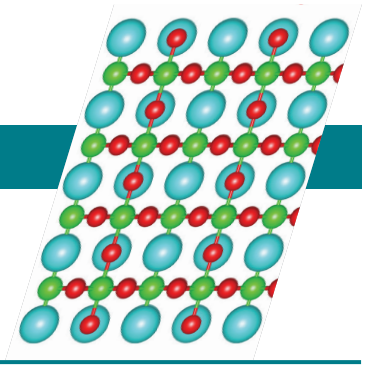
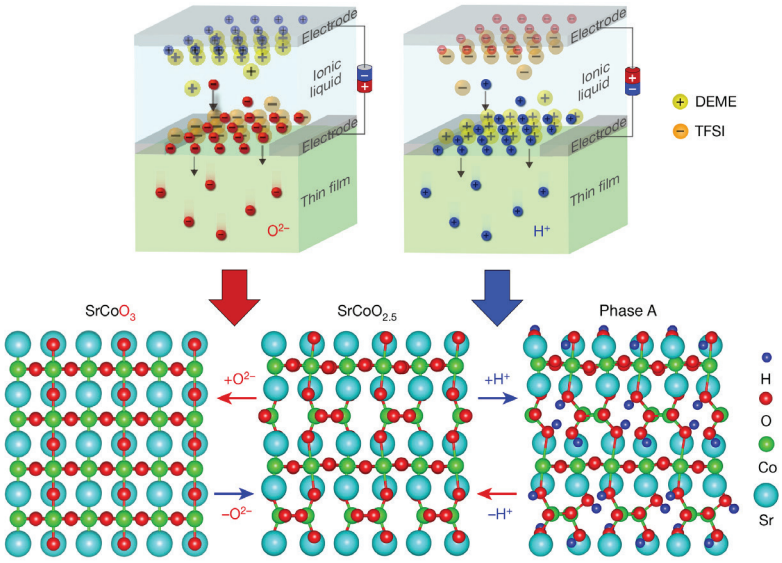


MATERIALS SCIENCES

# A Multifunctional Material with Electric-Field Control




**Electric-field control of phase transformations in thin-film $SrCoO_x$ by ion insertion. Three possible $SrCoO_x$ crystalline phases (obtained from first-principles calculations) are shown, including a hitherto unexplored phase, denoted "Phase A."**

With the flip of a switch, three distinct crystalline phases can be induced in one material, with each phase exhibiting very different electronic, magnetic, and optical properties. Materials capable of such versatility are desirable for a wide range of applications, from smart windows and batteries to spintronic devices. In this work, the properties of thin films of strontium cobalt oxide ($SrCoO_x$) were reversibly transformed through the insertion and extraction of oxygen and hydrogen ions, a process controlled by an applied electric field at room temperature. At the ALS, soft x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) experiments were used to verify and clarify the mechanism behind the phase transformations. Overall, the work represents a new approach to the manipulation of material properties that can be readily applied to a broad range of systems.

Earlier studies of ion-mediated phase transformations had focused mainly on the control of one ionic species at a time. In principle, however, increasing the number of ion species could allow access to multiple material phases and functional properties. Moreover, the use of an electric-field switch to drive ion diffusion would allow tunable control of the process and avoid the need for high-temperature thermal annealing. Such an approach had previously been reported for either oxygen or hydrogen ions, but control of both species in one system had not been explored until now.

In this work, the researchers focused on $SrCoO_x$, a simple material known to have at least two crystalline phases: a perovskite phase ($SrCoO_{3-\delta}$, where $\delta$ represents oxygen vacancies) and a "brownmillerite" phase ($SrCoO_{2.5}$). The well-ordered oxygen-vacancy channels in $SrCoO_{2.5}$ and multivalent cobalt ions were thought to provide favorable conditions for ion-mediated phase transformations.

Thin films of $SrCoO_{2.5}$ were coated with an ionic liquid—a gel-like layer containing dissociated organic ions (in this case, DEME and TFSI). A voltage

## One Material, Two Ions, Three Phases

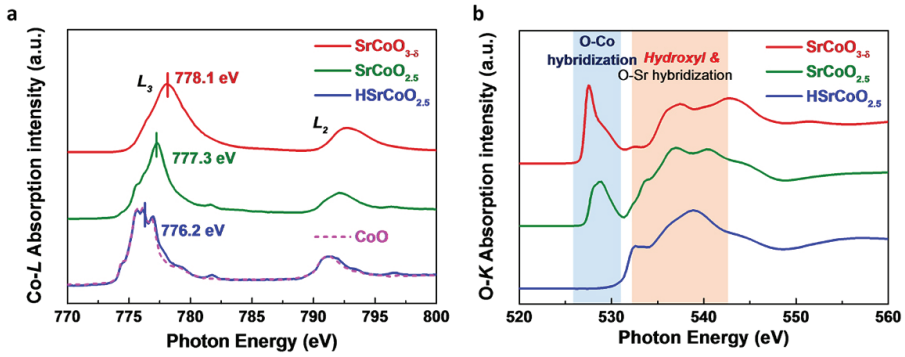
The trick of shuttling ions between electrodes is commonly used in electrochemical devices such as lithium-ion batteries and fuel cells to balance charges or feed chemical reactions. It's also used in "electrochromic" devices such as dimmable windows and mirrors, in which optical properties (transparency, color, or reflectivity) can be controlled by an applied voltage. So far, however, the shuttled particles have been of a single type: lithium ions in rechargeable batteries, for example, or hydrogen ions in fuel cells.

In this work, Lu et al. have discovered a very simple way to propel two types of ions in a single material, resulting in three distinct material phases with properties that can thus be switched on or off. These include electrochromic effects covering the spectrum from infrared through visible light (applicable to smart windows, heating/cooling), resistivity covering six orders of magnitude (relevant to resistive random-access memory), and changes in magnetic ground state (useful for magnetoelectric and spintronic devices). Given the incredible rate at which "new materials" are discovered these days and the simplicity of this approach, we will no doubt be seeing more examples and applications.

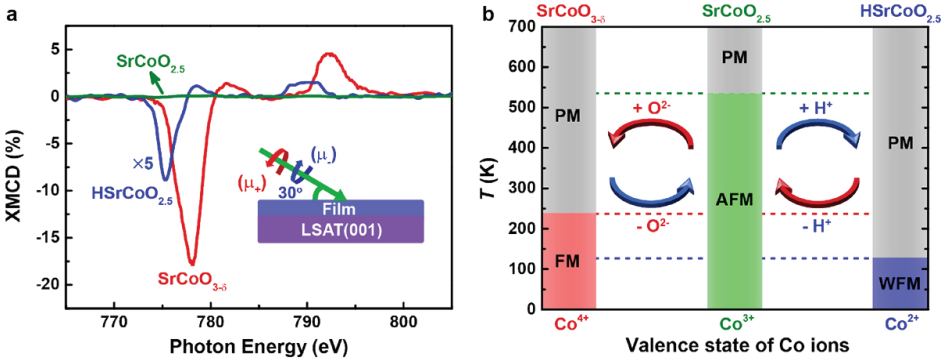
applied across the ionic liquid polarized it and drove either oxygen or hydrogen ions (produced by electrolysis of water in the ionic liquid) into the $SrCoO_{2.5}$. Detailed in situ analyses indicated that the $SrCoO_{2.5}$ reversibly transformed into two other nonvolatile phases as a function of voltage: $SrCoO_{3-\delta}$ upon insertion of $O^{2-}$, and an unidentified state (Phase A) upon insertion of $H^{+}$.

To identify Phase A, the researchers performed XAS measurements of cobalt L-edges and oxygen K-edges at ALS Beamline 8.0.1, as well as at synchrotron facilities in Beijing, Shanghai, and Hiroshima. The cobalt spectra correspond directly to cobalt 3*d* valence states, and a straightforward comparison of the Phase A spectrum with a reference CoO spectrum confirms that the cobalt cations in Phase A are dominated by the +2 oxidation state. Meanwhile, the Phase A oxygen spectrum displays the total suppression of oxygen–cobalt hybridization. This narrowed the identity of Phase A to either $SrCoO_2$ or $HSrCoO_{2.5}$. Subsequently, based on the above results and a series of other characterizations (scanning transmission electron microscopy, secondary ion mass spectroscopy, and theoretical calculations), Phase A was identified as $HSrCoO_{2.5}$.

The researchers also brought their samples to ALS Beamline 6.3.1 to perform XMCD measurements. Clear signals for $SrCoO_{3-\delta}$ and $HSrCoO_{2.5}$ and a nondetectable signal for $SrCoO_{2.5}$ provided solid evidence for changes in magnetic ground states. The rich magnetic phase diagram shows that at room temperature, the transformation between $SrCoO_{2.5}$ and the other phases is equivalent to turning the antiferromagnetic state on or off. Thus, a new and practical way to achieve electric-field control of antiferromagnetism has been identified. In general, the use of ion transport to change a material's lattice, orbital, and spin characteristics is very simple and can be readily applied to a wide variety novel materials with exotic functionalities, opening up exciting possibilities for future discoveries.




**Soft x-ray absorption spectra of (a) cobalt L-edges and (b) oxygen K-edges for the three phases: $SrCoO_{3-\delta}$ (red), $SrCoO_{2.5}$ (green), and "Phase A"—ultimately identified as $HSrCoO_{2.5}$ (blue).**




**(a) XMCD spectra at cobalt L-edges. The experimental configuration is shown in the inset. (b) Phase diagram of magnetoelectric effects in different temperature regions. PM: paramagnetism; FM: ferromagnetism; AFM: antiferromagnetism; WFM: weak ferromagnetism.**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