住友電工
SUMITOMO ELECTRIC

SQA02-2018-010

Exemption Request Form

Date of submission: 25/03/2019

1. Name and contact details

1) Name and contact details of applicant:

Company:	Sumitomo Electric Industries, Ltd.	Tel.:	+81-6-6466-5792
Name:	Yuichi Yamada	E-Mail:	yamada-yuichi@sei.co.jp
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2) Name and contact details of responsible person for this application (if different from above):

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

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2. Reason for application:

Please indicate where relevant:

☒ Request for new exemption in: Annex IV

☐ 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: _____

Proposed or existing wording: Lead in bismuth lead strontium calcium copper oxide superconductor cables and wire and lead in electrical connections to these wires.

Duration where applicable: Maximum validity period of 7 years

☐ Other: _____

3. Summary of the exemption request / revocation request

Superconductors with high critical temperatures have many technical advantages over the niobium-alloy low temperature superconductors that are currently used in NMR spectrometers and MRI scanners. Research has shown that the material that gives the best overall performance and reliability is lead-doped bismuth strontium calcium copper oxide (BSCCO). Powerful superconducting electromagnets have been constructed using lead-doped BSCCO and used for NMR and other applications. The use of lead-doped BSCCO allows the generation of more powerful and more stable magnetic fields than using other copper oxide superconductors, and these magnets have also been found to be more reliable than those made with other materials. Electrical connections are made to the superconducting wires using eutectic lead/tin solder because this has proven to be reliable and has low electrical resistivity at low temperatures. NMR spectrometers and other products that use lead-doped BSCCO cannot be sold in the EU until this exemption is granted.

4. Technical description of the exemption request / revocation request

(A) Description of the concerned application:

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

   Name of applications or products: Products where this exemption will be used include Magnetic Resonance Imaging (MRI) scanners, Nuclear Magnetic Resonance (NMR) spectroscopic analysers, mass spectrometers, superconducting cables, magnetic field strength measurement instruments and other electrical equipment in scope of RoHS that uses superconducting cables, motors and electromagnets. The superconductor will also be used in magnets for control of melting of silicon for single crystal manufacture and in particle accelerators for medical use (e.g. proton therapy), although these end use applications may be regarded as large-scale fixed installations and so would currently be excluded from the scope of the RoHS Directive.

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

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

   b. Please specify if application is in use in other categories to which the exemption request does not refer: _____

c. Please specify for equipment of category 8 and 9:

The requested exemption will be applied in

☒ monitoring and control instruments in industry

☐ in-vitro diagnostics

☒ other medical devices or other monitoring and control instruments than those in industry

2. Which of the six substances is in use in the application/product?

(Indicate more than one where applicable)

☒ Pb ☐ Cd ☐ Hg ☐ Cr-VI ☐ PBB ☐ PBDE

3. Function of the substance: Bismuth Lead Strontium Calcium Copper Oxide is a superconductor that is used to make conductors (wire and cables) that have zero electrical resistance below the critical temperature (Tc). Lead is also a constituent of solder used to make electrical connections.

4. Content of substance in homogeneous material (%weight): Lead as a dopant in bismuth strontium calcium copper oxide (BSCCO) (Bi2223 phase) gives stable superconducting material within a range of concentrations around 7% lead by weight. Solder alloy used for electrical connections contains about 36 – 37% lead.

5. Amount of substance entering the EU market annually through application for which the exemption is requested: Estimated to be ca. 1 kg per year for NMR on average during the next 10 years and eventually another 14.4kg for MRI per year, plus smaller amounts for other applications.

This quantity of lead in BSCCO was calculated by SEI based on a magnet coil designed by JASTEC[1]. The first main use in the EU of BSCCO superconductor is expected to be in 1GHz NMR spectrometer electromagnets. Approximately 100 kg of BSCCO wire will be used in each spectrometer and the lead content of the BSCCO-filled silver wire is 1.8%. So, the total amount of lead is 1.8 kg per NMR spectrometer. 5 units of 1 GHz NMR magnets are expected to be sold in the EU during the next 10 years, therefore 9 kg of lead in 10 years or 0.9 kg per year on average. The quantity that will be used in other applications that are in scope of RoHS in the EU is not known as manufacturers of other types of equipment have not yet determined their future plans for EU sales. However, SEI speculates that MRI may eventually require up to 100km wire per year containing 14,4kg lead, however this is uncertain and this quantity will not be required until commercial MRI that use BSCCO are developed and approved.

[1] JASTEC = Japan Superconducting Technology Inc. http://www.jastec-inc.com/e_about/

The quantity of lead in the solder electrical connections was calculated as follows:

NMR contain about 40 bonds containing 0.005 to 0.02grams (average 0.01 grams) lead per bond. As 1 NMR is expected to be sold every two years, the total amount of lead per year is 0.2 grams.

Other uses. These are expected to require about 400 bonds per year each containing 0.05 grams of lead. The total is 2 grams per year.

6. Name of material/component: The superconductor material has an approximate stoichiometry of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$. Lead is also used in eutectic solder typically containing 63%Sn37%Pb.

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?

Superconductor

Lead is used as a dopant in Bismuth Strontium Calcium Copper Oxide, which is referred to as BSCCO or as Bi2223 which is the optimal superconducting phase. This material is a superconductor with a critical temperature (Tc) of 110 to 116K (depending on lead content). The material has zero electrical resistance at temperatures below the critical temperature. A Tc of 110K and higher is sufficiently high to avoid the need to use liquid helium as a coolant (this boils at 4K) and so that liquid nitrogen cooling (boils at 77K) could be used. There is also research[2] into refrigerant-free superconducting electromagnets and at least one commercial product[3] has been developed. However, the main advantages of Bi2223 over low temperature superconductors that require liquid helium cooling, such as niobium-tin, is that their overall performance is superior and it is envisaged that finished equipment will operate at liquid helium temperatures to achieve the optimum performance. For example, the critical current and critical field strength[4] of lead-doped Bi2223 are much higher at 4K than at 77K. The performance characteristics of Bi2223 are described below in section 4 (C).

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2 S. Awaji, et. al., "First performance test of a 25 T cryogen-free superconducting magnet", Supercond. Sci. Technol. 30 (2017) 065001.

3 http://www.jastec-inc.com/products_nmr/detail5.html

4 See figure 12 of US Patent 4,880,771, R. J. Cava, "Bismuth Lead Strontium Calcium Cuprate Superconductors", Nov 1989. This shows that magnetic field performance for this superconductor increases as the temperature decreases.

Bi2223 is a ceramic material which is used inside a silver tube. Typically, the silver tube containing Bi2223 superconducting powder is drawn to create long lengths which can be used as wire.

An example of a commercial lead-doped Bi2223 wire is shown below.

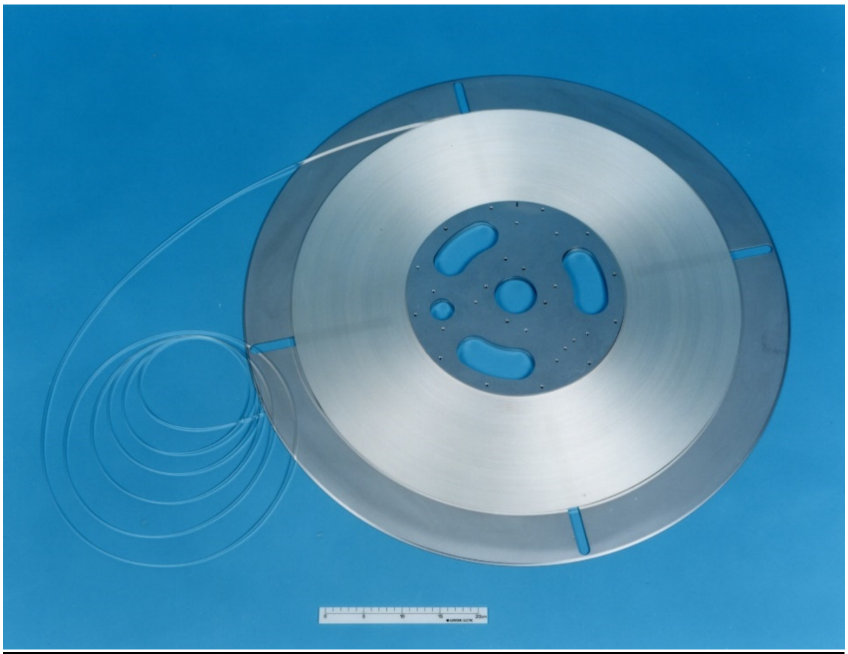

Figure 1. Lead-doped Bi2223 wire produced by Sumitomo Electric Industries

For some applications, superconducting wires are used in the form of multi-filamentary wire as this gives superior electromagnet performance. Optimal superconductivity of the Bi2223 inside the silver encapsulation is achieved by heat treatment in an oxygen atmosphere. Silver is ideal because it readily allows oxygen migration through the silver walls of the tube into the Bi2223 material inside when the wire is heated in an oxygen atmosphere.

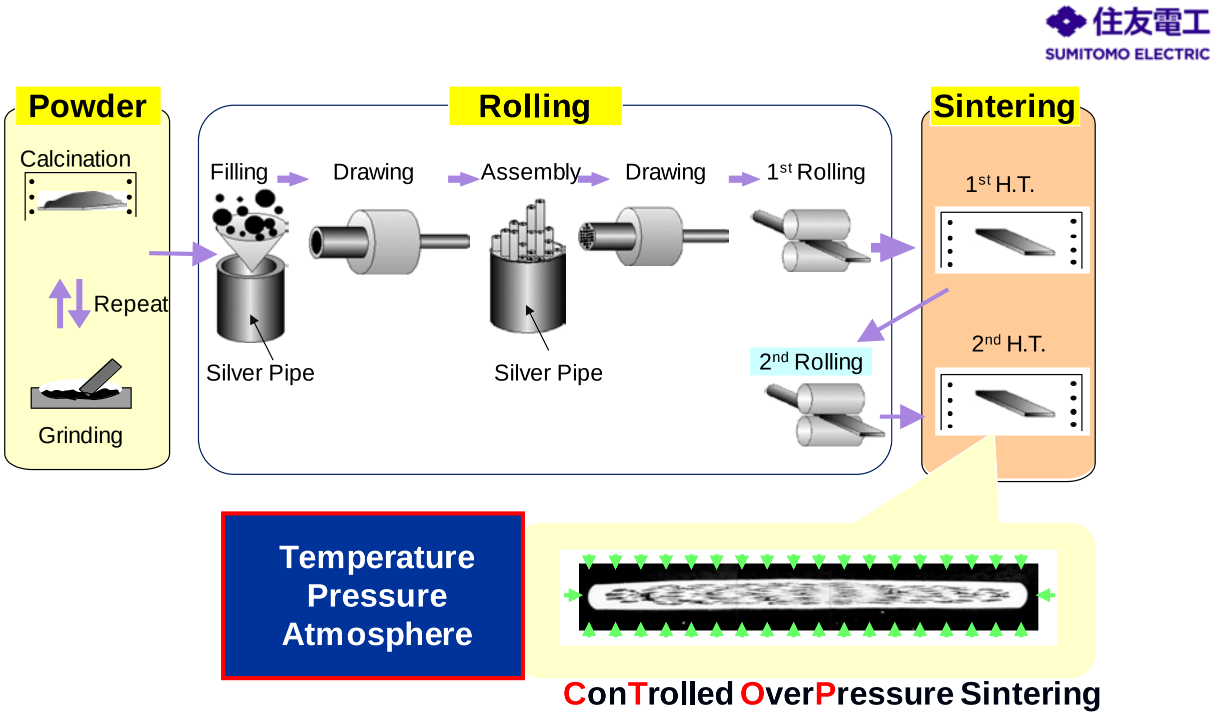

Figure 2. Schematic showing the process of making multi-filamentary wire using BSCCO

Superconducting wire is used in a variety of applications, some of which have been commercialised. Some applications are outside of the scope of RoHS. The main uses are as follows[5]:

- Powerful electromagnets for NMR spectrometers; these are in RoHS category 9. Increasing the magnet's field strength enables the spectrometer to analyse more complex molecules such as protein's dissolved in water, which cannot be analysed using conventional NMR spectrometers[6]. These spectrometers are likely to be the first commercial electrical equipment placed on the EU market to use lead-doped Bi2223 and these can be sold in the EU as soon as this exemption has been granted. Current designs utilise two coils; an outer low temperature superconductor coil and an inner lead-doped Bi2223 coil which are cooled with liquid helium or by a conduction cooling method using a cryo-cooler.
- Powerful magnets for MRI – Increasing the field strength of medical (category 8) and veterinary MRI electromagnets increases the image quality so that smaller features can be visualised[7]. Clearer images will also enable health professionals to more accurately determine what type of

5 "Research, Fabrication and Applications of Bi-2223 HTS Wires", edited by K. Sato, World Scientific Series in Applications of Superconductivity and Related Phenomena, Vol I. Published by World Scientific Publishing Co. Pte. Ltd, 2016, ISBN 978-981-4749-25-1.

6 "Recent Developments in High-Temperature Superconducting Magnet Technology (Review)", Hideaki Maeda and Yoshinori Yanagisawa, IEEE Transactions on Applied Superconductivity, Vol. 24, No. 3, June 2014.

7 This is clearly illustrated for an increase from 3T to 7T by the images from https://www.news-medical.net/news/20160712/Increasing-access-to-MRI-scanning-an-interview-with-Jane-Kilkenny.aspx

feature, such as a tumour etc., is being examined. This is clearly a benefit for detection of small tumours, damage to small blood vessels, etc. allowing more accurate and earlier diagnosis and treatment.

- Analytical equipment that utilises Bi2223 superconducting coils to measure the characteristics of magnetization and other properties of magnetic materials[8]. These instruments are commercially available in Japan and could be sold in the EU when this exemption is granted.
- Power transmission – usually will be excluded from RoHS as electricity transmission installations are usually regarded as types of large-scale fixed installations*, or they are rated at higher than 1500V (so out of scope)*
- The windings of electric motors – some uses of motors, such as in electric vehicles and in ships would be excluded from RoHS as these are forms of transport, but other uses may be in scope.
- Cables rated at 250 volts and less are in scope of the RoHS Directive. Superconducting power cables rated at more than 400V may be used in data centres or for other applications.
- Electromagnets for the controlled melting of silicon in single crystal manufacture. This equipment is usually used in production lines which will be regarded as large-scale fixed installations, but smaller scale equipment used for research or small-scale batch production may be in scope of RoHS.

The following diagram illustrates the technical complexity of a BSCCO superconducting power cable and the technologies required to support operation.

[8] B-H curve tracer https://www.j-ndk.co.jp/product/jikisokutei/bh_curve_tracer.html#sub_03 and a High Temperature Superconducting Type of Vibrating Sample Magnetometer http://www.toeikogyo.co.jp/english/products/sei-01/vsm-5hsc.html

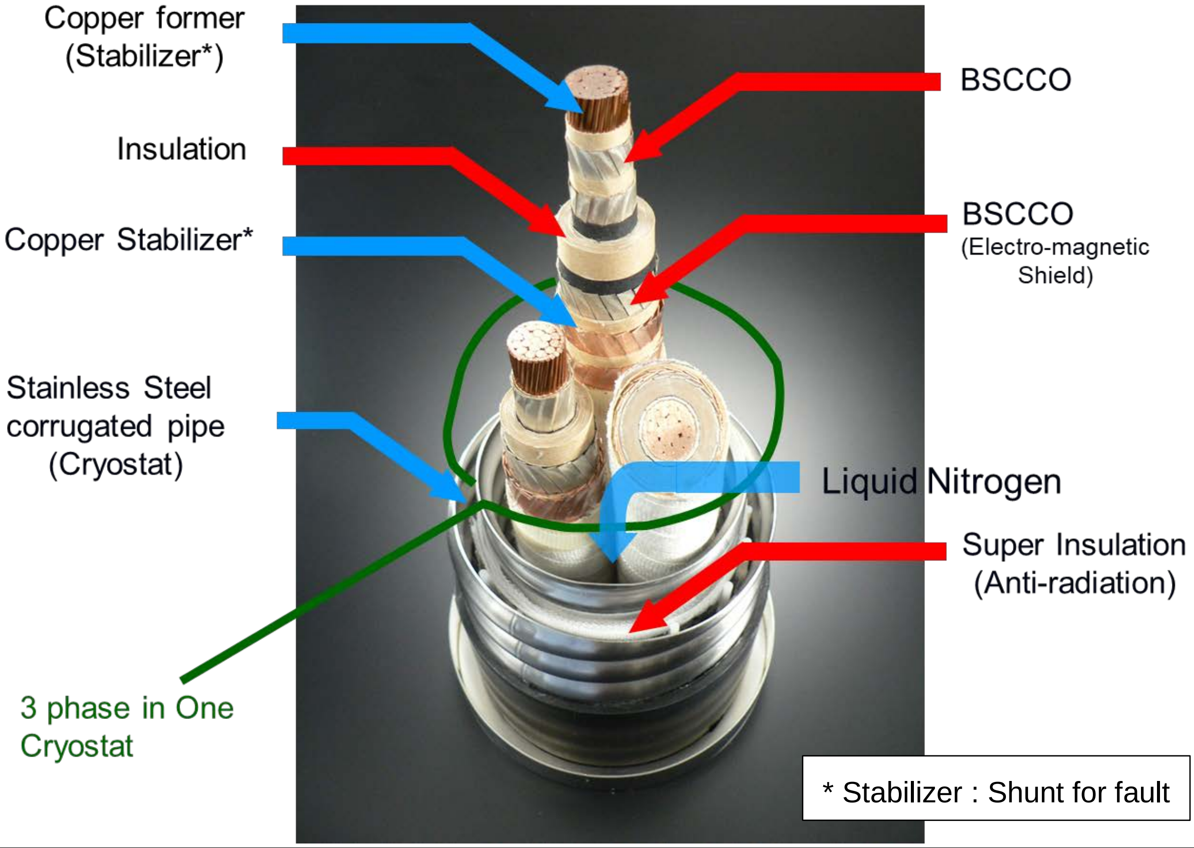

Figure 3. Construction of a superconducting cable system using BSCCO wire for power transmission

Electrical connections

High power electrical connections need to be made to the BSCCO superconductor. Forming of bonds needs to be easy to carry out to ensure that 100% of bonds are of good quality with very low electrical resistivity. To increase the strength of superconducting wire, these can be coated with stainless steel, nickel alloy or copper alloy. Soldering to copper is straightforward but it is very difficult to solder to stainless steel and nickel alloy and so these must first be coated with tin which is deposited by electroplating. Solder coating of tin is straightforward. Research has shown that a thin lamination coating of tin/silver/copper (SAC) lead-free solder alloy, with melting point 219°C, on the superconducting wire improves the strength of the material. It is necessary to make solder bonds to the ends of the superconducting wires without melting the SAC solder coating and so an alloy with a lower melting point must be used and tin/lead (SnPb) solder was selected. This has a melting point of 183°C, which is sufficiently lower than 219°C so that it can be used without melting or delaminating the SAC coating. This alloy is ductile at the very low temperatures used, has low electrical resistivity at low temperature and there is many years of experience with this alloy being used at low temperatures. The temperatures that the solder bonds will experience are typically:

- NMR about 4K
- Other magnet applications 20 to 40K

- Cable applications about 65 to 80K.

At these temperatures (and at very high field strength), the chosen solder material (SnPb) will not be a superconductor and so to minimise resistive heating, it must have a very low electrical resistivity. Due to the powerful magnetic fields, the solder bond must be reliable when exposed to cyclic stresses.

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

The superconductor materials are required to have:

- High critical temperature (Tc) – this is important even when used at very low temperatures because the material will remain as a superconductor even if the temperature were to rise, as long as it does not exceed Tc;
- High critical field strength – This is important for electric motors and electromagnet applications. Superconductivity is lost at magnetic field strengths that are larger than the critical field strength value. Applications such as MRI and NMR require very high field strengths. Over 24 Tesla has been achieved with lead-doped Bi2223, and it is important that superconductivity is not lost at these high values;
- High critical current density[9] – including when exposed to a powerful magnetic field. The maximum current that can be passed through a cable is the critical current. For many applications including power transmission, NMR and MRI, it is necessary to pass very large currents. NMR sensitivity and MRI image quality are proportional to the magnetic field strength which in turn depends on the current being passed. Critical current density is reduced however when the cable is exposed to a strong magnetic field and it is also temperature dependent. So, a high critical current density is required when exposed to a powerful magnetic field and at temperatures approaching the critical temperature.
- It is important that the critical temperature, critical magnetic field strength and critical current density are all high[10] to achieve the performance that is required as well as to avoid catastrophic failure that would occur when a large current is passed through a superconducting wire when superconductivity is lost or "quenched" (i.e. due to exceeding a critical parameter). When the coil becomes resistive, passage of current causes heat to be generated. This can cause thermal runaway, which can cause a fire when the coil's bonding materials (adhesives and resins) burn. These

[9] Current density is the electric current per unit area of the cross section of a conductor. The critical current density is the maximum that can be sustained before the superconductor stops superconducting.

[10] See slide 9 from https://www.slideshare.net/DebiPrasadDash3/superconductivity-68227517

bonding materials are required to prevent moving of the superconducting wires from electro-magnetic forces (which occurs when NMR and MRI operate) and rapid temperature changes (such as when coils are cooled with liquid helium).

Wires and coils made with wires must meet exacting requirements:

- It must be possible to fabricate the material into flexible superconducting wire with sufficient tensile strength;
- Wires must be sufficiently strong and have sufficient current carrying capacity for compact electromagnet coils;
- Wires and coils should exhibit insignificant magnetic field distortion, drift and hysteresis;
- Field strength inside coils must be high (e.g. for MRI and NMR applications).
- For NMR and MRI, a high magnetic field ramp rate is a significant advantage as this reduces the time before the equipment can be used.
- Coils must be reliable and not fail catastrophically in normal use.

Superconducting electromagnets are used to achieve superior resolution and sensitivity, which are especially important for NMR and MRI. Resolution (e.g. of NMR spectra) is proportional to the magnetic field and sensitivity is generally proportional to magnetic field (to the power of 3/2). NMR spectral analysis of very large complex molecules (such as proteins) is only possibly with the very high resolution achieved by use of superconducting electromagnets. Spectra can also only be obtained when the concentration of a substance is very low by using powerful superconducting electromagnets[11].

At present, the smallest magnetic field strength for which Bi2223 is likely to be used in electromagnet coils of NMR is 9.4T. The smallest magnetic field strength for MRI, magnetic field strength measurement, etc. is 1.5 Tesla. If there are shortages of helium in the future, lower field strength magnets may need to also use Bi2223 electromagnets as these can operate without using liquid helium as a refrigerant, but Bi2223 is not likely to be used for MRI of less than 1.5T.

Solder bonds must be:

- Low electrical resistivity
- Ductile at very low temperature
- Able to withstand cyclic stresses
- Easy to make consistently
- Bonds must be reliable over expected >25 years lifetime
- Low melting point solder bonding (<195°C), at least 25° lower than the SAC solder coating on the wire

[11] This is illustrated by the increase in spectral detail obtained by increasing from 42.5MHz to 300MHz at http://www.process-nmr.com/WordPress/?p=388.

- Resistant to corrosion and oxidation
- Shock resistant (sudden and strong forces are imposed when magnetic field is switched on or off).

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

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

Superconducting wire will be sold to manufacturers of NMR, MRI, etc. who will use it in their products which are all used by industry or by professionals. The equipment will be fairly large and complex and so will have a positive value in terms of metal content at end of life, making recycling for materials recovery highly likely. Although some of the equipment may be returned to the original manufacturer, the superconducting wire is not envisaged to be returned to the wire manufacturer and so an auditable closed loop will not exist.

2) Please indicate where relevant:

☒ Article is collected and sent without dismantling for recycling.

☐ Article is collected and completely refurbished for reuse

☐ Article is collected and dismantled:

- ☐ The following parts are refurbished for use as spare parts: _____
- ☐ The following parts are subsequently recycled: _____

☐ Article cannot be recycled and is therefore:

- ☐ Sent for energy return
- ☐ Landfilled

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

☐ In articles which are refurbished	_____
☒ In articles which are recycled	Eventually increasing from 1 to 15.5kg per year, but none for at least 15 years, which is the likely minimum lifetime of these types of equipment.
☐ In articles which are sent for energy return	_____
☐ In articles which are landfilled	_____

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6. Analysis of possible alternative substances

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

Superconductor

Since the first superconductor, mercury, was discovered in 1911 many superconducting materials have been discovered. Many metals are superconductors but these all have fairly low critical temperatures (Tc). NbTi and NbSn are used as superconductors in MRI scanners and NMR spectrometers. Superconductors with low Tc values (known as low temperature superconductors or LTS) need to be cooled with liquid helium (boiling point 4.2K), which is a big disadvantage as helium is a very scarce element and the cooling equipment required is complex and consumes large amounts of energy. As a result, scientists have searched for many decades to find superconductors with much higher Tc values with an ideal material being a superconductor that can be used at room temperature. While this has not yet been achieved, a large number of ceramic formulations have been developed that have higher critical temperatures than niobium including many that are superconductors at temperatures above the boiling point of liquid nitrogen (77K). These are referred to as “high temperature superconductors” (HTS) of which Bi2223 is one example.

Although many high temperature superconductors have been developed[12], very few can be fabricated into cables and wires that have properties, such as high critical current, that are useful commercially. Only a few types of high temperature superconductors have been fabricated into useful long lengths of wires or tapes that can be used to make electromagnets for MRI, NMR and other commercial applications. These include Bi2223, and compounds based on rare earths, barium and copper as mixed oxides (REBCO), such as Yttrium Barium Copper Oxide (YBCO), which is one kind of REBCO. However, only one material; lead-doped Bi2223 meets all of the criteria described above in section 4 (C). Although the HTS materials are superconducting at liquid nitrogen temperature, many of the current applications operate at liquid helium temperatures as critical current values are significantly higher (such as a larger critical current value) at the lower temperature. However, these HTS superconductors also have the big advantage over LTS that if the temperature were to rise by up to 100K, the material remains as a superconductor and so catastrophic failure due to thermal runaway is less likely to occur. The other reason why HTS are superior to LTS is that significantly more powerful electromagnets can be constructed as their critical current densities are higher than those of LTS such as NbSn and NbTi[13].

Currently LTS are used in commercial NMR and MRI but have a significant disadvantage if the

[12] For example those listed at http://superconductors.org/Type2.htm.

[13] See figure 4 of reference 5.

magnets have to be switched off, for example if a magnetic metal part accidentally comes into contact with the bore. Ramping up of LTS magnets to the operating field strength takes considerably longer than ramping up lead-doped Bi2223 superconducting magnets. A commercial MRI can take as long as 3 days to bring it back into full operation, including recalibration[14] which will cause potentially harmful delays in treating patients. Comparison of LTS and lead-doped Bi2223 magnetic field ramp rates, as used for NMR, measured by a superconducting electromagnet manufacturer are as follows:

Table 1. Comparison of magnetic field ramp rates for LTS and lead-doped Bi2223 magnets

Change in magnetic field strength	LTS magnet with 100mm bore	Pb-Bi2223 magnet with 88mm bore
0 to 6T	6 minutes	30 seconds
0 to 8T	8 minutes	30 seconds
0 to 10T	12 minutes	4 minutes

High temperature superconductors that contain mercury compounds have also been developed but cannot be considered as a substitute because mercury is also RoHS restricted. Thallium based compounds have also been developed, but thallium is very toxic. The main reason why mercury and thallium based superconductors have not been used successfully is that these materials have not proven relatively high critical current density values. Thallium and mercury also have relatively high volatility so are lost at superconductor synthesis temperatures (they vaporise), unlike lead and bismuth which, having much lower vapour pressures at these temperatures[5], are not lost.

The only substitute high temperature superconductors to lead-doped Bi2223 that have been made into useful lengths of wire or tape and which can be made in into magnets are:

- Undoped Bi2223 and Bi2212 oxide phases,
- YBCO (Yttrium Barium Copper Oxide, a type of REBCO),
- REBCO (rare earths, barium and copper as mixed oxides),
- Magnesium boride.

Most other ceramic HTS materials[12], however, cannot be produced as wire or tape in lengths suitable for electromagnets or transmission cables or they do not give suitable performance. One reason that many ceramic materials are unsuitable is that they are too brittle and so cannot be used in flexible wire[15].

[14] http://mriquestions.com/how-to-ramp.html

[15] US Patent 4,880,771, R. J. Cava, "Bismuth Lead Strontium Calcium Cuprate Superconductors", Nov 1989.

Lead doping of Bi2223 and other BSCCO phases

Lead doping of Bi2223 gives multiple benefits compared with undoped Bi2223[2] and is also superior to other BSCCO phases.

- The optimum superconducting phase is Bi2223, but other inferior BSCCO phases can also form when the superconductor is synthesised. Lead doping has been found to promote the formation of the optimum Bi2223 phase as the only phase[16]. A patent by Yamada compares different phases to show that the lead-doped Bi2223 phase has a higher critical temperature than undoped Bi2223, Bi2212 and also aluminium doped Bi2223 and other compositions[17]. Majewski showed that lead doping can be used to ensure that only the superior Bi2223 phase is formed when the lead and bismuth concentrations are within specific concentration ranges although the formation temperature is also critical[18].
- Lead increases the critical temperature (Tc) of the Bi2223 superconducting phase from about 110K to about 116K[19]. This increased Tc gives an advantage over other ceramic superconductors that are capable of being made into superconducting magnet coils as well as low temperature superconductors such as NbSn and NbTi. This is especially important in AC applications because operation of superconducting magnets can generate heat by a variety of mechanisms. When a current passes through a wire this creates a magnetic field. As the size of the current being passed changes either because AC is used or when power is switched on (i.e. from zero to the maximum) and off, this creates "hysteresis loss", which occurs when the magnetic field strength increases and decreases. These losses are converted into heat which causes the superconductor's temperature to rise. Eddy currents are also generated and can also create energy losses that create heat due to field gradients. The higher Tc of lead-doped Bi2223 is a big advantage over other materials with lower Tc in preventing catastrophic failure due to temperature rise to above Tc causing thermal runaway.
- One limitation of all ceramic superconductors is that they are anisotropic, which means that their properties are orientation dependent. The electromagnetic anisotropy parameter γ is relatively large for undoped Bi2223 and is much larger than REBCO. This is less important if the crystals of the superconductor can be aligned so that their orientation is such that the axis with the highest performance is parallel to the direction that current is passing, however having a lower γ values is beneficial if <100% of

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[16] High-Tc Phase Promoted and Stabilized in the Bi, Pb-Sr-Ca-Cu-O System, M. Takano, et.al., Japanese Journal of Applied Physics, Vol 27 (6), 1988, pp1041-1043.

[17] Yamada et.al., US Patent 5,317,007 "High Tc oxide superconductor and method for producing the same, granted May 1994.

[18] P. J. Majewski, „Phase Equilibria and Crystal Chemistry, Bismuth-based High-temperature superconductors", from Bismuth-Based High-Temperature Superconductors, Edited By Hiroshi Maeda, CRC Press, 1996, pp139-145.

[19] Shown by several publications including references 5 and 15.

crystals are optimally orientated. Lead doping of Bi2223 has the benefit of significantly lowering the γ value.

- Lead doping significantly increases the critical current density of undoped Bi2223[5].
- Porous structures are formed when Bi2223 is sintered. This porosity is removed by rolling and sintering in oxygen at higher pressure. This orientates grains into the optimum direction and ensures that the material is homogeneous along the full length of wires and cables. It is also non-porous so that crystal to crystal conduction can occur. Lead doping makes Bi2223 grains larger and enhances the Jc (critical current density) with this process.

Comparison with REBCO

A significant disadvantage of REBCO superconductors is that they can be formed only as thin films deposited onto tape containing <2% of superconductor, whereas lead-doped Bi2223 can be made as silver wire with 40% of its volume as the superconducting phase. Bi2223 can be formed into multi-filamentary wire using powder in tube method. This structure can realize the smaller screening current. Moreover, it has high strength against the peeling force by electromagnetic force and thermal stress. The ability to make multi-filamentary wires enables Bi2223 to be used to make powerful electromagnets with superior performance.

Limitations of all superconducting electromagnets are that they can exhibit[6]:

a) Screening of magnetic fields
b) Degradation of coil performance due to excessive mechanical stress
c) Difficulty protecting electromagnets from thermal runaway.

a) Screening magnetic fields can cause distortion of the magnetic field, which distorts MRI images, impairs NMR analysis and causes “field drift” due to screening currents being generated. This was originally an issue with low temperature superconductors such as NbTi, but was resolved by using twisted multi-filamentary wire for MRI and NMR superconducting magnets. Lead-doped Bi2223 can be used as untwisted multi-filamentary wire. REBCO wire can only be used as monolithic (thin-film) REBCO layer in tape. Both lead-doped Bi2223 wire and REBCO tape suffer from field drift and hysteresis, but lead-doped Bi2223 to a significantly lesser extent. The results of this distortion and drift is manifested as hysteresis in plots of coil current versus apparent magnetic field. Experiments have shown that the hysteresis from lead-doped Bi2223 is only one fifth that of REBCO. Hysteresis and the resultant distortion (of MRI images and NMR spectra) and drift are reduced by use of multi-filamentary wire compared with flat tape and may be reduced further if the filaments can be twisted. Hysteresis is, as explained above, also an issue as it generates heat.

Several organisations have successfully constructed and operated NMR and MRI using lead-doped Bi2223 superconductor. One organisation, RIKEN, has built prototype NMR with both lead-doped Bi2223 and REBCO. Both experience a drift in magnetic field which can be suppressed using a current sweep method, but the drift with REBCO was 20 times larger than that with lead-doped Bi2223.

Yanagisawa[20] has successfully built an NMR spectrometer using a lead-doped Bi2223 electromagnet. Bi2223 was chosen instead of REBCO because REBCO has the following limitations:

- Substantial field drift (due to REBCO being a thin film on tape);
- Reduced central magnetic field intensity resulting in reduced performance;
- Large field error harmonics. These are oscillations in the strength of the magnetic field. These seriously degrade performance if they cannot be eliminated using shim and field coils;
- Degradation of performance of superconducting shim coils and field correction coils. Shim coils are used with current commercial NMR and MRI to eliminate unwanted harmonics in the magnetic field.

Lead-doped Bi2223 was used for the NMR coil as it has insignificant screening currents and so does not suffer from the above limitations. The only potential limitation of Bi2223 is a lower tensile strength, but this was overcome by use of Ni-alloy reinforcement tapes to increase the coil's tolerance to hoop stress.

b) When superconducting wires in coils, used for NMR and MRI electromagnets, are cooled with liquid nitrogen or liquid helium or by conduction cooling method using a cryo-cooler, this imposes severe stresses that can damage the ceramic superconductor material. This limits the choice of superconductor material that can be used but lead-doped Bi2223 wires are not damaged by rapid cooling.

c) Thermal runaway will occur when a large current is passed through a superconducting wire when it ceases to be a superconductor. This can occur if the critical temperature, critical field strength or critical current are exceeded. Heat is generated when the wire becomes resistive according to I^2R (I = current and R = resistance) and as very large currents are used for powerful electromagnets, a very large amount of heat energy can be generated very quickly which causes a rapid temperature rise and thermal damage (to bonding resins used to prevent damage from vibration). Therefore, it is essential to ensure that critical temperature, critical magnetic field and critical currents are not exceeded because if any one of these is exceeded, superconductivity will be lost instantly and rapid heating will occur potentially leading to thermal runaway. Operation at a stable temperature, magnetic field and current will help to avoid exceeding critical temperature, critical magnetic field and critical currents. This is easier to achieve with lead-doped Bi2223 than with REBCO as drift in magnetic field and screening currents are considerably smaller. The Tc of lead-doped Bi2223 (~110K) is also higher than REBCO (YBCO is 92K, GdBCO is 94K). Several publications describe catastrophic failures of prototype REBCO electromagnets and these are described below in section 6 (B).

Sato[5] reports that superconductors that contain barium can be degraded by moisture and carbon dioxide. Superconductivity of ceramic materials relies on grain-to-grain conduction, but this is hindered if electrically insulating phases form at grain boundaries. Barium oxide readily

[20] Combination of high hoop stress tolerance and a small screening current-induced field for an advanced Bi-2223 conductor coil at 4.2K in an external field, Yanagisawa, et.al., Supercond. Sci. Technol. 28 (2015) 125005.

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reacts with moisture and carbon dioxide to form electrically insulating barium carbonate as an impurity that forms between grains and stops superconduction between grains. Elimination of moisture and carbon dioxide in commercial scale production is difficult but this is less critical with lead-doped Bi2223 as this superconductor does not contain barium and so does not as readily form electrically insulating carbonates.

Comparison with GdBCO or Gd123

One type of rare earth barium copper oxide (RE123) superconductor is Gd123 ($GdBa_2Cu_3O_7$ with a Tc of 94K). This has been used to make powerful superconducting electromagnets that have been compared with similar performance electromagnets made of lead-doped Bi2223[21]. The coils consisted of a low temperature superconductor coil combined with a high temperature superconductor coil of either Gd123 or of lead-doped Bi2223. The lead-doped Bi2223 coil gave superior performance to the Gd123 coil as follows:

- Gd123 superconductivity was quenched (lost superconductivity) at the upper magnetic field strength of 23.6 T. There was a difference of 0.4 T between the calculated and measured magnetic field which was due to hysteresis effects.
- The lead-doped Bi2223 coil achieved a magnetic field of 24.5 T without being quenched. The difference between calculated and measured magnetic fields was much smaller than for Gd123 at 0.07 T due to the smaller hysteresis effects (so less heat is generated).

Comparison with YGdBCO

Another type of rare earth barium copper oxide that has been researched is yttrium gadolinium barium copper oxide ($(Y_{0.5}Gd_{0.5})Ba_2Cu_3O_7$). This has a Tc of 97K.

Critical current performance of wires was measured and compared with lead-doped Bi2223, yttrium barium copper oxide (YBCO) and published data on YGdBCO were compared[22]. Measurements were made at relatively low field (up to 0.4 T) but this is relevant to currently available commercial NMR and MRI equipment. This clearly showed effects due to anisotropy of materials, including of Bi2223. The tests showed that critical current decreases with increasing magnetic field strength, as would be expected. However, the performance was different depending on whether the conductors were perpendicular or parallel to the magnetic field. When oriented perpendicular to the magnetic field Bi2223 was inferior to YBCO and YGdBCO, but in orientation parallel to the magnetic field, Bi2223 was superior to both of the other materials achieving significantly higher critical current values and being less affected by magnetic field strength. As the production process can orient crystals of Bi2223 in one specific direction, this can be used to ensure that Bi2223 is used in its optimum orientation to achieve superior performance compared to YBCO and YGdBCO.

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[21] "First performance test of a 25 T cryogen-free superconducting magnet“, S. Awaji, et.al., Supercond. Sci. Technol. 30 (2017) 065001.

[22] Comparative study on the critical current performance of Bi-2223/Ag and YBCO wires in low magnetic fields at liquid nitrogen temperature, F. Feng, et.al., Physica C 471 (2011) 293–296.

Comparison with YBCO

One type of rare earth barium copper oxide (RE123) superconductor is Y123 ($YBa_2Cu_3O_7$). Although YBCO, which has a Tc of 92K, was one of the first high temperature superconductors, Tc over boiling temperature of nitrogen, to be developed, it has been used much less in research and for commercial applications. Generally, the process of YBCO is less tolerant compared with other REBCO materials, so it is not used for commercial applications.

Comparison with Magnesium boride

Magnesium boride (MgB_2) has a Tc of 39K which is much lower than that of Bi2223. Although this is higher than the Tc values for LTS, such as NbTi, it is more likely to fail than Bi2223 if a temperature rise occurs. However, research has been carried out into powerful electromagnets using MgB_2 and YBCO coils for NMR by MIT[23]. The highest magnet field strength achieved by MIT was 21.1 T which is lower than the highest that has been achieved by lead-doped Bi2223. Two further disadvantages of MgB_2 over lead-doped Bi2223 are that it has a much lower critical current density[13] and a lower critical magnetic field value.

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

Reliability of end-products such as NMR is extremely important when HTS are used because sudden unexpected quenching of superconductivity can lead to catastrophic failure. This is covered in section 6 (A) in the discussion on thermal runaway. There are many publications that describe catastrophic failure of REBCO superconducting coils. Both mechanical damage and overheating causing thermal damage are reported to occur when unexpected quenching of superconductivity of coils at high field strength occurs[24,25,26]. These types of failure have been found during trials to be much less likely to occur with lead-doped Bi2223 tape-shaped conductors due to the reasons explained in 6 (A) above, such as its higher critical temperature.

Bonding Solder

Research has shown that if SAC solder is used for bonding, the SAC coating on the superconducting wire melts and delaminates and this weakens the wire. Therefore a lower melting point solder must be used for bonding. The electronics industry has many decades of experience with SnPb solder including when used at low temperatures such as in cold environments and it has proven to be reliable. There are only a few low melting point solders

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[23] High-Temperature Superconducting Magnets for NMR and MRI: R&D Activities at the MIT Francis Bitter Magnet Laboratory, Yukikazu Iwasa, et al., IEEE, available from https://dspace.mit.edu/handle/1721.1/69163.

[24] Degradation of the performance of an epoxy-impregnated REBCO solenoid due to electromagnetic forces, T. Matsuda et al., Cryogenics, 90 (2018), pp47–51.

[25] Selected Mechanical and Operational Issues of High Field No-Insulation High Temperature Superconductor Magnets, Seungyong Hahn, The 9th Workshop Mechanical and Electromagnetic Properties of Composite Superconductors, Korea, 2018.

[26] Degradation analysis of REBCO coils, D. X. Ma et al., Supercond. Sci. Technol. 27 (2014) 085014.

that are both lead-free and cadmium-free and these are all based on bismuth or indium, for example:

- In52%Sn48% m.pt. 118°C
- 58%Bi42%Sn m.pt. 138°C
- 67%Bi33%In m.pt. 109°C
- 97%In3%Ag m.pt. 143°C

Bismuth makes the alloys hard and brittle and this is exacerbated at very low temperatures. Indium alloys tend to be very soft and ductile, but indium is a relatively reactive metal so that it corrodes and oxidises much more readily than other types of solder. Also, due to its softness, bonds are easily deformed when force is applied such as when the magnetic field strength changes and this can cause bond failure. The following summarises the main reasons why lead-free and cadmium-free low melting point solders cannot be used instead of SnPb:

- Brittle bonds, especially bismuth-based alloys
- Inferior wetting properties, compared with SnPb
- Bad anti-shock properties
- Voids within bonds readily form. Larger size voids will weaken bonds
- Bad mechanical properties (bismuth too hard, indium too soft)
- Deformation by heat cycles (especially indium solders)
- Unknown long term reliability in this application
- When soldering to nickel alloy or stainless lamination, the indium or bismuth solder will not make strong bonds with nickel (or nickel in stainless steel) as the intermetallic phases that form result in weak bonding whose strength is insufficient.
- Inferior corrosion resistance - indium solders require aggressive fluxes as indium oxidises more readily than SnPb. These fluxes can cause corrosion
- Very little published research or experience at low temperature
- Less information on cold brittleness than for SnPb.

NMR, MRI and other electromagnet applications will experience cyclic stresses due to the powerful magnetic fields that are generated. Bond ductility is therefore highly beneficial. Tin/lead solder is known to be more ductile than lead-free solder alloys, bismuth based solders and also braze alloys and so SnPb is likely to be more reliable than these bonding options.

Conducting adhesives have not been evaluated because these are not specified for use at very low temperatures. Also, they would become very hard and brittle at low temperature and high resistivity bonds may develop if oxidation of base metals occurs.

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.

Although high temperature superconductors have been known since 1986 commercialisation is fairly recent and equipment manufacturers are at present selecting the best materials overall for each application, and for those described above in this exemption request this is lead-doped Bi2223. Research into high temperature superconductors has demonstrated many issues that limit their use as is described above in section 6. All materials have limitations which are often difficult to compensate. Research has been carried out to develop different superconducting materials, into equipment design using superconductors with various materials and to include compensating measures within equipment to overcome the limitations and boost performance. The optimal superconductor that gives the best performance and the least risk of failure will be used.

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

At present, lead-doped Bi2223 gives the best overall performance for the specific applications in scope of RoHS when compared with alternative materials. Further research is and will be carried out to boost performance of equipment and improve technology that is used to compensate for limitations. This will include assessment of lead-free superconductors in prototype equipment and these will be used commercially if these materials give the best overall performance and reliability. Research into commercial NMR and MRI equipment using high temperature superconductors started relatively recently.

The aim of manufacturers is to advance the performance of electrical equipment such as NMR and MRI and the materials which give the best overall performance will be used. At present, the optimum material overall is lead-doped Bi2223. It is envisaged that if other materials can be made into superconducting wire and coils, these will be evaluated and if superior performance is achieved and the equipment is reliable, then this will be used. It is not currently possible to predict when development of designs using lead-free superconductors will be possible. Lead-doped Bi2223 was originally discovered in 1988, but commercial wire was not available until 2004, 15 years later. Commercial equipment such as NMR is only now being realised, >14 years after commercial wire was available. Commercialisation of any new superconductors is likely to take a similar length of time once a material is found to be suitable and meets all essential requirements, i.e. a total of about 30 years.

Alternative solders can be investigated once long term reliability of BSCCO based products is proven. However, it will take many years to determine whether lead-free bonding will give long term reliability as testing needs to be carried out under realistic use conditions, which are at low temperatures, so accelerating failure modes significantly is not possible as behaviour at higher temperatures will not be representative.

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)? None are applicable to lead-doped Bi2223

☐ Authorisation

☒ SVHC Lead metal in solder
☒ Candidate list Lead metal
☐ Proposal inclusion Annex XIV
☐ Annex XIV

☐ Restriction

☐ Annex XVII
☐ Registry of intentions

☒ Registration lead has been registered – see https://ila-reach.org/our-substances/lead-metal/ and https://echa.europa.eu/registration-dossier/-/registered-dossier/16063

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

(B) Elimination/substitution:

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

☐ Yes. Consequences? _____

☒ No. Justification: Substitutes give inferior performance and poor reliability

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

☐ Yes.

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

☒ No.

Justification: Substitutes give inferior performance and poor reliability

3. Give details on the reliability of substitutes (technical data + information): See section 6 (B)

4. Describe environmental assessment of substance from 4.(A)1 and possible substitutes with regard to
    1) Environmental impacts: Not considered
    2) Health impacts: Not considered
    3) Consumer safety impacts: Not considered

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

(C) Availability of substitutes:

a) Describe supply sources for substitutes: See section 6
b) Have you encountered problems with the availability? Describe: Not applicable
c) Do you consider the price of the substitute to be a problem for the availability?
☐ Yes ☒ No
d) What conditions need to be fulfilled to ensure the availability? Not applicable

(D) Socio-economic impact of substitution:

⇨ What kind of economic effects do you consider related to substitution? Lead-doped Bi2223 is used solely because it gives superior performance and reliability compared to alternative superconductors. This exemption would allow EU organisations to buy and use NMR and MRI that use this material and this will give benefits to researchers (NMR, etc.) and the health of EU citizens (MRI). Without this exemption, this cannot be realised as substitutes are inferior.

☐ Increase in direct production costs

☐ Increase in fixed costs

☐ Increase in overhead

☒ Possible social impacts within the EU. There could be a possible loss of jobs if EU organisations could not use types of equipment (such as NMR) that use lead-doped BSCCO, if this exemption is not granted. These will be available to non-EU organisations in countries without the same RoHS restrictions as the EU. There may also be possible health impact as described above.

☐ Possible social impacts external to the EU

☐ Other: _____

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

9. Other relevant information

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

10. Information that should be regarded as proprietary

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