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Solid-state physics

Surface polarization feels the heat

A crystal's surface has been found to behave as a distinct material that has temperature-dependent electrical polarization — despite the rest of the crystal being non-polar.

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When crystals of certain materials are squeezed, the compression causes a polarization of internal charge that generates a voltage — a phenomenon known as piezoelectricity. Some piezoelectric materials also exhibit spontaneous polarization that changes in magnitude with increasing temperature. These materials are said to be pyroelectric, and are useful in heat sensors and for solid-state cooling (because pyroelectrics change temperature in an applied electric field)[1]. Pyroelectrics have thus been intensively investigated, with research naturally focusing on electrically polar materials. Writing in *Advanced Materials*, however, Meirzadeh *et al.*[2] report that the non-polar material strontium titanate ($SrTiO_3$) is also pyroelectric, suggesting that the net needs to be cast more widely in the search for pyroelectrics.

Conventional piezo- and pyroelectricity ultimately arise from the fact that the repeating unit (the unit cell) of the crystal lattice is asymmetric. A perfect, infinite crystal of strontium titanate is symmetric and therefore would not be pyroelectric. But perfection, alas, does not exist. Many crystals contain defects whose concentration varies across the crystal; the resulting concentration gradient breaks the macroscopic symmetry of the crystal, causing residual piezoelectricity and pyroelectricity[3].

Moreover, even the most perfect crystals are finite, which means that they inevitably have one kind of “defect”: surfaces. And surfaces break symmetry, because what is above the surface is different from what is below. Hence, irrespective of the intrinsic symmetry of the bulk, surfaces can in theory be polar and thus pyroelectric. This seems to be the case for strontium titanate, a cubic type of crystal commonly used as a substrate for growing films of other oxides.

Determining whether pyroelectricity comes from the surface, rather than from inside a crystal, is not trivial. Meirzadeh and co-workers did so by heating the surface with fast laser pulses, and measuring how the resulting pyroelectric current evolves with time. The rate at which the current decays is related to the rate at which the surface reaches thermal equilibrium, a process called thermalization: fast decay of the current implies quick thermalization and therefore suggests that the depth of the pyroelectric region is shallow.

From the time-dependence of the signal, the authors estimate that the depth of the polarized layer in strontium titanate is about 1.2 nanometres, equivalent to 3 unit cells. This depth coincides with the depth of an intrinsic region of polar distortion predicted by first-principles calculations due to surface tension in strontium titanate,[2,4]. The pyroelectric effect, therefore, seems to arise from inherent surface polarization.

The authors took precautions to discard alternative explanations: they showed that the direction of the heat-induced current does not depend on the orientation of the crystal, ruling out a bulk effect; and that the local heating produced by the laser is very small (the temperature increases are at the sub-kelvin scale), which means that the strain gradients induced by thermal expansion are insignificant. Other experiments and data analysis were carried out to exclude the possibility that the induced current is due to molecules (typically water) adsorbed to the surface, charges trapped by lattice defects, excitation of free charges induced by light or the thermoelectric Seebeck effect (which generates currents in semiconductors that contain temperature gradients). Importantly, the pyroelectricity disappeared when Meirzadeh *et al*. deposited an atomically thin layer of amorphous silica (SiO_2) on top of the strontium titanate, consistent with the idea that the phenomenon originates at the surface. Moreover, the temperature dependence of the surface polarization suggests that a phase transition occurs that is not observed in the bulk. This is interesting, because it implies that the pyroelectricity does not simply arise from thermal expansion of the piezoelectric surface[5], but from a true phase transition confined to the surface.

Surface layers of crystals that have properties different from those of the bulk, known as skin layers, are found in various materials[6,7] including strontium titanate[8]. However, such skin layers tend to be much thicker than the atomically-thin one described by Meirzadeh and colleagues, and are probably induced by defects introduced during polishing, rather than being intrinsic. Rearrangements of surface atoms in strontium titanate have also previously been reported[9], but it has not been established whether the resulting surfaces are pyroelectric. Meirzadeh and colleagues' findings are therefore new.

This discovery matters for many reasons. One is pointed out by the authors: multi-layer thin film devices could be specifically designed to take advantage of the surface polarization at the interface between each layer [10,11]. There are also consequences for bulk crystals. When a crystal of any symmetry is bent, it can become electrically polarized as a result of strain being produced non-uniformly in the material — a phenomenon called flexoelectricity. If the surface is polarized (as it would be if it is pyroelectric), the surface polarization will also contribute to the total flexoelectricity, [12, 13]. In fact, the surface termination of a strontium titanate crystal (that is, whether the last atomic layer is TiO_2 or SrO) can theoretically change the sign of the macroscopic flexoelectric voltage –even for macroscopic crystals[14].

Surfaces are also interesting in themselves, being two-dimensional entities in a three-dimensional world. If a pyroelectric phase transition does occur in the surface of strontium titanate, it would offer an excellent playground for testing theories about the relationships between phase transitions and dimensionality in general, because of the universality of the laws that underpin such transitions. It will also be interesting to study the nature of the dipoles that form at surfaces and, specifically, whether their orientation can be switched by voltage –in other words, whether the surface of $SrTiO_3$ is not just a two-dimensional pyroelectric but also a two-dimensional ferroelectric.

Electrical polarity might not be the only surprising thing about the surface of strontium titanate. Although this material is an insulator, its surface conducts electricity[15]. The surface might therefore be a polar metal: an exotic type of metal that contains electric dipoles[16,17]. Polar metals have been much sought after, partly out of fundamental curiosity (polar materials are normally insulators or, at most, semiconductors), but also because they are expected to have unique electronic properties[18]. Meirzadeh and colleagues' findings hint that polar metals might have been under our noses all along, non-intuitively on the surfaces of non-polar insulators.

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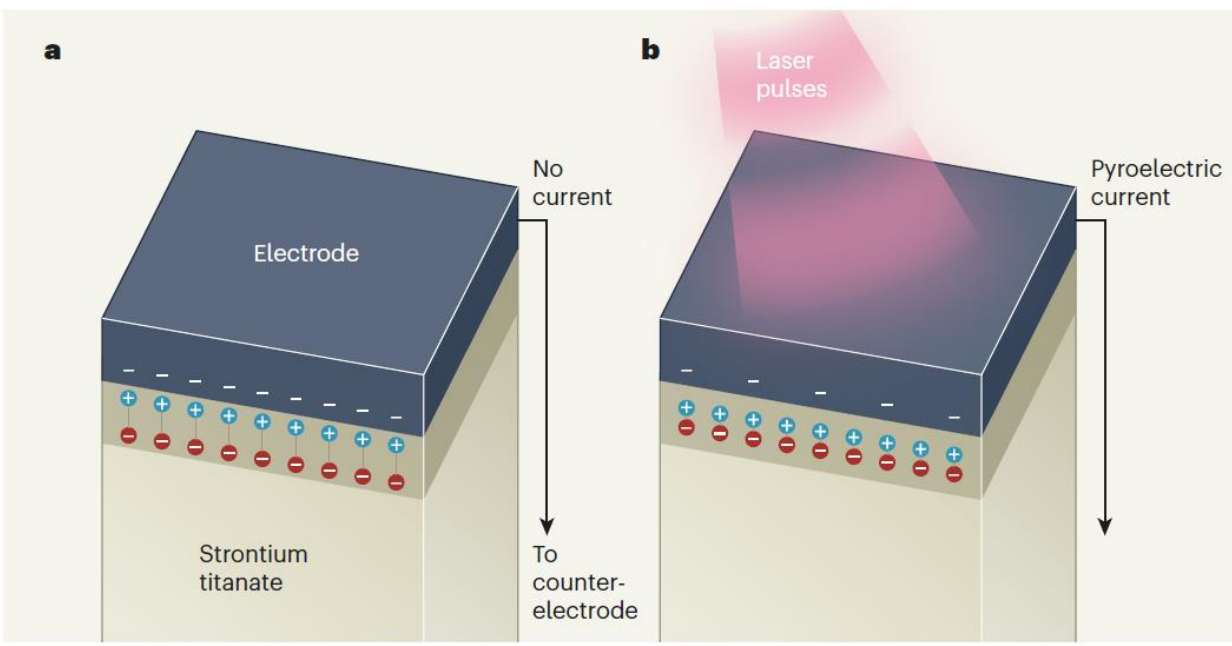

Figure 1 | Pyroelectricity at the surface of strontium titanate. Meirzadeh *et al*.[2] report that the surface layers of crystals of strontium titanate ($SrTiO_3$) undergo temperature-dependent changes of electrical polarization – a phenomenon known as pyroelectricity. **a**, At the beginning of the experiment, before laser irradiation, the surface layers already have an intrinsic amount of polarization, which is balanced (screened) by free charges at the electrode. **b**, Irradiation by laser light heats up the surface and lowers the polarization (shrinks the dipoles). This causes a current to flow in order to balance again the modified polarization. Contrary to thermoelectric currents, pyroelectric currents are transient: once the temperature stabilizes, the current disappears. The time that it takes for the current to disappear therefore carries information about the time that it takes to reach thermal equilibrium, which is proportional to the volume of pyroelectric material – a very small quantity for a thin surface layer.