

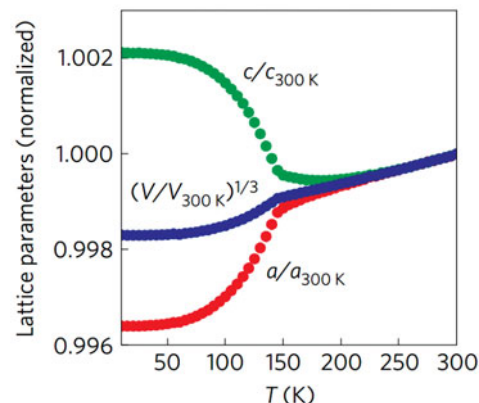
Ferroelectric-like phase transition observed in a metal

The phenomenon of ferroelectricity, in which a compound exhibits a spontaneous electric polarization, is generally thought to be incompatible with metallicity. This seems intuitive, since unbound carriers would quickly act to screen any polarization in a metal. In a strange twist, researchers Youguo Shi of the National Institute for Materials Science in Ibaraki, Japan, and co-workers from China, Japan, and the United Kingdom, now report a ferroelectric-like transition in metallic LiOsO_3 at 140 K. Their results open the door to an entirely new class of materials and shed light on fundamental electron behavior in ferroelectrics.

Writing in the November issue of *Nature Materials* (DOI: 10.1038/NMAT3754; p. 1024), the researchers describe structure refinement studies of

rhombohedral LiOsO_3 . Using neutron powder diffraction, they find that this compound forms a LiNbO_3 -type crystal structure; at room temperature, it can be described by a centrosymmetric $R\bar{3}c$ space group, which is not compatible with ferroelectricity. However, upon cooling below 140 K, the structure undergoes a phase transition to a noncentrosymmetric $R3c$ space group, which is compatible with ferroelectricity. The researchers confirmed this symmetry change using convergent-beam electron diffraction.

Interestingly, they find that the material remains a metal through the phase change, and they find no associated change in magnetic behavior across the phase transition. This suggests that the transition to ferroelectric behavior in this compound is driven by a displacive, order-disorder-type transition, rather than collective electron motion. The group said that their study may guide other researchers as they seek to



Temperature dependence of the LaOsO_3 unit cell parameters as it undergoes a structural transition at 140 K. Refinement of this structure demonstrates a transition to a noncentrosymmetric space group. Reproduced with permission from *Nat. Mater.* **12** (2013), DOI: 10.1038/NMAT3754; p. 1024. © 2013 Macmillan Publishers Ltd.

understand high-temperature ferroelectric transitions in related LiNbO_3 and LiTaO_3 compounds.

Steven Spurgeon

Vanadium oxide metamaterial structure appears to cool as it heats

When an object is heated, it gets hotter and emits more thermal radiation, right? Well, not always. Researchers at Harvard University have developed a thin-film/substrate structure that emits decreasing amounts of thermal radiation when heated over the temperature range of 75–85°C. Viewing this process through an infrared camera, the object appears to be getting colder even though it is really heating up.

Mikhail Kats, a graduate student in the group of Federico Capasso at Harvard University, calls this phenomenon “a very unusual situation—almost pathological.” He explains that the amount of radiation emitted at all frequencies from an object at temperature T (Kelvin scale) is proportional to its emissivity times T^4 . “So the only way you can see the effect that we saw is if the emissivity goes down faster than T^4 goes up.” This is a huge change in

emissivity. The structure that shows such dramatic properties is a thin (150 nm) film of VO_2 on a sapphire substrate.

“Vanadium oxide is extremely special because the insulating and metallic phases have very different dielectric properties that give you these spectacular changes in the interaction with radiation over very small temperature windows,” said Shriram Ramanathan, a Harvard faculty member and co-author of the research published in the October–December 2013 issue of *Physical Review X* (DOI: 10.1103/PhysRevX.3.041004; 041004).

Scientists have long known that VO_2 undergoes an insulator-to-metal transition (IMT) at 67°C in the bulk material, and they are exploring this phase transition as an on/off switch for optical and electronic applications in thin-film form. But by observing the transition from insulator to metal slowly, in steps of 0.5°C, and in the particular configuration of a thin film of VO_2 on sapphire, Kats, Ramanathan, Capasso, and their colleagues were able to observe this unusual

negative differential thermal emittance phenomenon in great detail.

As the VO_2 thin-film/sapphire substrate heats up in the phase transition region, small islands of metal begin to form in the insulator matrix, forming what the researchers call a “naturally disordered metamaterial.” At one point in the phase transition, a lot of IR absorption is exhibited and hence a lot of emissivity, Kats said, while at a point further along in the phase change less IR absorption occurs and therefore less emissivity. Thin-film interference causes incoming infrared radiation to bounce back and forth between the VO_2 thin film and the sapphire substrate, making both components essential in causing the negative differential thermal emittance.

So instead of artificially combining a metal with an insulator in the manual construction of a metamaterial, the researchers have found a way to do this more naturally. “You don’t have to pattern very complicated features, and you don’t need to worry about mixing and matching composite materials,” Ramanathan said. “It’s