

## COLOSSAL PERMITTIVITY MATERIALS

## Doping for superior dielectrics

The search for materials with colossal permittivity for use in capacitors has been met with limited success. A newly discovered co-doped titanium oxide material has an extremely high permittivity and negligible dielectric losses, and is likely to enable further scaling in electronic and energy-storage devices.

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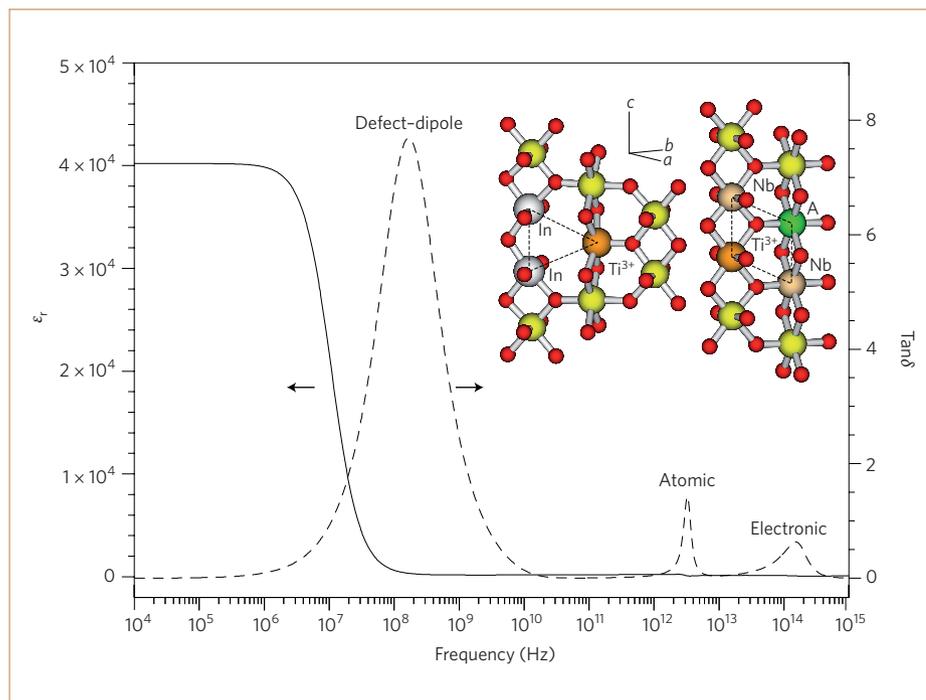
The capacitor is a ubiquitous device used in applications ranging from microelectronics to large-scale power appliances. The capacitance of a simple capacitor with two parallel plates of area  $A$  separated by a distance  $d$  is approximately given by  $C = \epsilon_r \epsilon_0 A/d$ , where  $\epsilon_r$  is the relative permittivity and  $\epsilon_0$  is the permittivity of vacuum. In essence,  $\epsilon_r$  is a measure of the polarizability of a material and its ability to isolate charge. For instance, in a metal  $\epsilon_r$  is negative, and charge placed on the surface will quickly dissipate, whereas in a dielectric  $\epsilon_r$  is positive, and charge placed on the surface will dissipate slowly (the larger the  $\epsilon_r$ , the slower the dissipation).

Although geometric optimization is one strategy to increase  $C$  by extrinsic means, this has arguably reached its limits, and a better approach is to increase  $\epsilon_r$  itself. One such way is to use supercapacitors in which the conventional solid dielectric between the plates is replaced by an electrolyte with special electrodes, resulting in an electrochemical device<sup>1</sup>. Another promising avenue, reported by Hu and co-workers<sup>2</sup> in *Nature Materials*, is to make colossal permittivity materials with  $\epsilon_r$  values that are several orders of magnitude higher than conventional solid dielectrics. This requires engineering the competing materials' interactions by creating and locally

containing electrons using appropriate chemical doping.

In a simple dielectric, the value of  $\epsilon_r$  is related to absorptions arising from lattice vibrations displacing the intrinsic dipole moments typically observed at infrared frequencies. This effect is captured by the Lyddane–Sachs–Teller relation,  $\epsilon_r/\epsilon_\infty = \omega_{\text{LO}}^2/\omega_{\text{TO}}^2$ , in which the strength of the absorption mode is proportional to the splitting between the frequencies of the longitudinal- and transverse-optic modes,  $\omega_{\text{LO}}$  and  $\omega_{\text{TO}}$ , respectively, and  $\epsilon_\infty$  is the high-frequency (usually in the visible region) contribution to  $\epsilon_r$ . In principle, a strong lattice vibration could yield a very large value for  $\epsilon_r$ , but in practice the largest values that are observed are of the order of 250 in rutile<sup>3</sup> (TiO<sub>2</sub>). However, the Lyddane–Sachs–Teller relation may be generalized for other types of dipole-active process in a material, in a manner that may provide a route to large values of  $\epsilon_r$  (the calculated value of  $\epsilon_r$  is shown for several different processes in Fig. 1).

There are several promising candidate systems for achieving colossal permittivity, with materials such as CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> displaying  $\epsilon_r \sim 10^5$  (refs 4,5). Although the extrinsic and intrinsic mechanisms responsible for the high permittivity in this particular material are still a matter of some debate, it is puzzling that the processes that give rise to the high values for  $\epsilon_r$  also result in significantly higher dielectric losses. Niobium doping, frequently used as a way to increase  $\epsilon_r$ , only worsens the overall performance of the dielectric in a capacitor<sup>6</sup>. Doping dielectric oxides such as rutile with electron-donors such as Nb<sup>5+</sup> creates electrons by reducing Ti<sup>4+</sup> to Ti<sup>3+</sup>. Although this electron-doping process raises the permittivity to values above 10<sup>4</sup> at 1 kHz, it also increases the dielectric loss above 0.1, an unacceptably high value. Dielectric loss occurs when the relaxation time and frequency of the applied field are similar, and as a result a phase lag occurs and energy is absorbed. Often the increased permittivity is due to extrinsic effects such as interfacial polarization of highly delocalized electrons at grain boundaries.



**Figure 1** | Ambipolar co-doping in a rutile structure where electron donors (Nb<sup>5+</sup>) create diamond-like complexes; the oxygen vacancies associated with the acceptors (In<sup>3+</sup>) result in triangular complexes<sup>2</sup>. The close proximity (or overlap) of these structures create defect-dipoles that give rise to colossal permittivity and low dielectric losses. Depending on the precise configuration of these two entities, A (green) could be Ti<sup>3+</sup>, Ti<sup>4+</sup> or In<sup>3+</sup>. The unlabelled atoms are Ti<sup>4+</sup> (yellow) and O (red). The relative permittivity (solid line) and the loss tangent,  $\tan\delta = \epsilon_r/\epsilon_r$  (dashed line), where  $\epsilon_r$  is the imaginary part of the dielectric function, are shown for electronic, atomic and defect-dipole processes. The combination of electronic and atomic processes typically result in a maximum value for the relative permittivity of about 250; however, defect-dipoles yield very high values for the relative permittivity in the radiofrequency range.

Doping electron-acceptors such as  $\text{In}^{3+}$  into rutile has little or no effect on the permittivity but results in lower dielectric losses at higher frequencies.

Hu and co-workers<sup>2</sup> have shown that co-doping  $\text{In}^{3+}$  and  $\text{Nb}^{5+}$  into rutile produces local lattice defects that are highly correlated, a conclusion supported by density functional modelling. The complex stoichiometry of  $(\text{In}_{z^{3+}}\text{Nb}_{z^{5+}}\text{Ti}_{z^{3+}})\text{Ti}_{1-3z}^{4+}\text{O}_{2-z/2}$  gives rise to defect clusters where the electrons created by both  $\text{Nb}^{5+}$  doping and the reduction of  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$  are contained by the presence of  $\text{In}^{3+}$  close by. Without the latter, electrons would delocalize and lead to high dielectric losses. These intrinsic defect complexes formed by co-doping give rise to strong dipoles that

are responsible for the extraordinarily high intrinsic values of  $\epsilon_r \geq 10^4$  without having to rely on, for instance, textured ceramic materials or other extrinsic effects that achieve colossal permittivity through the internal barrier layer capacitance effect<sup>7</sup>. More significantly, this material displays exceptionally low dielectric losses over most of the radiofrequency range with excellent thermal stability.

This remarkable new approach of chemically balancing the competing materials interactions with ambipolar co-doping is precisely the advance needed to allow the use of colossal permittivity materials in high-performance capacitors and permit further scaling advances in electronic devices. □

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## CELL MIGRATION

# Towards the void

Cells at the edges of migrating epithelial sheets pull themselves towards unfilled space regardless of their direction of motion.

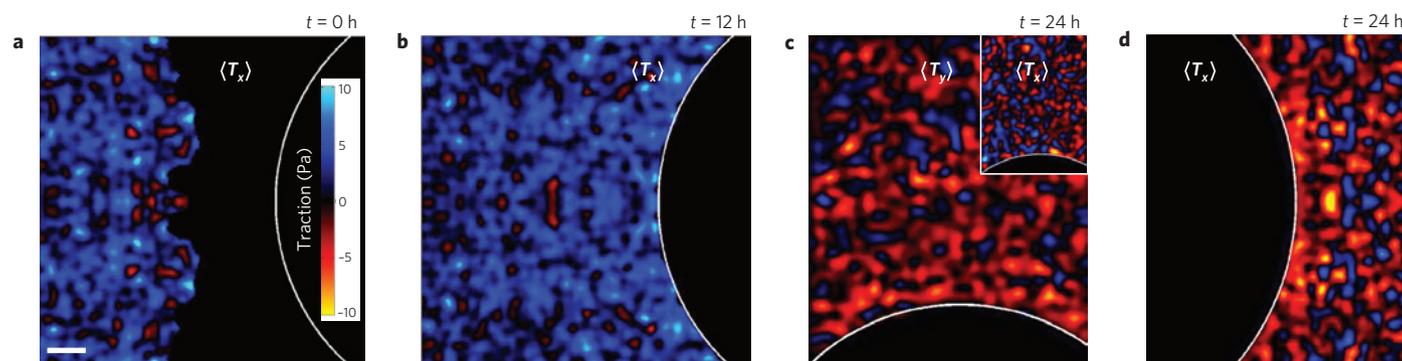
Eric R. Dufresne and Martin A. Schwartz

Wound healing, gastrulation and migration of carcinomas all involve coherent movements by large groups of interconnected cells<sup>1</sup>. Although *in vitro* studies of migrating single cells have clarified many of the critical regulatory mechanisms that govern individual cell migration, we know much less about how ensembles of cells coordinate their movements. The current view is that soluble molecules, signals from adhesion receptors (such as integrins and cadherins)

and mechanical stresses all mediate cell–cell communication in these systems<sup>2</sup>. The challenges are to identify the specific cell-autonomous regulatory mechanisms and to explain how they lead to emergent behaviour in collective migration. In this regard, Jeffrey Fredberg and colleagues report in *Nature Materials* an analysis of the collective motion of a migrating epithelial sheet past an area where the cells could not adhere. They found a surprising disconnect between the motion of the cells located

near the non-adhesive area and the forces they exerted<sup>3</sup>.

Fredberg and co-workers examined the sheet of cells at an intriguing intermediate length scale, where they could resolve individual cells while still capturing large-scale flow. The motion of the cell sheet resembled a fluid flowing past an obstacle: the sheet of cells neatly split into two just upstream of the non-adhesive island and reconnected in a disorganized wake. Far from the non-adhesive island, the directions



**Figure 1** | Colour maps of traction forces exerted on an underlying elastic substrate by a migrating cell sheet approaching and surrounding a non-adhesive island (values are averages of six identical cell sheets)<sup>3</sup>. **a,b**, As the cell sheet (which moves from west to east) approaches the non-adhesive island (white outline), the directions of traction forces and velocities align ( $T_x$  indicates the x-component of the traction forces, where x is a horizontal axis running from west to east). **c,d**, The y- (vertical, **c**) and x- (horizontal, **d**) components of the traction forces for cells north (**c**) and east (**d**) of the island point towards it. The inset in **c** shows that north of the island there is no predominant direction for  $T_x$ . Scale bar, 100  $\mu\text{m}$ .