Topotactic transformation of single crystals: From perovskite to infinite-layer nickelates

Pascal Puphal1*, Yu-Mi Wu1, Katrin Fürsich1, Hangoo Lee1, Mohammad Pakdaman1, Jan A. N. Bruin1, Jürgen Nuss1, Y. Eren Suyolcu2, Peter A. van Aken1, Bernhard Keimer1, Masahiko Isobe1, Matthias Hepting1*

Topotactic transformations between related crystal structures are a powerful emerging route for the synthesis of novel quantum materials. Whereas most such “soft chemistry” experiments have been carried out on polycrystalline powders or thin films, the topotactic modification of single crystals, the gold standard for physical property measurements on quantum materials, has been studied only sparsely. Here, we report the topotactic reduction of La1−xCaNiO3 single crystals to La1−xCaNiO2+δ using CaH2 as the reducing agent. The transformation from the three-dimensional perovskite to the quasi–two-dimensional infinite-layer phase was thoroughly characterized by x-ray diffraction, electron microscopy, Raman spectroscopy, magnetometry, and electrical transport measurements. Our work demonstrates that the infinite-layer structure can be realized as a bulk phase in crystals with micrometer-sized single domains. The electronic properties of these specimens resemble those of epitaxial thin films rather than powders with similar compositions.

INTRODUCTION

Synthetic routes to materials in which anions are partially removed, inserted, or exchanged are rapidly gaining attention in solid-state physics and chemistry (1–3). In particular, soft chemistry topotactic reductions (4) of perovskite-related transition metal oxides have opened up possibilities to prepare entirely new families of functional electronic and magnetic materials. Prominent examples include the infinite-layer compounds SrFeO2 (5) and SrVO2H (6) obtained via targeted removal of oxygen from the parent perovskites SrFeO3 and SrVO3 using CaH2 as the reducing agent.

A breakthrough in the field was achieved recently with the discovery of superconductivity in infinite-layer nickelate thin films (7). More specifically, epitaxial films of Sr or Ca substituted RENiO2 (RE = La, Pr, and Nd) obtained via topotactic reduction of the perovskite phase show superconducting transitions below 9 to 15 K (7–12) and overdamped spin excitations with a bandwidth as large as 200 meV (13). These extraordinary properties attracted considerable interest because infinite-layer nickelates are isostructural to cuprate superconductors and were proposed to engender their electronic and magnetic structure (14). While the relationship between infinite-layer nickelates and cuprates is still an active field of research (13, 15–19), it was found that polycrystalline powders with similar compositions show insulating behavior and superconductivity remains elusive (20, 21). This raises the question of whether film-substrate interface effects, including epitaxial strain, polar reconstructions, and interfacial phonons, are prerequisites for the emergence of superconductivity in infinite-layer nickelates (22, 23).

However, intrinsic factors such as enhanced disorder and diminishing sizes of infinite-layer single domains in powder grains (24, 25) can possibly lead to physical properties distinct from the genuine bulk properties, which obscure a direct comparison between powders and thin films.

Thus, single-crystalline specimens with at least micrometer-sized single domains are highly desired to unveil the intrinsic properties of the infinite-layer phase of nickelates. Moreover, single crystals allow to take advantage of the application of complementary measurement techniques and can exhibit superior crystalline quality. Yet, synthesis and comprehensive spectroscopic characterization of macroscopic infinite-layer nickelate crystals have not been accomplished, which is also the case for most other topotactically reduced transition metal oxides (1, 4–6, 26–28).

A major challenge concerning the preparation of infinite-layer nickelate crystals, besides the highly invasive topotactic reduction, is the synthesis of the precursor perovskite phase RENiO3, which requires extreme oxidizing conditions to stabilize the Ni3+ valence state. This can be realized through high external oxygen gas pressure (29, 30) or hydrostatic pressure in a Belt-type apparatus while adding perchlorates as oxidizers (31). Similarly, salt flux mixtures and perchlorate oxidizers can be used under hydrostatic pressure and at high temperatures, which yields micrometer-sized RENiO3 single crystals (32–34). Millimeter-sized LaNiO3 (35) and PrNiO3 (36) crystals can be grown by the high-oxygen pressure optical floating zone (OFZ) method. However, OFZ-grown nickelate crystals might be prone to inclusions of higher-order Ruddlesden-Popper and oxygen-deficient phases (36–38). To date, the synthesis of Sr or Ca substituted RENiO3 single crystals has not been reported.

Here, we report the high-pressure growth of La1−xCaNiO3 single crystals using a 1000–metric ton press equipped with a Walker module. We obtained crystals with a typical size of 150 μm by 150 μm by 150 μm and Ca substitution levels of 10(5)% in the bulk and 16(3)% in proximity to the surface. The perovskite crystals were reduced to the infinite-layer phase La1−xCaNiO2+δ using CaH2 and the structural, electronic, and magnetic properties were characterized. Notably, local electron energy-loss spectroscopy (EELS) reveals close similarities between the electronic structures of our high-quality infinite-layer crystals and thin films. Moreover, we find that the metal-like electrical conductivity of the reduced

1Max Planck Institute for Solid State Research, Heisenbergstraße 1, 70569 Stuttgart, Germany. 2Department of Materials Science and Engineering, Cornell University, Ithaca, NY 14853, USA.
*Corresponding author. Email: puphal@fkf.mpg.de (P.P.); hepting@fkf.mpg.de (M.H.)
crystals is reminiscent of weakly hole-doped infinite-layer thin films, which is in stark contrast to previous results on powder samples.

**RESULTS AND DISCUSSION**

**High-pressure growth of Ca-substituted perovskite nickelates**

The substitution of the RE ion in RENiO$_3$ perovskite nickelates with a divalent ion, such as Sr or Ca, requires Ni to take on an oxidation state even higher than 3+. Thus, for the synthesis of the La$_{1-x}$Ca$_x$NiO$_3$ substitution series, we choose a strongly oxidizing environment using salt flux growth with a perchlorate oxidizer under external pressure from a multi-anvil press implemented in a Walker module (Fig. 1A), which is an established route for the synthesis of RENiO$_3$ crystals (32–34). To optimize the synthesis process of flux-grown crystals, the salt flux (white) and the nickelate precursor (black) were spatially separated (see Fig. 1B and Materials and Methods for details). The growth is carried out under an external temperature gradient intrinsic to the setup using a graphite heater and dependent on the size of the ampule. Because of the spatial separation of flux and precursor, a transport growth is realized in an external gradient, enabling the growth of relatively large single crystals with sizes limited predominantly by the durability of the crucible. Tests with several different ampule materials and thicknesses showed that Pt is the most suitable crucible material, although it dissolves slowly at the used temperatures (Fig. 1C). In particular, if the temperature exceeds a certain point, or the holding times are too long for the specific Pt foil thickness, then the flux can dissolve too much of the Pt ampule and the oxygen pressure is released, which results in the decay of any grown specimen. We found that sufficiently long holding times can be achieved with a Pt foil with a thickness of 50 μm. During heating, the underlying chemical processes can be monitored via a change in the external pressure curve (Fig. 1C). First, the flux mixture starts to melt, enabling the decay of the perchlorate. The following release of oxygen then leads to a slow oxidation of the nickelate. Second, at elevated temperatures around 1300°C, the nickelate is slowly dissolved and the transport growth starts. The dissolved nickelate crystallizes during the holding time at the top and bottom of the Pt ampule, as depicted in Fig. 1C, after which the ampule is quenched.

A secondary electron (SE) image of an as-grown crystal acquired with a scanning electron microscope (SEM) is shown in Fig. 1D. Characterization by energy-dispersive x-ray spectroscopy (EDS) (fig. S3) and single-crystal x-ray diffraction (XRD) indicates that the Ca substitution level in the obtained crystals is strongly reduced compared to the nominal level of 20 atomic % (at %), expected from the educts (see Materials and Methods for details). In more detail, our EDS analysis performed on a large number of crystals with sizes up to 200 μm shows that a nominal substitution level of 20 at % yields La$_{1-x}$Ca$_x$NiO$_3$ crystals with 0.06 ≤ x ≤ 0.16. Furthermore, we identify concentration gradients toward the center of the crystals (fig. S4) and slight variations of the substitution level among crystals from...
the same batch. In particular, we find that the average Ca substitution on as-grown crystal surfaces is \( x = 0.16(3) \), whereas cleaved surfaces, which are representative for the bulk of the crystals, exhibit \( x = 0.10(5) \) in average (see also fig. S4). Moreover, we determine the presence of CaO crystallites on the surface of some crystals with SEM-EDS (fig. S4) suggesting that the reduced Ca substitution level is associated with the challenges to stabilize a Ni\(^{3.2+} \) oxidation state. We emphasize that the agglomeration of CaO crystallites occurs only on the as-grown crystal surfaces and was not observed on cleaved surfaces, i.e., in the bulk of the crystals.

From single-crystal XRD (fig. 1E and fig. S1), we identify the crystallographic space group of as grown crystals as \( R5'c \) (#167), which is the same space group as reported for single crystalline and powder LaNiO\(_3\) (38, 39). The refined atomic coordinates and lattice parameters of an as-grown crystal with \( x = 0.06(2) \) are given in Table 1A. We note that the unit cell dimensions of the Ca-substituted perovskite crystals are slightly larger than those of OFZ-grown LaNiO\(_3\) crystals (35), despite the closely similar ionic radii of Ca\(^{2+}\) and La\(^{3+}\) (40). This variation could result from the different synthesis methods and/or different oxygen contents, although we did not detect any superstructure reflections in XRD (figs. S1 and S2), which are indicative of oxygen deficient phases, such as the La\(_2\)Ni\(_4\)O\(_{11}\) and La\(_2\)Ni\(_2\)O\(_x\) phases (37, 38).

**Topotactic reduction**

The next step after synthesis of high-quality Ca-substituted perovskite single crystals (Fig. 1, A to F) is the topotactic oxygen reduction (Fig. 1, G to I). Previously, the reduction process has been investigated in detail for nickelate thin films and polycrystalline powder samples using \( H_2 \) (25) or the reducing agents CaH\(_2\) or NaH (7–12, 20, 21, 24, 41).

Here, we used the CaH\(_2\) variant with spacial separation between reducing agent and sample. Several as-grown crystals were wrapped in aluminum foil and loaded into quartz tubes with approximately 600 mg of CaH\(_2\) powder, which were then evacuated to a high vacuum below \( 10^{-7} \) mbar and sealed to ampules with dimensions \( \phi_{\text{out}} = 1.7 \) mm, \( \phi_{\text{in}} = 1.5 \) mm, and \( h = 10 \) cm. We found that after 1 day of reduction at 300°C, the crystals transformed into an intermediate phase (likely the La\(_{1-x}\)Ca\(_x\)NiO\(_{2.5}\) phase). The subsequent reduction to the infinite-layer phase can be accomplished with a substantially longer reduction time of approximately 2 weeks. The optimal duration of the reduction is individual for each crystal and depends on details, such as crystal size, shape, and the Ca substitution level. Overall, we find that an extension of the 2-week time period by a few days did not induce obvious changes in crystals with \( 0.06 \leq x \leq 0.16 \) and sizes between 75 and 200 μm. However, we observed that substantially longer reduction times increase the brittleness of the crystals. After 4 weeks of reduction, crystals decompose into smaller fragments that mostly exhibit rectangular shapes and are only loosely attached to each other. The SEM-SE image in Fig. 1G displays a representative example for such an overreduced polycrystal. Figure 1H shows a reconstructed map of the \((h0l)\) planes from XRD on a crystal with \( x = 0.08(2) \) that was reduced for 2 weeks. The XRD data can be refined when assuming three orthogonal domains of the tetragonal space group \( P4/mmm \) (#123). Note that the notable differences in the XRD maps of the as-grown perovskite and the reduced crystal (Fig. 1, E and H) are due to the rhombohedral and tetragonal symmetries of the respective crystal lattices. The refined \( P4/mmm \) symmetry is the same as reported for polycrystalline LaNiO\(_3\) powder in the infinite-layer phase, which, in comparison (Table 1B) exhibits slightly smaller in-plane lattice parameters and a larger \( c \) axis (24). This difference in lattice parameters can be indicative of a further progressed transformation of the crystals into the infinite-layer phase with less excess oxygen compared to previous powder studies (24). While the presence of three infinite-layer domains is unambiguous from the XRD refinements (Table 1B), their average sizes cannot be extracted. However, the shapes of the crystal fragments of the extensively reduced crystal shown in Fig. 1G suggest that they are in the order of tens of micrometers. Note that substantially smaller domains or

| Atom  | \( x/a \) | \( y/b \) | \( z/c \) | \( U[Å^2] \) | Occ. |
|-------|-----------|-----------|-----------|-------------|------|
| La (6a) | 0 | 0 | 0.25 | 0.0097(4) | 0.937(15) |
| Ca (6a) | 0 | 0 | 0.25 | 0.0097(4) | 0.063(15) |
| Ni (6b) | 0 | 0 | 0 | 0.0072(6) | 1 |
| O (18e) | 0.4559(9) | 0 | 0.25 | 0.0163(8) | 1 |

| Atom  | \( x/a \) | \( y/b \) | \( z/c \) | \( U[Å^2] \) | Occ. |
|-------|-----------|-----------|-----------|-------------|------|
| La (1d) | 0.5 | 0.5 | 0.5 | 0.0184(5) | 0.921(18) |
| Ca (1d) | 0.5 | 0.5 | 0.5 | 0.644(10) | 0.079(18) |
| Ni (1a) | 0 | 0 | 0 | 0.0190(8) | 1 |
| O (2f) | 0 | 0.5 | 0 | 0.0204(19) | 1 |

Table 1. Single-crystal x-ray diffraction results. (A) Refined lattice parameters and atomic coordinates of an as-grown crystal. The refinement was performed in the rhombohedral space group \( R3c \) (hexagonal axes). A Ca substitution level of \( x = 0.06(2) \) was extracted. The reliability factor is \( \chi^2 = 1.496 \). (B) Refined parameters of a reduced crystal in the tetragonal space group \( P4/mmm \). A Ca substitution level of \( x = 0.08(2) \) was extracted. The reliability factor is \( \chi^2 = 1.227 \).
Electron microscopy investigation of the topotactic transformation

The local crystal structure and the elemental distribution in the perovskite and infinite-layer crystals was investigated by scanning transmission electron microscopy (STEM) including EELS. Figure 2 (A to C) shows the simultaneously acquired atomic-resolution STEM-EELS elemental maps of Ni, La, and Ca in a perovskite crystal recorded using the Ni L$_{3,2}$, La M$_{5,4}$, and Ca L$_{3,2}$ edges, respectively. The maps signify a homogeneous distribution of the elements, including the substitution species Ca. The Ca substitution amount in the STEM specimen was determined with STEM-EDS as $x \sim 0.16$ and remains unchanged within a region of at least 2 μm in proximity to the top surface of the STEM specimen (fig. S5). The substitution level is consistent with an EDS measurement in a SEM on the surface of the as-grown crystal. However, XRD on a fragment of the same crystal revealed $x = 0.08(2)$, thus suggesting a strong substitution gradient toward the bulk of the crystal on length scales of several tens of micrometers. The low-magnification STEM–high-angle annular dark-field (HAADF) images in Fig. 2 (D and G) reveal the absence of crystallographic defects on length scales of several tens of nanometers for both the perovskite and infinite-layer phase. The observed high crystalline quality is in line with the single-crystal XRD characterization (Fig. 1, E and H). Note that the two STEM specimens were prepared from the same crystal, before and after the reduction. The similarity of the crystal lattices in Fig. 2 (D and G) indicates that the integrity of the A-site cation sublattice remains intact during the reduction process. Profound changes of the A-site cation sublattice can be extracted from the fast Fourier transformed (FFT) amplitudes of the images, which are displayed as insets in Fig. 2 (D and G). Along the horizontal direction of the FFT images, the distance between features increases upon reduction, corresponding to a contraction of the c-axis lattice parameter in real space, which is consistent with the removal of oxygen ions. In the vertical direction, the distances remain almost unchanged. Specifically, the ratio between lattice parameters $c/a \sim 0.85$ calculated from the FFT maxima for the reduced crystal is similar to the result obtained with XRD (Table 1B). The trend of a collapse of the $c$ axis in real space can also be observed in the high-magnification STEM-HAADF images in Fig. 2 (E and H).

Detailed information about the distribution of oxygen ions in the lattice can be provided by STEM–annular bright-field (ABF) imaging (Fig. 2, F and I). While Ni in the cross-sectional STEM-ABF image of the perovskite crystal (Fig. 2F) is coordinated with four oxygen ions, we observe in the reduced crystal that Ni is coordinated with two oxygen ions for the most part of the specimen (Fig. 2I), which signals the presence of the infinite-layer structure. The resulting orientation of the NiO$_2$ planes within the infinite-layer structure is indicated in Fig. 2I. However, we note that in some regions in Fig. 2I, the supposedly nonoccupied oxygen positions also exhibit a slightly dark contrast, which suggests that some apical oxygens withstand the reduction. Furthermore, a subtle variation

---

**Fig. 2. Topotactic transformation of the crystal structure.** (A to C) Atomic-resolution STEM-EELS elemental maps of an as-grown perovskite crystal ($x = 0.16$) demonstrating the homogeneous distribution of Ni (A; blue), La (B; green), and Ca (C; orange) atoms. The maps were acquired simultaneously. (D and G) Low-magnification STEM-HAADF images of the perovskite and the reduced crystal, respectively, showing the absence of extended crystallographic defects. Insets correspond to the fast Fourier transformation of the HAADF images. (E and F) High-magnification STEM-HAADF and STEM-ABF images of the perovskite crystal. Both images were acquired from the same part of the STEM specimen. The superimposed cartoon indicates a pseudocubic unit cell with different elements highlighted according to their color in the elemental maps (A to C). Oxygen atoms can be identified specifically in the STEM-ABF image (F). (H and I) STEM-HAADF and STEM-ABF images of the reduced crystal, in analogy to (E and F).
of the contrast among the occupied oxygen positions of the NiO$_2$ planes can be indicative of an occasional depletion within the NiO$_2$ planes upon reduction. Overall, we stress that the STEM-HAADF and ABF images of the reduced crystal in Fig. 2 (G to I) confirm a clear, high-quality infinite-layer structure, while local nonstoichiometries of the oxygen ions can be identified in Fig. 2I. In consequence, we conclude that the infinite-layer structure is realized in our crystals within volumes of several cubic micrometers, whereas for thin films, the thickness of the infinite-layer phase was reported to be less than 10 nm (9). Moreover, Ruddlesden-Popper phase inclusions or stacking faults in the crystal lattice, which have typically been identified in thin films (9), were not observed in our crystals.

**Electronic structure of reduced crystals**

Having established the details of the crystal structure, we proceed with an investigation of the electronic structure of our samples. The characteristic multiband electronic structure of infinite-layer nickelate thin films has been revealed in previous x-ray absorption spectroscopy (XAS) and STEM-EELS studies (15, 17, 16, 42, 43). Specifically, the degree of Ni-O hybridization can be deduced from the near-edge fine structure of the O K edge. In the as-grown perovskite crystal ($x_{\text{EDS}} \sim 0.16$), we detect a pronounced prepeak at ~527 eV (Fig. 3A), characteristic of a strong hybridization between ligand O 2p and Ni 3d states in RENiO$_3$ nickelates (44). Noticeably, the spectral weight at this energy vanishes after reduction, which is in line with XAS and STEM-EELS studies on reduced films, where the lack of the prepeak was interpreted as the absence of Ni-O hybridization, while a Mott-Hubbard character emerges (15–17). Concomitant with the vanishing of the 527 eV prepeak, a recent STEM-EELS study reported the appearance of additional spectral weight around 528 eV as a function of hole doping (fig. S7), which could be reminiscent of the Zhang-Rice singlet peak in isostuctural cuprates (17). We observe a similar feature centered around 529 eV in our reduced and Ca-substituted crystal. In addition, we notice that a broad feature of the perovskite spectrum centered around 542 eV, which is likely associated with hybridized Ni 4sp states (44), vanishes upon reduction. A similar trend was observed in NdNiO$_3$/NdNiO$_2$ STEM-EELS spectra (17), which calls for future STEM-EELS and XAS studies to clarify the origin of this behavior.

Further insights into the electronic structure can be gained from STEM-EELS across the La $M_{5,4}$ and Ni $L_{3,2}$ edges. Figure 3B shows that upon reduction, the La $M_4$ peak remains unchanged within the experimental error, as expected for an empty 4f shell of La$^{3+}$ and an unchanged valence state (43). The La $M_4$ and Ni $L_2$ edges overlap strongly, but nevertheless, a redistribution of spectral weight of the Ni $L_2$ edge toward lower energy can be recognized for the infinite-layer phase, which is consistent with XAS studies (15, 42, 43). The Ni $L_2$ edge is well separated from other features and shifts toward lower energies, as expected from the lowering of the 3+ valence state of Ni in the reduced phase.

**Lattice dynamics**

While STEM-EELS provided information about the local electronic structure, next we use Raman spectroscopy to probe lattice dynamics averaged over length scales of several micrometers. Figure 3C shows the Raman spectra of a perovskite and an infinite-layer crystal ($x = 0.06(3)$). As expected (45), five Raman active modes (one $A_{1g}$ and four $E_g$) are observed for the perovskite crystal with space group $R3c$ (Table 1A). The Raman frequencies are similar to those reported for LaNiO$_3$ films (46, 47). For the reduced sample in the infinite-layer structure and space group $P4/mnm$ (Table 1B), no first-order Raman active modes are expected (48). Accordingly, we do not detect any phonon-like feature in the Raman spectra of crystals that are reduced to such an extent that their average crystal structure can be assigned to the infinite-layer phase (Fig. 3C).

**Magnetic susceptibility and electronic transport**

Figure 4 (A and B) shows the magnetic susceptibility of an as-grown perovskite and a reduced crystal measured in small and large external magnetic fields, respectively. As displayed in Fig. 4B, we observe paramagnetic behavior for our Ca-doped perovskite single crystal [$x = 0.07(2)$], similar to polycrystalline LaNiO$_3$ (49) and OFZ-grown LaNiO$_3$ single crystals (37, 38). Signatures of a magnetic transition around 170 K as reported for some OFZ crystals (35) and LaNiO$_3$ with La$_2$Ni$_2$O$_5$ and/or Ruddlesden-Popper inclusions (38) were not detected. This is consistent with the absence of such lattice defects in the STEM analysis (Fig. 2).

Measurements in small fields (Fig. 4A) reveal a bifurcation between the field-cooled (FC) and zero field–cooled (ZFC) susceptibility for
the reduced crystal that persists up to the highest measured temperature (375 K) but is not present in measurements in strong fields (Fig. 4B). In addition, the ZFC curve in small fields shows a cusp-like feature around 10 K. Such behavior (fig. S8A) is typical for spin glasses (50) and is likely not an intrinsic property of the infinite-layer phase but can originate from local oxygen nonstoichiometries, which were identified with STEM-ABF (Fig. 2I). Furthermore, a small bifurcation between the FC and ZFC susceptibility also exists in the case of the nonreduced perovskite crystal (inset in Fig. 4A). Moreover, a bifurcation and glassy properties were recently detected in perovskite Sm$_{1-x}$Sr$_x$NiO$_3$ powders (51). This supports the notion that the spin glass behavior is not an intrinsic property of the infinite-layer phase. Instead, a small number of oxygen vacancies due to challenges associated with the stabilization of a Ni valence state higher than 3+ in the Ca- or Sr-substituted perovskite phase and local oxygen nonstoichiometry in the infinite-layer phase presumably lead to the observed bifurcations. Alternatively, a FC-ZFC splitting can be due to ferromagnetic impurities, such as elemental Ni particles, which were reported for reduced nickelate powder samples (24). Our XRD, STEM, and EDS characterization of the crystals did not indicate any such impurities. Nevertheless, it is still possible that our crystals contain minute Ni inclusions of the order of a few percent or less (fig. S6).

Along the lines of paramagnetic LaNiO$_3$, we fit the susceptibility of the perovskite crystal by a Curie-type law $\chi(T) = \chi_0(1 - a T^2) + C/T$ (49), which includes Pauli and van Vleck paramagnetism as well as Landau and core diamagnetism. $\chi_0$ is a temperature-independent constant and C the Curie constant. The fit yields $a = 2.66(2) \cdot 10^{-6}$ 1/K$^2$, $C = 7.1(1) \cdot 10^{-4}$ electromagnetic unit (emu) K/mol, and $\chi_0 = 4.922(7) \cdot 10^{-4}$ emu/mol, which is similar to LaNiO$_3$ (49). Hence, a Ca substitution of $x = 0.08$ (2) does not substantially affect the magnetic correlations in the perovskite case (fig. S8B). The enhanced signal of the infinite-layer polycrystal is fitted with a Curie-Weiss law $\chi(T) = \chi_0 + C/(T - \theta_W)$, and we obtain $C = 0.099(2)\text{ emu K/mol}, \chi_0 = 0.0111(1)\text{ emu/mol}$, and a Curie-Weiss temperature $\theta_W = -16.3(5)\text{ K}$.

The electrical transport properties of a perovskite and a reduced crystal are displayed in Fig. 4 (C and D), respectively. For the perovskite crystal $[x = 0.07(3)]$, the expected metallic behavior is observed (Fig. 4C and fig. S8C), and we determine a residual-resistivity ratio (RRR) of 11. This value is slightly larger than the reported RRR of ∼9.6 of OFZ-grown LaNiO$_3$ single crystals (35) and can be related to the Ca substitution and/or the increased quality of our flux-grown crystals. While the resistivity of the perovskite crystal (Fig. 4C) was determined via a four-point measurement, the reduced crystal was measured in two-point configuration (Fig. 4D) owing to the smaller size of reduced crystals (see inset in Fig. 4D), which tend to break into smaller pieces along the domain boundaries (Fig. 1G). The resistance $R(T)$ of a reduced crystal $[x = 0.08]$ normalized to the room temperature resistance is shown in Fig. 4D. Notably, we find that the resistance decreases with decreasing temperature and exhibits a subtle upturn below ∼50 K. This is in stark contrast to powder samples, which show insulating behavior at all temperatures (20, 21). Instead, the electrical resistance of our reduced crystal is reminiscent of lightly hole-doped nonsuperconducting $\text{RENiO}_3$ thin films (7, 8, 9, 10, 11, 12) and underdoped cuprates (52) that exhibit metallic behavior at high temperatures and a weakly insulating
upturn at low temperatures (fig. S8D). The upturn in nickelate films was recently interpreted as a signature of strong electron correlations (53). We note that the upturn in Fig. 4D coincides approximately with the onset temperature of the strong upturn in the magnetic susceptibility (Fig. 4B). Future studies will be required to clarify the origin of the discrepancy between the electrical transport properties of powders and crystals, which could be due to inferior crystalline quality, imurities (20, 21, 24, 51), domain/grain boundaries, or enhanced hydrogen intercalation (54) in the powders.

In summary, we synthesized perovskite La$_{1-x}$Ca$_x$NiO$_3$ crystals in the perovskite phase via a perchlorate-chlorate flux mixture in an external temperature gradient growth under extreme pressures. The perovskite crystals were successfully reduced to the infinite-layer phase La$_{1-x}$Ca$_x$NiO$_{3-8}$ with three orthogonally oriented crystallographic domains. Excessive reduction increased detachment between domains. Nevertheless, micrometer-sized domains remained robust and showed excellent crystalline quality with homogeneous Ca distribution and no detectable defects on length scales exceeding the thickness of previously reported films by orders of magnitude. The observed large domain sizes suggest that a targeted extraction of single domains from multidomain crystals will be feasible in future studies using microstructuring techniques, such as focused ion beam (FIB) preparation. The oxygen sublattices in the reduced crystals are consistent with the infinite-layer structure but exhibited local nonstoichiometries of residual apical oxygen and/or vacancies.

The observed large domain sizes suggest that a targeted extraction of single domains from multidomain crystals will be feasible in future studies using microstructuring techniques, such as focused ion beam (FIB) preparation. The oxygen sublattices in the reduced crystals are consistent with the infinite-layer structure but exhibited local nonstoichiometries of residual apical oxygen and/or vacancies within the NiO$_2$ planes. To date, detailed information about the corresponding local oxygen stoichiometry in thin films is sparse. Yet, the metal-like electrical transport observed for the crystals suggested a close similarity to weakly hole-doped thin films. In consequence, with somewhat higher Ca substitution in the bulk, infinite-layer crystals are a promising candidate for hosting superconductivity. In a broader context, our work signifies that topotactic reductions can be applied to bulk single-crystalline specimen. To the best of our knowledge, this was previously only realized for perovskite-derived layered materials (55). Hence, our successful reduction of the perovskite to the infinite-layer structure provides new perspectives for the transformation of three-dimensional to quasi–two-dimensional materials. In particular, we anticipate that topotactic reductions are feasible for a wide variety of perovskite oxides with distinct morphologies, including nanowires, fibers, and cubes (56, 57). While these perovskites are already widely used as functional materials for energy storage and conversion (58), catalysis (59), and ionic conduction (60), they might show superior performances or new functionalities after topotactic transformation.

MATERIALS AND METHODS

Single-crystal growth

For the high-pressure growth, La$_2$O$_3$ powder (0.39056 g, 1.2 mmol; Alfa Aesar, 99.99%) was dried at 1000°C for 1 day. Subsequently, we mixed and ground the powder in a 0.8:0.2:1 molar ratio with CaO (0.03361 g, 0.6 mmol; Sigma-Aldrich, 99.9%) and NiO (0.22384 g, 3 mmol; Alfa Aesar, 99.998% metal powder) to obtain stoichiometric La$_{0.8}$Ca$_{0.2}$NiO$_3$ single crystals. The spatially separated salt flux was prepared by mixing a molar ratio of 0.1:0.3:0.6 of KCl (0.02234 g, 0.3 mmol; Roth, 99.5%), K$_2$CO$_3$ (0.12456 g, 0.9 mmol; Sigma-Aldrich, 99.99% metal basis) and NaCl (0.10509 g, 1.8 mmol; Sigma-Aldrich, 99.999% metal basis). The mixtures were sealed in a platinum-foil ampule (φ = 7 mm and h = 10 mm) in a sandwich structure of flux–nickelate mixture–flux. The ampule was heated to 1380°C for 1 to 2 hours under a pressure of 4 GPa in a Max Vogenreiter mavo press LP 1000-540/50 equipped with a Walker module for 32-mm WC (WC stands for the elements tungsten carbide) cubes and subsequently quenched to room temperature.

Topotactic reduction

The reduction was carried out using CaH$_2$ as a reducing agent in spacial separation to the nickelate crystals. In more detail, several as-grown perovskite crystals were wrapped in aluminum foil and transferred to a glove box. A glass crucible was loaded with approximately 600 mg of CaH$_2$ powder (0.600 g, 14 mmol; Sigma-Aldrich, 97%) and put into a DURAN glass tube. The wrapped crystals were inserted into the glass tube and placed above the crucible with CaH$_2$. Subsequently, the glass tube was evacuated (~10$^{-7}$ mbar) and sealed to ampules with dimensions of $\phi_{\text{out}}$ = 1.7 mm, $\phi_{\text{in}}$ = 1.5 mm, and $h$ = 10 cm. The reduction was carried out by heating slowly to 300°C in an optimized low-temperature furnace and held for several weeks (see Results and Discussion) before slowly cooling down to room temperature. Depending on the progression of domain separation, the extracted crystals were somewhat fragile during mechanical handling. Nevertheless, we did not detect any signs of moisture sensitivity or degradation within the course of several weeks after extraction.

Single-crystal XRD

Because only very tiny crystal pieces turned out to be suitable for single-crystal XRD, perovskite crystals were broken under high-viscosity oil. A small piece was mounted with some grease on a loop made of Kapton foil (Micromounts, MiteGen, Ithaca, NY). Diffraction data were collected at room temperature with a SMART APEXI charge-coupled device x-ray diffractometer (Bruker AXS, Karlsruhe, Germany), using graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda$ = 0.71073 Å). The reflection intensities were integrated with the SAINT subprogram in the Bruker Suite software package. For the rhombohedral perovskite La$_{1-x}$Ca$_x$NiO$_3$, a multiscan absorption correction was applied using SADABS. Crystals of the tetragonal, reduced infinite-layer nickelate showed systematic twinning by reticular merohedry. The threefold axes of the (pseudo)cubic perovskite structure become twinning elements, and the three twin domains are related by transformation matrices: (1 0 0) (0 0 1), (1 0 0) (0 1 0), (0 0 1) (0 1 0), and (0 0 1) (0 0 1) (0 1 0). To handle this, the reflection intensities were integrated with the help of the orientation matrices of all three twin domains, and a multiscan absorption correction was applied using TWINABS. Both structures were solved by direct methods and refined by full-matrix least square fitting with the SHELXL software package.

Further details of the crystal structure analysis can be found in the Supplementary Materials, and technical details may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de, www.fiz-karlsruhe.de/request for deposited data. html) on quoting the depository numbers CSD-2086960 and CSD-2086915, respectively.

Scanning transmission electron microscopy

Electron-transparent TEM specimens of the as-grown and reduced sample were prepared on a Thermo Fisher Scios I FIB using the standard liftoff method. The lateral dimensions of the specimens were 20 μm by 1.5 μm with thicknesses between 50 and 100 nm.
Energy-dispersive x-ray spectra were recorded with a NORAN System 7 (NSS212E) detector in a Tescan Vega (TS-5130MM) SEM. HAADF, ABF, and EELS were recorded by a probe aberration-corrected JEOL JEM-ARM200F scanning transmission electron microscope equipped with a cold field-emission electron source and a probe Cs corrector (DCOR, CEOS GmbH), and a Gatan K2 direct electron detector with a large solid-angle JEOL Centurio SDD-type EDS detector was used at 200 kV. STEM imaging and EDS and EELS analyses were performed at probe semicorrection angles of 20 and 28 mrad, resulting in probe sizes of 0.8 and 1.0 Å, respectively. Collection angles for STEM-HAADF and ABF images were 75 to 310 and 11 to 23 mrad, respectively. To improve the signal-to-noise ratio of the STEM-HAADF and ABF data while minimizing sample damage, a high-speed time series was recorded (2 μs per pixel) and was then aligned and summed. A collection semiangle of 111 mrad was used for EELS investigations. A 0.5-eV/μCh dispersion with an effective energy resolution of ~1 eV was used for overall chemical profiling, and 0.1-eV/μCh dispersion with an effective energy resolution of ~0.5 eV was chosen particularly for the O K edges.

Raman spectroscopy

The Raman measurements were performed with a Jobin-Yvon LabRam HR800 single-grating (1800) Raman spectrometer using the 632.8-nm excitation line of a HeNe laser. Spectra were taken at 300 K in backscattering geometry with parallel and crossed polarization, respectively. The data displayed in Fig. 3C correspond to the sum of the spectra recorded with the two polarization configurations.

Physical properties measurements

Magnetic susceptibility measurements were carried out in a range of 1.8 to 400 K and 0 to 7 T using a Quantum Design Magnetic Property Measurements System. We used silver paint to contact the samples for resistivity and resistance measurements, which were carried out using the standard resistivity option of a Physical Property Measurements System. As explained in the main text, the perovskite crystal was measured in a four-probe geometry, and a two-contact resistance measurement was used for the substantially smaller infinite-layer crystal. We note that our two-contact measurement of the infinite-layer crystal cannot quantitatively determine intrinsic transport properties, as this measurement configuration adds contributions from electrical contact resistances. Nevertheless, assuming that the temperature dependence of the contact resistances is small and/or monotonic, the R(T)/R(300 K) data in Fig. 4D are qualitatively representative for the temperature dependence of the intrinsic electrical transport.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at https://science.org/doi/10.1126/sciadv.abl8091

REFERENCES AND NOTES

1. H. Kageyama, K. Hayashi, K. Maeda, J. P. Attfield, Z. Hiroi, J. M. Rondinelli, K. R. Poeppelmeier, Expanding frontiers in materials chemistry and physics with multiple anions. Nat. Commun. 9, 772 (2018).
2. H. Jeen, W. S. Choi, J. W. Freeland, H. Ohta, C. U. Jung, H. N. Lee, Topotactic phase transformation of the brownmillerite SrCoO2.5 to the perovskite SrCoO3−δ. Adv. Mater. 25, 3651–3656 (2013).
3. V. R. Nallagatla, T. Hegisig, C. Banumer, V. Feyer, M. Jugovac, G. Zambrolini, C. M. Schneider, R. Weaver, M. Kim, C. U. Jung, R. Dittmann, Topotactic phase transition driving memristive behavior. Adv. Mater. 31, 1903391 (2019).
33. T. Saito, M. Azuma, E. Nishibori, M. Takata, M. Sakata, N. Nakayama, T. Arima, T. Kimura, Y. E. Suyolcu, Y. Wang, W. Sigle, F. Baiutti, G. Cristiani, G. Logvenov, J. Maier, J. L. García-Muñoz, J. Rodríguez-Carvajal, P. Lacorre, J. B. Torrance, Neutron-diffraction study of the perovskite nickelate PrNiO$_3$.

34. N. Chaban, M. Weber, S. Pignard, J. Kreisel, Phonon Raman scattering of perovskite LaNiO$_3$ thin films. Appl. Phys. Lett. 97, 031915 (2010).

35. J. Zhang, H. Zheng, Y. Ren, J. F. Mitchell, Oxygen inhomogeneity and reversibility in single crystal LaNiO$_{3−x}$ films. J. Mater. Chem. A 3, 2730–2735 (2015).

36. A. Reller, J. M. Thomas, D. A. Jefferson, M. K. Uppal, Superstructures formed by antiferromagnetic defect structure inLaNiO$_{3−x}$ under compressive strain. Phys. B Condens. Matter 460, 10196–10198 (2015).

37. G. Burns, M. K. Crawford, F. H. Dacol, E. M. McCarron, T. M. Shaw, Phonons in CaCuO$_2$. Phys. Rev. B 40, 6717–6720 (1989).

38. J.-S. Zhou, L. G. Marshall, J. B. Goodenough, Mass enhancement versus Stoner enhancement in strongly correlated metallic perovskites: LaNiO$_3$ and LaCuO$_3$. Phys. Rev. B 89, 245138 (2014).

39. S. Huangfu, Z. Guguchia, D. Cheptiakov, X. Zhang, H. Luetkens, D. J. Gawryluk, T. Shang, F. O. von Rohr, A. Schilling, Short-range magnetic interactions and spin-glass behavior in the quasi-two-dimensional nickelate PrNi$_3$O$_5$. Phys. Rev. B 80, 054423 (2020).

40. C. He, X. Ming, Q. Li, X. Zhu, S. Ji, H.-H. Wen, Synthesis and physical properties of perovskite Sm$_{1−x}$Sr$_x$NiO$_3$ (x = 0, 0.2) and infinite-layer Sm$_{0.8}$Sr$_{0.2}$NiO$_3$ nickelates. J. Phys. Condens. Matter 33, 265701 (2021).

41. B. Keimer, N. Belk, R. J. Birgeneau, A. Cassanho, C. Y. Chen, M. Greven, M. A. Kastner, A. Aharony, Y. Endoh, R. W. Erwin, G. Shirane, Magnetic excitations in pure, lightly doped, and weakly magnetic La$_2$CuO$_4$. Phys. Rev. B 46, 14034–14053 (1992).

42. Y.-T. Hsu, B. Y. Wang, M. Berben, D. Li, K. Lee, C. Duffy, T. Ottenbros, W. J. Kim, M. Osada, S. Wiedmann, H. Y. Hwang, N. E. Hussey, Insulator-to-metal crossover near the edge of the superconducting dome in Nd$_{1−x}$Sr$_x$NiO$_3$. Phys. Rev. Res. 3, L042015 (2021).

43. J. Zhang, H. Zhao, H. Zhao, Y. Zhao, Z. Liu, Z. Li, J. Gao, H. Chen, Hierarchical mesoporous perovskite La$_{2}$Sr$_{3}$CoO$_{11}$ nanowires with ultrahigh capacity for Li-air batteries. Proc. Natl. Acad. Sci. U.S.A. 109, 15966–15974 (2012).

44. D. Chen, C. Chen, Z. M. Baijey, Z. Shao, F. Ciucci, Nonstoichiometric oxides as low-cost and highly-efficient oxygen reduction/evolution catalysts for low-temperature electrochemical devices. Chem. Rev. 115, 9869–9921 (2015).

45. W. G. Coors, D. W. Readey, Proton conductivity measurements in yttrium barium cerate by impedance spectroscopy. J. Am. Ceram. Soc. 85, 2637–2640 (2004).

Acknowledgments: We thank G. McNally for discussions about high-pressure physics. We also thank M. Minola for helpful discussions about the Raman measurements. The use of facilities and resources of the Quantum Materials Department of H. Takagi at MPI-FKF is gratefully acknowledged. Funding: This project has received funding from the European Union’s Horizon 2020 research and innovation program under grant agreement no. 823717-ESTEEM3. Author contributions: M.H., P.P., M.I., and B.K. conceived the project. P.P. and M.I. grew the perovskite crystals and P.P. carried out the reduction. The Raman measurements were executed by H.L. under the supervision of K.F. and M.H. The resistivity measurements were conducted by P.M and J.A.N.B and discussed with K.F. The single-crystal measurements were executed by H.L. under the supervision of K.F. and M.H. P.P. and M.I. gratefully acknowledged.

Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials.

Submitted 11 August 2021
Accepted 14 October 2021
Published 3 December 2021
10.1126/sciadv.abl8091