

Sustainable Functional Materials (SFM) 2016

Challenges and New Directions for Dielectrics and Piezoelectrics

Prof Clive A Randall

*Department of Materials Science and Engineering, Pennsylvania State University, University Park,
Pennsylvania, USA*

As we consider future opportunities for dielectric and piezoelectric materials over the next decade, there have to be new developments in material compositions, new applications, and revolutionary new processing techniques to drive the field forward. In the case of high temperature and high power applications, new dielectrics are required for the power electronics community. One group of dielectrics for power and pulse capacitors that is lacking in variety and understanding is the antiferroelectrics. We recently have identified and predicted a group of potential antiferroelectrics compositions based on solid solutions with NaNbO_3 . In terms of piezoelectrics, there are new applications that could be introduced. The future developments of power electronics, such as piezoelectric voltage sensors and transformers, offer new opportunities. Materials that need to be developed are lead-free hard piezoelectric materials with inner, highly conducting electrodes, such as Ag and/or Cu, that can be co-fired into multilayer structures. Recently, we have demonstrated that we can co-fire soft NKN materials with copper inner electrodes. In the case of functional electroceramics, there is a need to integrate materials and lower temperatures to permit the integration of ceramic and polymer technologies. Such a technology would open up new products and processes that impact additive manufacturing, flexible electronics, and electrochemical energy storage devices, such as batteries and supercapacitors.

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Will the next generation of piezoelectric components be dominated by Potassium–Sodium Niobate?

Prof Paula Maria Vilarinho

Department of Materials and Ceramic Engineering, Center for Research in Ceramics and Composite Materials, CICECO, University of Aveiro, 3810–193 Aveiro, Portugal

This talk intends to contribute to the answer to the following question: Will the next generation of piezoelectric components be dominated by Potassium–Sodium Niobate?

This talk is about the comparison between the electromechanical properties of single crystals and polycrystals (ceramics and thick films) of sodium potassium niobate (KNN), towards the development of materials with improved electromechanical performance able to substitute lead based compositions.

Piezoelectrics and ferroelectrics are currently the basis of the most important smart materials used in micro-electromechanical systems (MEMS), for applications as optical displays, acceleration sensing, radio-frequency switching, drug delivery, chemical detection, and power generation and storage. The increasing importance of MEMS in microelectronics industry has also been addressed by the International Road Map for Semiconductors (ITRS) within the concept of functional diversification called “More than Moore”.

The market for piezoceramic components is dominated by lead zirconate titanate (PZT) materials. Indeed compositions in the solid solution of PbZrO_3 - PbTiO_3 ($\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT)) and PZN-PbTiO_3 exhibit some of the highest electromechanical coupling coefficients, being consequently key piezoelectric materials. Nevertheless, environmental restrictions are triggering the rapid replacement of lead based components. Compositions in the NaNbO_3 – KNbO_3 system are leading lead free candidates for some of these applications.

This talk revises the state of the art on NaNbO_3 – KNbO_3 (KNN) materials. Though with some advantages over the classical PZT the performance of KNN based materials needs to be improved. To support this discussion the results of our systematic studies on the comparison between the performance of single crystals and polycrystalline $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (Figure 1) [4-6] are presented. From the domain structure to the charge transport the differences between KNN single crystals, ceramics and thick films are established. Based on these differences strategies for sustainable, economical viable and optimised performance of KNN based materials are proposed.

References:

1. Muhammad Asif Rafiq, M. Elisabete V. Costa, Paula M. Vilarinho, *Science of Advanced Materials*, 2014, **6**, 426-433.
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3. Morgane Dolhen, Amit Mahajan, Rui Pinho, M. Elisabete Costa, Gilles Trolliard, Paula M. Vilarinho, *RCS Advances*, 2015, **5**, 4698-4706.
4. Muhammad Asif Rafiq, Maria Elisabete Costa, Paula Maria Vilarinho, *Crystal Growth & Design*, 2015, **15**, 1289 – 1294.
5. Muhammad Asif Rafiq, Maria Elisabete Costa, Paula Maria Vilarinho, *Physical Chemistry Chemical Physics*, 2015, **17**, 24403 – 24411.

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What is a Sustainable Piezoelectric Material?

Prof Andrew J Bell

*Institute for Materials Research, University of Leeds, Leeds, LS2 9JT
& Ionix Advanced Technologies Ltd, Huddersfield, HD1 3BD*

The answer to the question “what is a sustainable functional material?” is complex and comprises the responses to several subsidiary questions that address aspects of a range of scientific, technical and economic issues. The four most important issues are:

1. Does the material meet the performance requirements for specific device applications ?
2. Is it legal ?
3. Is it widely available now and in the future ?
4. Is it commercially viable ?

This presentation will address each of these questions in turn, focussing on the example of piezoelectric materials, and will attempt to provide an holistic response to the question of sustainability that goes beyond the single issue of the replacement of lead in PZT.

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Making a Potential Difference

Jonathan Booth

Johnson Matthey

Johnson Matthey is committed to the principles of sustainable development. We aim to more than double earnings per share while halving our carbon intensity, achieve zero waste, and halve the key resources we consume per unit of output. This will create a business that will continue to grow and prosper in its third century. For the benefit of our customers, we aim to apply our expertise to the development of a new generation of sustainable products and services. This talk will discuss many of the technology areas in which Johnson Matthey is involved and demonstrate how by doing more with less we hope to achieve our ambitions.

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Recent advances in sulphur based thermoelectric compounds

E. Guilmeau,^{a)} T. Barbier,^{a)} P. Lemoine,^{a)} M. Eriksson,^{b)} G. Guélou,^{c)} P. Vaqueiro,^{c)} A. Powell^{c)}

a) CRISMAT, UMR 6508 CNRS-ENSICAEN, 6 Bld Maréchal Juin, 14050 Caen, France

b) Diamorph AB, Stureplan 3, SE-11145 Stockholm, Sweden

c) University of Reading, Reading, RG6 6AD, United Kingdom

The high thermoelectric performance together with the potential for economical and large scale production makes tetrahedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$) compounds very promising candidates for the construction of competitive thermoelectric generators for low and medium temperature range. Indeed, the very low thermal conductivity, due to on one hand to its complex structure and on another hand to a rattling effect of copper atoms in triangular coordination, allows to reach a ZT value around the unit at 700 K. Due to the absence of reported data on the phase stability against temperature, we have studied the influence of the temperature on purity, structure and TE properties of some tetrahedrite phases by high temperature powder X-ray diffraction measurements up to 830 K. The results demonstrate the benefits of Ni substitution in terms of phase crystallisation and stability against temperature [1] and thermoelectric performances. In addition, we will show how the high-energy ball-milling from pure and non-toxic elements coupled with Spark Plasma Sintering (SPS) process constitutes a rapid and reproducible method for synthesizing pure and highly dense tetrahedrite material [2]. We will also report some recent advances in the up-scaling of the sintering process [3]. For that purpose, dense pellets of 15 mm diameter, synthesized in CRISMAT lab, will be compared to large square monoliths (50 mm side), sintered using an industrial device.

Recent results obtained in other ternary systems, such as Cu-Sn-S and Cu-Fe-S will be also presented.

[1] T. Barbier, et al. Structural stability of the synthetic thermoelectric ternary and nickel-substituted tetrahedrite phases. *J. Alloys Compd.* 634 (2015) 253.

[2] T. Barbier et al. Thermoelectric Materials: A New Rapid Synthesis Process for Nontoxic and High-Performance Tetrahedrite Compounds. *J. Am. Ceram. Soc.* 99 (2016) 51

[3] T. Barbier, et al. Up-scaled synthesis process of sulphur-based thermoelectric materials. *RSC Adv.* 6 (2016) 10044.

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Biomediated Crystal Growth of High Temperature Oxide Phases

Dr Simon Hall

School of Chemistry, Cantock's Close, University of Bristol, Bristol, BS8 1TS, UK

Scalability in the synthesis of high temperature oxide phases can be achieved via biotemplated sol-gel syntheses. On calcination, the individual metal salts undergo multiple chemical transformations before finally reacting to form the correct stoichiometry. The precise mechanism of sol-gel synthesis of the superconductor $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ (Bi-2212) is to-date unknown. Synthetic protocols invariably result in the formation of large crystallites of SrCO_3 (decomp. 1,494 °C) that are stable throughout calcination (typically around 900 °C) altering the final stoichiometry of the superconductor. It has been postulated that calcium may be present in the synthesis at elevated temperatures as calcium carbonate, which aids in the melting of SrCO_3 by forming a low-melting eutectic mixture. This would ensure full melting of the strontium phase and its subsequent availability for reaction to form Bi-2212, but this has never been conclusively determined. By employing a biopolymer, which chelates multivalent cations, we can restrict the nucleation of SrCO_3 to the nanoscale and easily follow via X-ray diffraction and thermogravimetric analysis, the development of a mixed carbonate eutectic as the synthesis of Bi-2212 progresses. Positive identification of a eutectic-based mechanism of formation enables us to further lower the eutectic melting point by the incorporation of a biopolymer rich in potassium, resulting in the formation of Bi-2212 at 50 K lower than has been previously observed.