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Integrated Hybrid Life Cycle Assessment and Supply Chain Environmental Profile Evaluations of Lead-based (Lead Zirconate Titanate) versus Lead-free (Potassium Sodium Niobate) Piezoelectric Ceramics

Ibn-Mohammed, T.[1, 2]*, Koh, S.C.L[1, 2], Reaney, I.M.[3], Acquaye, A.[4], Wang, D.[3], Taylor, S.[5], Genovese, A.[6]

[2]Advanced Resource Efficiency Centre, University of Sheffield, Sheffield, S10 1FL, UK
[3] Departments of Materials Science and Engineering, University of Sheffield, Sheffield, S1 3JD, UK
[4] Kent Business School, University of Kent, Canterbury, CT2 7PE, UK
[5] School of Civil and Building Engineering, Loughborough University, Loughborough, LE11 3TU
[6] Logistics and Supply Chain Management Research Centre, University of Sheffield, Sheffield, S10 1FL, UK

*Corresponding email: t.ibn-mohammed@sheffield.ac.uk

Abstract

The increasing awareness of the environmental and health threats of lead as well as environmental legislation, both in the EU and around the world targeted at decreasing the use of hazardous substances in electrical appliances and products has reinvigorated the race to develop lead-free alternatives to lead zirconate titanate (PZT), which presently dominates the market for piezoelectric materials. Emphasis has been placed on one of the most likely piezoelectric materials, potassium sodium niobate (KNN), as a lead-free replacement for PZT. KNN has been speculated to have better environmental credentials and is considered as a "greener" replacement to PZT. However, a comparative environmental impact assessment of the life cycle phases of KNN versus PZT piezoelectric materials has not been carried out. Such a life cycle assessment is crucial before any valid claims of "greenness" or environmental viability of one material over the other can be made and is the focus of this paper. Against this backdrop, a methodologically robust life cycle supply chain assessment based on integrated hybrid life cycle framework is undertaken within the context of the two piezoelectric materials. Results show that the presence of niobium in KNN constitutes far greater impact across all the 16 categories considered in comparison with PZT. The increased environmental impact of KNN occurs in the early stages of the LCA due to raw material extraction and processing. As a result, the environmental damage has already occurred before its use in piezoelectric applications during which it doesn't constitute any threat. As such, the use of the term "environmentally friendly" for the description of KNN should be avoided. Cost-benefit analysis of substituting PZT with KNN also indicates that the initial cost of conversion to KNN is greater, especially for energy usage during production. This environmental assessment has allowed us to define and address environmental health and safety as well as sustainability issues that are essential for future development of these materials. Overall, this work demonstrates insightful findings that can be garnered through the application of life cycle assessment and supply chain management to a strategic engineering question which allows industries and policy makers to make informed decisions regarding the environmental consequences of substitute materials, designs, fabrication processes and usage.

1. Introduction

In recent times, there has been a drive to develop new piezoelectric materials for a wide range of applications with properties comparable with lead zirconate titanate (Pb (Zr, Ti) O$_3$, PZT). One main driver has been the growing awareness of the environmental impact and health concerns due to the toxicity of lead [1-6] which has led to existing environmental legislations and restrictions both in the EU and across the globe under the auspices of Waste Electrical and Electronic Equipment (WEEE) and Restriction of Hazardous Substances (RoHS) directives which concern the reduction of the use of hazardous substances in electrical equipment and the management of the ensuing waste.[3, 7, 8] In addition, there is keen interest in developing

environmental friendly lead-free substitutes in biological and surgical settings due to increased interest in actuators and sensors that can be directly implanted into living tissues. [2, 3, 7, 9] Finally, there is a need for piezoelectric devices that are suitable for high temperature applications (e.g. control actuation in aero-engines to enhance fuel efficiency)[7, 9, 10] as well as a general demand for piezoelectrics to function at higher performance levels in a number of emerging market sectors. [1, 7, 9]

Piezoelectricity is a phenomenon which entails the ability of certain class of materials (i.e. anisotropic crystals) to generate an electrical potential when subjected to a mechanical stress or load. [11] Such materials also have a unique opposite property of generating a stress, if the voltage-generating crystals are exposed to an electric field. These modes of operation are known as the direct and inverse piezoelectric effects, respectively. These effects, whether they are individually, resonantly or sequentially coupled, have been extensively adopted for various applications in actuation, sensing and digital signal processing.[7, 12] Piezoelectric materials are indeed multifunctional given their existence at the heart of devices, rendering an exceptionally wide array commercial applications such as sensors, military hardware, low-power, high-power and multilayer actuators, acoustic and axial transducers, voltage and ultrasonic generators and smart structures. The global market for piezoelectric materials is presently estimated at ~$1 billion per annum, with a growth rate of roughly 10% per annum. [7] This figure includes the piezoelectric materials as well as simple devices and components but excludes more complex subsystems for which the piezoelectric is the main functional component and which accounts for a market worth many times the aforementioned figure.[7] For instance, the prospective market for piezo-injection actuators is worth more than 80 million euros per annum in the UK alone despite the technology being in its infancy at present. [7]

The understanding of the phenomenon of piezoelectricity has led to the discovery of a number of ceramics and innovations centred on PZT, upon which the majority of commercial devices are based. The use of PZT in applications requires various forms such as single crystals, thick films, thin films, monolithic ceramics, multilayer ceramics and composites with reliable and reproducible properties. [7] However, in recent time, there has been an increasing awareness of environmental and health issues posed by the use of PZT due to the presence of more than 60 wt% composition of lead – a toxic heavy material [3, 12] Given the importance of PZT for piezoelectric applications, an enormous amount of lead oxide is emitted into the atmosphere during the life cycle of the materials. Emission can occur due to evaporation of lead oxide from

the starting oxides during calcination and sintering in the production phase but also PbO is lost to the environment during machining. These issues are further compounded by challenges such as recycling and waste disposal after usage. Furthermore, the recycling and final waste disposal of devices containing lead-based piezoelectric materials has become a matter of huge concern, given that these materials are now employed in many consumer goods including automobiles, medical devices, and sound equipment amongst other areas. Consequently, the EU through its WEEE and RoHS legislations is tightening the use of lead oxide in a wide range of applications. This legislation has prompted the production of lead-free solder and glasses, although at present electro ceramics containing lead are exempt from these directives until such time as viable alternatives are deemed available. [12]

A number of lead-free piezoelectric materials to replace PZT have been developed or considered. Select but not exhaustive examples of such materials include: lithium niobate ($LiNbO_3$) [13]; barium titanate ($BaTiO_3$), [14, 15] lead-free substitutes based on the tungsten-bronze structured (e.g. $KBa_2Nb_5O_{15}$, $(Sr_{0.7}Ba_{0.3})_2NaNb_5O_{15}$), [16, 17] perovskite-like compounds based on bismuth layer structures [18], and bismuth sodium titanate (BNT). [19-21] Many of the aforementioned lead-free materials exhibit technical challenges including relatively weak piezoelectric effect; [13] low-phase transition temperature; high costs of fabrication and uncertainty about the feasibility of the fabrication technique for large scale production; [14, 15] problems pertaining to the actualisation of samples with high-density and fine-grained microstructures; [22] inappropriate crystallographic symmetry causing problems of domains control; [16] as well as high conductivity which yields ineffective polling. [19, 23] These limitations have inhibited progress to market of many potential piezoelectric materials but two candidate materials have emerged, head and shoulders above all others: the aforementioned compositions based on BNT [19-21] and potassium sodium niobate, (K, Na)NbO_3 (KNN)-based compositions which will be the focus of this comparative life cycle analysis. [1, 9, 10]

Although KNN-based compositions still pose challenges for densification and fabrication, the high piezoelectric constant of recent doped and modified KNN-based compositions coupled with their high Curie temperature (T_C) [1, 3, 9, 10] are very attractive to manufacturers of bulk materials and multilayer actuators (MLAs). Moreover, KNN is compatible with low cost Ni internal electrodes for MLAs unlike its competitor BNT which requires complex non-standard metallisation solutions or the use of inert noble metals such as Pt and Ag-Pd. [24-26] Hence, KNN is gradually becoming regarded as the leading candidate to replace PZT for

piezoelectric applications [4, 10, 12, 27] should WEEE and RoHS exemptions be lifted.[4, 12] Given these attributes, KNN is thus the focus of comparison with PZT in the current work.

It is universally speculated that KNN has better environmental credentials and is "greener" than its PZT-based counterpart. However, a comparative environmental impacts assessment of the life cycle stages of KNN lead-free and PZT lead-based piezoelectric material has not been carried out. This type of life cycle and environmental profile assessment is vital before any valid assertions of "greenness" or environmental viability of one material over the other can be made. Given the potential of KNN to replace PZT, it is important to verify the claim by several leading authors that the advantages gained from this material system far outweighs the impact of the use of toxic lead-based PZT piezoelectric material by conducting a detailed comparative environmental profile assessment along the entire supply chain. This will provide an indication as to whether KNN-based materials constitute new environmental challenges or not.

A comprehensive environmental profile assessment and evaluations of any material system must account because of the tendency of the environmental impact to shift to other phases of the life cycle. Information regarding the consequences of alternative material substitute and design are required for effective environmental decision making. For consumers, industries and policy makers to make informed decisions, the environmental consequences of substitute materials, designs, fabrication processes and usage must be established. Against this backdrop, a methodologically robust life cycle supply chain assessment based on integrated hybrid life cycle framework is undertaken within the context of the two piezoelectric materials under consideration. This allows us to define and address environmental health and safety as well as sustainability issues that are essential for future development and upscaling of this material architecture.

In the light of the above, the remainder of the paper is structured as follows. In Section 2, a brief review of extant literature on application of LCA for comparative environmental profiling, detailing specific LCA methods and the rationale for choosing the integrated hybrid LCA for the current work is provided. A brief description of the processes involved in PZT and KNN fabrication are presented in section 3. Details of the general methodological notes and theoretical formulations underpinning the integrated hybrid LCA model and the framework for cost-benefit analysis are provided in Section 4. In Section 5, the key findings of the results are

analysed and discussed as well as highlighting the implications of the research to new piezoelectric material development leading to the summary and concluding remarks in Section 6.

2.   Overview of LCA approaches and rationale for using integrated hybrid LCA

As highlighted above, it is important for materials designers, consumers and policy makers to have reliable information regarding the consequences of alternative material substitute and design for effective environmental decision making. Life Cycle Assessment (LCA) is a methodical tool that can provide such information.[28, 29] It is a well-established systematic approach used for the identification, quantification and assessment of the associated environmental impacts throughout the entire value chain of an activity, product or process.[28, 30] The adoption of LCA framework allows for the identification of pathways to production processes associated with high energy and resource usage, pollution and emissions of greenhouse gases, for which suitable basket of intervention options and strategies can be devised and implemented in order to address them.[29, 31]

Two main LCA modelling techniques, namely the process (bottom-up) models or the macro-economic environmental input-output (top-down) models,[32] can be used to evaluate the environmental footprints of competing products within a supply chain production system[33]. Process-based analysis is more suitable for adoption in instances where the flows of a range of goods and services for specific processes, products, or chains of manufacturing are easy to trace and track at a physical level[31]. It works by establishing a system boundary dictated by the scope of the study, accounting for individual emissions contributions within the system. However, the degree of the incompleteness and inaccuracy posed by setting a system boundary varies, subject to the type of product or process under consideration and how thorough the study is, but it can be as high as 50% or more.[34] As such, it is not able to handle the complex and global nature of supply chains of products.[31, 35] The EIO make use of country and/or regional input–output data linked to averaged sectoral emissions to calculate environmental impacts, yielding an all-encompassing result. The method offers comprehensiveness and completeness because it captures nearly the entire system boundary,[30, 36] by taking into account the entire activities along the chain of supply of a product including those accrued by indirect suppliers, allowing the tracking of the complete range of inputs to a process, thus avoids systems boundary issues that characterises the process-based approach.[29, 37] However, the method suffer from a number of well-recognised limitations, including proportionality and homogeneity assumption, conversion

of economic quantities into physical quantities and less specific due to aggregation of a range of activities in one sector. [36-40]

Integration of the two methods via a hybrid method augments the specificity of process LCA with the inclusivity of EIO [31, 35, 41-43]; hence hybrid LCA models can be implemented in practice to broaden the system boundary whilst complying with ISO standards.[41, 44] In the hybrid LCA system, process LCA is interlinked with the complete supply chain system boundary provided by EIO model, which captures the entire economic supply chain along with its sectorial changes and production and consumption patterns.[45] As shown by a number of authors,[41, 44, 46, 47] the use of hybrid LCA ensures a LCA system that is systematically complete is achieved through the augmentation of upstream and downstream inputs within the LCA system in instances where specific process LCA data are lacking. Specifically, hybrid LCA places more emphasis on the process data whilst avoiding truncation of system boundary and double counting of process inputs.[41, 43, 48]

Given the strategic importance of piezoelectric materials because of their wide array of applications, their entire supply chain must be assessed to identify environmental hotspots. It is therefore essential to adopt an environmental profile assessment technique that captures all impacts (direct and indirect), whilst ensuring complete supply chain visibility, which is a fundamental prerequisite in environmental impacts assessment across supply chains.[49] The hybrid LCA ensures that this visibility requirement is sustained in any environmental assessment accounting analysis, hence its adoption in this work. Data for conducting a detailed LCA study are hard to obtain and it is time consuming to gather sufficient data for a credible LCA study since it is not possible to obtain enough information to produce a detailed inventory for all the areas identified in the goal and scope definition stage of the study. For instance, in the current work, data including contributions from upstream activities such as transportation, use of imported equipment, special purpose machinery, research and development, telecommunications etc. which forms part of the overall development of piezoelectric materials are not available but it is important not to ignore the impact of the contributions from such activities. An estimation of such contributions using a well-established framework, hybrid LCA, is therefore the preferred methodology of dealing with this issue within this manuscript. Against this backdrop, the current work adopts a Multi-Regional Input-Output (MRIO) model within a hybrid LCA framework, to conduct a life cycle supply chain comparative assessment, within a cradle-to-grave scenario, of the two piezoelectric materials namely PZT and KNN. This provides opportunities for the

identification and pursuance of a continuous environmental improvement of product supply chains of the two material systems.

A number of LCA studies have been carried out using integrated hybrid framework based on a single sustainability metric, notably greenhouse gas emissions. However, Hoekstra and Wiedmann[50] identifies the importance of multiple sustainability metrics (e.g. land, water, material and other footprints) along supply chains in understanding the sustainability, efficiency and equity of resource use from the viewpoint of producers, consumers and policy makers. To this end, the LCA in this work is carried out, from cradle-to-grave, within a hybrid framework, across multiple sustainability metrics namely GHG emissions, material use (i.e. cumulative energy demand), land use, pollution (acidification and eutrophication potentials) and toxicology (marine, fresh water etc.). Accordingly, the current work represents the first LCA study to adopt the aforementioned multiple sustainability metrics within a consistent hybrid framework.

LCA has been used in a number of studies for comparative life cycle assessment of products or materials. A select but not exhaustive list include studies by Miller et al.[51] on the comparative LCA of petroleum and soybean-based lubricants; Peters and Rowley[52] on environmental comparison of biosolids management systems; Zhang et al.,[53] on the LCA of ionic liquid versus molecular solvents and their applications. To the best of our knowledge, no LCA work currently exists for comparative environmental assessment of piezoelectric materials. This work therefore represents the first and comprehensive comparative environmental sustainability assessment of piezoelectric materials with specific focus on PZT and KNN.

To summarise, the novelty and contribution of the current work is as follows:

(i)   The expansion or extension of the hybrid LCA model to incorporate additional sustainability metrics including materials usage, land use, eutrophication, acidification and toxicology. This is an important contribution given the increasing importance of multiple metric LCA analysis which ensures visibility and allows for thorough trade off analysis.

(ii)   The application of the multiple metric-enabled hybrid LCA framework to identify supply chain hotspots in the environmental profile of PZT versus KNN piezoelectric functional materials. The work demonstrates the predictive capability of LCA for the environmental impact assessment of new materials versus existing materials. In particular, it highlights the fact that the replacement of PZT with KNN will not be driven purely by environmental consideration and

negates the conventional knowledge which suggests that KNN is "environmentally greener" as compared to PZT piezo because it does not contain lead, a toxic heavy material.

(iii)   Overall, this work demonstrates an important application of integrated hybrid life cycle assessment and supply chain management to a strategic engineering question which allows industries and policy makers to make informed decisions regarding the environmental consequences of substitute materials, designs, fabrication processes and usage.

3.   Production route for PZT and KNN

In this section, simplistic procedures for fabricating both the PZT and KNN piezoelectric materials are presented. For comparison, we are using laboratory-based temperatures and sintering times for undoped KNN and PZT. However, we duly note that procedures vary from manufacturer to manufacturer and also as a result of the use of dopants and substituents to modify and improve properties in each composition and to engender compatibility with different internal electrode technologies in the case of MLAs.

3.1   Manufacturing route for PZT

PZT ceramics is typically fabricated using conventional powder processing technology which entails the four basic steps: i) preparation of powder; ii) shape forming; iii) sintering at high temperature and iv) component finishing.[54] As shown in Figure 1 (R.H.S), the starting materials for PZT are lead oxide (PbO), titanium oxide (TiO_2) and zirconium dioxide (ZrO_2). Each starting material is precisely weighed based on the formulation being fabricated. The PZT powder mixture is then batched stoichiometrically and synthesised through solid-state reaction by ball or attrition milling a mixture of the oxides in isopropanol, to achieve a uniform particle size distribution. This exact control over particle size distribution is important to ensure a homogeneous distribution of constituents and good reaction during calcination. Following on from the milling process, the resulting slurry is dried and prepared for calcination. The slurry is calcined in high-purity, refractory kiln furniture to minimise contaminants in the final product. The calcination is carried out in air at ~800 °C-900 °C for ~4 hours to synthesise the perovskite compound.

Given that the major constituents in the PZT material is PbO, a hazardous material that is volatile at temperatures above 800 °C,[55] proprietary measures are adopted to minimise the loss

of PbO, so that the desired composition is not altered due to the tendency of allowing too much lead to evaporate during calcination. After calcining, the PZT powder is ball milled again in isopropanol for 12 hours to ensure homogeneity. The slurry is then dried again at 90 °C and pressed for the final net shape. For complex shapes, a binder such as polyethylene glycol (PEG) is sometimes added to minimise pressing flaws. If a binder is used it must be removed by an intermediate step at ~450-500 °C during a sintering profile which peaks at ~1000 - 1200 °C, depending on exact composition. Care must be taken to control PbO emissions during calcination and sintering. If necessary, parts are machined to create the required geometry of the actuator, sensor or transducer.

3.2   Manufacturing route for KNN

The manufacturing route for KNN-based compositions (Figure 1, L.H.S) is similar to that of PZT with the starting materials being sodium carbonate (Na_2CO_3), niobium pentoxide (Nb_2O_5) and potassium carbonate (K_2CO_3). The correct stoichiometric quantities are calculated for the desired composition before the mixture is wet-milled to ensure that all powders are mixed together thoroughly. The resulting slurry is dried at ~90 °C and calcined ~6h at ~850 °C. It is well known that slight modifications to the stoichiometric composition of the KNN powder can lead to the formation of secondary phases which impair the piezoelectric performance. Hence X-ray diffraction is adopted to establish the phase assemblage after calcination in the case of all ceramic processing routes. The resulting KNN powder is re-milled for 12 hours and dried again at ~90 °C after which they are pressed into pellets of the required geometry. Pellets are then sintered for 3h at ~1100 °C to obtain densified ceramics followed by machining to obtain the required device geometry.
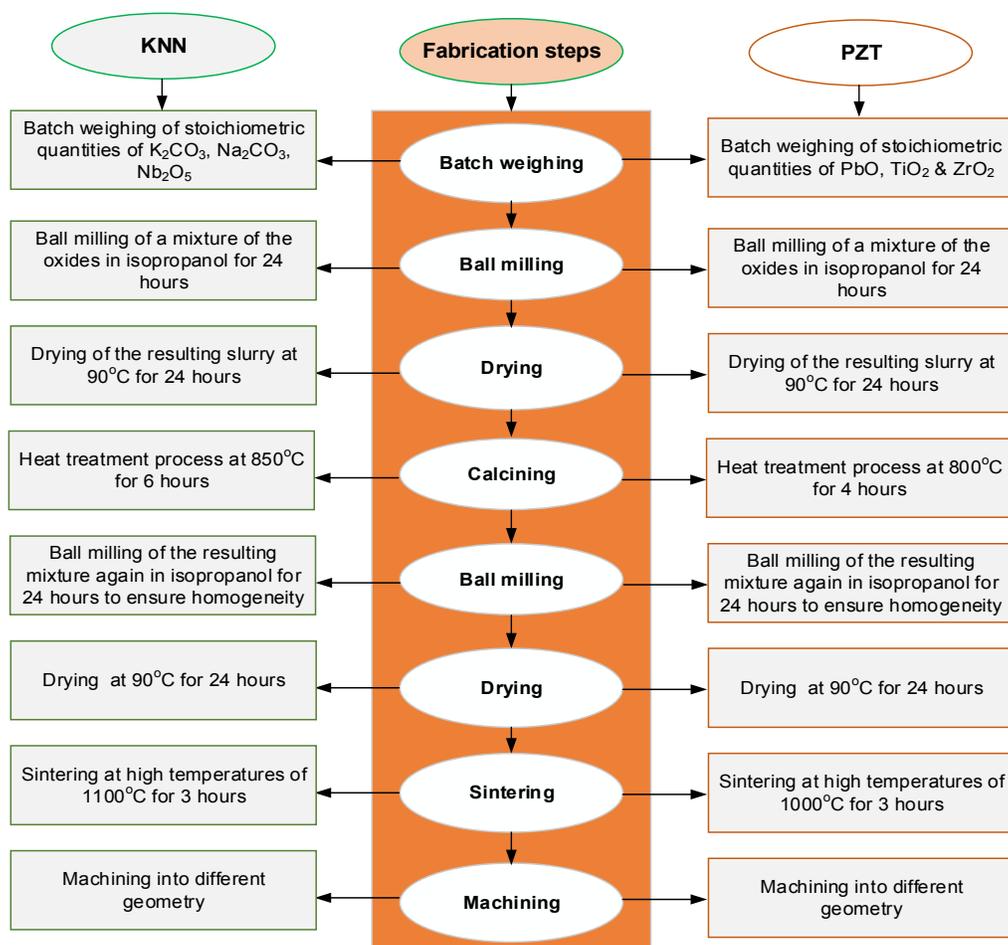
Figure 1: Fabrication route of PZT and KNN piezoelectric materials. Please note that for simplicity we are quoting typical laboratory-based times and temperatures for comparison but it is anticipated that these may be modified slightly for commercial production for different manufacturers.

4.   Research Methodology

The production, usage, recycling or disposal of products can generate damaging impacts to human wellbeing and the natural environment.[28, 30] As such, Life Cycle Assessment (LCA) can been used as a powerful tool to systematically track the broad spectrum of environmental impacts throughout the entire value chain of an activity, product or process and assess them from a systems perspective, identifying approaches for improvement without burden shifting.[28, 30, 31, 35, 53] LCA entails the gathering and evaluation of the inputs, outputs, and potential environmental impacts of a product system throughout its lifespan and involves four key steps namely [56]: (i) goal and scope definition, where the objectives of the study are defined and where the systems boundaries are set; (ii) inventory analysis where inputs and outputs of each process in the life cycle are compiled, summing them across the whole system; (iii) life cycle impact

assessment, where emissions and resources are grouped into their respective impact categories and converted into common impact units for comparative analysis; (iv) the interpretation of the inventory and impact assessment of results in order to actualise the objectives of the study.

To analyse the contributions of individual process exchange entries into the inventory based on a number of sustainability metrics, the LCA in this work is carried out, from cradle-to-grave, across multiple sustainability metrics, based on CML method,[57] namely GHG emissions, land use, pollution (acidification and eutrophication potentials) and ecotoxicity (marine aquatic, marine sediment, fresh water sediment, fresh water aquatic, terrestrial etc.), human toxicity, malodours air and ionisation radiation. Three endpoint indicators (ecosystem quality, human health and resources) following the Eco indicator 99 methodology[57] were also considered. The sustainability metric, material use (i.e. cumulative energy demand), was based on primary energy which denotes the extraction of energy embodied in natural resources that are yet to be transmogrified into any form of usable energy such as gas, electricity, etc. Examples of such natural resources include fossil fuels, solar energy, nuclear energy, geothermal energy, wind energy and biomass. The cumulative energy demand of a product is therefore the addition of the aforementioned forms of primary energy as adopted in many LCA studies.[58-62] Accordingly, all the inputs in cumulative energy demand were summed up to derive the consumption of a material based on natural resources including fossil, solar, nuclear, geothermal, wind, primary forest, water and biomass.[57]

The current work adopts an integrated hybrid LCA approach which overcomes boundary limitations of a process approach, by combining the process LCA inventories and Environmental Input-Output (EIO) data, [29, 31, 35] to evaluate the environmental profile of a laboratory-based PZT versus KNN piezoelectric materials. In the subsections that follows, details of how process LCA and EIO are combined to form hybrid LCA is presented.

4.1   Process-based LCA framework

The process LCA entails the unit process exchange and supply chain inputs that are employed directly in the fabrication of the product or material under consideration. It evaluates the amount of supply chain inputs required to produce a given functional unit (i.e. 1kg of PZT vs. KNN in this study). Using life cycle inventories, the process LCA can be expressed mathematically as:

$$Process\ LCA = \sum_{i=1}^{n} A_{p(i)} * E_{p(i)} \qquad (1)$$

11

where: A_p is the inputs (i) into a product's (i.e. PZT vs. KNN piezoelectric materials) supply chain including raw material extraction, energy consumption, material production and manufacturing processes, etc.; n is the total number of process input (i) into the product's supply chain and E_p is the emissions intensity across a number of environmental and sustainability metrics (e.g. GHG emissions, land use etc.), for each input (i) into a product's supply chain emissions. For details of how the matrix A_p is represented in vector form, see ESI.

4.2   Environmental Input Output LCA framework

The EIO LCA is carried out by linking national IO tables with direct industrial emissions intensities to produce results that can be adopted in the LCA of a product. [38, 45] The general IO model is a quantitative technique[63] which details how products and services flow from one economic sector (i.e. producer) to other economic sectors (consumers).[38] It is adopted as the methodological basis to compute the upstream indirect emissions associated with the inputs into the supply chain for the production of the final product. The process entails the conversion of economic flows into physical flows (in this case $CO_{2\text{-eq}}$ emission within the overall IO framework, using well-established assumptions of IO analysis. Given that A_{io} represents the technical coefficient IO matrix, (I) the identity matrix, E_{io} the direct emissions intensities across a number of sustainability metrics for each IO industry and (y) the final demand [64], the EIO can therefore be defined in a generalised form as:

$$EIO\ LCA = E_{io}.(I-A)^{-1}.y \qquad (2)$$

where: $E_{io}.(I-A)^{-1}$ is the total (direct and indirect) emissions intensities of each industry required to produce a unit of product.

4.2.1 Multi-Region Input-Output (MRIO) model

The distinguishing characteristics of Multi-Region Input-Output (MRIO) framework is that it enables the tracking of the production of a given product in a given economic sector, quantifying the contributions to the value of the product from different economic sectors in various countries or regions captured in the model.[65, 66] The model which is in tune with current United Nations Accounting Standards,[67-69] therefore provides an account of the global supply chains of products consumed given it is globally closed and sectorally highly disaggregated thereby facilitating international supply chains tracking and produce more robust and complete results.[70, 71] MRIO framework combines, in a robust way, the matrices of domestic or local

technical coefficient with the matrices of import from numerous countries or regions into one big coefficient matrix. This has the overall influence of capturing the supply chains associated with trade between all the participating trading partners as well as provide feedback pathways and effects.[71] For detailed mathematical analysis of how EIO framework is expanded upon and adopted within a Multi-Region Input-Output (MRIO) model in this study, see ESI.

4.2.2 Construction of upstream requirement matrix C_u and avoidance of double counting

To realise a hybrid LCA framework for the PZT versus KNN supply chain, upstream cut-offs from the process-based LCA system were computed using IO analysis (see Figure 2). For instance, to calculate the contributions of a particular upstream activity, say research and development, for a particular process inventory (e.g. lead oxide), which is already captured within the process matrix, A_p, the following procedures were taken. The unit cost $(i.e. £/kg)$ of lead oxide was obtained. All cost data were obtained from the powder manufacturer's website[72] and from direct quotation from manufacturers. The unit cost is then multiplied by the input (i.e. the physical quantity) of the input process (in this case lead oxide).

$$u_{ik} = C_{ik} \times p_k \tag{3}$$

This gives the total cost (u_{ik}) (i.e. the price-weighted coefficients in upstream matrix) of the input process $(i.e. [£/kg] * [kg])$ and represents the amount of lead oxide in monetary equivalent $(£)$ that is required to produce 1 kg of final demand of PZT ceramics. This total cost (u_{ik}) is then used for scalar multiplication with the a_{ij} column of the input-output technology matrix, A_{i-o} where j corresponds to the chemical industry where lead oxide is produced. To ensure that certain inputs are not double counted, all inputs which are already taken into consideration in the process matrix are no longer counted (i.e. deleted) from the resulting column vector $u_{ik}a_{ij}$.

$$u_{lk} = 0 \; if \; x_{lk} \neq 0 \tag{4}$$

The computed values $u_{ik}a_{ij}$ then become individual elements of the matrix U which represents the upstream input. The research and development expenditure which links the process LCA lead oxide to the IO table corresponds to $u_{ik}a_{ij}$ where i corresponds to research and development as a product and j lead oxide as an industry.
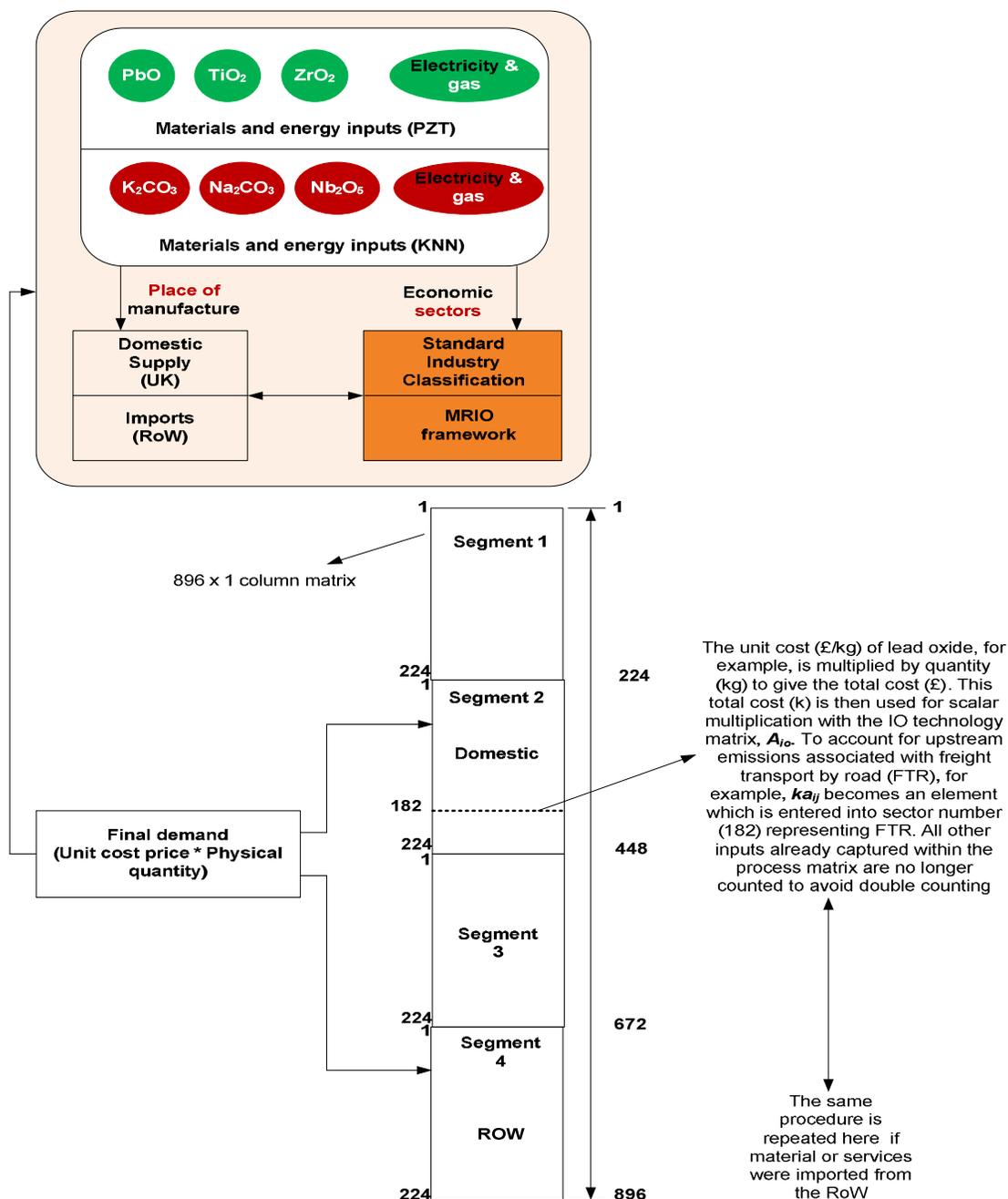
Figure 2: Illustration of how upstream requirement matrix, C_u is integrated within the overall hybrid LCA framework to avoid double counting

4.2.3 Multi-Regional Input-Output (MRIO) Hybrid LCA model

In this contribution, by combining the matrices notations process-based and EIO LCA as well as the C_u and C_d matrices, a fully integrated hybrid LCA based on the work of Suh and Huppes [43] as shown in Equation 5 is established. It then form the basis for the computation of embodied emissions across multiple sustainability metrics other than GHG, whose sectoral

emissions intensity IO data are available, namely material use, land use, pollution (eutrophication and acidification), and toxicity, within a hybrid framework. This spectrum of indicators is also consistent with the Indicators of Sustainable Development identified by the United Nations Commission's Sustainable Development Framework. [73] Due to computational complexity, the use of hybrid LCA is relatively sparse [43] but a number of authors [31, 35, 41, 74] have adopted the methodology for LCA. The consistent mathematical framework incorporating the aforementioned metrics, for the hybrid LCA methodology, is therefore defined as follows:

$$\text{Hybrid LCA} = \begin{bmatrix} E_{P_{(g,m,l,p,t)}} & 0 \\ 0 & E_{io_{(g,m,l,p,t)}} \end{bmatrix} \begin{bmatrix} A_p & -C_d \\ -C_u & I - A_{io} \end{bmatrix}^{-1} \begin{bmatrix} y \\ 0 \end{bmatrix} \tag{5}$$

$E_{P_{(g,m,l,p,t)}}$ Process inventory environmental extension matrix for GHG, material and land use, pollution (e.g. acidification and eutrophication potentials), and toxicity; All metrics are measured in their respective units (e.g. $kgCO_2$-eq) and are diagonalised, (dimension: $m \times s$)

$E_{io_{(g,m,l,p,t)}}$ MRIO environmental extension matrix for GHG, material use, land use, water use, pollution and toxicity; All metrics are measured in their respective units (e.g. $kgCO_2$-eq per £ for GHG) and are diagonalised (dimension: $m \times s$)

A_p Square matrix representation of the process LCA inventory, (dimension: $s \times s$)

A_{io} Input- Output technology coefficient matrix, (dimension: $m \times m$)

I Identity matrix, (dimension: $m \times m$)

C_u Matrix representation of upstream cut-offs to the process system, (dimension: $m \times s$)

C_d Matrix of downstream cut-offs to the process system, (dimension: $s \times m$)

$\begin{bmatrix} y \\ 0 \end{bmatrix}$ Functional unit column matrix with dimension: $(s + m, 1)$, where all entries are 0 except y

A summary of the description of the key elements in the mathematical framework in Equation 5 is presented here. Hybrid LCA (i.e. total emissions) is the direct and indirect environmental impact (e.g. CO_2-eq emissions) associated with one unit of final demand y for the

product (here PZT or KNN). Matrix A_p describes the product inputs into processes as captured in the unit process exchanges (i.e. process LCA system). A_{i-o} in this study is a (896 × 896) multi regional input-output (MRIO) technology matrix and describes input and output coefficients requirements from one sector to another within the UK vs. Rest of the World (ROW) Supply and Use MRIO framework. Matrix U which is assigned a negative sign, represents the higher upstream inputs from the MRIO system to the process system. Matrix D, also assigned a negative sign, represents the (downstream) use of goods/process inputs from the process to the background economy (MRIO system). The negative signs represent the direction of flow of inputs.

The final demand y for KNN or PZT denotes the functional unit of the LCA system, set to ***1 kg*** of both materials produced on the laboratory scale for the sake of direct comparison in this study. Functional unit is a quantified reference unit and its choice can frequently be decisive for the outcome of a specific LCA. Given that the functional unit describes and quantifies those properties of the product which must be present for the studied substitution to happen, it is therefore pertinent that the functional unit is chosen with diligence. Examples of such properties include the functionality, stability, appearance, ease of maintenance, durability, etc., and are in turn determined based on requirements in the market in which the product will be auctioned. Accordingly, a detailed procedure is chiefly important for such applications where the products or materials for comparison differ in any of the aforementioned properties. In this work, functional unit is not selected based on stability, appearance, operational characteristics etc. given that piezoelectric applications based on KNN are yet to be implemented. Our choice of functional unit is therefore based on the obligatory property that is required by the relevant market sector induced by environmental legislations and restrictions, which in this case are the raw material constituents of the two products, which ensures like for like comparison. Accordingly, the current work adopts a mass-based as against performance-based functional unit given that currently there are no devices that are operationally functional based on KNN piezoelectric materials. In fact, at the moment, none of the piezoelectric material alternatives are drop-in substitutes for PZT which invariably has superior performance than proposed alternatives.

4.3 Data sources

The overall assessment includes five main steps: i) gaining an understanding of the KNN/PZT piezoelectric materials in terms of raw material requirements, production and manufacturing processes; ii) system characterisation (i.e. establish systems boundaries, functional

unit, material composition, etc.); iii) construction of system inventory (e.g. input requirements (physical units), supply chain information and embodied emissions, process flow, energy flow, material flow, and reference flow; iv) overall impact assessment and environmental profile evaluations across multiple sustainability metrics; v) performance evaluation and cost-benefit analysis.

4.3.1   Process analysis data

Process data for inputs into the LCA were based on inventory data estimated from laboratory processes based on engineering heuristics and study assumptions, Ecoinvent database and well established data from within the literature. Process data input into the LCA system boundary (Figure 3) includes emissions arising from raw material extractions, production and purification processes, electrical and thermal energy processes involved in PZT/KNN production, the fabrication of the piezoelectric materials, and the synthesis of the compounds required during their production. Data sources of chemical synthesis steps were taken from patents and well-established literatures. For certain materials, emissions data are difficult to find. As such, emissions intensity data were derived on the basis of stoichiometric reactions based on previously published guidelines [75]. The unit process exchanges (i.e. individual material entries) representing the process analysis data from all sources are presented in the Electronic Supplementary Information (ESI).
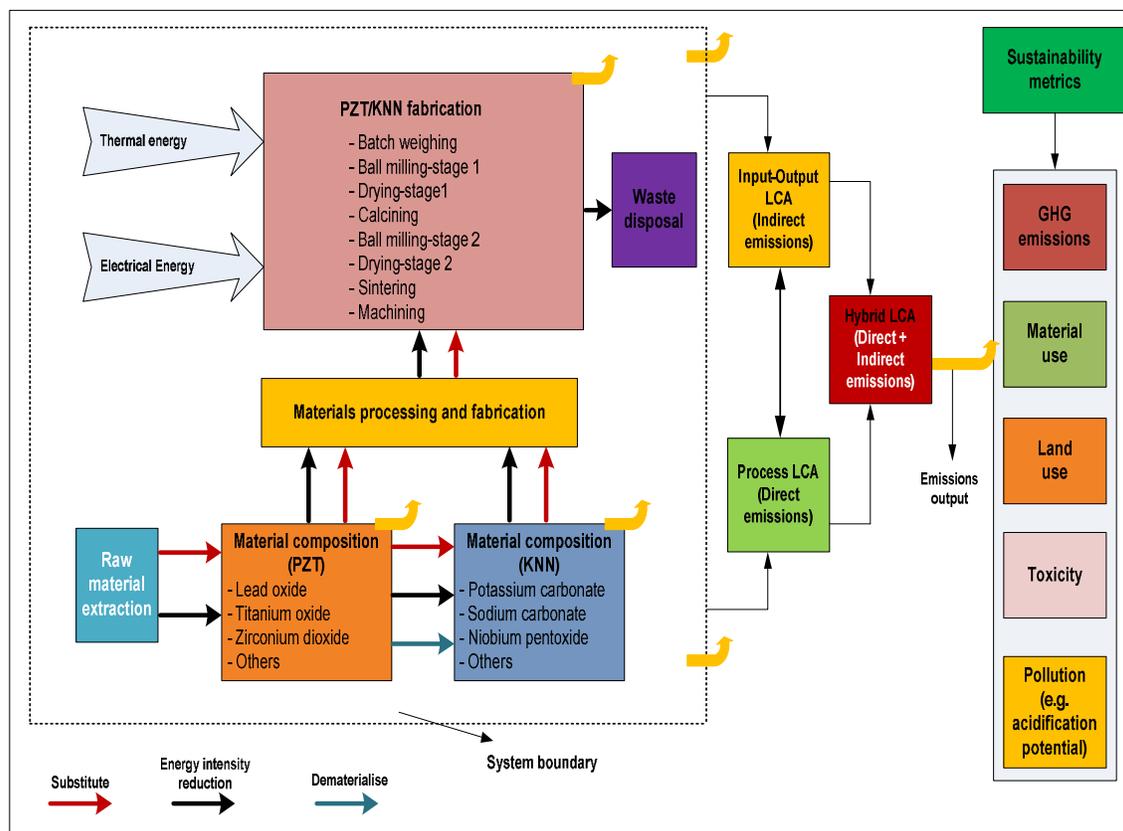
Figure 3: System boundary considered in the LCA, detailing relevant material and energy flows recorded in the inventory. Only the main constituent materials are shown for simplicity. For detailed breakdown of other input resources, see ESI.

4.3.2 Electrical and thermal energy consumption

The required energy for each of the fabrication processes is calculated using the electrical power of the specified device as described by the manufacturer, and the time during which the specific temperature is maintained for each of the processes:

$$Q = P \times t \tag{6}$$

where Q = energy required for temperature maintenance (kWh); P = electrical effect of the heating equipment (W); t = time required to maintain the temperature (sec).

Also, to account for the heating demand for the fabrication processes, where temperature is increased from an ambient to a desired temperature, the required energy is calculated using the following heat equation:

$$Q = Cp \times m \times \Delta T \tag{7}$$

Where: Q = energy required in the process (J); C_p = specific heat capacity of the material heated (J/kg·K); m = mass of material heated in the process (kg) and ΔT = temperature difference (K or °C)

4.3.3 Input-Output data

In this work, we employed the 2008 MRIO S&U tables for the UK and the ROW represented as (896 × 896) technology matrix to compute upstream indirect emissions in the LCA framework. Additionally, data for all the sustainability metrics were obtained representing the sectorial environmental intensities (i.e. kg CO_2-eq/£ for GHG, kg SO_2-eq/£ for acidification potential, kg NO_x-eq /£, for eutrophication potential, kg/£ for toxicity, m^2a/£ for land use and MJ/£ for material usage for the environmental matrix, $E_{i\text{-}o}$). The IO environmental intensities for the aforementioned indicators other than GHG, were retrieved from World Input-Output Database (WIOD)[76] and expanded upon to conform to the 896 × 896 MRIO framework based on supplementary Figure 1. The WIOD consist of national IO tables, MRIO tables, environmental accounts for forty countries and one ROW category comprising all other regions. These 40 countries include all European Union (EU) member countries, Non-EU OECD countries (e.g. the USA, Canada, Japan), and some large emerging economies (e.g. China, India, Brazil). Most of countries in the ROW region are developing countries in Africa, Asia, and Latin America. The IO table in each country includes 35 × 35 economic sectors. Given that the technology matrix A_{io} in this study is a (896 × 896) MRIO technology matrix and describes input and output coefficients requirements from one sector to another within the UK vs. ROW Supply and Use MRIO framework, it is important to make the IO environmental intensities of other indicators to conform with the same framework. As such, 39 countries (i.e. excluding the UK) and one ROW were aggregated to become an "integrated" ROW.

The direct intensity matrix, DIM (i.e. the sectoral direct emissions intensities derived for metric k across j industries) is given by:

$$D_{IM} = \frac{\text{Environmental Extension Matrix}}{\text{Total output}} = \frac{E}{X} \qquad (8)$$

As such the direct intensity matrix for the integrated ROW is given by:

$$\frac{\sum_i^n DIM_i T_i}{\sum_i^n T_i} \qquad (9)$$

Where DIM_i is the sectoral direct emissions intensities of individual country (i) within the WIOD; T_i is total sectoral outputs (£) from individual country(i); n is the total number of countries represented in the ROW within the WIOD database.

For the UK, the direct intensity matrix is derived using:

$$\frac{\sum DIM_{UK} T_{UK}}{\sum T_{UK}} \tag{10}$$

Where DIM_{UK} is the sectoral direct emissions intensities from the UK; T_i is total sectoral outputs (£) from the UK.

These sectors are therefore disaggregated to conform to the 896 × 896 (i.e.4 by 224 × 224) technology matrix used in this study based on similar technique adopted by Wiedmann et al.[41] For example, the agriculture sector alone was further disaggregated into 28 sub-economic sectors (see Table S14 in ESI for details of how the main 35 × 35 economic sectors are disaggregated into 224 × 224 sub-sectors). For toxic emissions intensities, a newly developed set of data was originally derived from the toxic release inventory database for the US. [77]

4.3.4   Cost benefit analysis of substituting PZT with KNN functional materials

Material or product substitution is an activity whereby a given material, a product or a process is replaced by suitable alternatives. When making a decision about material or component substitution, an integral consideration is the comparative value which include the substitution costs, price ratio, and in some instance the end user's propensity to change.[78] The motivation for material or product substitution could range from improving the overall service performance such as longer life and higher reliability or taking advantage of new materials or operational procedure or processes; or meeting new legal or environmental requirements.[78-80] Against this backdrop, for any material substitution project to take place, the following questions might be asked. (i) Is the benefit of implementing a novel and untested material worth the risk of abandoning the current material that are already well established? (ii) Does the cost of changing to the new material surpass the overall benefits? (iii) Will such changes require new equipment and plant? (iv) What are the implications of that substitution on the overall system at large,

assuming substitution has been carried out, (v) Are there any institutional, legal, social and environmental consequences? These are questions that require an engineering solution as much as an economic one.

We therefore employ cost-benefit analysis to ascertain the benefit of replacing PZT with KNN. This is because new materials are usually more complex, requiring closer control and in some instances, new technologies and methods for their processing. As a result, components or devices made from such materials might become more expensive. As such, for a material substitution effort to be deemed feasible economically, the economic or financial gain as a result of improved performance ΔB should be greater than the extra cost incurred due to the substitution ΔC .[78] This implies that:

$$\Delta B - \Delta C > 1 \qquad (11)$$

The cost of material substitution is usually divided into three categories namely: cost difference in direct material and labour, cost of redesign and testing and cost of new equipment and tools [78]. Therefore, the entire cost ΔC of replacing a new material, n, with an original material, o, in a given part or process is given by [78]:

$$\Delta C = (P_n M_n - P_o M_o) + f\left(\frac{C_t}{N}\right) + (T_n - T_o) + (L_n - L_o) \qquad (12)$$

Where:

P_n, P_o is the price per unit mass of new and original materials used in part;

M_n, M_o is the mass of new and original materials used in part;

f is the capital recovery factor which can be taken as 15% in absence of data;

C_t is the cost of transition from original to new materials;

N is the total number of new parts produced;

T_n, T_o is the tooling cost per part for new and original materials;

L_n, L_o is the labour cost per part using new and old materials;

The gains as a result of improved performance ΔB can be evaluated on the basis of the expected improved performance of the material, which can be related to the increase in performance index of material compared with the currently used material. Such increases or

improvements include reduced energy consumption, saving gained as a result of weight reduction or increased service life span of the component [78]:

$$\Delta B = A(\gamma_n - \gamma_o) \tag{13}$$

where: γ_n, γ_o is the performance indices of new and original materials respectively; A is the benefit of improved performance of component expressed in $£$ per unit increase in materials performance index, γ.

5.   Results, analysis and discussion

As stated in Section 4, life cycle impact assessment (LCIA) is the third step in LCA where environmental pressures related to the life cycle inventory (LCI) are characterised by calculating the impact category sustainability metrics. Currently, there is no universal list of impact categories that exist, [52, 81, 82] but LCA professionals choose categories based on the scope of the study [52]. Accordingly, Hybrid LCA as discussed in Section 4.2.4, was implemented to evaluate the environmental profile of PZT and KNN and is calculated as the addition of the process and indirect upstream emissions for five sustainability metrics whose IO sectoral emissions intensity data are available and are consistent with the Indicators of Sustainable Development identified by the United Nations Commission's Sustainable Development Framework. [73] The metrics for which hybrid model was used include GHG (kg CO_2e), material use (MJ/kg), land use (m^{2}a), eutrophication (kg NO_x-eq) and acidification (kg SO_x-eq).

For the toxicology metric, six variants of impacts namely: (i) freshwater aquatic ecotoxicity (FAETP 100a); (ii) freshwater sediment ecotoxicity (FSETP 100a); (iii) marine sediment ecotoxicity (MSETP 100a); (iv) marine aquatic ecotoxicity (MAETP 100a); (v) human toxicity (HTP 100a) and (vi) terrestrial ecotoxicity (TAETP 100a) were evaluated using process-based LCA but the upstream impact due to toxicity were calculated as toxic release per unit output in terms of air, land, water and underground combined together. This was largely due to the numerous number of chemicals included in the input-output inventory of toxic release database which makes it difficult to express this upstream toxic impacts in kg 1, 4-DCB-eq. This separation is reasonable given that the process and IO results are normally added together to give an integrated hybrid output. However, for toxicity categories considered, the process outputs are all expressed in kg 1, 4-DCB-eq while the IO are expressed in kg of toxic release. Two other metrics namely ionisation radiation (DALYs) and malodours air (m^3 air) were considered based on process LCA only, due to lack of IO sectoral emissions data. Three Eco-indicators namely ecosystem quality, human health and resources, based on Eco-indicator 99

methodology were also considered. Results are presented graphically as indicated in the following subsections.

5.1   Life cycle impacts of PZT fabrication

5.1.1   Primary energy consumption for fabrication of laboratory-based PZT ceramic

Primary energy consumption (both electrical and thermal) and material embedded for the fabrication of the PZT material are shown in Figure 4, totalling 1463.57 MJ/kg. As indicated in Figure 4(a), the primary energy consumed in fabrication contributed to about 96% (77% thermal energy and 19% electrical energy consumption) of the total primary energy consumption. Raw material requirements constitute the remaining 4%. A breakdown of the thermal energy consumed (Figure 4(b)) during manufacturing indicate that relatively long duration and high temperature sintering results in the highest thermal energy demand with calcination and drying operations responsible for 35% and 22% of the thermal energy demand.

In order to reduce the primary energy consumption due to sintering, alternative approaches for sintering PZT ceramics at lower temperatures can contribute to the overall reduction in thermal energy demand during fabrication as well as help in reducing the problem associated with the volatile nature of lead oxide under high sintering temperatures. A number of well-established procedures for reducing the sintering temperature of PZT have been reported. For instance, researchers including: Dong et al., [83] Zeng et al.,[84] Collier et al. [85] and Ohtaka et al.[86] have used dopants with low melting perovskite-type oxides such as Ba $(Cu_{0.5} W_{0.5}) O_3$ and $BiFeO_3$ to lower sintering temperature of PZT. We note that the aforementioned dopants can have differing effects on the performance of PZT, but the goal here is to reduce thermal energy consumption due to high temperature sintering which can in turn lessen the overall carbon footprint of PZT.

Regarding electrical energy consumption (Figure 5(c)) during fabrication, ball milling operation is responsible for 82% of the total electrical energy demand with sintering, calcining and drying operations contributing 8%, 7% and 3% respectively. A breakdown of the materials embedded in PZT ceramic manufacturing (Figure 5 (d)) shows that lead oxide is the most influential component, contributing 58% of the material impact category. Zirconium oxide and titanium oxide are responsible for 25% and 17% respectively of materials embedded in PZT ceramics fabrication.
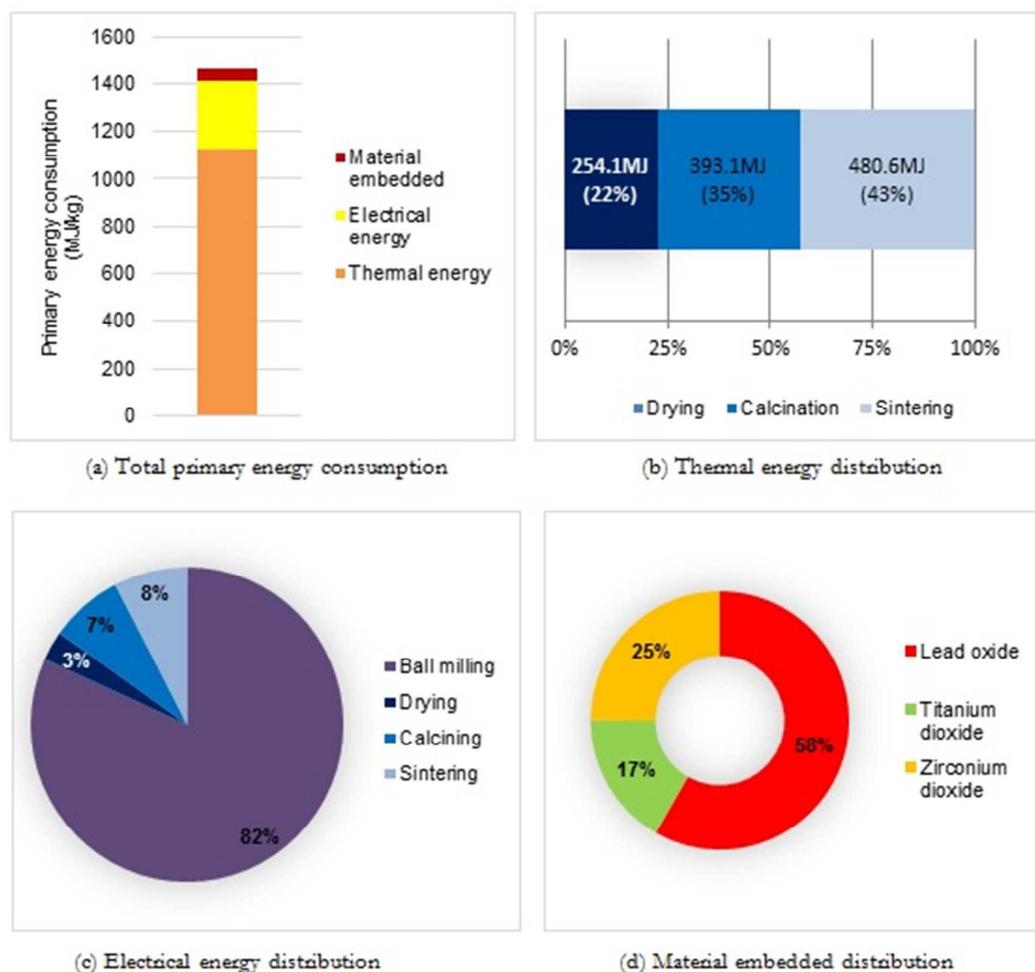
Figure 4: Distribution of the primary energy consumption for the fabrication of a laboratory-based PZT material. (**a**) Total primary energy consumption including thermal and electrical energy and materials embedded all expressed in MJ/kg. Figures 5 (b), (c) and (d) indicate the percentage contributions of each process or material relative to Figure 5(a).

5.1.2   Hybrid life cycle assessment of laboratory-based PZT ceramics

The life cycle emissions of the PZT material system is estimated as the integration of the process-based LCA and the IO indirect emissions based on five sustainability metrics. Indirect upstream emissions comprise embodied emissions attributed to inputs in the upstream supply chain, amongst others, utilities, equipment, chemicals, mining, maintenance, research and development, banking and finance, telecommunications, insurance and advertising. The results, in terms of actual values, of how process-based results compared to EIO results are shown in Table 1 and represented in graphical form in Figure 5 based on percentage contributions.

Table 1: Hybrid LCA results for PZT material system

| Impact category	Process	EIO	Hybrid (Total)
Climate Change	46.67	9.08	55.74 kg CO_2-eq
Acidification potential	0.20	0.03	0.23 kg SO_x-eq
Eutrophication potential	0.12	0.02	0.14 kg NO_x-eq
Land use	1.26	0.87	2.12 m²a
Material use	2069.25	62.75	2,132 MJ/kg
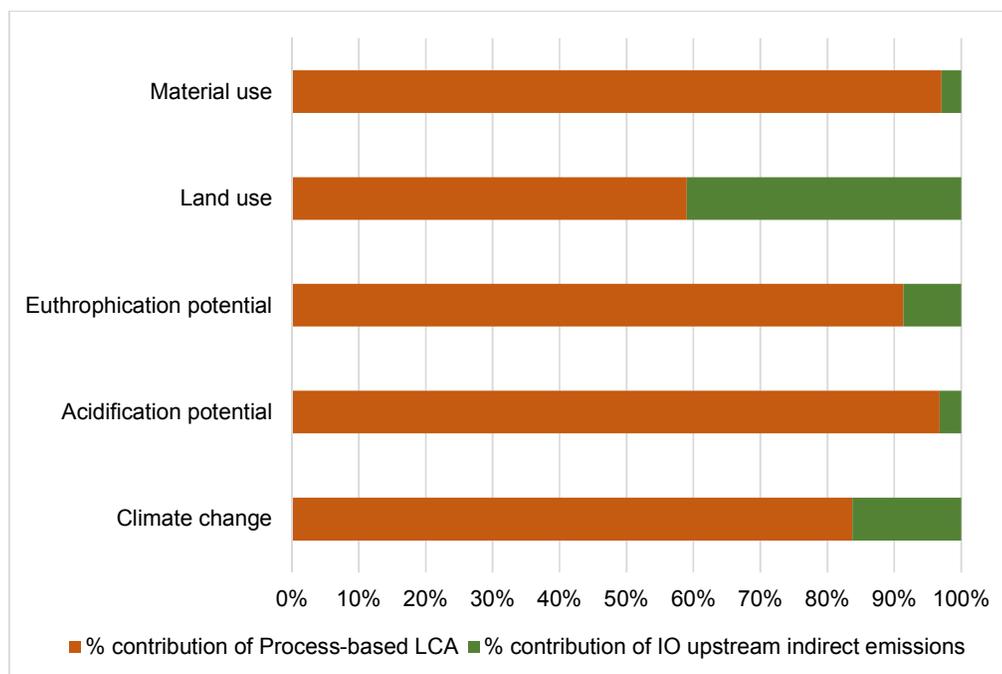
Figure 5: Results of hybrid LCA (process + IO) of PZT across a number of sustainability metrics

An examination of the toxicology environmental impacts (Figure 6) along the production routes of PZT ceramic indicates that marine sediment ecotoxicity has the highest toxicology impact. Due to the numerous number of chemicals included in the input-output inventory of toxic release database, it was difficult to express upstream toxic impacts in kg 1, 4-DCB-eq.
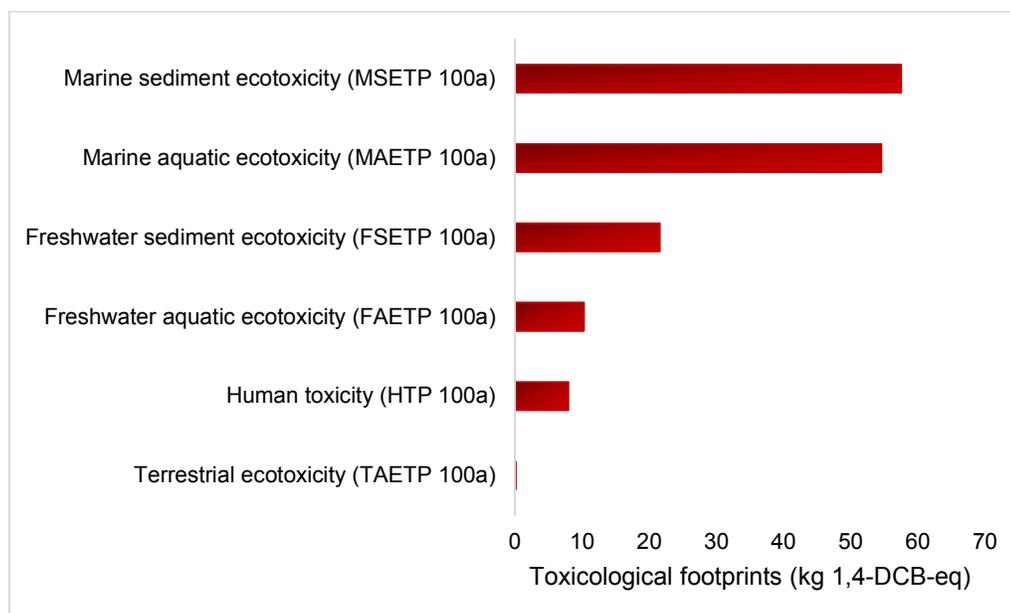
Figure 6: Results of footprint of PZT across six variants of toxicity

In the subsections (5.1.3 and 5.1.4) that follow, component level analysis based on process LCA as well as sectoral level analysis based on IO LCA of the environmental impacts of PZT fabrication is presented to identify the most influential components and materials as well as economic sectors in light of the sustainability metrics under consideration. For instance, as shown in Figure 6, based on climate change sustainability metric, the total footprint is 55.74 kg CO_2-eq with the split between processed-based and IO-based components being 46.67 and 9.08 kg CO_2-eq respectively. The goal of the next two sub-sections is therefore to identify the proportion of each material or process within the life cycle inventory that contributes to 46.67 kg CO_2-eq for example and the key economic sectors that constitute the 9.08 kg CO_2-eq. This will allow us to identify hotspots and the corresponding materials/process responsible for such hotspots for which intervention options can then be recommended.

5.1.3 Analysis of the environmental profile of PZT ceramics based on the contributing processes

Figure 7 shows the environmental profile of all the unit process exchanges representing the process analysis data of 1kg of PZT ceramic fabricated in the lab. All the thirteen sustainability metrics are normalised, ensuring that the absolute indicator of each category of impact is 100%. The principal toxic impact is marine sediment ecotoxicity (see Figure 6 for the order of the ecotoxicity impact categories). As indicated in Figure 7, most of the environmental impact emanates from primary energy consumption due to electrical and thermal energy due to associated high emissions intensity due to the numerous processes involved during the

generation of electricity. The contributing processes to marine sediment ecotoxicity category, for example, include electricity (83%), thermal energy or gas (28%) and lead oxide (5%). Waste disposal and zirconium dioxide each contribute 2% with the remaining 1% contributed by titanium oxide.
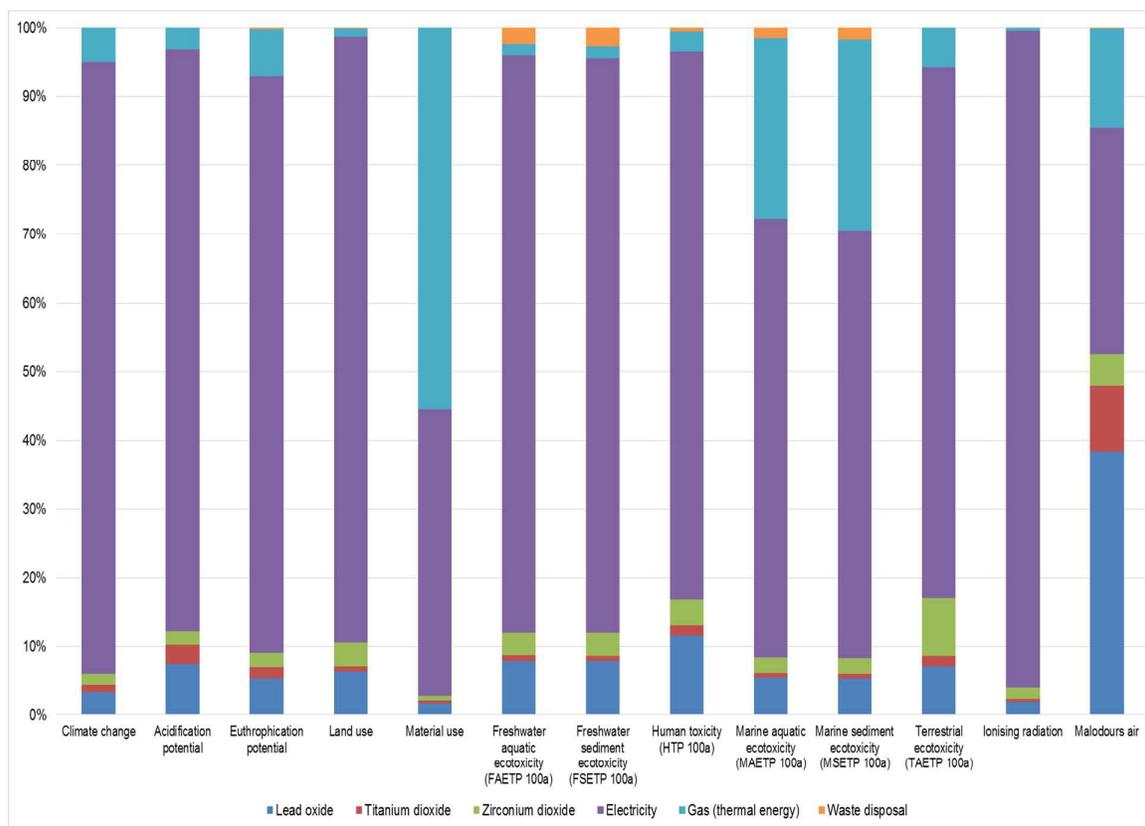

Figure 7: Environmental profile of 1 kg of laboratory-based PZT ceramic showing relative proportions of each of the 14 impact categories due to contributing processes.

In PZT, PbO is the dominant component, representing 69% of the composition with TiO_2 and ZrO_2 constituting 11% and 19% respectively. However, a close look at environmental profile of PZT represented in Figure 8 indicates that the biggest impact comes from electricity. The reason why the contributing impact from electricity generation overwhelms that of PbO can be explained as follows. The weighted impact is calculated as a product of quantity of the unit process input and the corresponding emissions intensity of that input (see Equation 1). The quantity of the unit process input for electricity and PbO to produce a 1kg functional unit of PZT is 79.21 kWh and 0.69 kg with corresponding emissions intensity of 0.5246 kg CO_2-eq/kWh (UK (DECC) electricity emissions data) and 2.19 kg CO_2-eq/kg, under climate change impact category, for example. It follows that the impact from electricity and PbO equals 41.55 kg CO_2-eq and 1.51 kg CO_2-eq respectively. Although the emissions intensity of PbO is higher than

that of electricity, a larger quantity of the unit process for electricity overwhelms that of PbO. The use of emissions intensity for electricity from other parts of the world does not alter this conclusion. See Supplementary Figure 3 for sensitivity analysis of effect of using emissions intensity data of electricity generation from other parts of the world on the impact results.

Given that PbO is the most influential component of PZT and is the main driver behind the need for replacement with alternatives that are lead free, it is important to examine its individual contributions to the impact categories. For ecotoxicity impact category including marine aquatic ecotoxicity, freshwater sediment ecotoxicity, freshwater aquatic ecotoxicity, human toxicity and terrestrial ecotoxicity, lead oxide contributes 6%, 8%, 8%, 12% and 7% respectively. These impacts from lead stem from the extraction or use phase which can penetrate water systems through runoff and from sewage as well as industrial waste streams. Elevated levels of lead in waterbodies cause damage to reproductive systems of some aquatic life which in turn cause blood changes and neurological disorders in fish and other animals whose habitat is the waterbody. In the context of human toxicity, human beings, animals and fish can be exposed to lead through breathing and ingesting it in food, water and soil or dust. Given that lead accumulates in blood, muscles, bones and fats, it ultimately damages organs and affects the brain, nerves, heart and blood.

In terms of terrestrial ecotoxicity, domestic and wild animals can ingest lead while grazing and can compromise their major organs as in humans. In fact, low concentrations of lead slow down the growth of vegetation near industrial facilities. Lead oxide also contributes to acidification (7%), eutrophication (5%), land use (6%) and malodours air (38%). The impact of lead due to malodours air is high because the use of lead oxide in production releases Pb into the environment, generating massive direct air emissions as well as soils and water contamination. These effects remain as dust indefinitely in the environment due to accumulation over time [87-89].

5.1.4   The case for the use of recycled lead to lower environmental impact of lead

Given that the presence of lead in PZT piezoelectric materials is a major concern, it is important to carry out sensitivity analysis based on the lead type used in the material composition across a number of toxicity indicators. Three scenarios are considered namely: a) the entire lead needed for the production of the PZT is derived from lead concentrate at beneficiation; b) required lead are derived from recycling and c) half of the lead required are derived from lead concentrate and the other half derived from recycling. The analysis is carried out based on the material composition of PbO in the PZT based on data sourced from

Ecoinvent [57]. Using a mixture of recycled lead and lead derived from concentrate is important if the gap between annual production of lead and its abundance in the earth's crust as well as the tendency of the use of lead obtained from recycling becomes insufficient This particularly true given the disparity of recycling rates in different parts of the world. Figure 8 indicates that the use of recycled lead represents the best case scenario across all the toxicity indicators, which will further lessen the overall impact of lead in the PZT materials architecture.
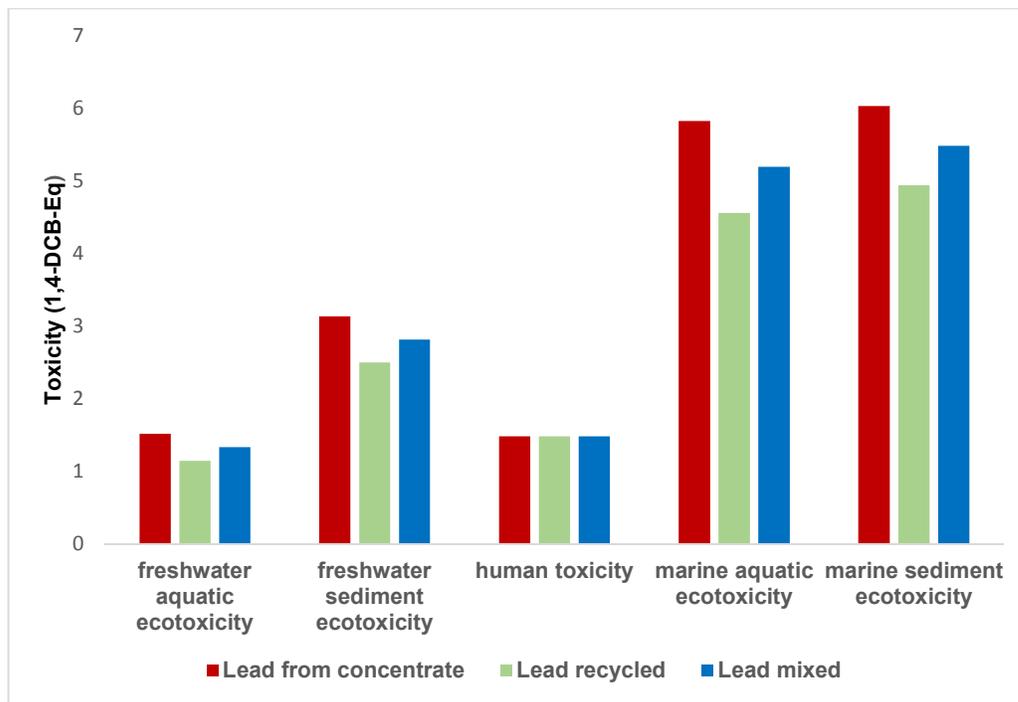

Figure 8: Sensitivity analysis based on type of lead used in PZT materials architecture

5.1.5   Input-output (upstream) emission analysis of PZT ceramics

Here, we consider the impact of indirect (upstream) emissions estimated using IO in the production of PZT across six sustainability indicators with respect to key economic sectors as shown in Figure 9.
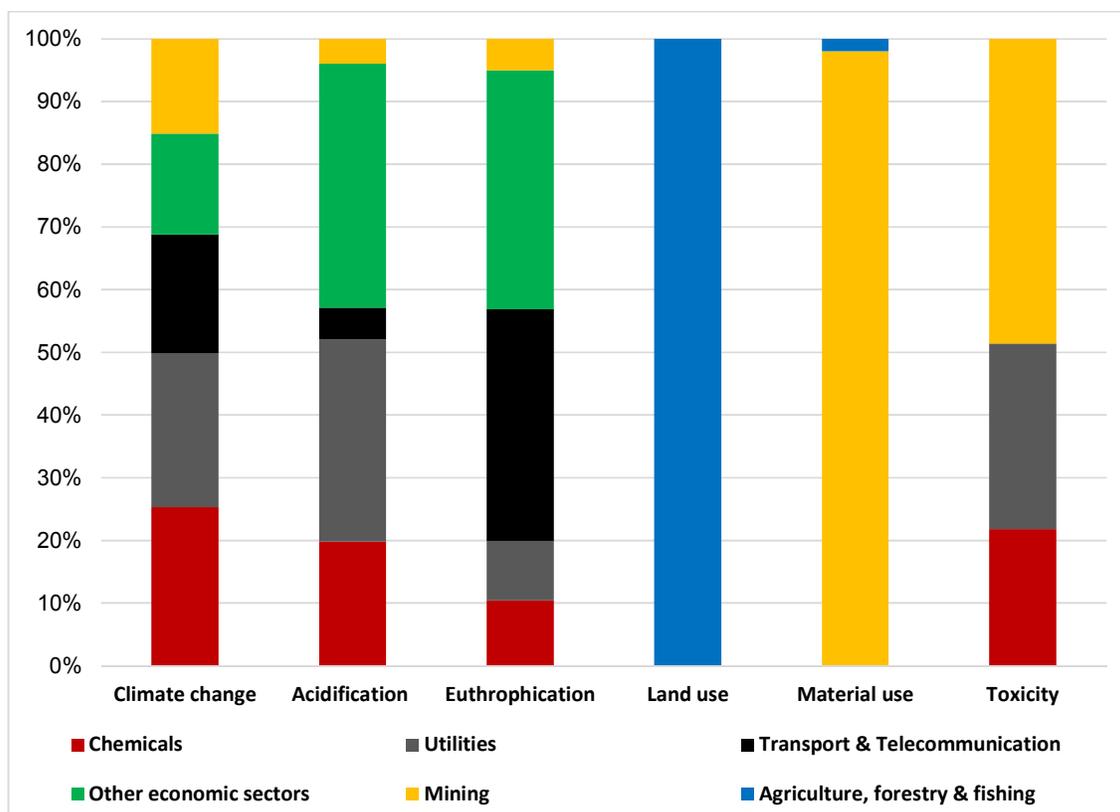
Figure 9: IO (upstream) analysis showing the contributions of each economic sector towards the fabrication of PZT ceramic.

As shown in Figure 9, for the case of GHG emissions (i.e. climate change), the most significant upstream emissions emanated from chemical (25%), utilities (25%), transport & telecommunication (19%) and mining (15%). All other economic sectors combined are responsible for 16% of the indirect upstream emissions. In terms of upstream eutrophication impact, transport and telecommunication contribute 52% with chemical, utilities, mining and other economic sectors contributing 15%, 13%, 7% and 12% respectively. For land use, the main IO contribution is the agriculture sector representing almost 100% of the impact. This is due to the fact that land used by all sectors are attributed as a resource emanating from agricultural sector which consist of arable, permanent crop, pastures and forest lands (See ESI, Table S16). The two main economic sectors that contributed to the upstream material usage are mining (98%) and agriculture (2%). It is important to state here that of the 98% upstream emissions attributed to mining activities, 83% of the impact came from the rest of the world (RoW) with only 17% attributed to the UK.

5.1.6 Eco-indicator assessment of PZT ceramic fabrication

Ecosystem quality includes effects on species diversity especially as it relates to vascular plants and lower organisms based on four indicators namely ecotoxicity, acidification, eutrophication and land use. Resources entail the surplus or extra energy required in the future to extract minerals and fossil resources that are of lower quality. Human health includes the number and duration of diseases and life years lost due to premature death resulting from environmental causes that stem from issues such as climate change and carcinogenic effects. [90]. The Eco-indicator 99 results for PZT in terms of damage to the ecosystem, human health and resources are shown in Figure 10. As indicated, the highest impact from the PZT production comes from waste disposal of lead which constitutes a threat to human as well as aquatic species. The use of recycled lead in the PZT material architecture may likely reduce this impact.
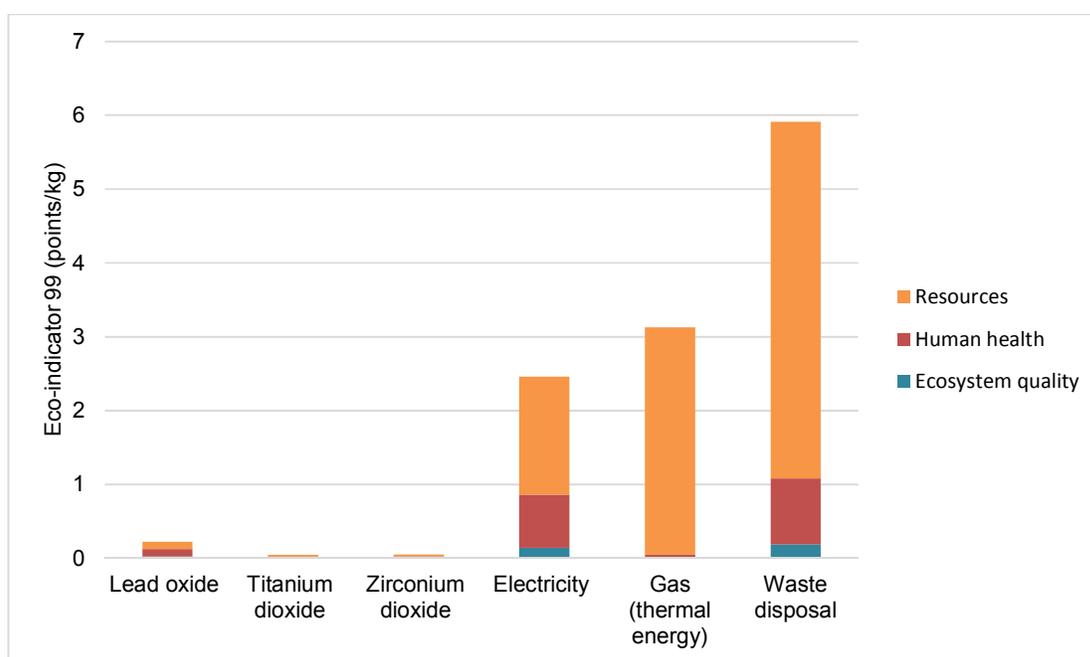

Figure 10: Eco indicator 99 results for 1 kg of PZT ceramic

5.2 Life cycle impacts of KNN fabrication

5.2.1 Primary energy consumption for fabrication of laboratory-based KNN

The material embedded in the fabrication of KNN and the primary energy consumption (both electrical and thermal) totalling 4123.65 MJ/kg, is shown in Figure 11. As indicated in Figure 11 (a), raw materials is responsible for roughly 60% of primary energy usage in KNN fabrication, with thermal and electrical energy contributing 33% and 7% respectively. This split, is in contrast to PZT which shows that raw material extraction for KNN constitutes the main source of environmental impact. A breakdown of the thermal energy, electrical energy and materials embedded are shown in Figures 11 (b), (c) and (d), respectively.

As with PZT, the sintering process which involves the consolidation of the KNN powdered particles by heating them to a high temperature below the melting point results in higher energy demand which consumes 43% of thermal energy required as shown in Figure 8b. Calcination and drying operations constitute 35% and 22% respectively. Electrical energy distribution is shown in Figure 11c. Optimised sintering approaches such as the use of sintering aids and low temperature processing technology can therefore contribute to the overall reduction in thermal energy demand for KNN and for that matter PZT fabrication.

A breakdown of the material embedded in KNN manufacturing (Figure 11d) shows that niobium pentoxide is the only outweighing component, contributing 99.53% of the material impact category. The reason for a 99.53% share residing in niobium pentoxide in KNN is that niobium is a transition metal found in a range of mineral species[91-93] with a considerably high primary energy utilisation and embodied carbon footprint. The extraction of niobium requires highly intense energy from related activities including mining (e.g. blasting of mine open pit); concentration (i.e. crushing, milling); refining and smelting, conventional and centrifugal separation, magnetic separation etc.[93-96]
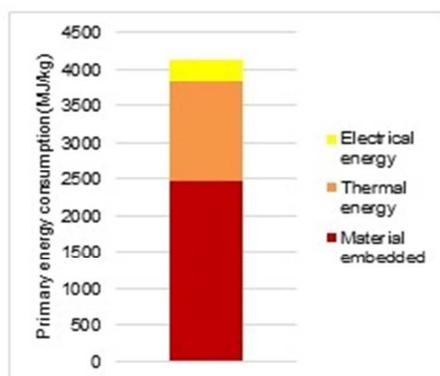
(a) Total primary energy consumption
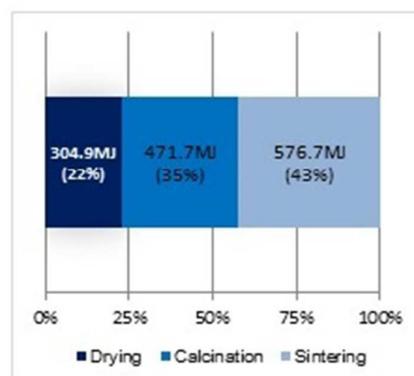
(b) Thermal energy distribution
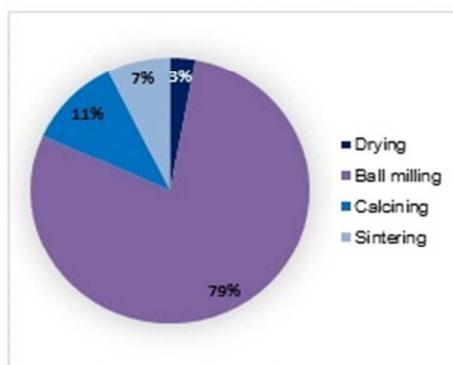
(c) Electrical energy distribution
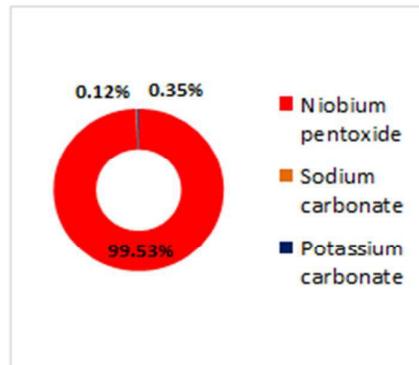
(d) Material embedded distribution

Figure 11: Distribution of the primary energy consumption for the fabrication of a laboratory-based KNN material. (**a**) Total primary energy consumption including thermal and electrical energy and materials embedded all expressed in MJ/kg. Figures 11 (b), (c) and (d) indicate the percentage contributions of each process or material relative to Figure 11 (a).

5.2.2   Hybrid LCA of laboratory-based KNN piezoelectric material

The results, in terms of actual values, of how process-based results compared to EIO results are shown in Table 2 and represented in graphical form in Figure 12 based on percentage contributions.

Table 2: Hybrid LCA results for KNN material system

Impact category	Process	EIO	Hybrid (Total)
Climate Change	194.45	54.10	248.55 kg CO_2-eq
Acidification potential	1.28	0.04	1.32 kg SO_x-eq
Eutrophication potential	1.08	0.07	1.15 kg NO_x-eq
Land use	43.82	5.17	48.99 m²a
Material use	4735.26	373.93	5109.19 MJ/kg
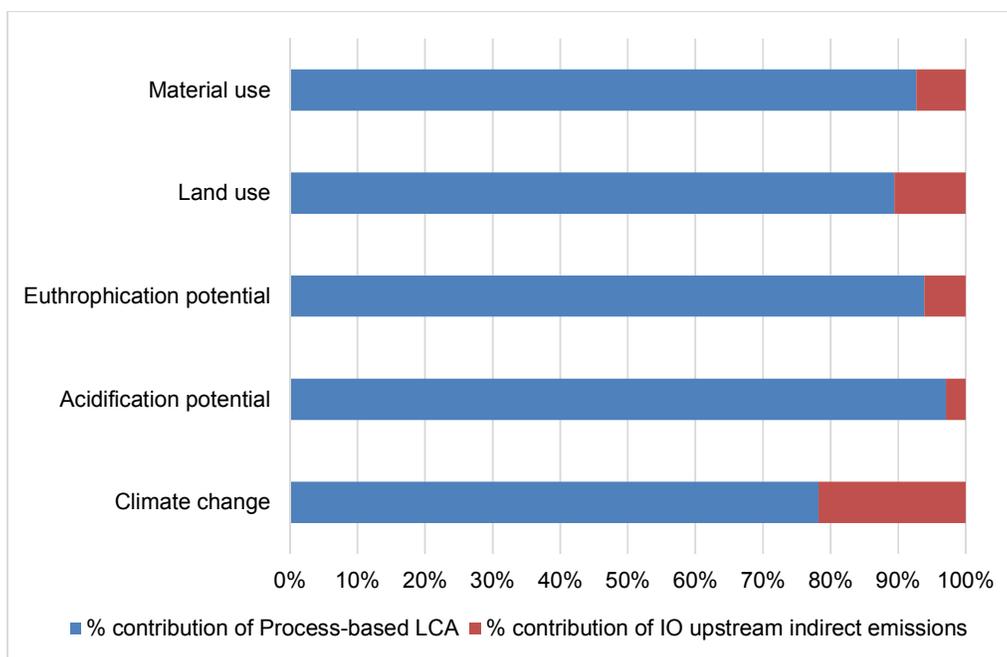
Figure 12: Results of hybrid LCA of KNN across a number of sustainability metrics

An inspection of the toxicology impacts along the production routes of KNN (Figure 13) indicates that marine sediment ecotoxicity has the highest toxicology impact of 278.16 kg 1, 4-DCB-eq (see section 5.2.3 for rationale behind this figure). The combined (air, water, land and underground) upstream toxic impact account for 0.014 kg of toxic release per unit output.
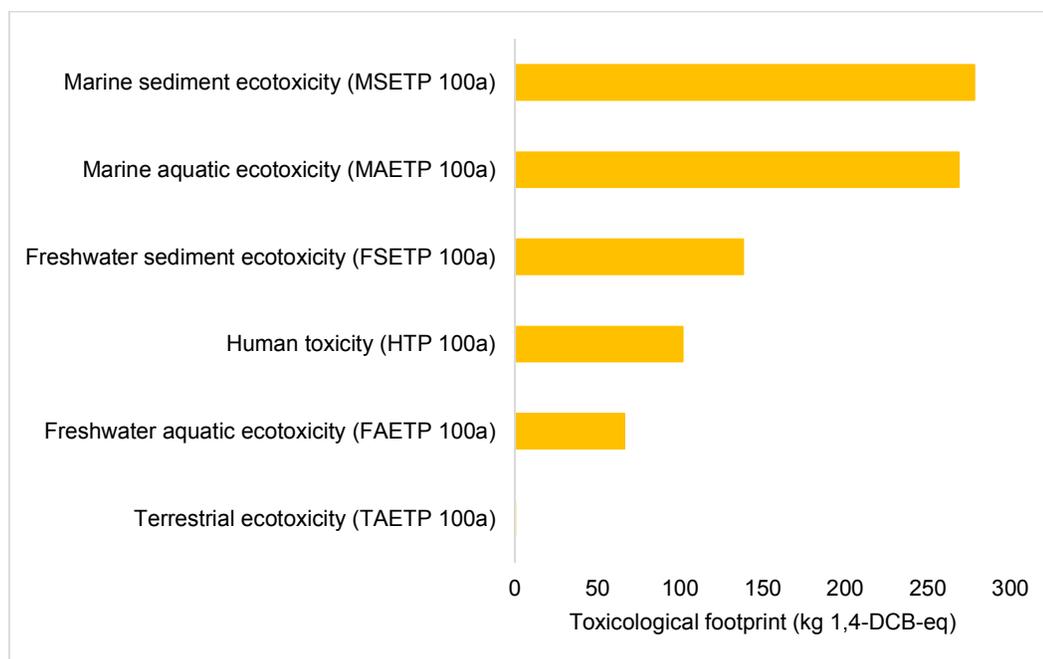
Figure 13: Results of footprint of KNN across six variants of toxicity

5.2.3 Analysis of the environmental profile of KNN based on the contributing processes

In this section, component level analysis of the environmental impacts of KNN fabrication is undertaken to identify the most influential components and materials vis-à-vis the sustainability metrics under consideration. Figure 14 shows the environmental profile of all the unit process exchanges representing the process analysis data of 1kg of KNN fabricated in the laboratory. All the thirteen sustainability metrics are normalised, ensuring that the absolute indicator of each category of impact is 100%. As indicated in Figure 14, the use of niobium pentoxide is the singular most outweighing contributor to climate change (76%), acidification (86%) eutrophication (89%), land use (97%) fresh water aquatic ecotoxicity (85%), fresh water sediment ecotoxicity (85%), human toxicity (93%), marine aquatic ecotoxicity (79%), marine sediment ecotoxicity (79%), terrestrial ecotoxicity (82%), ionising radiation (72%), malodours air (93%). Niobium pentoxide also has influence on material utilisation (52%), with thermal and electrical energy demand contributing 29% and 19% respectively. It is to be noted that the electrical energy required to produce 1kg of KNN (82.21 kWh) surpasses that of PZT (79.21 kWh). However, as indicated in Figure 14, the environmental impact of KNN is dominated by the presence of niobium due to its high emissions intensity compared to electricity, across all indicators.
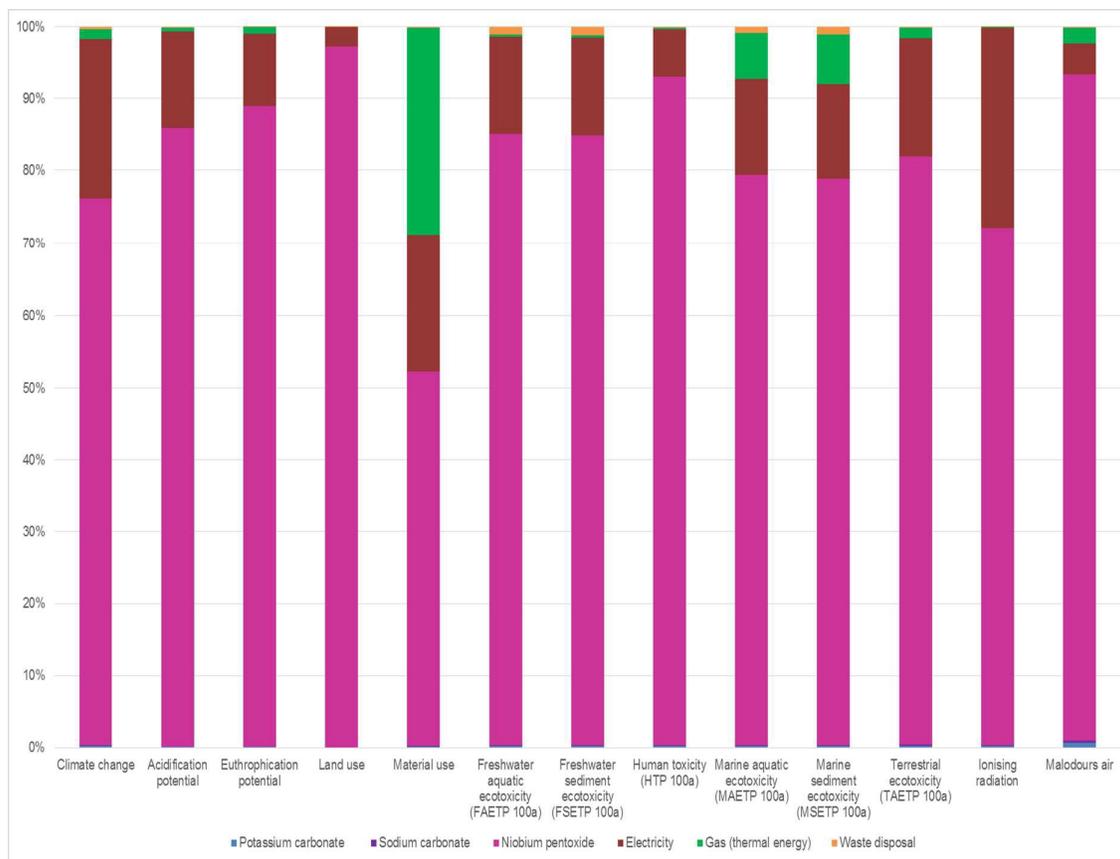
Figure 14: Environmental profile of 1 kg of laboratory-based KNN ceramic showing relative proportions of each of the 14 impact categories due to contributing processes.

5.2.4 Environmental impact of extraction of niobium and potential mitigation strategies

During the mining and production of niobium, heavy metals and radioactive metals leach into water bodies since there is a requirement to dig through several types of radioactive rock to reach the niobium deposit. [93-95] Therefore, during the process of uncovering niobium, rivers, and watercourses used for the mining of niobium become contaminated with toxic discharge of carcinogenic e.g. uranium. By extension, these toxic discharges contain substances such as arsenic, nitrates, antimony, and sulphides etc. which are responsible for the toxicity, eutrophication and acidification that constitute threats to aquatic life. In addition, a significant portion of radon gas is released into the atmosphere to the detriment of human health. [94]

The extraction of niobium can also affect air quality, land use, soil, ground water, biodiversity and visuals. [93-95] The key impact of niobium in terms of air quality is the dispersion of dust and thus responsible for its high malodours air impact. Air quality can be badly affected

and may exceed international health risk guidelines in areas of key activities during the mining of niobium. The mining of niobium also leads to change in landform and landscape character during excavation and civil engineering works. Such mining activities may cause sterilisation of soil resources due to the development of open pit waste rock dump and soil contamination which may arise through leakage of hazardous chemicals including hydrocarbons.[93-95] The extraction of niobium may also cause damage to the ferricrete layer of soil during excavation of foundations for infrastructure.

Inappropriate disposal of hazardous and general wastes attributed to the mining of niobium may cause contamination of ground water resources, lower groundwater table whilst reducing ground water supply. It may also lead to contamination of rivers and watercourses due to release of effluent and contaminants into the environment and also due to sediment loads because of erosion of exposed surfaces. Additionally, erosion of soil resources can result due to wind and storm water erosion of stockpiles and exposed soil surfaces. There are other hot issues surrounding the extraction of niobium that pertain to biodiversity (e.g. damage to sensitive habitats and increased pressure on ecological resources); cultural heritage (e.g. disturbance of archaeological and cultural sites during site clearance and excavations); visuals (e.g. disturbance of line of sight); socio-economics (e.g. resettlement of members of the community and reduced access to land for agriculture and fuel collection) and noise (e.g. disturbance of noise receptors during day and night due to movement of machinery and vehicles and mechanical operation of plant components).

As highlighted above, most of the impact from KNN emanated from the raw material extraction of niobium, implying that the environmental damage has already happened before the material is put into use at the production phase. Consequently, improvements towards minimising the overall environmental impact of KNN will come from advancement in raw material extraction techniques and implementation of mitigation strategies. For example, to minimise the impact of land use during the extraction of niobium, utilisable soil could be stripped and stockpiled before the extraction process begins.[94] Also, to minimise air quality disturbance, dispersion modelling can be used to project the amount of dust that can be potentially generated and mitigation strategies such as installation of wet suppression at key sources and surfacing of roads with chemical dust suppressants which can further minimise the amount of dust generated, can be implemented.

To minimise the effects of sterilisation, contamination, erosion of soil resources as well as contamination of rivers and watercourses, dams constructed should be deconstructed at the end of life of the mining operation and the original landform restored. All hazardous chemicals should be stored and handled in specifically engineered facilities to prevent spillage or seepage of contaminants into soil or groundwater. At the same time, all effluents are to be contained and treated prior to release. Long term stockpiles should also be vegetated to allow for stability of surfaces. Regarding the potential mitigation of contamination of groundwater resources, facilities for temporary storage of general and hazardous waste should be made available to prevent run-off or seepage into the environment. Also, disposal of waste should be conducted offsite at available facilities until such a period when general and hazardous waste sites are developed. For biodiversity issues such as damage to sensitive habitat, fuel resulting from the clearance of site should be made available for use by the surrounding communities. It is to be noted that there is no silver bullet to mitigation of environmental impact of extraction of niobium due to difference in mine locations and related activities.

Environmental regulations and governmental policy should therefore be more effective and stricter when it comes to granting mining permissions for the extraction of niobium from its ore. Improvements in emissions associated with extraction of niobium can be achieved using technology and methods for efficient and cheaper extraction. Examples include innovation in: (i) exploration (i.e. identification of minerals, chemical compositions and physical properties directly in the field); (ii) ore deposit definition (i.e. modelling mineral deposits, their potential economic assets and challenges from the earliest stages of exploration); (iii) ore extraction; (iv) transport and communication; (v) ore processing; (vi) health and safety and (vii) remediation. By leveraging on such advancement in extraction and processing techniques backed with effective mining policy, only then can KNN fully realise its potential as a 'greener' alternative to PZT for piezoelectric applications.

5.2.5 Input-output analysis of KNN piezoelectric material

In this section, consideration is given to the impact of IO indirect (upstream) emissions in the production of KNN across six sustainability indicators with respect to vital economic sectors as indicated in Figure 15.
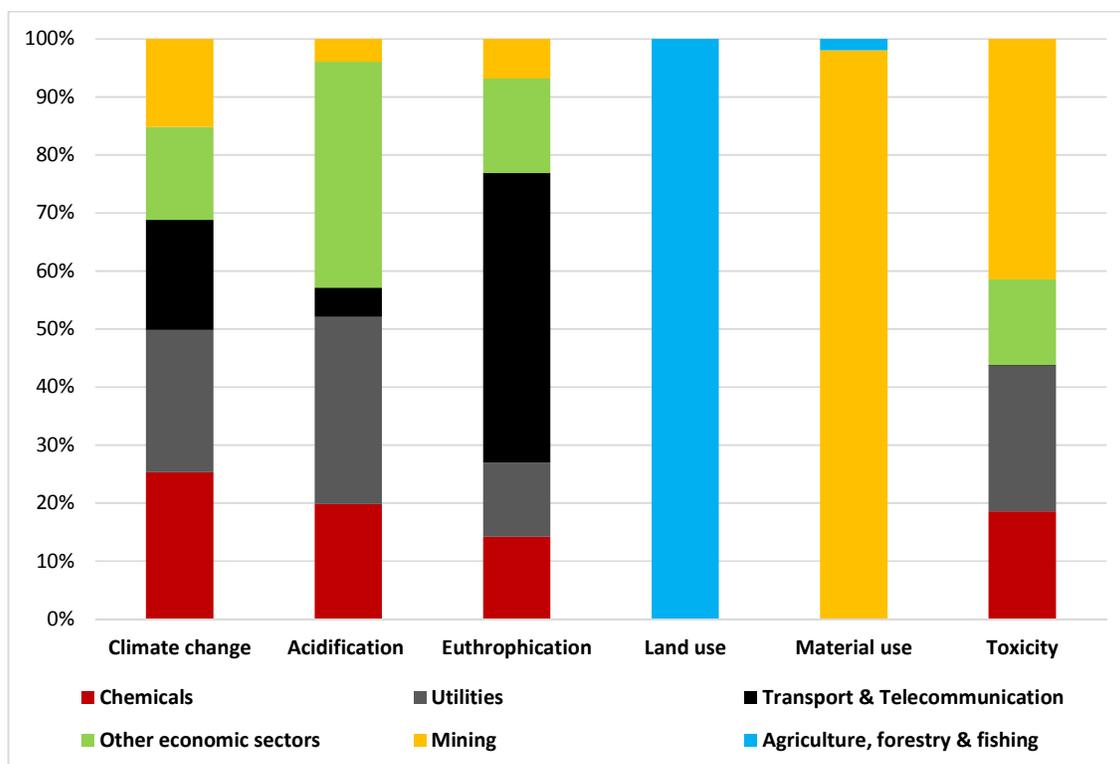
Figure 15: IO (upstream) analysis showing the contributions of each economic sector towards the fabrication of KNN.

As shown in Figure 15, for the case of GHG emissions the most significant upstream emissions came from chemical (25%), utilities (25%), transport & telecommunication (19%) and mining (15%) industries. All other economic sectors combined are responsible for 16% of the upstream emissions. In terms of upstream land use impact, agriculture sector is the dominant sector responsible for almost 100% of the emissions. This reason for this is similar for the case of PZT as explained in section 5.1.5. The two main economic sectors that contributed to the upstream material usage are mining (98%) and agriculture (2%). As with the upstream emissions of PZT, 83% of the upstream emissions attributed mining activities related to KNN came from the rest of the world (RoW) with only 17% attributed to the UK.

5.2.6 Eco-indicator assessment of KNN piezoelectric material fabrication

The Eco-indicator 99 results for KNN based on damages to ecosystem, human health and resources is shown in Figure 16. As indicated, the highest impact from KNN production comes from the raw material extraction of niobium with a negligibly small impact from the waste disposal process. This is further confirmation that the main impact from the production of KNN came from the early stages of raw material extraction and purification processes.
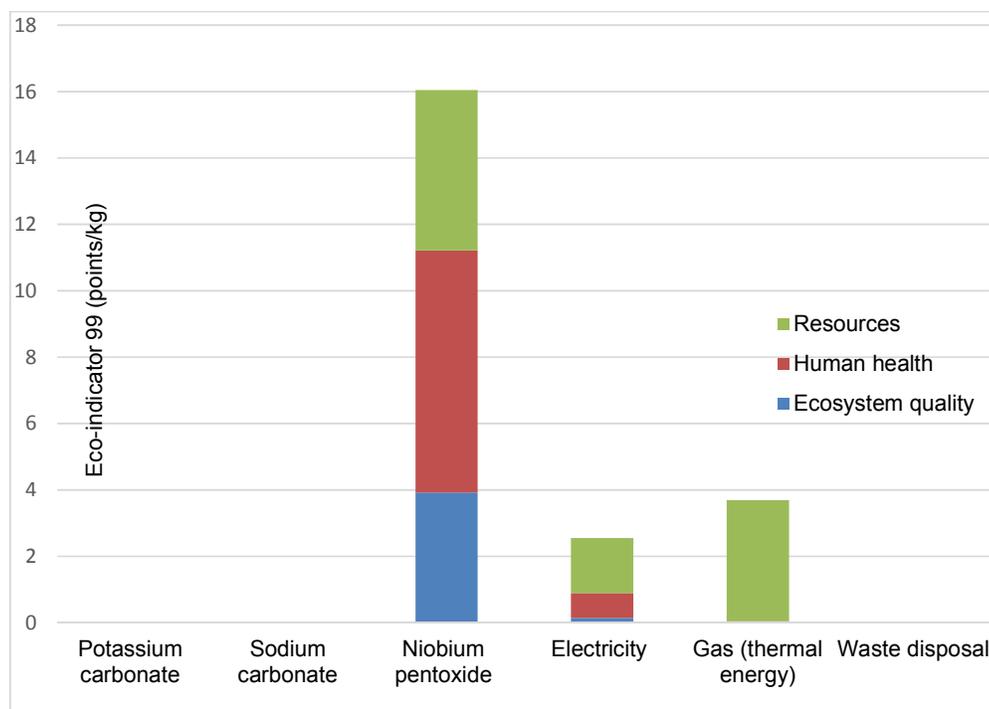
Figure 16: Eco indicator 99 results for 1 kg of KNN

5.3   Comparison of environmental profile of PZT versus KNN piezoelectric material

Figure 17 shows the comparison of the environmental profile of PZT versus KNN across 14 environmental indicators. As shown, KNN results in significant environmental impacts across all the 14 categories of impact considered with environmental impact of PZT surpassing that of KNN by an incredibly high margin only under the waste disposal scenario based on three endpoint indicators which stems from the Eco-indicator 99 approach (see Figures 10 and 17 for comparison). The environmental impact and associated pollution due to KNN, shifted to the earlier stages (i.e. raw material extraction and purification processes) of the lifecycle, causing more environmental burden compared to PZT. For instance, under the climate change and material use impact category, 96% of the impact came from the production phase (thermal and electrical energy demand) in the case of the PZT.
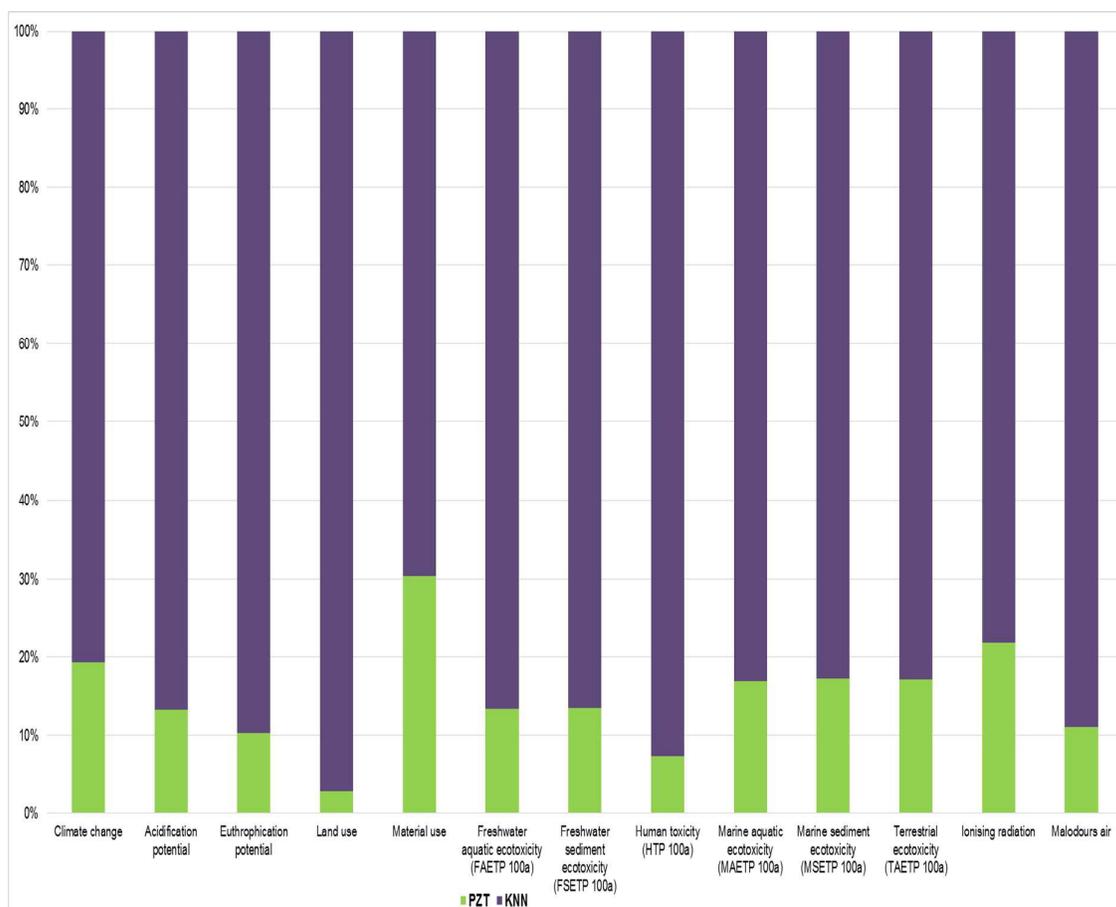
Figure 17: Comparison of environmental profile of PZT versus KNN piezoelectric material (Note: the comparison between KNN and PZT is based on ratio. For instance, the combined impact (process LCA) of the two materials under climate change impact category is 241.11 kgCO$_2$-eq with PZT contributing 46.67 kgCO$_2$-eq (19%) and KNN 194.45 kgCO$_2$-eq (81%). See Supplementary Table S13 for actual data)

As shown in Figure 18 (a) and (b), KNN consumes more thermal and electrical energy across all the fabrication activities namely, drying, calcination and sintering except in the ball milling operation where they consume equal amount of electrical energy. The wide margin between the energy consumption of KNN and PZT lies in the fact that KNN possess a higher specific heat capacity and high curie temperature. As such, it requires a high amount of energy to heat up, thus driving up the primary energy demand of KNN and raising its environmental impact. In terms of the ecosystem quality, resources and human health, the overall impact of KNN is far greater than that of PZT as shown in Figure 18 (c). However, when the Eco-indicator 99 result is expanded upon as shown in Figure 10 (PZT) and Figure 16 (KNN), the impact for PZT occurs mostly at the use phase and end of life (i.e. waste disposal) but for KNN at the end of life, the disposal of KNN material does not result in any environmental damage. Finally, as shown in Figure 18 (d), KNN causes more upstream IO GHG than PZT across all the economic sectors shown with the most significant upstream emissions coming from the

chemical sector for both materials. What underlies the differences in this result between the two compounds are the material cost, substitution cost and energy (i.e. electrical and thermal energy) consumption costs. Currently, the overall cost of production of KNN is higher than that of PZT. Given that in IO analysis, economic data such as energy tariffs are converted into physical quantities (e.g. kWh of electricity), a higher conversion output will cause more upstream emissions across the supply chain. Nevertheless, cost price of KNN may lessen in the future, due to negotiated energy tariffs which might in turn lower the IO upstream emissions of KNN.
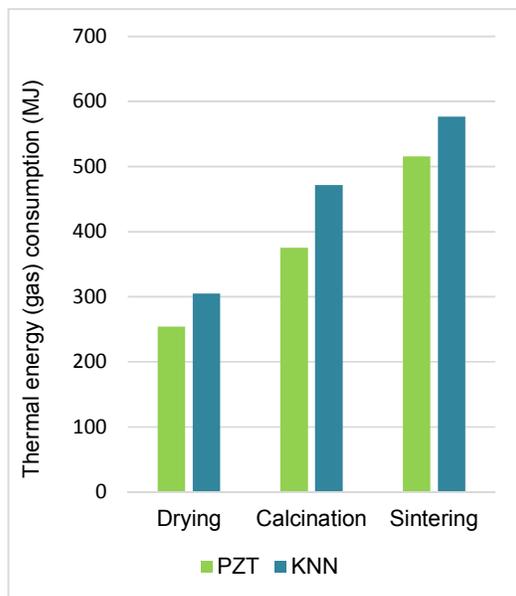
(a) Thermal energy comparison
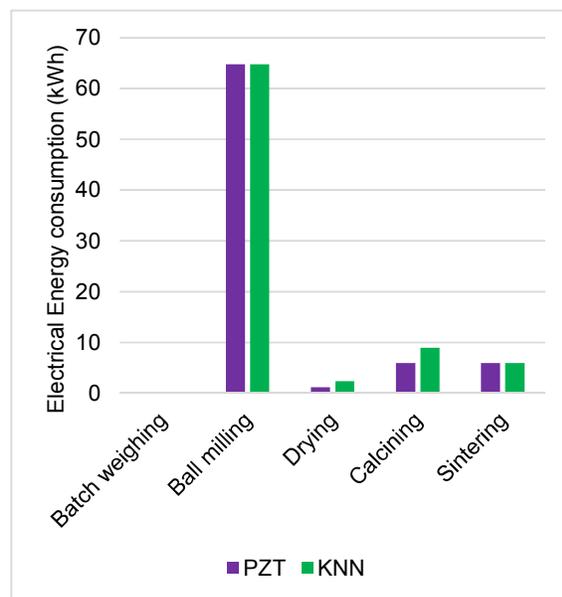
(b) Electrical energy comparison
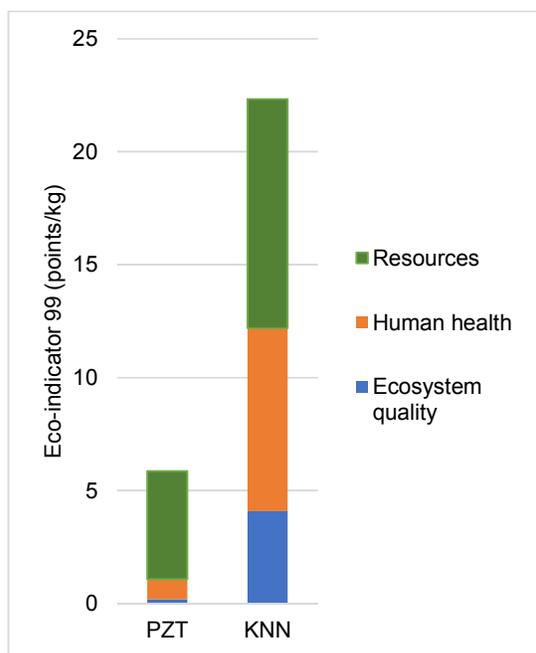
(c) Eco-indicator comparison
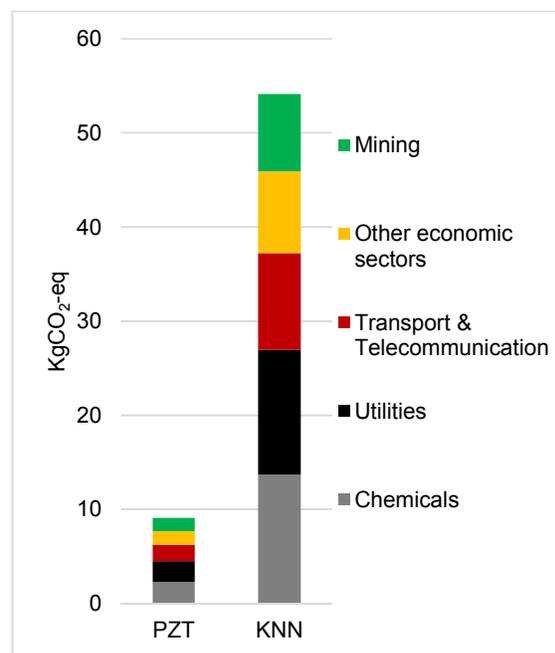
(d) IO upstream GHG comparison

Figure 18: Comparison of PZT versus KNN (a) Thermal energy (b) Electrical energy (c) Eco-indicator 99 (d) IO upstream GHG emissions

5.3.1 Health hazards and biological problems of PZT piezoelectric material

It is important to note that although the overall environmental impact of KNN surpasses that of PZT, the current assessment does not show that the impact from lead is negligible and as such the consequences that high exposure to lead can have on human health and the environment cannot be overemphasised. Poisoning through exposure to lead has long been established as an environmental health hazard, given its adverse effects on intellectual and neurological development. Accordingly, the concern about lead has become increasingly important given that PZT materials are now adopted in a number of consumer goods. Lead is a naturally occurring metal with most of its concentration in the atmosphere emanating from human activities such as mining and extraction, fossil fuels or municipal waste burning, vehicle fuel combustion and disposal of car batteries without recycling. [97] Once released into the environment, lead cannot be degraded by natural means. It can only be changed into other forms. [97] Humans can therefore be exposed to lead poisoning through breathing in air containing lead particulates or through eating food or drinking water or by accidentally swallowing dust with lead content. [98] In fact, when humans accidentally come in contact with chemicals containing lead, there are three routes namely gastrointestinal, respiratory and dermal uptake, by which it can get into the body, causing damage to essential body organs such as kidney, liver and the nervous tissues.[99] As such, an excessive amount of lead in air or soil can therefore be dangerous not only to humans, but also to animals and local ecosystems.[97, 98] The probable occupational and non-occupational exposure associated with the fabrication of PZT piezoelectric materials should therefore be treated with extreme caution.

Furthermore, despite the advantages of PZT about cost of production, processing energy, and pollution compared to KNN, the lead component in PZT is extremely harmful and hazardous for biomedical applications and body-attachable devices. For instance, PZT must not be used for bio-implantable MEMS, generators, foetal heart monitors and in vivo piezoelectric sensors amongst other application[100]. In contrast, lead-free materials such as KNN can be used for the biological applications, although there are some demerits of KNN about processing energy demands and pollution at its beginning of life as highlighted in this work. Given that up-to-date bio-implantable systems utilizing piezo ceramics are increasingly becoming more and more important for future bioelectronics[101], the use of KNN for such applications therefore becomes pertinent despite its associated environmental problems.

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5.4   Result of Cost benefit analysis of replacing KNN with PZT functional materials

Using the mathematical relationship in Section 4.3.4, the evaluation of the cost benefit of replacing one material with another material is presented in this section. The price per unit mass of new (KNN) and original materials (PZT), P_n, P_o were estimated to be £695 and £235 respectively based on information from manufacturers. M_n, M_o, the mass of KNN and PZT were 1kg each. The cost of transition from PZT to KNN was calculated to be £460. T_n, T_o were taken to be same, since the same equipment were used for the fabrication of both piezoelectric materials. Number of new parts produced N was taken to be 3 and the labour cost per part L_n, L_o of producing KNN and PZT were taken to be £350 and £250 respectively. The total cost ΔC (based on Equation 12) of replacing PZT with KNN was therefore calculated to be £583.

Taking thermal energy demand (kWh) as the performance indicator (γ_n, γ_o) under consideration, then the total thermal energy demand for producing KNN and PZT is 376 kWh and 318 kWh respectively. So that $\gamma_n - \gamma_o = 376 - 318 = 58\ kWh$. At a cost of £0.022/ kWh for gas, the cost incurred in terms of thermal energy (gas) usage in producing KNN and PZT in the lab is £6.99 and £8.26 respectively. Therefore A , which is the benefit expressed as a function of thermal energy demand is calculated to be £8.26 − £6.99 = £1.27. So that $\Delta B = A(\gamma_n - \gamma_o) = £73.66$. It then follows that the condition $\Delta B - \Delta C > 1$ is not met, suggesting that economic feasibility of replacing PZT with KNN is not favourable based on the thermal energy demand.

The cost-benefit analysis presented is just a simple illustration of the benefits of replacing one material with another and it by no means represents overall economic assessment of KNN versus PZT. However, the analysis is in tune with risk assessment based on a number of factors including material and substitution cost as shown in Supplementary Figure 2 in the ESI. Other functional performance indicators are difficult to assess at this stage since materials are still at their development phase but we note that none of the lead-free alternatives are drop-in substitutes for PZT and they invariably have lower performance and higher associated production costs.

5.5   LCA of PZT versus KNN functional materials - a conundrum

The comparative LCA of PZT versus KNN functional materials presents a conundrum given that the overall environmental impact of KNN across all indicators considered far outweighs that of PZT due to the presence of niobium in KNN, whose extraction is responsible

for its overall high environmental impact. As such, environmental damage has already occurred before its adoption for piezoelectric applications, despite the fact that niobium and its oxides are innocuous, causing no harms or damage at the use phase. In fact, at the application level, niobium and its oxide can be swallowed without any health threats, hence their usefulness in bio-compatible applications. On the other hand, the overall impact of PZT is significantly lesser than that of KNN, yet at the application level, the use of PZT for piezoelectric applications is extremely harmful due to the presence of lead oxide which is extremely toxic and potentially hazardous. Their impact on human health is intense at the use and disposal phase. If the impact from early stage of the life cycle assessment of KNN is neglected, then its environmental impact will be minimal but the overall aim of LCA would have been defeated. This scenario represents a massive conundrum that requires careful consideration before strategic environmental decisions are taken.

Consider the following scenario, for example. During the extraction of niobium from its ore, toxic discharges containing substances such as nitrates (pressure in form of emissions intensity), for example, causes acid rain (still pressure), that makes lakes acidic (impact) and kills fish (impact!). This impact due to extraction of niobium has occurred at the early stage of life, resulting into climate change effects which far outweigh that of lead. Accordingly, the comparative sustainability performance of materials such as KNN versus PZT as demonstrated in this study can become a complex problem due to the overlapping nature of the multiple and sometimes competing factors such as energy consumption during fabrication, financial costs of the raw materials, environmental impact, health and safety, strategic applications and the influence of regulation from national authorities and policy makers.

In the light of the above, an important question to ask in terms of environmental sustainability is: which of PZT and KNN is better? This question will be considered in different ways by an investor, an environmentalist, a material chemist and a policy maker. The sole desire of the investor is to realise a high financial savings and generate favourable economic return from the development of applications based on KNN piezoelectric materials, whereas the environmentalist who wants to prevent damage to communities may prioritise emission reduction from source. Similarly, a material chemist whose desire is to develop piezo-based products that can be directly implanted into living tissues may prioritise biocompatibility. In the same vein, a policy maker may weigh the prospects of creation of new jobs and expansion of tax base against concerns about environmental damage. This is particularly the case in Florence,

Arizona, in the US, where housing developers intend to construct a master-planned community that can guarantee between 25,000 - 30,000 residential apartments, but a few miles away, a mining company intends to develop a mine. In this instance, the state governor of Arizona supported the mining project given that it promises jobs and state excise-tax revenue over the next 20 years, despite the submissions by urban and town planning officials that the longer-term advantages of property taxes derived from residential and commercial development surpasses the economic benefits of a mine.

Overall, answering the above question, taking all factors into consideration is a difficult proposition. However, if the global definition of LCA still remains the same, irrespective of the final decisions made afterwards, regarding the choice between KNN and PZT, the conclusion, in plain English, is given an overall environmental consideration, KNN is worse as compared to PZT. Foreseeable environmental hazards, especially as it pertains to climate change and ecotoxicity induced by the adoption of transient metal like niobium and its oxide, may unfortunately hinder KNN from becoming a thriving piezoelectric material. As such, the case for replacing PZT with KNN for piezoelectric applications will not be driven mainly by environmental consideration. It may be based on the need for piezoelectric devices that are suitable for high temperature applications and for applications in biological and surgical settings where the use of PZT is simply impossible.

5.6 Limitations and uncertainties of the work

In this study, all measurements (e.g. power ratings, materials weighing and temperature values for the evaluation of both electrical and thermal energy) that serves as part of input data into the LCI were taken using state-of-the-art and highly calibrated equipment within the functional materials and devices laboratory of the department of materials science and engineering. Accordingly, errors due to experimental measurements are minimised. In terms of the potential uncertainties associated with the fabrication route of PZT versus KNN piezoelectric materials, typical laboratory-based times and temperatures for comparison were quoted. However, it is anticipated that these may be modified slightly for commercial production for different manufacturers which may result in different energy consumption values.

Given that the manufacturing route of PZT is already well-established compared to KNN, economies of scale in an industrial setting when estimating energy intensity of producing the materials were not taken into consideration. Conducting a sensitivity analysis is difficult due

to the lack of baseline data from the industry. Nevertheless, it is highly unlikely that such variations will have any significant effect during scale up of the materials. In fact, even if the manufacturing route of KNN becomes well-established at the industrial scale, the cost of substitution and energy consumption will still be relatively higher than for PZT provided properties remain the same. For instance, given that the specific heat capacity of KNN is greater than that of PZT, thermal energy consumption of KNN will always be higher. At the moment, none of the piezoelectric material alternatives are drop-in substitutes for PZT and device redesign based on inferior properties is considered inevitable[102] with cost estimates ranging from £100k per item for transducers to £1m for more complex systems such as ink-jet heads.

The process-based data used in this LCA study emanates from quantitative estimates and extant literature. In instances where the characterisation factors, CF (i.e. emissions intensity data) are available in Ecoinvent database, such data are extracted and adopted in the LCIA, as such the precision of the CFs are high. In instances where such data is absent (e.g. lead oxide), CFs of such materials are evaluated based on stoichiometry based on raw materials whose emissions intensity data are reported in Ecoinvent. Accordingly, the precision of such newly derived LCI data is high. Hybrid LCA was adopted in this study to ensure supply chain visibility and for completion of system boundary limitations of process-based LCA using EIO LCA data. However, the choice to include or exclude certain inventories from the EIO LCA data with the view to account for missing inputs whilst avoiding the double counting of inputs remains potentially subjective. An in-depth understanding and knowledge of the supply chain and process LCA data is therefore required to make correct decisions about missing inputs to exclude or include. Such understanding was demonstrated in this work which ensures like for like comparison between KNN and PZT. Examples of some missing supply chain inputs considered in this work include transportation (UK), research and development (UK and RoW), computers and other office machinery and equipment (UK), other special purpose machinery (RoW) to mention a few. Furthermore, despite the use of the S&U table with high disaggregation into sub-economic sectors, large amount of aggregation still exist. For instance it is hard to draw a fine distinction between a product that is manufactured based on a highly efficient supply chain and a similar product made using inefficient supply chain mechanism.

6.   Summary and conclusion

The current work demonstrates the crucial role that environmental and sustainability science and in particular LCA plays within innovation and the process of new product

development. Within this process, as demonstrated by this study, very useful insight garnered from environmental profiling of new and innovative products across a wide spectrum of indicators can be used to aid the decision-making process within a mix of other objectives in relation to product innovation.

Conventional knowledge suggests that KNN is "environmentally greener" as compared to PZT because it does not contain lead, a toxic heavy material. However, the current work is able to establish that this assertion may not be entirely valid, and must be assessed via a detailed and holistic life cycle and environmental profile assessment. As such, a life cycle supply chain comparative assessment, based on hybrid LCA framework, within a cradle-to-grave scenario, of the two piezoelectric materials was carried out. Results indicate that the environmental impact and associated pollution due to KNN, shifted to the earlier stages (i.e. raw material extraction and purification processes) of the life cycle, causing more environmental burden than PZT. Although, it was not found that the toxic impact of lead in PZT is negligible, the presence of niobium in KNN, constitute greater environmental impacts across all the 16 categories of impact considered. It is only in the waste disposal phase under the Eco-indicator 99 category that the environmental impact of PZT surpasses that of KNN by an incredibly high margin, which still constitutes a source of major concern in terms of environmental profile of PZT.

In general, the current work reveals that the replacement of a conventional piezoelectric material such as PZT with new compositions such as KNN may be considered environmentally friendly if these compositions constitute lower life cycle impact, guarantee higher tendency of reusability and results in lower energy demand during fabrication. These characteristics are not satisfied by KNN based on the LCA carried out in this work. As such, the case for replacing PZT with KNN is not driven mainly by purely environmental consideration. Despite the advantages of PZT regarding the aforementioned factors compared to KNN, the lead component is still extremely harmful and hazardous for biomedical applications and body-attachable devices. For example, PZT cannot be used for bio-implantable MEMS, generators, and in vivo piezoelectric sensors to mention a few applications.

The LCA conducted in this work inherently faces some form of uncertainties and challenges due to the emerging nature of the material systems and processes analysed, especially as it relates to understanding the material architecture of new piezoelectric material. Given that conventional LCA databases are insufficient for this type of study, a profound understanding of the pertinent literature detailing the materials technology is necessary for assessing, at minimum, a part of the dataset captured within the life cycle inventory as this study as demonstrated.

Despite the lack of company or industrial data and associated challenges, the current work demonstrates the usefulness of LCA during these early phases before a new material technology is widely adopted.

The methodological framework used in the current work should be useful for the LCA and environmental profile assessment of other emerging materials architectures and technologies and at the early stages before key design decisions are made. This work highlights the importance of considering life cycle analysis and environmental profile assessment among the core principles of material substitution and optimisation and before claiming any material or product or process to be environmentally friendly. It shows that LCA must become a fundamental part of the toolbox for a materials developer. Overall, this work demonstrates an application of LCA and supply chain management to a strategic engineering question which allows industries and policy makers to make informed decisions regarding the environmental consequences of substitute materials, designs, fabrication processes and usage.

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Additional information

Electronic Supplementary Information (ESI) accompanies this paper

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Broader context

Recently, the importance of replacing lead-based piezoelectric materials such as PZT with lead-free equivalents have grown tremendously, given the increased environmental concern and subsequent EU and worldwide legislation and restrictions to reduce the use of hazardous substances such as lead-based materials in all sectors. Additionally, there is keen interest in developing environmental friendly lead-free substitutes in biological and surgical settings due to increased interest in actuators and sensors that can be directly implanted into living tissues. With the high piezoelectric constant of recent doped and modified KNN based compositions coupled with their high Curie temperature, KNN has captured a tremendous research attention and has become very attractive to manufacturers of bulk materials and multilayer actuators (MLAs) as a potential replacement for PZT. However, a comparative environmental impact assessment of the life cycle phases of KNN versus PZT remains in the shadow, despite the universal speculations that KNN has better environmental credentials and is "greener" than its PZT-based counterpart. In this work, life cycle assessment within the context of the two piezoelectric materials across 16 sustainability metrics was performed. We found that foreseeable environmental hazards, most importantly climate change induced by the intensive energy consumption during raw material extraction and manufacturing and the ecotoxicity caused through the use of transition metal like niobium and its oxides, may question their viability as environmentally friendly piezoelectric materials. Advances in extraction techniques induced by government policy and environmental regulations, for the extraction of niobium from its ore may offer improvement in the overall environmental impact of KNN.