Converting a layer perovskite into a non-defective higher-order homologue: topochemical synthesis of Eu$_2$CaTi$_2$O$_7$

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Topochemical reduction of CaEu$_2$Ti$_2$O$_8$, a new $n = 1$ mixed Ruddlesden–Popper/Dion–Jacobson phase prepared by divalent ion-exchange of NaEuTiO$_4$, yields the non-defective $n = 2$ Ruddlesden–Popper phase Eu$_2$CaTi$_2$O$_7$.

Transition-metal oxides that possess the perovskite structure are important materials that exhibit a wide range of useful properties, including ferroelectricity, superconductivity, colossal magnetoresistance, and catalytic activity. Layered perovskites that belong to the Ruddlesden–Popper, $\text{A}^n\text{B}^{n+1}\text{O}_{3n+1}$, and Dion–Jacobson, $\text{A}^{[n+1]}\text{B}_n\text{O}_{3n+1}$, families are known to possess similar properties, which often depend sensitively on the thickness of the perovskite block. As an example, the Curie temperature and magnetoresistive effects vary with increasing $n$ (the number of octahedra that stack in the perovskite block) in the Ruddlesden–Popper manganese series $\text{(La, Sr)}_{n-1}\text{Mn}_n\text{O}_{3n+1}$.

Many layered perovskites also undergo interlayer ion-exchange reactions, so they are ideal precursors to new metastable materials. For example, Dion–Jacobson phases that contain divalent interlayer cations, as well as perovskite/copper-halide and vanadate intergrowths, can be synthesized at relatively low ($< 500^\circ\text{C}$) temperatures from layered perovskite precursors. Similarly, A-site defective three-dimensional perovskites can be synthesized by dehydrating proton-exchanged Ruddlesden–Popper phases, and non-defective perovskites can be synthesized by topochemically reducing the appropriate Dion–Jacobson precursors. In general, it is not possible to make these same ordered phases by direct, high temperature synthesis.

Since the electronic and magnetic properties of layered perovskites vary with the perovskite block thickness, the ability to convert among similar homologues in a series is a potentially useful tool for fine-tuning their properties. Recently, Gopalakrishnan and coworkers converted HLnTiO$_4$ (Ln = La, Nd, Sm, Gd), a family of $n = 1$ Ruddlesden–Popper phases, into Ln$_2$TiO$_3$, an A-site defective $n = 2$ Ruddlesden–Popper series, by carefully dehydrating the $n = 1$ precursor. The unique ordering of the lanthanide cations and the protons in HLnTiO$_4$ (or alkali cations in the parent phase NaLnTiO$_4$) in alternate rows imparts interlayer reactivity only to every other layer, which is necessary for the conversion from an $n = 1$ to an $n = 2$ phase.

Topochemical reduction is a powerful alternative to dehydration, because it can create non-defective condensed structures. One can envision a similar conversion reaction that transforms NaLnTiO$_4$ into a non-defective $n = 2$ phase (Fig. 1). NaEuTiO$_4$, the $n = 1$ Ruddlesden–Popper parent phase, contains the easily reducible Eu$^{3+}$ cation, which converts to Eu$^{2+}$ when heated in hydrogen. The concomitant loss of oxygen from the lattice is necessary for the topochemical collapse to occur. NaEuTiO$_4$ contains twice the number of interlayer Na$^+$ cations than are needed to fill the A-sites of a perovskite block, so divalent ion exchange must first be done to give the correct stoichiometry of interlayer cations, forming A$^{n+1}$EuTiO$_4$. Subsequent reduction can collapse the perovskite layers over the divalent A-site cations, resulting in the $n = 2$ Ruddlesden–Popper phase A$^{n+1}$Eu$_2$Ti$_2$O$_7$ (or Eu$_2$A$^{n+1}$Ti$_2$O$_7$).

NaEuTiO$_4$ was synthesized as reported in the literature and reacted with 1 M Ca(NO$_3$)$_2$ for 1 week at 45 $^\circ\text{C}$ to form Ca$_x$Eu$_{1-x}$TiO$_4$ (or CaEu$_2$Ti$_2$O$_8$). Energy-dispersive X-ray analysis (EDAX) confirms that 85% of the sodium is replaced by calcium, which is consistent with the efficiencies of other aqueous and non-aqueous divalent ion-exchanges. (Attempts at ion exchange using Sr$^{2+}$ and Ba$^{2+}$ resulted in significantly less exchange, presumably due to the size mismatch between Na$^+$ and the large divalent cations.)

Fig. 2(b) shows the X-ray diffraction patterns for (a) NaEuTiO$_4$, (b) CaEu$_2$Ti$_2$O$_8$, and (c) Eu$_2$CaTi$_2$O$_7$. Fig. 1 Topochemical transformation of an $n = 1$ Ruddlesden–Popper phase into a non-defective $n = 2$ phase, which includes (a) NaEuTiO$_4$, (b) CaEu$_2$Ti$_2$O$_8$, and (c) Eu$_2$CaTi$_2$O$_7$.

Fig. 2 XRD patterns for (a) NaEuTiO$_4$, (b) CaEu$_2$Ti$_2$O$_8$, and (c) Eu$_2$CaTi$_2$O$_7$.
diffraction (XRD)\textsuperscript{[12]} pattern for CaEu\textsubscript{2}Ti\textsubscript{2}O\textsubscript{8}. The proposed structural model of CaEu\textsubscript{2}Ti\textsubscript{2}O\textsubscript{8} contains alternating staggered and eclipsed layers, as shown in Fig. 1b. Thus, CaEu\textsubscript{2}Ti\textsubscript{2}O\textsubscript{8} can be considered as a mixed n = 1 Ruddlesden–Popper/Dion–Jacobson phase. After drying for 1 h at 400 °C to remove interlayer water, CaEu\textsubscript{2}Ti\textsubscript{2}O\textsubscript{8} was indexed on a tetragonal unit cell (Table 1) with a doubled c-axis due to the staggered alternate layers. A pyrochlore impurity is identified in Fig. 2(b), which is consistent with the expected increase from the eclipsed perovskite slabs. Likewise, the decrease in the layer spacing for Eu\textsubscript{2}CaTi\textsubscript{2}O\textsubscript{7} (ca. 12.1 Å) relative to Eu\textsubscript{2}CaTi\textsubscript{2}O\textsubscript{6} can only be explained by the bridging of octahedra from the perovskite slabs. Reduction without topochimical collapse (i.e., an oxygen-deficient n = 1 phase) would result in a larger layer spacing than Eu\textsubscript{2}CaTi\textsubscript{2}O\textsubscript{7} due to the larger Eu\textsuperscript{2+} cation, so the (002) peak would have shifted to lower angles instead of higher angles.

While the topochimical conversion of an n = 1 to a defective n = 2 Ruddlesden–Popper phase has already been demonstrated,\textsuperscript{[2]} this work represents the first route to a non-defective higher order layered perovskite. This kind of topochimical reaction could have interesting implications for fine-tuning the properties of carefully designed magnetic and ferroic phases. Additionally, it is an important extension of the topochimical reduction reaction that converts layered perovskites into three-dimensional perovskites, since it involves lower-order Ruddlesden–Popper homologues and results in a two-dimensionally bonded product. Indeed, this work demonstrates that topochimical reduction can be viewed as a generalized approach for the rational synthesis of metastable non-defective perovskites.

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Notes and references

11 EDAX data was recorded using a JEOL-JSM 5400 scanning electron microscope at the Electron Microscope Facility for the Life Sciences in the Biotechnology Institute at the Pennsylvania State University.
12 X-Ray diffraction patterns were obtained on a Philips X-Pert MPO diffractometer using monocrystallized Cu-Kα (λ = 1.5418 Å) radiation.