NON-LINEAR DIELECTRICS

University of Aveiro researchers share their discoveries in non-linear dielectrics, from electronics to biological communication

Linear dielectrics are referred to as dielectrics (insulators) whose dielectric constant increases linearly with the applied electric field accompanied by an increase in the polarisation. Additionally, there is a special class of dielectrics called non-linear dielectrics that exhibits large dielectric constants and non-zero polarisation in the absence of the electric field and non-linear dielectric constant. Besides this, non-linear dielectrics may also display relevant special physical phenomena such as coupling strain and electric field (piezoelectric effect), temperature dependence of the polarisation (pyroelectric effect) and the presence of large polarisation in the absence of the electric field (spontaneous polarisation) that can be reversed by the application of an external electric field (ferroelectric effect). Based on these properties and effects, non-linear dielectrics are extremely useful in different applications that range from sensors, actuators, motors, transducers, temperature detectors, imaging and data storage, for a wide range of industries including the automobile, aeronautics, computer, military, consumers and medical.[1]

Most of these non-linear dielectrics are oxides and the properties are directly dependent on the chemical composition, singularities of the crystallographic structure and manufacturing process. The knowledge of the relationships between composition, structure, processing and properties allows the production of improved materials for known applications as well as for new uses and in an economic way.[1]

Among the functional materials which exhibit piezoelectric-, pyroelectric-, ferroelectric- and ferroelectric-related properties, four main groups of materials have been considered: hydrogen bonded systems, ionic crystals, narrow gap semiconductors and organic polymers. One of the most important is the ionic crystals group and among these, perovskites (ABO_3) are particularly significant from the point of view of applications. Such materials undergo a phase transition on cooling from a high symmetry temperature phase (cubic paraelectric phase) to a non-centrosymmetric ferroelectric phase.[1]

The materials with the highest piezoelectric co-efficient belong to the lead-based perovskite family. Materials with a high ferroelectric transition temperature show piezoelectricity at room temperature, whereas those with transitioning near or below room temperature exhibit an important electrostrictive effect. For these, due to the large anharmonicity of the ionic potential, electrostriction is extraordinarily large. Besides the ability to design the physical properties required for certain applications, by formation of solid solutions, the possibility of fabrication as single crystals, ceramics, textured ceramics and thin and thick films adds value to this family of materials.[1]

Electroceramics Group (www.electroceramicsgroup.org) is engaged in fundamental and applied research in the synthesis, properties and processing of functional materials for electronics, microelectronics and related applications.

Paula Vilarinho's Research Group, has focused on electrical polarisation phenomena in solids, aiming to understand mechanisms that control electrical polarisation at the macroscopic and nanoscale level, and applying such understanding to the development of advanced nano- and microelectronic devices. For that the group has used electrical and structural characterisation tools (impedance spectroscopy, piezo-ferroelectric analysis, scanning probe microscopy, electron microscopy, Raman spectroscopy, among others) at the highest level.

Materials under investigation include perovskite type ferroelectric, piezoelectric, dielectric and multiferroic oxides and piezoelectric polymers (PLLA and PVDF). Applications of these materials include microelectronic devices as memories, sensor and actuators, energy harvesters, thermoelectric devices, tunable dielectrics, and, more recently, bio-related uses such as bio-compatible piezoelectric platforms for tissue growth and biosensors, among others.

While understanding materials properties is central in many of Vilarinho's R&D activities, the synthesis of sustainable functional materials in different geometries (1D, 2D and 3D) at low temperatures for compatible materials integration and using low-cost approaches and lead-free oxides is becoming increasingly important in the group's research activities. Within this context the group has been exploiting hydrothermal synthesis, their own proprietary solution-based Seeded Photosensitive Precursor Method and electrophoretic deposition (EPD) for the preparation of nanoparticulates, nanocomposites, thin and thick films of functional materials.

Towards room temperature

In collaboration with the group of Professor Lourdes Calzada (CSIC, Madrid, Spain) a novel solution method was developed that enables the processing of functional oxides under low-temperature conditions so that direct-large-area integration of active layers with flexible electronics becomes reality. We started by demonstrating the concept on the most important multifunctional oxide, $PbZr_{1-x}Ti_xO_3$ (PZT), which reaches the lower limit temperature of crystallisation at 300°C, using a strategy that combines seeded diphasic precursors and photochemical solution deposition. Properties of

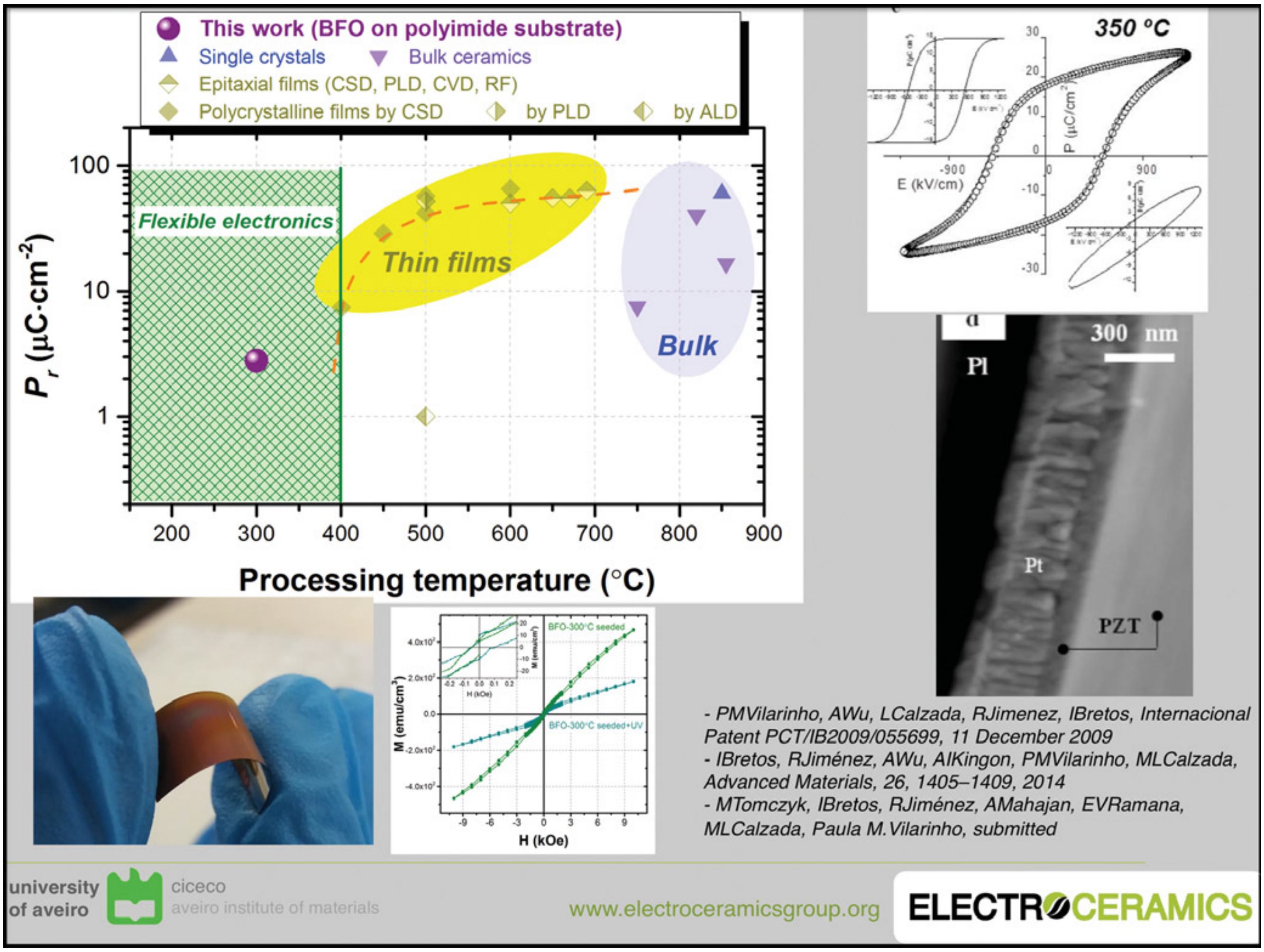

Fig. 1 Direct fabrication of $PbZr_{1-x}TixO_3$ and $BiFeO_3$ thin films on polyimide substrates for flexible electronics. Adapted from reference 3 and 4

these ferroelectric layers on flexible plastic fulfil the major requirements demanded for devices, showing a wider temperature range of applicability and functionality than those of the high-K dielectrics or organic ferroelectrics.[2,3]

More recently, lead-free multifunctional and multiferroic $BiFeO_3$ thin films have been fabricated for the first time at a temperature as low as 300°C, directly on flexible polyimide substrates. Despite this low thermal budget a remanent polarisation (Pr) of 2.8µC/cm^2 is obtained for these $BiFeO_3$ films, with a coercive field (Ec) of 300kV/cm and notably exhibit a room temperature ferromagnetic response, corresponding to a broken or significantly distorted cycloid-like magnetic modulation.[4]

This is a platform that can be used for many other functional oxide layers as the concept allows direct fabrication of complex oxides thin films on polyimide substrates targeted for flexible and miniaturised electronic components to produce light, low cost, low power consumption, and portable electronic devices. It contributes to the development of technological approaches with drastic reduction of energy consumption towards a more sustainable processing of microelectronics (Fig. 1).

Looking for lead-free piezoelectric oxides, R&D activities of the Electroceramics Group include studies on potassium sodium niobate, $K_{1-x}Na_xNbO_3$ (KNN). Among the several families of lead-free piezoelectrics currently under consideration, KNN is one of the most promising. The electromechanical properties of KNN are still inferior to the ones of PZT, but the high transition temperature of KNN (Tc=420°C) is an important added value permitting applications at high temperatures. It is then critical to develop KNN-based ceramics that possess high electromechanical properties together with phase transitions as much as possible far from room temperature and high Tc.

Enhanced piezoelectricity

Attempts to improve the electromechanical response of KNN traditionally encompass the use of dopants but at the expense of lowering Tc. We have shown that using KNN single crystals as seeds for template grain growth (TGG) of KNN ceramics enables dramatic improvements in the electromechanical properties while maintaining a high Tc. (001)-oriented KNN-based ceramics engineered by TGG using KNN crystals as templates exhibit a high d_{33} of 280pC/N, while maintaining the high Tc of 430°C.

Enhanced piezoelectricity is attributed to long-range ordered ferroelectric domain patterns consisting of 90° and 180° domains, similar to single crystals. We proved that pairing high d_{33} and high Tc in KNN keeping a high PPT temperature without resorting to heavily doped compositions, is feasible. Our approach opens the door to high-performance, rare-earth free, compositionally simple

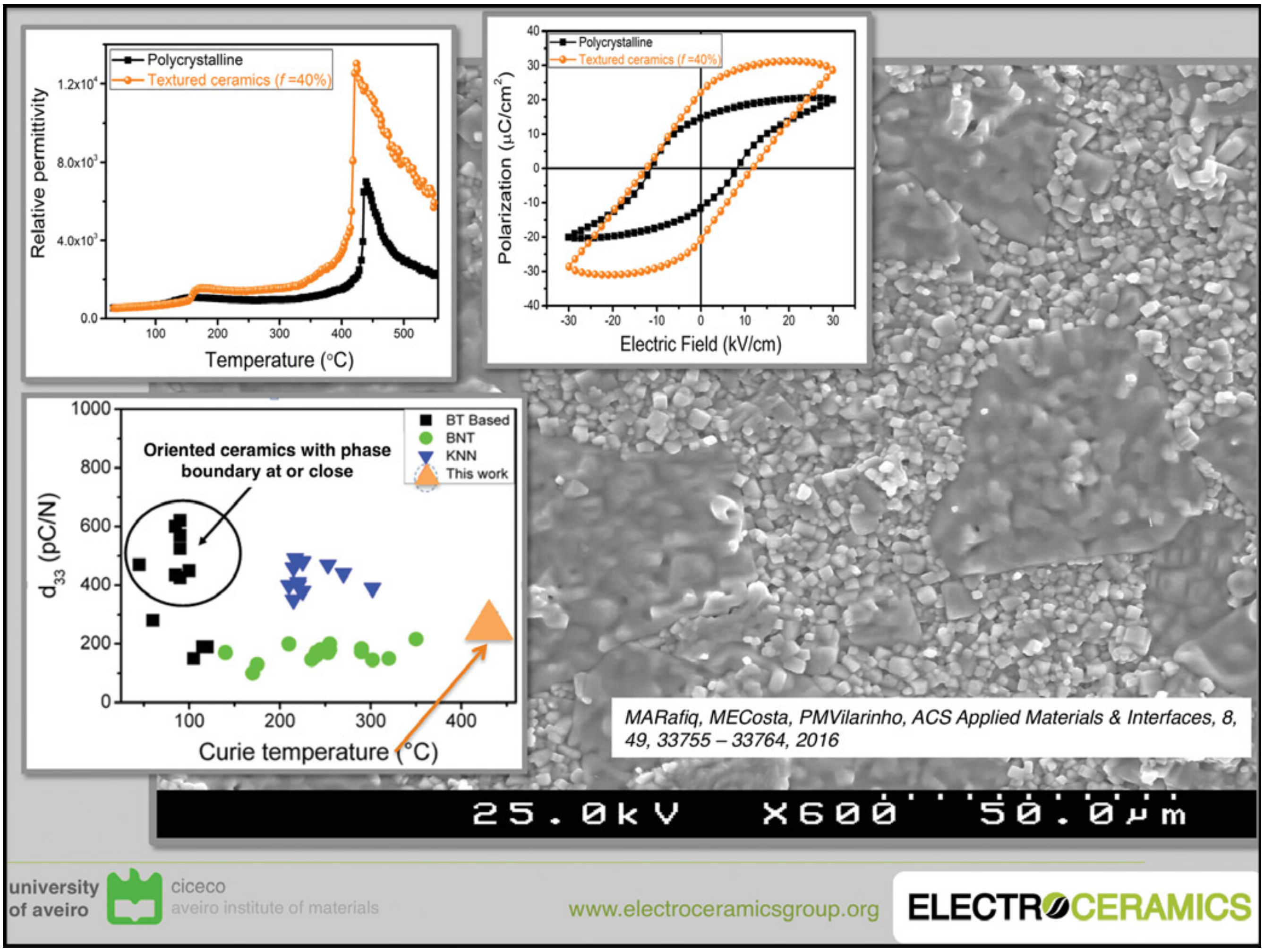

Fig. 2 Pairing high piezoelectric coefficient d_{33} with high Curie temperature (Tc) in lead-free $(K,Na)NbO_3$. Adapted from reference 5

lead-free and low-cost electromechanical compounds, which can largely expand lead-free piezoelectrics applications (Fig. 2).[5]

We also demonstrated that an eco-friendly aqueous solution-based process can be used to produce KNN thick coatings with improved electromechanical performance. KNN thick films on platinum substrates with thickness varying between 10 and 15μm have a dielectric permittivity of 495, dielectric losses of 0.08 at 1MHz, and a piezoelectric coefficient d_{33} of 70pC/N. At Tc these films display a relative permittivity of 2,166 and loss tangent of 0.11 at 1MHz. A comparison of the physical properties between these films and their bulk ceramics counterparts demonstrates the impact of the aqueous-based electrophoretic deposition (EPD) technique for the preparation of lead-free ferroelectric thick films. This opens the door to the possible development of high-performance, lead-free piezoelectric thick films by a sustainable low-cost process, expanding the applicability of lead-free piezoelectrics.[6]

From electronics to biological communication

The major medical applications of piezoelectrics include *ex vivo* imaging; *in vivo* tissue growth applications are seldom, if any. Starting from the relatively well-known role of electrical stimulation on living tissues, and assuming that *in vivo* endogenous electric potentials can control cell functions as growth, migration and mitosis rate, we are currently exploiting the use of piezoelectrics as *in situ* smart platforms for biological communication targeted to tissue growth. Our work explores the effects of electrically induced polarisation in piezoelectric polymer such as poly L-lactic acid platforms (among others) to be used as *in situ* tissue engineering scaffolds.

The process of protein adsorption is highly favoured in the poled areas of PLLA. When polarisation occurs above glass transition temperature PLLA films present a durable polarisation, up to ten days.[7,8] The effects of the morphologies and polarisation of these platforms were evaluated with respect to the proliferation and differentiation of neuroblastoma cells and embryonic cortical neuronal cultures. Polarisation promotes a cell's differentiation capability. Aligned nanofibres were revealed to be the best platform as it delivers a synergistic effect between topographical cues and polarisation, promoting neuritogenesis. These mimic the natural cell environment, greatly enhance neuritogenesis and exhibit a long shelf life. *Ex vivo*, these platforms can also be used to study the effect of charged platforms on cellular processes, or to manipulate protein adsorption and cell behaviour towards improved regenerative strategies. The long lasting induced polarisation can be envisaged as a long shelf life therapeutic device for neural repair (Fig. 3).[9]

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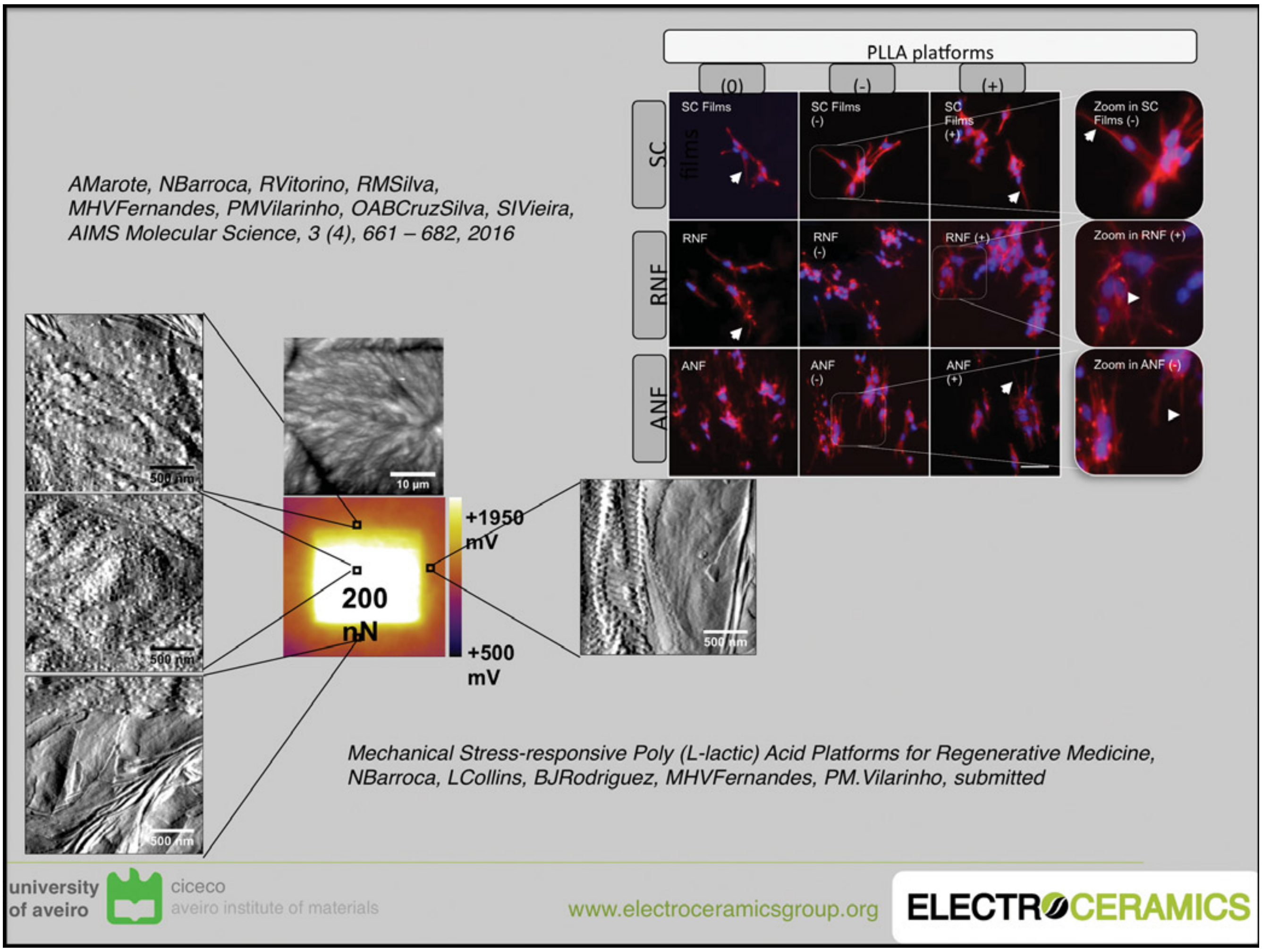

Fig. 3 Piezoelectric Poly (L-lactic) acid thin films and fibbers as platforms for tissue growth. Adapted from reference 9 and 10

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