

These magnetic photonic crystal wrappers offer an intriguing combination of ease of handling, independence of droplet size, potential for *in situ* analysis and spectral bar-coding. Porous silicon is a highly versatile and straightforward medium, but it remains to be seen if specificity and recognition elements can be successfully incorporated onto the surfaces of the porous silicon, while keeping the appropriate hydrophobic/hydrophilic balance for self-assembly. Judicious choice of surface chemistries and terminations may deliver the promise of this new manipulation technique making it a standard part of future lab-on-chip systems.

References

1. Aussillous, P. & Quere, D. *Nature* **411**, 924–927 (2001).
2. Vilknier, T., Janasek, D. & Manz, A. *Anal. Chem.* **76**, 3373–3386 (2004).
3. Colyer, C. L., Tang, T., Chiem, N. & Harrison, D. J. *Electrophoresis* **18**, 1733–1741 (1997).
4. He, B., Burke, B. J., Zhang, X., Zhang, R. & Regnier, F. E. *Anal. Chem.* **73**, 1942–1947 (2001).
5. Stroock, A. D. & Whitesides, G. M. *Acc. Chem. Res.* **36**, 597–604 (2003).
6. Dorvee, J. R., Derfus, A. M., Bhatia, S. N. & Sailor, M. *Nature Mater.* **3**, 896–899 (2004).
7. Nagarajan, R. *Langmuir* **18**, 31–38 (2002).
8. Link, J. R. & Sailor, M. J. *Proc. Nat. Acad. Sci.* **100**, 10607–10610 (2003).
9. Schmedake, T. A., Cunin, F., Link, J. R. & Sailor, M. J. *Adv. Mater.* **14**, 1270–1272 (2002).
10. Rack, J. J., McCleskey, T. M. & Birnbaum, E. R. *J. Phys. Chem. B.* **106**, 632–636 (2002).

MAGNETOELECTRICS

A new route to magnetic ferroelectrics

Materials that exhibit both ferromagnetism and ferroelectricity could be useful, but they are unfortunately very rare. Could a new proposal for combining the two properties point the way forward?

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Materials that are simultaneously ferroelectric and ferromagnetic are gaining more and more attention within the scientific community. Such magnetoelectric multiferroics are an example of the broader class of multifunctional or smart materials that combine several useful properties in the same substance to produce new phenomena that are more

than just the sum of the individual parts. For example, one can envisage a coupling between ferroelectric and ferromagnetic properties that could lead to electric-field-switchable magnetization or vice versa. Such coupling would lead to totally new possibilities in the design of data-storage devices, in addition to revealing fascinating new basic physics. Dmitry Efremov and colleagues have now proposed an entirely new route to combining ferromagnetism and ferroelectricity in a single material¹. Their proposal is exciting because very few magnetoelectric multiferroics exist.

In fact, the mechanism driving the ferroelectricity in typical perovskite ferroelectrics such as BaTiO_3

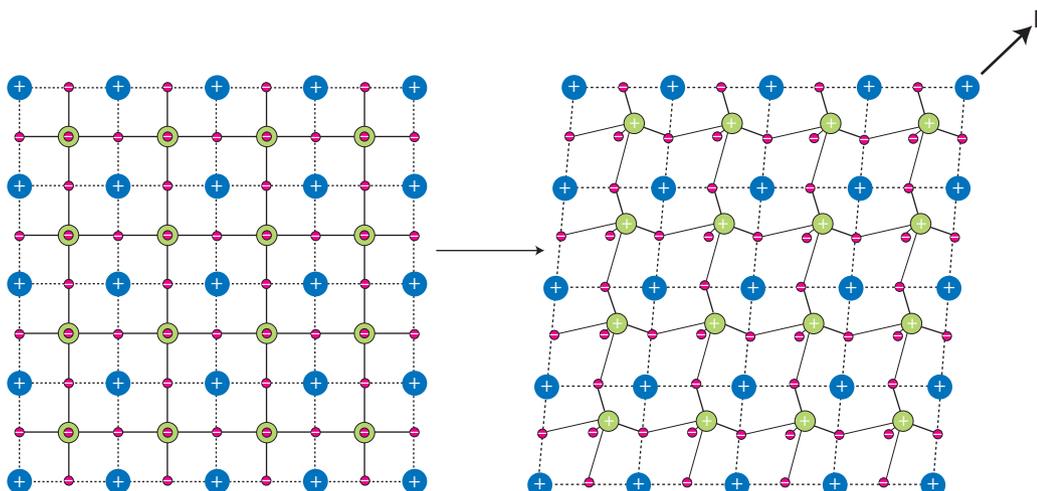
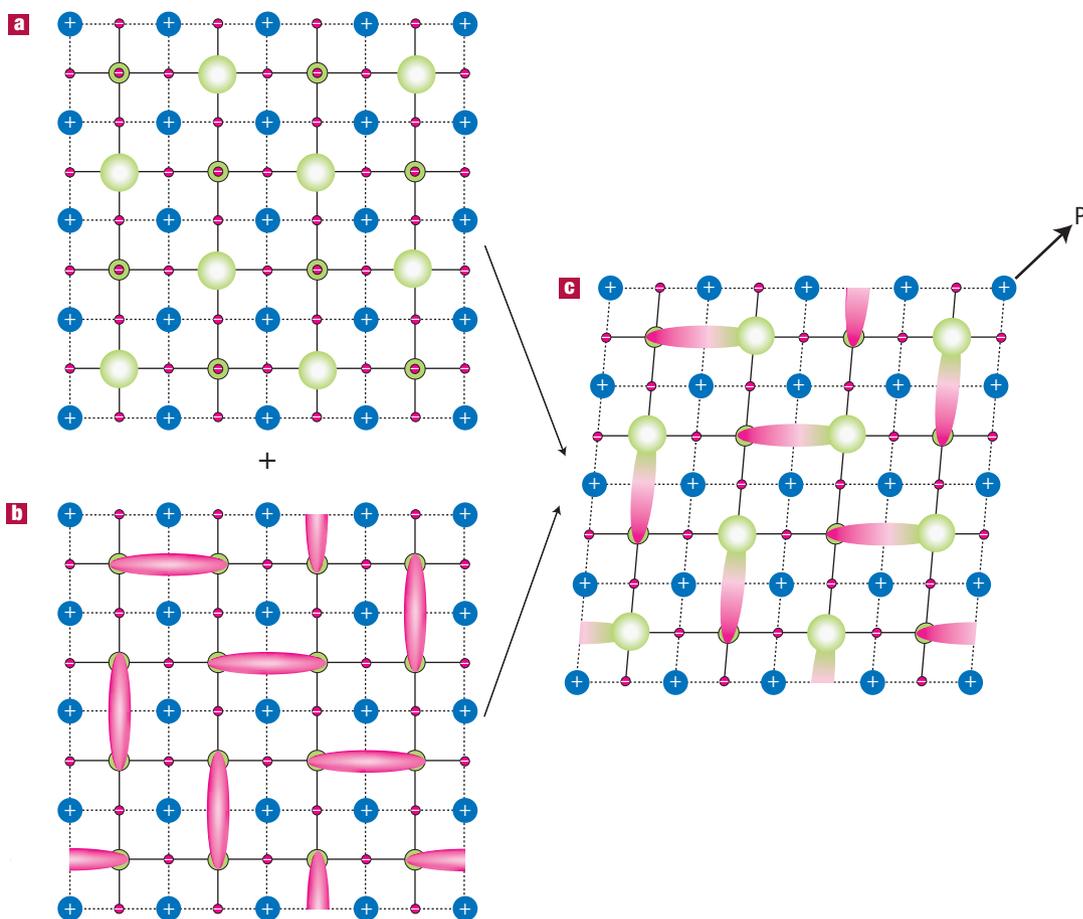


Figure 1 Ferroelectricity in typical perovskite manganites, such as BaTiO_3 . The green Ti ion is shifted away from its position in the centre of the (pink) oxygen octahedra. This creates a ferroelectric polarization (P), but is incompatible with any spontaneous magnetic moment.

Figure 2 Models of charge ordering in doped perovskite-structured manganites. **a**, Mn- or site-centred ordering, in which formally 3+ and 4+ Mn ions (green) orbitally order in a checkerboard pattern. The additional charge (green circles) is localized on the Mn sites. **b**, The bond-ordering model proposed in ref. 7, in which the Mn sites have equal charge and the variation in charge is localized on the Mn–Mn bonds (pink ellipses). **c**, The intermediate state proposed by Efremov and colleagues⁸ combines both Mn-centred and bond-centred ordering, and leads to ferroelectric polarization.



or KNbO_3 is incompatible with the existence of a spontaneous magnetic moment². The Ti ion in BaTiO_3 is shifted from its position in the ideal perovskite structure (the centre of its surrounding oxygen octahedron) towards the corner of its unit cell (Fig. 1), creating an electric polarization characteristic of the ferroelectric state. This off-centring is stabilized by energy-lowering covalent bond formation, in which charge transfers from the filled oxygen 2p orbitals into the d states of the transition metal ion, which must be empty for this mechanism to be favourable. On the other hand, a partly filled d shell is necessary for magnetism to occur in transition metal ions. Therefore, alternative mechanisms for off-centring are required in magnetic ferroelectrics, such as the stereochemical activity of the Bi lone pair in Bi-based compounds BiMnO_3 and BiFeO_3 (ref. 2), geometric ferroelectricity in YMnO_3 (ref. 3), or the recently reported ferroelectricity driven by magnetoelastically induced lattice modulations in rare-earth manganites such as TbMnO_3 , DyMnO_3 (ref. 4) and TbMn_2O_5 (ref. 5).

The mechanism proposed by Efremov and colleagues is entirely new, and relies on the concept of charge ordering in doped perovskite-structure manganites. When LaMnO_3 (or related compounds in which the charge on the Mn ions is formally 3+) and CaMnO_3 (in which the Mn charge is formally 4+) are alloyed, the resulting arrangement of Mn^{3+} and Mn^{4+} ions can be ordered; this is called charge ordering.

Because the oxygen octahedron surrounding a formally Mn^{3+} ion is elongated along one axis, whereas a Mn^{4+} ion should have ideal octahedral surroundings, there is a strong interplay between the arrangement of electronic charge in the atomic orbitals and the resulting structural symmetry. Recently there has been active debate over the validity of the traditional picture⁶ in which formally 3+ and 4+ Mn ions orbitally order in a checkerboard arrangement with so-called CE-type antiferromagnetism (Efremov *et al.* call this site-centred ordering, Fig. 2a). An alternative model of ferromagnetic Mn–Mn dimers (the bond-ordering model of Efremov *et al.* Fig. 2b) has been predicted for $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (ref. 7) and reported for $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$ (ref. 8). In their work, Efremov and colleagues propose an intermediate state, a kind of superposition of these two different charge-ordering patterns, and show that it leads to local dipole moments that add up to a macroscopic ferroelectric polarization (Fig. 2c). Moreover, they show theoretically that such a superposition can be stable at CaMnO_3 concentrations between 40 and 50%. Because the charge ordering in these systems is intimately coupled with the magnetic ordering, the proposed mechanism for ferroelectricity not only allows the simultaneous development of magnetic order, but actually requires it. This should lead to magnetoelectrics with a strong coupling between the electric and magnetic order parameters, a prerequisite for many potential applications.

Some very recent neutron diffraction studies (E. E. Rodriguez, Th. Proffen, A. Llobet, J. J. Rhyne & J. F. Mitchell, manuscript in preparation) lend additional support for this new model. Using combined Rietveld and pair distribution function analyses, the neutron work extracts the most detailed map to date of the atomic positions in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. In addition to providing convincing support for the CE structure (although with much smaller charge alterations on the Mn ions than the naïve $3+/4+$ picture), it confirms an earlier suggestion that distortions of the oxygen octahedra occur around the formally $4+$ Mn ions⁹. These distortions create local dipole moments. In $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, adjacent dipole moments point in opposite directions so there is no overall electric polarization. However, for compositions away from 50% CaMnO_3 , complete cancellation should not be expected, and a net polarization could result.

Unfortunately, these proposed charge-ordered multiferroics are unlikely to be of immediate practical use in terms of device applications. The electric polarization is predicted to be very small and the magnetic ordering is essentially antiferromagnetic. Also, the electric and magnetic ordering temperatures of the proposed systems will probably be far below room temperature. Nonetheless, such an alternative route to ferroelectricity, which is necessarily strongly interwoven with the associated magnetic ordering, is a very exciting concept that will surely stimulate further research towards practical magnetoelectric multiferroics.

References

1. Efremov, D. V., van den Brink, J. & Khomskii, D. *Nature Mater.* **3**, 853–856 (2004).
2. Hill, N. A. *Annu. Rev. Mater. Res.* **32**, 1–37 (2002).
3. van Aken, B. B. *et al. Nature Mater.* **3**, 164–170 (2004).
4. Kimura, T. *et al. Nature* **426**, 55–58 (2003).
5. Hur, N. *et al. Nature* **429**, 392–395 (2004).
6. Radaelli, P. G. *et al. Phys. Rev. B* **55**, 3015–3023 (1997).
7. Ferrari, V., Towler, M. & Littlewood, P. B. *Phys. Rev. Lett.* **91**, 227202 (2003).
8. Daoud-Aladine, A., Rodriguez-Carvajal, J., Pinsard-Gaudart, L., Fernandez-Diaz, M. T. & Revcolevschi, A. *Phys. Rev. Lett.* **89**, 097205 (2002).
9. Garcia, J. *et al. J. Phys. Condens. Matter* **13**, 3243–3256 (2001).

MATERIAL WITNESS

Watching paint dry

“As a picture ages, and the paint dries out — it takes about fifty years — it cracks in a certain pattern. What we call the craquelure.” In Robertson Davies’ novel *What’s Bred In The Bone*, Francis Cornish is learning the fine points of art forgery from an expert named Saraceni. They place anonymous old portraits, freshly repainted to show grander (and more valuable) subjects, into a furnace. “After about fifteen minutes of slow baking they emerged with, sure enough, tiny hairlines that satisfied the Meister.”



Saraceni knew his business. Some forgers have been considerably less sophisticated; they have even been known to paint on a fine web of craquelure by hand — a deception that might fool the eye of a careless buyer but which would be immediately obvious under a magnifying glass.

Craquelure is a subtle fingerprint of authenticity. Its precise structure may vary according to where the picture was painted — there are French, Italian, Dutch and Flemish ‘styles’ of craquelure. And it provides a record of the treatment the painting has received over the course of its lifetime: the handling, transportation and changes in ambient environment.

This web of cracks provides a non-destructive means of analysing the artist’s materials and techniques. The features of the pattern can reveal the nature of the support (canvas or wood) and of the white undercoat or ‘ground’ (typically gypsum or chalk, bound with glue or oil). For example, many late-medieval altarpieces were painted on poplar, an unstable wood prone to shrinkage or swelling. That’s why a lot of effort has gone into developing methods for digitally scanning paintings to classify the craquelure pattern.

It’s of paramount importance, then, to know how cracking of paint surfaces happens in the first place. Although poor handling can wreak havoc — Titian’s *Bacchus and Ariadne* was twice removed from its wooden support and rolled up — craquelure is also an unavoidable consequence of the slow drying of paint. So a paper by Wai Peng Lee and Alexander Routh (*Langmuir* **20**, 9885; 2004) which posits a new mechanism for cracking in thin films ought to be of considerable interest to art conservators and historians.

The standard idea is that, as the film dries and contracts, the spacing of cracks is determined by a balance between the elastic energy released and the cost of rupturing the film and creating new surfaces. This suggests that the average size of the fragments is proportional to the film thickness. But Lee and Routh present evidence that cracking may instead have a hydrodynamic origin, governed by the capillary pressure set up due to depletion of the solvent at the drying front.

This introduces a new length-scale to the crack spacing, which has specific power-law relationships to the film thickness t (varying as $t^{0.8}$), the evaporation rate and the size of the particles in the film (the pigment particles in paint, say). The ‘signature’ of craquelure — the characteristic size of the cracks — might then encode revealing aspects of the painter’s technique, such as how thinly he mixed his paints or how the works were stored as they dried.

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