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Converting a layer perovskite into a non-defective higher-order homologue: topochemical synthesis of $Eu_2CaTi_2O_7$

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Topochemical reduction of $CaEu_2Ti_2O_8$, 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 $Eu_2CaTi_2O_7$.

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,[1] $A_2[A'_{n-1}B_nO_{3n+1}]$, and Dion–Jacobson,[2] $A[A'_{n-1}B_nO_{3n+1}]$, 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 manganate series $(La,Sr)_{n+1}Mn_nO_{3n+1}$.[3]

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,[4] as well as perovskite/copper-halide[5] and vanadate[6] intergrowths, can be synthesized at relatively low (< 500 °C) temperatures from layered perovskite precursors. Similarly, A-site defective three-dimensional perovskites can be synthesized by dehydrating proton-exchanged Ruddlesden–Popper phases,[7] and non-defective perovskites can be synthesized by topochemically reducing the appropriate Dion–Jacobson precursors.[8] 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 $Ln_2\square Ti_2O_7$, an A-site defective $n = 2$ Ruddlesden–Popper series, by carefully dehydrating the $n = 1$ precursor.[9] 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 $A^{II}_{0.5}EuTiO_4$. Subsequent reduction can collapse the perovskite layers over the divalent A-site cations, resulting in the $n = 2$ Ruddlesden–Popper phase $A^{II}_{0.5}EuTiO_{3.5}$ (or $Eu_2A^{II}Ti_2O_7$).

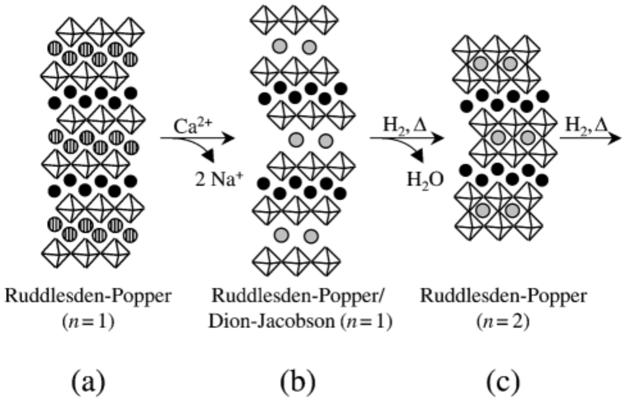

Fig. 1 Topochemical transformation of an $n = 1$ Ruddlesden–Popper phase into a non-defective $n = 2$ phase, which includes (a) $NaEuTiO_4$, (b) $CaEu_2Ti_2O_8$, and (c) $Eu_2CaTi_2O_7$.

$NaEuTiO_4$ was synthesized as reported in the literature[10] and reacted with 1 M $Ca(NO_3)_2$ for 1 week at 45 °C to form $Ca_{0.5}EuTiO_4$ (or $CaEu_2Ti_2O_8$). Energy-dispersive X-ray analysis (EDAX)[11] 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.[4,8] (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

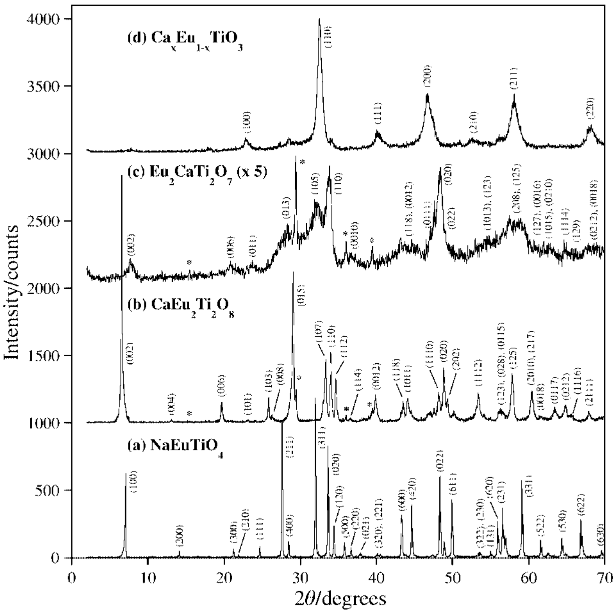

Fig. 2 XRD patterns for (a) $NaEuTiO_4$, (b) $CaEu_2Ti_2O_8$ formed by divalent ion exchange of $NaEuTiO_4$, (c) $Eu_2CaTi_2O_7$ synthesized under H_2 at 650 °C, and (d) $Ca_xEu_{1-x}TiO_3$, the thermodynamically stable product formed at 800 °C. A pyrochlore impurity is labeled with an asterisk in (b) and (c). Note that the vertical scale in (c) is expanded by a factor of 5.

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Table 1 Lattice parameters and selected data for layered perovskites

Compound	Description	Colour	Space group	Lattice parameters/Å
$NaEuTiO_4$	n = 1 RP	White	*Pbcm*[a]	a = 12.5471(2) b = 5.3307(2) c = 5.3328(1)
$CaEu_2Ti_2O_8$	n = 1 RP/DJ	White	*I*4/*mmm*	a = 3.7302(2) c = 27.125(3)
$Eu_2CaTi_2O_7$	n = 2 RP	Black	*I*4/*mmm*	a = 3.78(2) c = 24.2(3)

[a] The space group is taken from ref. 10.

diffraction (XRD)[12] pattern for $CaEu_2Ti_2O_8$. The proposed structural model of $CaEu_2Ti_2O_8$ contains alternating staggered and eclipsed layers, as shown in Fig. 1b. Thus, $CaEu_2Ti_2O_8$ 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, $CaEu_2Ti_2O_8$ 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), and $CaEu_2Ti_2O_8$ decomposes completely to CaO and pyrochlore-type $Eu_2Ti_2O_7$ upon further heating in air.

Interestingly, a related compound, $Ca_{0.43}Na_{0.14}LaTiO_4$ (prepared by Wiley and coworkers by divalent ion-exchange in anhydrous calcium nitrate),[4b] is also a mixed $n = 1$ Ruddlesden–Popper/Dion–Jacobson phase, but unlike $CaEu_2Ti_2O_8$, each layer remains staggered as in the parent $NaLaTiO_4$ phase. In this case, as well as for $ZnEu_2Ti_3O_{10}$ reported earlier,[8] aqueous ion exchanges give the perovskite sheets lateral mobility to adopt an eclipsed conformation, while ion-exchanges using anhydrous nitrates or molten chlorides retain the staggered symmetry of the parent crystal.

When $CaEu_2Ti_2O_8$ is heated in hydrogen to reduce Eu^{3+} to Eu^{2+} and remove oxygen from the lattice, the perovskite layers above and below the Ca^{2+} cations collapse, encasing Ca^{2+} in the A-sites of the two bridged perovskite slabs to form the $n = 2$ Ruddlesden–Popper phase $CaEu_2Ti_2O_7$, or $Eu_2CaTi_2O_7$ (written in the traditional form to emphasize the location of Eu^{2+} in the interlayer). Unfortunately, $Eu_2CaTi_2O_7$ [Fig. 2(c)] is a low temperature phase, since it decomposes to perovskite-type $Ca_xEu_{1-x}TiO_3$ [Fig. 2(d)] when heated above 650 °C in hydrogen. (While Eu^{3+} fits well in the rocksalt-type interlayer sites, Eu^{2+} is too large to adopt the same coordination, so the reduced structure is unstable.) As with the metastable $Ln_2\square Ti_2O_7$ series, a short reaction time is needed in order to isolate the topochemical product. Thus, $Eu_2CaTi_2O_7$ has a limited stability window and is formed only by heating $CaEu_2Ti_2O_8$ for 30 min in hydrogen at 625 °C. Below 600 °C, the reduction does not occur.

The XRD pattern of $Eu_2CaTi_2O_7$ is shown in Fig. 2(c). A highly crystalline pyrochlore impurity, which was a minor impurity phase in Fig. 2(b), remains unchanged upon heating in hydrogen. Thus, Fig. 2(c) can be indexed as a mixture of phases—a crystalline $Ca_xEu_{2-x}Ti_2O_7$ pyrochlore phase, and the n = 2 Ruddlesden–Popper phase $Eu_2CaTi_2O_7$, which is characterized by much broader peaks. The broad peaks and low intensity indicate that the product is not very crystalline and that the topochemical collapse introduces disorder over large regions. Although broad, all of the peaks can be indexed to a tetragonal unit cell consistent with that of an $n = 2$ Ruddlesden–Popper phase (Table 1). $Eu_2CaTi_2O_7$ appears to be isostructural with $K_2SrTa_2O_7$.[13] The a axis lattice parameter of $Eu_2CaTi_2O_7$ is contracted relative to $K_2SrTa_2O_7$ (a = 3.9768, c = 21.7062 Å, from ref. 13) and related n = 2 phases, while the c axis lattice parameter is significantly larger (Table 1), which is consistent with the size variations between Ti^{4+}/Ta^{5+} and Eu^{3+}/Eu^{2+}. The absence of a major peak around $2\theta = 41°$ in Fig. 2(c), which corresponds to the (111) cubic perovskite peak, indicates minimal decomposition to $Ca_xEu_{1-x}TiO_3$ (the thermodynamically stable phase upon further heating in hydrogen). Likewise, the presence of an intense low angle reflection, as well as higher-index peaks consistent with a tetragonal unit cell, indicates that a layered structure is retained.

The progression of low-angle XRD peaks for $NaEuTiO_4$, $CaEu_2Ti_2O_8$ and $Eu_2CaTi_2O_7$ (Fig. 2) shows the layer spacings expected for an n = 1 Ruddlesden–Popper phase, an n = 1 Ruddlesden–Popper/Dion–Jacobson intergrowth, and an n = 2 Ruddlesden–Popper phase, respectively. $CaEu_2Ti_2O_8$ has a larger layer spacing (13.56 Å) than $NaEuTiO_4$ (12.55 Å), which is consistent with the expected increase from the eclipsed perovskite slabs. Likewise, the decrease in the layer spacing for $Eu_2CaTi_2O_7$ (*ca.* 12.1 Å) relative to $CaEu_2Ti_2O_8$ can only be explained by the bridging of octahedra from the perovskite slabs. Reduction without topochemical collapse (*i.e.* an oxygen-deficient $n = 1$ phase) would result in a larger layer spacing than $CaEu_2Ti_2O_8$ (due to the larger Eu^{2+} cation), so the (002) peak would have shifted to lower angles instead of higher angles.

While the topochemical conversion of an $n = 1$ to a defective n = 2 Ruddlesden–Popper phase has already been demonstrated,[9] this work represents the first route to a non-defective higher order layered perovskite. This kind of topochemical 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 topochemical 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 topochemical reduction can be viewed as a generalized approach for the rational synthesis of metastable non-defective perovskites.

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