 t

Total Recycling and reuse: ~3300 t

See file reference: [EEE Waste Pb Amount.xlsx]

References: [1] Eurostat

http://epp.eurostat.ec.europa.eu/portal/page/portal/waste/key_waste_streams/waste_electrical_electronic_equipment_weee

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**

As described in the annexes, there is no suitable substance for substituting lead.

The results of industry's efforts to analyze possible alternative substances are shown in the annexes.

For details please refer to Annex 1 (Ceramic), Annex 2 (Piezoelectric ceramic), Annex 3 (Positive Temperature Coefficient Semiconductor ceramic) and Annex 4 (Glass).

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

As described in the annexes, there is no suitable substance for substituting lead.

The results of industry's efforts to analyze possible alternative substances are shown in the annexes.

No data available, for details please refer to Annex 1 (Ceramic), Annex 2 (Piezoelectric ceramic), Annex 3 (Positive Temperature Coefficient Semiconductor ceramic) and Annex 4 (Glass).

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 (piezoelectric) properties are inferior when compared with lead-containing ceramic and cannot be stably achieved throughout a wide temperature range.

Moreover, the properties described in the research papers listed in Annex 5 were obtained in the laboratory and experience has shown that these cannot generally be achieved stably at a

mass production scale. There are still many remaining technical 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 research has shown that the required properties for substituting almost all of the applications cannot be obtained.

For details please refer to Annex 1 (Ceramic), Annex 2 (Piezoelectric ceramic), Annex 3 (Positive Temperature Coefficient Semiconductor ceramic) and Annex 4 (Glass).

(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 (21 July, 2021)

For further details please refer to Product Examples in Annex 1 (Ceramic), Annex 2 (Piezoelectric ceramic), Annex 3 (Positive Temperature Coefficient Semiconductor ceramic) and Annex 4 (Glass).

For details please refer to Annex 1 (Ceramic), Annex 2 (Piezoelectric ceramic), Annex 3 (Positive Temperature Coefficient Semiconductor ceramic) and Annex 4 (Glass).

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 [1]

Candidate list [1]

Proposal inclusion Annex XIV

Annex XIV

[1]: Lead Titanium Zirconium Oxide / EC 235-727-4 / CAS 12626-81-2 and Lead Titanium Trioxide / EC 235-038-9 / CAS 12060-00-3

Restriction

Annex XVII

Registry of intentions

Registration

2) Provide REACH-relevant information received through the supply chain.

Name of document: None

(B) Elimination/substitution:

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

Yes. Consequences? _____

No. Justification: No substitutes with required properties exist.

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

Yes.

Design changes:

Other materials:

Other substance:

No.

Justification: No substitutes with required properties exist

3. Give details on the reliability of substitutes (technical data + information): Not applicable as no substitutes with required properties exist

4. Describe environmental assessment of substance from 4.(A)1 and possible substitutes with regard to

1) Environmental impacts: N/A

2) Health impacts: N/A

3) Consumer safety impacts: N/A

⇒ Do impacts of substitution outweigh benefits thereof?

Please provide third-party verified assessment on this: N/A

(C) Availability of substitutes:

a) Describe supply sources for substitutes: None

b) Have you encountered problems with the availability? Describe: N/A

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? N/A

(D) Socio-economic impact of substitution: N/A

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

Increase in direct production costs

Increase in fixed costs

Increase in overhead

Possible social impacts within the EU

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:

Up to the present moment substitution technology has not been found, but many potential compositions have been investigated in order to develop reliable technical solutions on industrial scale however below are further examples of environmental and health and production impacts of major candidates:

Potential future candidates under investigation are expected to have more difficult raw materials and process, even under mass production considerations.

Niobium, bismuth-based substitutes: have a higher impact on environment during extraction and purification than lead, as lead is already recycled with high recovery and is relatively abundant in nature (10 to 70 times more than Bi and 3 times more than Nb).

The environmental impact of lead in ceramic and glass is low, because of the low water solubility of lead contained in ceramic and glass, therefore, leakages into the environment are very low. Current PZT production is based on water; potential substitutes would require alternative technology based on organic solvents (e.g. isopropyl alcohol, ethanol, acetone). Such solvent-based technologies and the requirement to meet ATEX regulations would result in higher efforts and risks in health and environment protection, e.g. to avoid emission of solvents (Isopropyl alcohol, Ethanol, Acetone) that are VOCs (volatile organic carbon) which also need to be minimized in the EU due to the Industrial Emissions Directive 2010/75/EU.

PZT is used in industry for processing of ceramic for many years under controlled worker conditions. Health impact has been well investigated. Please refer to references below.

References:

[1] Worker Exposure to Lead Titanate Zirconate in an Ontario Company M.L. Roy, MD, PhD; S.Siu, Md; W.Waddell, MD; P.Kennedy, BSc

See file reference: [Worker Exposure to lead.pdf]

[2] COMMENTS ON AN ANNEX XV DOSSIER FOR IDENTIFICATION OF A SUBSTANCE AS SVHC AND RESPONSES TO THESE COMMENTS

See file reference: [rcom_lead_titanium_zirconium_oxide_en.rtf]

Below are examples of availability of the major candidate materials.

Twenty critical raw materials were identified as critical from the list of fifty-four candidate materials in 2013:

Antimony	Beryllium	Borates	Chromium	Cobalt	Coking coal	Fluorspar
Gallium	Germanium	Indium	Magnesite	Magnesium	Natural Graphite	Niobium
PGMs	Phosphate Rock	REEs (Heavy)	REEs (Light)	Silicon Metal	Tungsten	

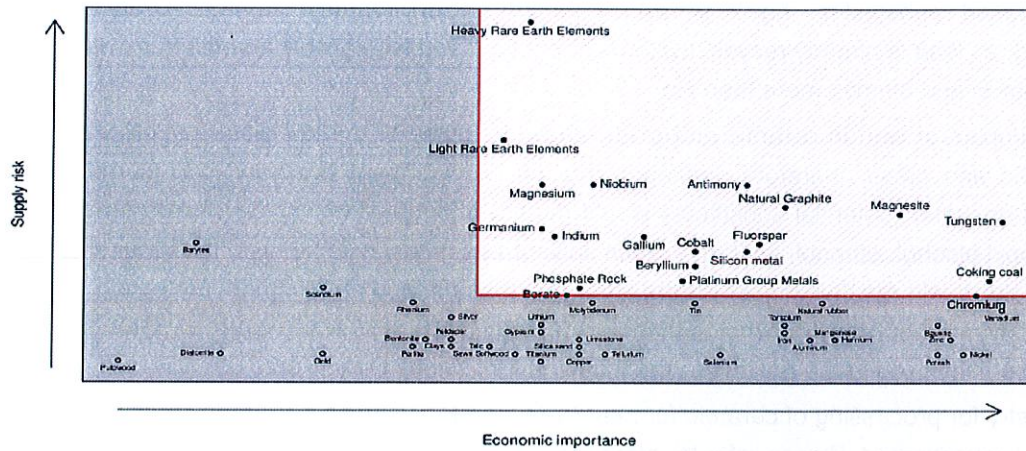
Rem: Tantalum was on the previous critical raw materials list

References:

[1] http://ec.europa.eu/enterprise/policies/raw-materials/critical/index_en.htm

See file reference: [CELEX_52014DC0297_DE_TXT.pdf]

The overall results of the 2013 criticality assessment are shown below; the critical raw materials are highlighted in the red unshaded criticality zone of the graph.



Supply risk: in order to measure the supply risk of raw materials, the World Governance Indicator (WGI) was used. This indicator takes a variety of influences into account such as voice and accountability, political stability and absence of violence, government effectiveness, regulatory quality, rule of law or control of corruption.

References:

[1] http://ec.europa.eu/enterprise/policies/raw-materials/critical/index_en.htm

[2]

See file reference: [EU-Rohstoffinitiative.pdf]

[2]

See file reference: [File:COM_2011_0025_FIN_DE_TXT.pdf]

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:

Technical Document – Annex 1:

Product category: Electrical and electronic components containing lead in a ceramic
Authors: JEITA experts

4. Technical Description of the Exemption Request/Revocation Request

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

Ceramic constituted by oxides of tetravalent cations of Group 4 elements¹ and divalent cations of lead (Pb) have the outstanding special characteristics of stably bringing out electrical properties (dielectric, piezoelectric, pyroelectric, ferroelectric, semiconductor, magnetic properties) over a wide use range (temperature, voltage, frequency).

These lead-containing ceramic are not only widely used as main constituent materials of electrical and electronic components, but are also utilized as important additives for controlling and enlarging the usable environment range (temperature, voltage) of other ceramic.

Moreover, lead-containing ceramic has characteristics of densely sintering throughout a wide range of sintering conditions, low energy consumption in manufacturing and high electrical and mechanical durability of the product after sintering. By controlling the sintering conditions, a fine layered structure can be internally formed and the functionality of the electronic components can be largely improved.

At the present moment, no substitute material not containing lead capable of bringing out equivalent electrical properties, environment adaptability range, reliability, workability and productivity has been found. Consequently, lead-containing glass and/or ceramic are indispensable for bringing out the required functionality and properties of the electrical and electronic components applicable to exemption 7(c)-I.

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

As described below in 7(A), there is no suitable substance for substituting lead. Therefore such information and analysis are not applicable for this case.

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

As described below in 7(A), lead-containing ceramic in certain electrical and electronic components are essential elements of EEE and there are no suitable lead-free substitutes for them. Therefore, such information is not applicable for this case.

¹ Elements belonging to the 4th column of the periodic table such as Ti, Zr, etc. They have the characteristics of easily becoming tetravalent or divalent cations.

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.

Electrical properties of ceramic strongly depend on their crystal structure. According to Pauling's rule, in order to form the same crystal structure constituent elements of ceramic which can substitute lead are restricted to those ions having a divalent valence and an ionic radius of 0.93-1.81Å. On a purely scientific basis the elements which meet these conditions are limited to the following four: cadmium and the alkaline-earth metals (calcium, strontium, and barium). Of these, cadmium is much more toxic than lead and is already restricted by the RoHS Directive, and thus is not appropriate even for consideration as a substitute material. "Lead-free" ceramics formed from alkaline-earth metals and Ti, Zr, etc. have electrical properties strongly dependent on the operating environment temperature and voltage, and as they lack stability throughout a wide use environment range (temperature, voltage, frequency), which is an advantage of lead-containing ceramic, they (alkaline-earth metals) cannot be used as substitute materials of lead.

For this reason, we are investigating substitution by ceramic having a completely different composition as a substitute material for lead-containing ceramic. In spite of that, up to the present moment it has not been possible to achieve mass production of electrical and electronic components using substitute materials and having the same level of functionality. For example, there is a report² concerning the achievement of electrical properties (piezoelectric properties) by using a (K, Na)NbO₃-type ceramic constituted of potassium, sodium and niobium. However, those electrical (piezoelectric) 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 at 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.

As described above, for lead-containing ceramic falling into the technical scope of exemption 7(c)-I it is not possible to substitute lead by simply replacing it by another element. Moreover, attempts to obtain equivalent electrical properties from a completely different perspective have not progressed beyond ultimately obtaining similar results at best for a small part of the properties at laboratory level, and there are absolutely no technical perspectives to comprehensively eliminate lead from ceramic as of now.

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

² Jing-Feng Li, Ke Wang, Fang-Yuan Zhu, Li-Qian Cheng and Fang-Zhou Yao. "(K, Na) NbO₃-Based Lead-Free Piezoceramics: Fundamental Aspects, Processing Technologies and Remaining Challenges", J. Am. Ceram. Soc., 1-20 (2013)

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 (21 July, 2021).

Technical Document – Annex 2:

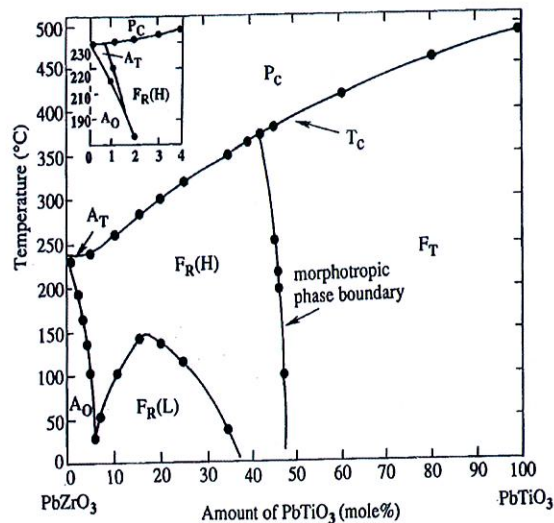
Product category: Ceramic Piezoelectric

Authors: Dr. HJ Schreiner, Mr. Eberhard Hennig

4. Technical Description of the Exemption Request/Revocation Request

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

Lead Titanium Zirconium Oxide abbreviated as PZT is the main constituent for piezoelectric devices. Lead (Pb^{2+}) is the main constituent in the solid solution of Lead Titanium Oxide with a tetragonal crystal structure and Lead Zirconium Oxide with a rhombohedral crystal structure forming a morphotropic phase boundary which is unique in the morphotropic phase boundary which is vertical above temperature as shown in the following phase diagram.



(ref.: Jaffe, Cook Jaffe; Piezoelectric ceramics)

This special perovskite structure in combination with the unique electron structure of Pb brings out the unique combination of piezoelectric properties over a wide temperature range like

- High Curie temperatures
- High Piezoelectric Charge constants
- High electromechanical coupling factors
- High quality factors and low losses for ultrasonic devices
- High stability under different driving and environmental conditions (especially temperature)
- High reliability

Those properties are required for the applications. Therefore, a simple replacement of Pb in Titanium

Zirconium Oxide based piezoelectric materials is impossible as shown by comparison with all other piezoelectric materials that have been evaluated (see reference Leadfree_PZT_comparison).

This was discussed and concluded during earlier Stakeholder consultations and is documented in the Final reports:

Adaption to the scientific and technical progress under Directive 2002/95/EC (20 Feb. 2009) and Adaption to the scientific and technical progress of Annex II to Directive 2000/53/EC (ELV) and the Annex to 2002/95/EC (RoHS) (28 Jul. 2010). Since then, research has continued but no new materials have been found that match the performance of lead-based materials, as discussed in section 6.

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

Intensive work has been done in the past to identify alternatives for PZT. PZT is by far the most effective composition in the combination of all properties. Research into other materials systems such as KNN and BNT go back to the

1950s. A comprehensive description of the tasks is given by Shrout et.al. [1]. Based on this early work, intensive research took place in the last years especially after the publication of the pioneering work of Saito et.al. [2] and have not realised any new basic formulations. Nevertheless, today some hundreds of compositions are known from the scientific literature which are marked as promising alternatives for PZT. The most important review papers published between 2009 and 2014 are summarized in the appendix.

On the other hand, more than 2500 patent publications are known (see e.g. <http://www.geocities.jp/kusumotokeiji/wadi.htm>), in which most of them go back to the known base compositions and indicate the development effort to improve the piezoelectric properties related to the base lead-free compositions.

The members of the consortium continuously review the possibility of using of alternative lead-free piezoelectric materials and have done internal and external developments towards lead-free materials (REALMAK Germany BMBF, DELLEAD Germany BMBF; sfb 595, TU Darmstadt).

Based on the state of art in the development of lead-free alternatives for PZT three main groups of compositions could be identified as barium titanate based, bismuth sodium titanate (BNT)

based and potassium sodium niobate (KNN) based, but none can be considered as a suitable overall substitute for PZT.

Barium titanate, the first piezoceramic ever, is still used in some limited applications, but it is sometimes modified by lead titanate to increase the Curie temperature. In the lead-free versions the working temperature is limited to the low Curie temperature of about 120 °C.

BNT based compositions are characterized by a so called depolarization temperature, at which the macroscopic piezoelectric properties are lost within a very narrow temperature range, which is much lower than the Curie temperature. Therefore, the usable working temperature range is limited to about 200 °C. BNT based compositions show a strong anisotropic behaviour, which means that these materials have a low planar mode but a high thickness mode piezoelectric coupling with low piezoelectric charge coefficients, a low dielectric permittivity and moderate dielectric losses. Sometimes a high normalized charge coefficient d_{33}^* (induced strain / applied electric field strength) is mentioned in the literature suggesting a strong piezoelectric effect. At this point it must be clarified that this so called "giant piezoelectric effect" is caused by a field induced phase transition and it is not a linear piezoelectric effect. For PZT or similar components it is known, that field induced phase transitions or domain switching processes lead to reliability issues due to crack propagation in the grains. Nonetheless, no reliability study is to our knowledge, currently available.

KNN based compositions textured or non-textured have the highest potential to be an alternative to PZT because the Curie-temperatures are comparable to the PZT family and piezoelectric coefficients are between the BNT based materials and PZT. But it must be pointed out, that this strong piezoelectric coupling is found around polymorphic phase transitions and shows therefore a remarkable temperature dependence. Furthermore, this group of materials is the most challenging with respect to the synthesis (preparation using organic solvents with impact to production safety, see below). It is well known that the properties are strongly dependent on real stoichiometric composition which can be hardly controlled because of the volatility of the alkaline metals.

In summary, none of the known Lead-free piezoelectric materials is a suitable overall substitute for PZT.

Beside the dielectric and piezoelectric properties for the possible alternatives for PZT the technological requirements for production on an industrial scale must be considered. 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 different 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 piezoceramic elements must be considered. Especially the mixing and milling

process plays a crucial role because of the water solubility of most of the necessary raw materials must be switched from a water-based process to a solvent-based process with a high impact on the health and environment protection.

A ban on PZT would also hinder technical developments towards safety applications, medical applications, to avoid batteries in some energy harvesting 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 which will reduce the CO2 amount in the exhaust.

Literature:

- [1] T. R. Shrout et. al.; J. Electroceram (2007) 19: 111-124
- [2] Saito et. al.; Letters to Nature, 2004

See file reference: [Leadfree_PZT_comparison.pdf]

See file reference: [Summary Review Papers for Annex 2.pdf]

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

Reliability is not ensured because there are no alternatives to PZT available on an industrial scale. To our knowledge, no reliability data have been published so far.

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.

Potential of lead free material under investigation in the last 10 years are included in the document provided.

None of the known lead-free materials reached the properties level met by lead containing materials which is the absolute necessary level for actual application of EEE.

For some extremely limited special applications the use of lead free materials seems to be possible and is already done (mostly on the basis of BaTiO3).

At the moment there is no industrial technology for the lead-free materials.

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

Achievable material properties are known

First demonstrations of applications published

Technologies for industrial production must be developed

Simple replacement of PZT components not possible

Adaption or new development of EEE, reliability investigations

Certain replacements: time frame >5 years, overall replacement not foreseeable

Refer to roadmap of DKG published before 2010 but still valid. This roadmap is until 2025.



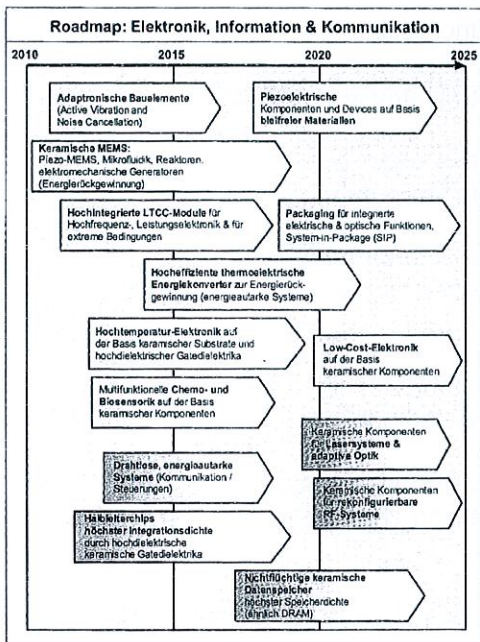


Abb. 5(1): Roadmap für die Bereiche „Elektronik, Information & Kommunikation“

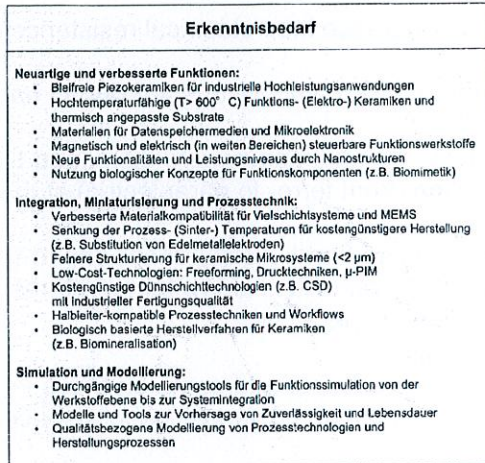


Abb. 5(2): Erkenntnisbedarf für die Bereiche „Elektronik, Information & Kommunikation“

Technical Document – Annex 3 :

Product category: Positive Temperature Coefficient Semiconductor ceramic

Authors: Dr. B. Steinberger

4. Technical Description of the Exemption Request/Revocation Request

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

PTC ceramics (Positive Temperature Coefficient) is the description of an electrical material functionality.

PTC ceramics increase their electrical resistance with increasing temperature.

Examples of material compositions are doped barium (BT) and lead titanate (PT) mixtures.

The basic PTC material barium-strontium-lead-titanate is a perovskite which undergoes a phase transition (from ferro- to paraelectric) at the Curie temperature.

If properly processed and slightly donor doped (<1mol%) such materials are PTCR active so to speak; semiconductive at low temperatures and quite highly resistive at temperatures above the Curie temperature.

It is possible with dopants and some changes in proportions of components and additives to tune the properties of a composition to a specific targeted application.

PTCR active materials can be divided into four sections based on resistivity and Curie temperature for sake of simplicity. Each individual section contains hundreds of material recipes based on BT and PT.

The first section describes Curie temperatures below 120°C and low resistance values (< 1000 ohm.cm).

With this materials applications like overload protection, inrush current limitation, heating, telecom line protection, motor protection, motorstart and temperature sensing are served.

Lead titanate is added to the recipes which serve this section to decrease the resistivity and increase performance because lead increases the ferroelectricity in the ceramic material. Lead-free materials are available for this region but the performance and durability that can be achieved is significantly lower and such materials can therefore not be used for most applications. Based on the current state of the art breakdown voltages are lower by approximately 30% for lead free ceramics.

As a result, the present situation is that no lead replacement has been found yet to produce a PTC with a Curie temperature below 120°C, low resistance values and sufficient performance.

The most commonly used section is the region with low resistance and Curie temperatures

above 120°C where lead is added to the recipes to achieve both higher Curie temperatures and lower resistance. With this materials applications like overload protection, inrush current limitation, telecom line protection, motor protection, motor start, temperature sensing and heating are served.

A bismuth-based perovskite material which exhibits higher Curie temperatures and can therefore be used to increase the Curie temperature of a solid solution with barium titanate was investigated as a substitute most in the literature.

However it has been demonstrated that such components as BNT (bismuth sodium titanate) have limited solubility in barium titanate and can increase the Curie temperature only to regions around 160°C.

At the same time electrical parameters including important ones like steepness of resistance change and breakdown voltage strength deteriorate dramatically. Especially the energy efficiency for switching applications like motor starters will be influenced strongly. The break down voltage for typical motorstart elements would be reduced by approximately 30% and the resistance stability during application would decrease as well. The performance in terms of reliability are effected most. Tests according the industry standard IEC 60738-1 like electrical endurance, electrical cycling, temperature storage show by an order of magnitude higher resistance change compared to the current standard. For IEC 60738-1 test procedures like humidity even higher changes up to two order of magnitudes are observed.

The section which is quite high ohmic and still with low T_c is one of the most critical ones in regard to material development. With this materials applications like overload protection, inrush current limitation, temperature sensing and heating are served mainly.

Nevertheless Industry has started some further investigations in this direction. The reduction of lead would induce reduced breakdown voltage performance of approximately 30%.. Additionally it must be noted that this high ohmic regime is especially problematic in terms of reproducibility and resistance spread if we get rid of lead, respectively.

In the fourth section, high ohmic and with high T_c, lead titanate compounds in the ceramic are necessary because of the high T_c up to 300°C (as already explained).

With this materials applications like overload protection, inrush current limitation and especially heating are served.

So far no material system beside BT and PT has been developed which is able to achieve the required Curie temperatures above 200°C not at all.

Adding lead to the barium titanate matrix of the PTC ceramic is the only known procedure to raise the Curie temperature of the basic barium titanate without loss of important properties and functionality.

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

For the applications with $T_c < 120^\circ\text{C}$ in general certain temperature ranges might be achieved by an adaption of strontium titanate.

However, beginning with the low ohmic section at $T_c < 120^\circ\text{C}$ it must be noted that the reduction of lead will be disadvantageous because this will reduce the ferroelectricity (permittivity, polarization) of the material involved. Which can be explained by the fact that BNT and BKT are reported to have a relative permittivity of less than 5000 where lead titanate show a relative permittivity of around 10000.

The effectiveness of the charge compensation which appears at temperatures below T_c is due to the magnitude of the ferroelectric material involved. Therefore the mechanism which causes the PTC effect is decreased if relative permittivity at the grain boundary is reduced. [6]

It should also be noted that when compared with lead-containing materials, replacement to Pb will decrease the lifespan of the product as well as its voltage breakdown strength in order of 30% depending on the material type in question This means that even if PTC materials are produced without lead for T_c lower than 120°C it will have to be by cost of a reduced performance [1]. So increased dimensions, more material and energy needs to be used to produce the individual product. Furthermore some applications and functions cannot be served by lead free materials.

This demonstrates that still many problems which need to be solved until a "lead-free" material can be produced in practice.

The ceramic materials for the section with low T_c and high resistance will be a major challenge in upcoming development projects which aim for "lead-free" materials because of the difficulties with reproducibility and resistance spread.

For high temperature sections the most promising materials to push the lead-free limit are BNT (bismuth sodium titanate) and BKT (bismuth potassium titanate).

Those materials work best at higher resistances above 1000 ohm-cm. In this high ohmic section above 120°C a T_c could be reached up to 200°C , as claimed by [5].

This limitation is mainly caused by the volatility of Bi which changes the composition and incorporation mechanism and thereby the sintering characteristics and achievable resistance, respectively.

Other works suggest that there is a limit at 160°C because above that the ceramic becomes highly resistive [3].

However, the best performances were reported at Curie temperatures below 150°C and even they are distinctly inferior to the traditional materials containing lead titanate.

See for example the following diagram taken out of a work of Takeda [1].

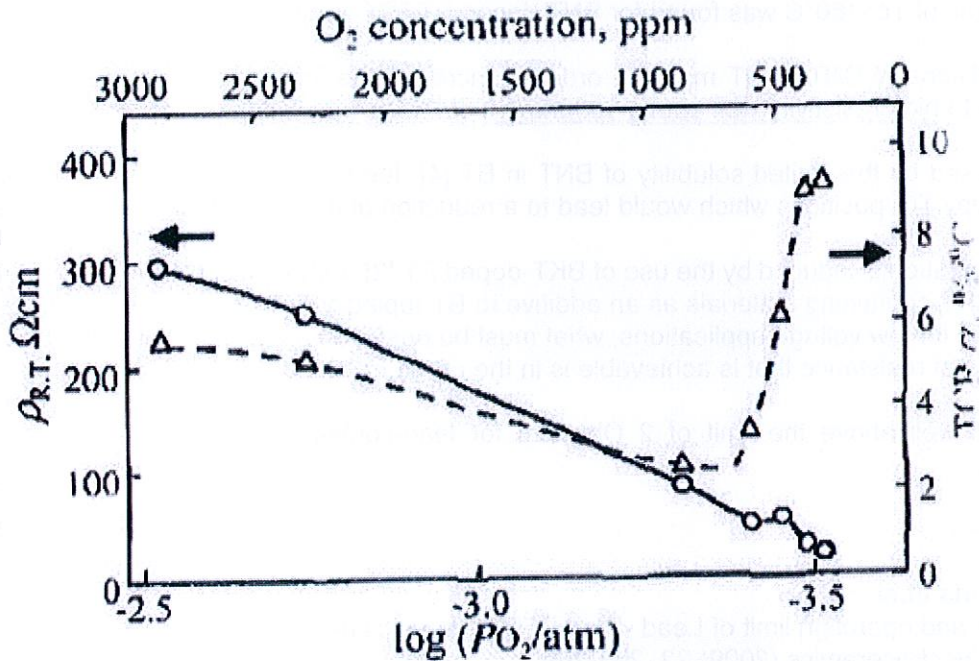


Fig. 6 Dependences of resistivity at room temperature (25°C) ρ_{RT} and temperature coefficient of resistivity (TCR) α of the BNT 6 mol% ceramics on oxygen partial pressure during sintering process

The breakthrough voltage is expected to be rather low, due to the fact that the PTCR steepness α [%/C] around T_c is below 10%/C which influences the maximum resistance which is directly related to the break down voltage. For comparison, values of 60%/C can be achieved with the standard technology using lead titanate

At the moment it is not possible to make a reliable statement about the T_c reproducibility. However due to the volatility of Bi a poor T_c reproducibility and predictability is expected.

It should be noted that the results obtained so far are at laboratory (research) level, and reliability and mass production technology have not been ensured. Consequently, there are no prospects for actual mass production supply being provided, and the current situation does not allow substitution in the next few years.

Everything becomes even more challenging if we look at the low ohmic section above 120°C which is the economically most important section.

Naturally the PTC effect is weaker than for higher resistances which is due to the very basic

principles involved.

So the drawback of the new BNT and BKT based materials in terms of steepness; break down voltage and so on becomes even more dominant than at high ohmic quarters.

In [4] the limit of $T_c=160^\circ\text{C}$ was found for BNT doped BT PTC materials.

Higher additions of BNT to BT made in order to increase the T_c to higher temperatures would lead to high resistivity well above 1000hmcm of PTC's, which is unacceptable.

This is caused by the limited solubility of BNT in BT [4] due to which Bi^{3+} as an acceptor would occupy Ti^{4+} positions which would lead to a reduction of free charge carriers.

A similar limitation is induced by the use of BKT-doped BT [2]. Although there are reports of BNT and BKT-containing materials as an additive to BT replacing lead titanate in the range up to 160°C , for low voltage applications, what must be observed as most important of all is that the lowest resistance that is achievable is in the range of 100 Ohm-cm.

This is still well above the limit of 2 Ohm-cm for lead-containing materials (traditional technique).

Cited articles:

[1] H. Takeda et.al.

Fabrication and operation limit of Lead -Free PTCR ceramics using BT-BNT
Journal of Electroceramics (2009) 22, 263-269

[2] S. Leng et.al.

Synthesis of Y doped BT-BKT Lead-Free Positive Temperature Coefficient of resistivity ceramic and their PTC effects
Journal of American Ceramic Soc. (2009) 92 [11], 2772-2775

[3] J. Wei et.al.

Effects of BNT Addition on the Microstructure and PTC Properties of La-Doped BaTiO_3 -Based PTCR Ceramics
Ferroelectrics, 403; 91-96, (2010)

[4] B.Y. Wu et.al.

A Study of PTC Ceramics Based on $(\text{V}_{1-x}\text{Cr}_x)_2\text{O}_3$
Electroceramics.British Ceramic Proceedings No.41 Stoke-on-Trent, 1989, p.195-203
Institute of Ceramics

[5] H. Takeda et.al.

$\text{BaTiO}_3-(\text{Bi } 1/2 \text{ Na } 1/2) \text{TiO}_3$ Solid-Solution Semiconducting Ceramics with $T_c > 130^\circ\text{C}$
Appl. Phys. Lett. 87 (2005) 102104

**[6] W.Heywang. Semiconducting Barium Titanate. J Mater Sci 1971;
6:1214-1226**

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

Not applicable as no alternatives exist

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.

So far material studies on BNT reveal that these lead-free PTC materials still have a lower performance and a lower reliability compared to the standard lead-containing materials.

Actual results show 30% lower breakdown voltage, 30% lower steepness of the RT-curve and >1000% less stability at temperatures above 160C.

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

As a general approach, introducing of new chemical compounds and materials in order to replace PT even only in a certain resistance-Tc range would need an overall change in powders conception used in the production of PTC at the moment.

This is because not just one powder is used in production of a certain product but usually a mixture of two or more powders is used.

With the alternative materials examined up to now only ceramic for applications with low Curie temperatures might be meaningful to undergo further investigation and development because of the strong limitations in regard to certain properties as mentioned above. And also for these low Tc applications there still exist several constraints as explained above.

Technical Document – Annex 4 :

Product category: Glass

Authors: James P. Vetro; Wolfgang Werner

4. Technical Description of the Exemption Request/Revocation Request

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

Glass for electronic components is an amorphous isolating solid. In electrical and electronic components, together with making use of the various properties exhibited by glass, the desired function is obtained by the combination of glass with other materials such as metal, ceramic, etc.

By using lead as a constituent element of glass the melting and softening points are lowered, workability (machinability) is improved, wettability (affinity) with metal and ceramic is increased the bonding strength with other materials is improved, and it becomes possible to control electrical properties (conductivity, resistance values) obtained by the combination with other materials over a wide range, etc., and it is possible to provide excellent functionality.

In addition, chemical stability and mechanical strength of glass are improved, and excellent reliability can be obtained.

That is to say that only after we use glass containing lead as a constituent element, we are able to provide the high functionality required for electrical and electronic components. Furthermore, as such glass can also bring out the necessary characteristics for simultaneously satisfying high reliability requirements, it can be used over a wide range of applications.

Examples of intended use related functional group as follows,

Insulating / Protection / Resistance / Adhesives / Bonding / Hermetic sealing.

Some examples can be found in the Annex 5 document.

REM: This document is an illustrative list (not comprehensive list) of uses of glass in electronic components, which explains the reason why lead in glass is needed and lead-free substitutes are not technically suitable.

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**

As described below in 7(A), there is no suitable substance for substituting lead.

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

Please refer to reliability of example for hermetic sealing described in 7(A).

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.**

Research by manufacturers for boron, phosphorus, zinc, tin, bismuth, etc. have been investigated as potential elements for substitution of lead as a constituent element of glass. "Lead-free" glasses using these elements can partially promote machining efficiency (ability to minimize energy consumed to apply heat, mechanical pressure, etc. in manufacturing processes) and affinity (ability for mutually wetting and bonding different materials such as metal and ceramic) which are necessary properties for achieving the required functionality of electrical and electronic components. 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.

As shown above, boron, phosphorus, zinc, bismuth, etc. are, in a general manner, inadequate for substituting lead as constituent elements of glass and as of now there are absolutely no technical perspectives for comprehensively eliminating lead from glass of electrical and electronic components.

As a further example, electronic component packages with hermetic sealing characteristics using a ceramic body with a ceramic or glass lid require glass with Pb as the sealing material between the

Example 3.3

Electronic components with hermetically sealed ceramic package

Electronic component packages with hermetic sealing characteristics using a ceramic body with a ceramic or glass lid require glass with Pb as sealing material between the 2 parts of the package. The Pb in glass is used to reduce the melting temperature to a level low enough to not harm the functional element itself, at the same time however high enough to withstand the reflow soldering temperatures without losing its strength and sealing properties even temporarily (this is important as in many cases the inside of the hermetically sealed package is under vacuum).



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