Solid-state refrigeration with ferroelectrics

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1. Introduction and background – purpose of the visit

This report summarizes research carried out at the Cavendish Laboratory, University of Cambridge, during a short-visit by the author from the Fondazione Bruno Kessler (FBK) in Trent, Italy.

The purpose of the visit was to initialise a collaborative programme of research investigating the refrigeration possibilities of ferroelectric or nearly-ferroelectric materials exhibiting the electro-caloric effect. The electro-caloric effect involves the isothermal polarization of electric dipoles, by application of an electric field, followed by adiabatic depolarization. The process may then be cycled to achieve continuous cooling. An idealised thermal cycle (a to b to c) is illustrated in the schematic entropy-temperature plot below.

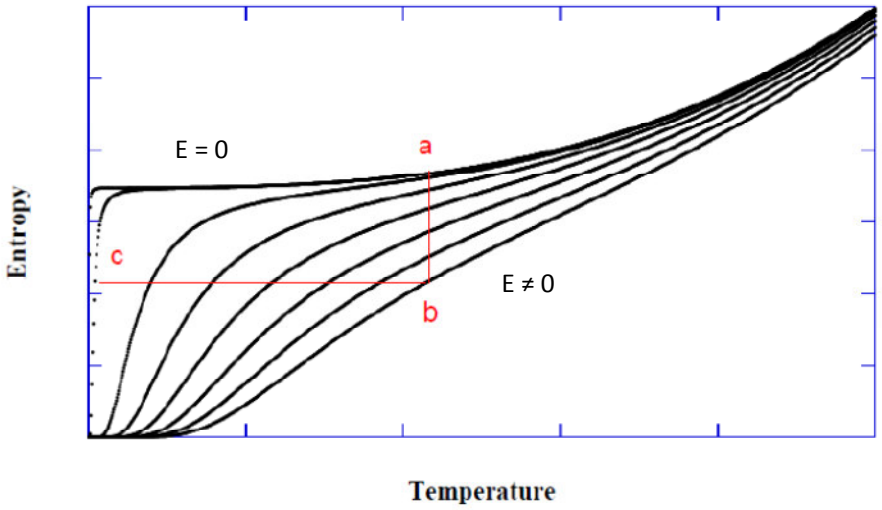

Figure 1 – Schematic plot of entropy against temperature for a material suitable as a refrigerant using the electro-caloric effect.

The isothermal step (a to b) is achieved by sweeping an electric field while the sample is thermally connected to a heat bath. After this, the adiabatic step (b to c), is carried out by disconnecting the thermal link with the heat bath and sweeping down the field to zero sufficiently slowly, during which cooling occurs.

We have in mind a range of materials that are suitable for both room temperature and low temperature (1 mK to 4 K) refrigeration applications. Using the expertise in materials fabrication at the Fondazione Bruno Kessler, single and multi-layer thin-film capacitors were made using $Pb_{0.88}La_{0.12}Zr_{0.65}Ti_{0.35}O_3$, (PLZT) as the

dielectric material, which has previously been reported to exhibit the electro-caloric effect [1]. The electrode and oxide layers were grown using a radio-frequency sputtering technique. An example of the types of devices fabricated are indicated in Fig. 2. The visit to Cavendish Laboratory in Cambridge was necessary to make use of the advanced measurement apparatus and theoretical support available there. Measurements required included electrical polarization and dielectric constant as a function of temperature and electric field.

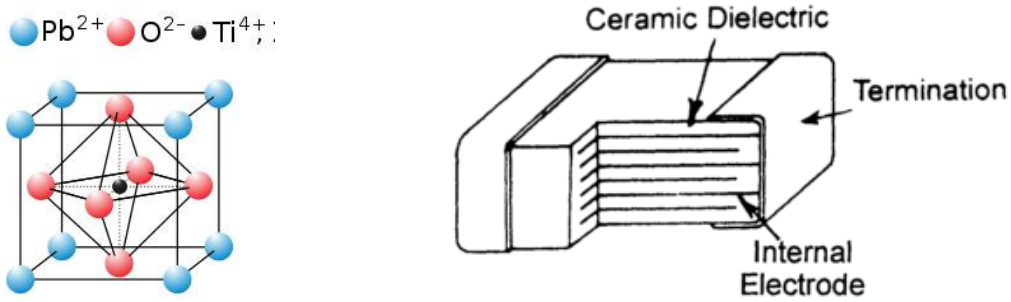

Figure 2 – Left image shows a unit cell of the perovskite lattice of $PbTiO_3$, the prototype compound on which our room temperature PLZT electro-caloric devices are based. The right figure shows a schematic diagram of a multilayer capacitor fabricated at FBK for electrical and thermal measurements to investigate the electro-caloric effect.

2. Work carried out during the visit

A study of the theory of displacive, order-disorder and relaxor ferroelectrics was carried out including the differences between these classes of materials in their application as electro-caloric coolers. The development of a working model for the electro-caloric effect in certain types of ferroelectric or nearly ferroelectric materials was achieved.

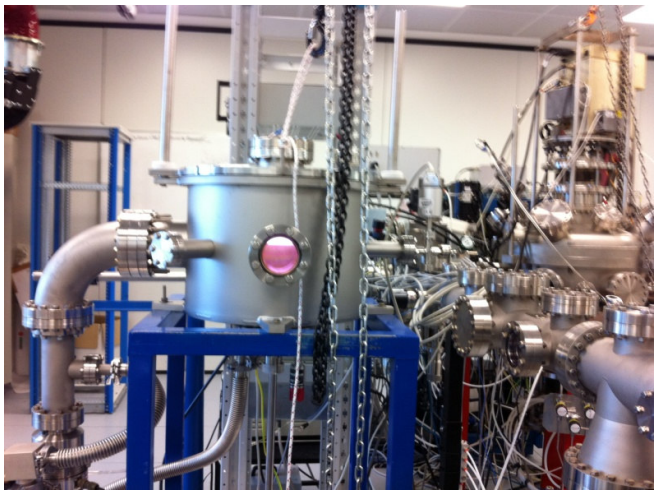

Figure 3 – Photograph showing the sputtering equipment used to fabricate thin film capacitors for this project. An active plasma of PLZT with argon gas can be observed through the window to the vacuum chamber.

Eight samples (labelled S1 to S8) synthesised using the sputtering apparatus shown in Fig. 3 were tested using a low frequency impedance analyser to characterize their electrical properties prior to detailed

measurements. The samples were approximately 500nm thick with an electrode area of roughly 0.25 cm^2, an example of which is shown in Fig. 4. Of the working samples, the dielectric constant was measured as a function of temperature around room temperature, in zero applied field, using a QuadTech capacitance bridge. The frequency response of the devices could also be measured up to 1 MHz. Electrical polarization and leakage current were then measured as a function of electric field from 0 to 800 kV/cm at various fixed temperatures between 20°C and 100°C. The break-down field for the device was also determined.

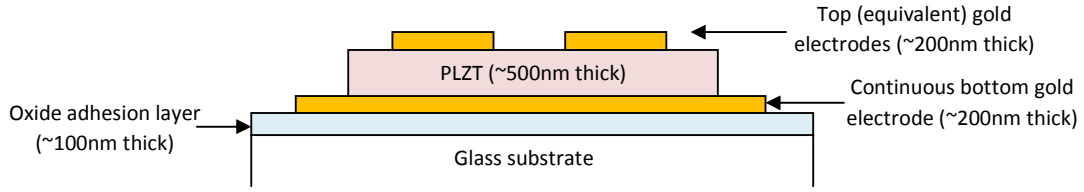

Figure 4 – A schematic diagram showing an example of a single layer thin-film ferroelectric capacitor. Single and multi-layer devices of this kind were used in the experiments.

3. Model for the electro-caloric effect

The possible temperature change achievable for a given electro-caloric material may be measured directly using a thermometer and heat switch enabling the cooling device to be thermally connected or disconnected from the surrounding heat bath. However, to save time, the cooling potential of candidate materials may first be determined from measurements of their dielectric properties in electric fields at different temperatures without the use of heat switching equipment. From the simple thermodynamic relations $(\partial P/\partial T)_E = -(\partial S/\partial E)_T$ and $S = (\partial S/\partial T)dT + (\partial S/\partial E)dE = 0$ during a process as seen in Fig. 1, one may find the following

$$\left(\frac{\partial T}{\partial E}\right)_S = -\frac{T}{C_E}\left(\frac{\partial P}{\partial T}\right)_E \qquad (1)$$

where *P* is the polarization, *E* the electric field, *S* the entropy, *T* the temperature and *C* the heat capacity. This may be integrated to find the temperature change

$$\Delta T = -T\int \frac{1}{C_E}\left(\frac{\partial P}{\partial T}\right)_E dE. \qquad (2)$$

Thus from measurements of $P(T)$ in different fields, one may estimate the cooling potential of a given device. This equation may be simplified further if one assumes the fields are small enough that the polarization depends linearly on field, in SI units $P = \varepsilon_0 \chi E$, where χ is the zero field electrical susceptibility, related to the dielectric constant ε by $\chi = \varepsilon - 1$ and ε_0 is the permittivity of free space.

$$\Delta T = -T\varepsilon_0\int \frac{\mathrm{E}}{C_E}\left(\frac{\partial \chi}{\partial T}\right)_E dE \qquad (3)$$

In this form, measurements of $\chi(T)$, or a model for example of the form $\chi = A/(T - T_C)^\gamma$ where *A* is a material specific constant and γ a power depending on the type of phase transition, may be used to determine possible temperature changes.

From these equations we can infer that a material with a high dielectric constant tuned close to its ferroelectric Curie temperature is favourable for electro-caloric cooling. The material should also have a break-down field as high as possible and a heat capacity that is not too large.

An alternative to using these equations is to calculate the entropy curves such as those in Fig. 1 directly using a statistical model for the type of ferroelectric of interest (displacive, order-disorder or relaxor). From such curves the temperature change for a given device may also be predicted.

4. Key experimental results

Seven of the eight samples were short-circuited as determined by measuring the real and imaginary parts of the electrical impedance z, between the bottom and top electrodes. They had an angle θ ($z = |z|e^{i\theta}$) close to zero and a resistance less than 100 Ω. This was also confirmed by attempting to measure the polarization as a function of field, the results of which were spurious. One of the samples was capacitive and selected to perform further experiments. This working sample had θ = -88° and $|z|$ = 13.9 kΩ. The success rate of 1 in 8 is considered quite good for this first batch of devices, especially as the electrode areas were quite large which increases the probably of a pin-hole occurring between the plates. The large electrode area is favourable as it increases the amount of material available for cooling. We anticipate that the next batch of single and multi-layer devices will improve on this success rate and in fact this has already been shown to be true at the time of writing by varying the parameters of the growth process during sputtering.

Of the working sample, the dielectric constant and loss tangent as a function of temperature were measured and found to be monotonically increasing with temperature up to 100°C. The dielectric constant was much smaller than that expected from previous reports [2]. We believe this is due to the amorphous nature of the film and the fact that the stoichiometry may not be exactly as intended.

The polarization was found to be linear with electric field up to 600 kV/cm at every temperature tested. No hysteresis was observed indicating that the films were paraelectric. The devices suffered break-down by 800 kV/cm signified by a large leakage current. The maximum polarization at the high field end, before break-down, was observed to be much smaller than should be the case for our target composition and crystallinity of PLZT. We are confidant these results may be improved in the next batch of samples as suggested in the next section.

5. Conclusions and recommendation for further work

The results from electrical measurements so far have enabled us to guide the future fabrication of devices in correspondence with the chemical and structural analysis of the films. The visit has enabled us to set-up up and test a measurement facility specifically for experiments on the electro-caloric effect. The initial measurements on this first batch of samples and our theoretical study have shown that despite no appreciable cooling power observed so far, the development of multi-layer capacitors with improved dielectric films have a strong potential as solid-state refrigerants.

By using platinum electrodes grown on top of a TiO_2 adhesion layer, heating the substrate during the sputtering process and post-annealing the sample, we anticipate that the crystallinity and composition of

the PLZT will be greatly improved. Our future samples will be based on these and other types of dielectric refrigerants.

6. Future collaboration

We are pleased with the initial results and understanding gained from the short-visit. Based on this we are planning to continue the collaboration between FBK and the Cavendish. We envisage this will take the form of improved devices being fabricated at FBK based on the guidance from the short-visit. The new devices may then be measured at the Cavendish for their potential as solid-state refrigerators. This work has already begun and we would hope to publish the results in the future as supported by the European Science Foundation.

7. References

1. S. G. Lu et al, Applied Physics Letters, 97, 162904 (2010)
2. G. H. Haertling and C. E. Land, J. American Ceramic Soc., 54, 1 (1971)