

Microstructural Activation of a Topochemical Reduction Reaction

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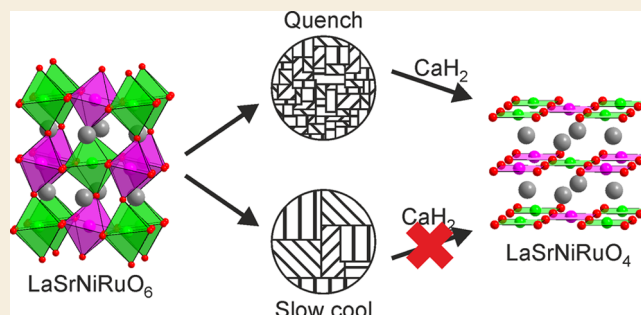
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ABSTRACT: The progress of the topochemical reduction reaction that converts LaSrNiRuO_6 into LaSrNiRuO_4 depends on the synthesis conditions used to prepare the oxidized phase. Samples of LaSrNiRuO_6 that have been quenched from high temperature can be readily and rapidly converted into LaSrNiRuO_4 . In contrast, samples that have been slow-cooled cannot be completely reduced. This reactivity difference is attributed to the differing microstructures of the quenched and slow-cooled samples, with the former having much smaller average crystalline domain sizes and larger lattice strains than the latter. A mechanism to explain this effect is presented, in which the greater “plasticity” of small crystalline domains helps lower the activation energy of the reduction reaction. In addition, we propose that the enhanced lattice strain in quenched samples also acts to destabilize the host phase, further enhancing reactivity. These observations suggest that the microstructure of a material can be used to “activate” topochemical reactions in the solid state, expanding the scope of phases that can be prepared by this type of reaction.

KEYWORDS: *Topochemical reduction, Transition-metal oxides, Solid-state microstructure, Solid-state synthesis, Phase transitions*



INTRODUCTION

Solid-state syntheses performed under “conventional” high-temperature conditions tend to form products that are “selected” on the basis of their thermodynamic stability. This behavior can be attributed to the large energetic barriers that oppose diffusion in the solid state. These large barriers not only necessitate the use of high reaction temperatures but also tend to dominate the activation energies of the many possible reactions that could occur between solid components. As a result, these competing reactions establish an equilibrium at the high temperatures required for reactions to proceed, yielding products that are selected on the basis of their thermodynamic stability. As a consequence, there are many metastable phases that cannot be prepared under these high-temperature conditions.

Low-temperature topochemical (structure conserving) reactions can overcome the dominance of thermodynamic product selection in the solid state, by utilizing the observation that while the energetic barriers to diffusion are high in solids, they do not apply uniformly. There are many solid compounds in that a subset of the species present are more mobile than the “host framework” in that they are embedded. This difference in mobility amounts to a difference in reactivity, allowing the more mobile species to be removed, inserted, or exchanged within the immobile framework, facilitating preparation of metastable phases with chemical compositions and structures that can be considered as modifications of the original host phase.¹

This topochemical approach is particularly valuable in the preparation of complex transition-metal oxides, as conventional high-temperature synthesis techniques tend to prepare phases with transition-metal cations in the limited subset of oxidation-state/coordination-geometry combinations that are the most thermodynamically stable. Topochemical manipulations, particularly when applied to modify the anion lattices of phases, allow the range of oxidation-state/coordination-environment combinations that can be stabilized within extended oxide phases to be increased dramatically.^{2–12}

While the products of high-temperature reactions can only be changed by modifying the relative thermodynamic stability of competing product phases, the kinetic control that is in operation during topochemical reactions offers many opportunities to direct and modify the product phases formed, by tuning the many features of the reagents and reaction conditions that come together to determine reaction rates. Recently, we reported the preparation of LaSrNiRuO_4 via the topochemical reduction of LaSrNiRuO_6 , as shown in Figure 1.¹³ While investigating the preparation of this phase, we observed a highly unusual behavior, in which the reactivity of the “host” LaSrNiRuO_6 phase depends on the exact conditions

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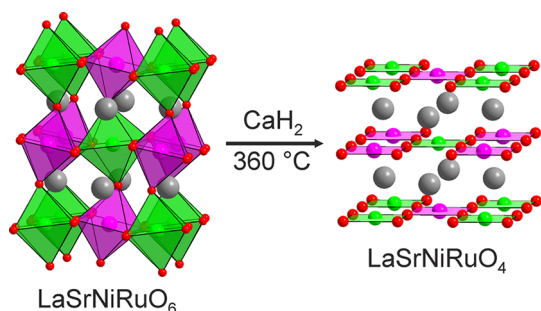


Figure 1. Reduction of LaSrNiRuO_6 with CaH_2 yields LaSrNiRuO_4 via a topochemical reduction reaction. La/Sr, Ni, Ru, and O positions are represented by gray, green, purple, and red spheres, respectively.

under which the material was prepared. Samples of LaSrNiRuO_6 rapidly cooled from high temperature could be readily converted to LaSrNiRuO_4 by reaction with CaH_2 . In contrast, samples of LaSrNiRuO_6 that had been cooled slowly could not be completely reduced to form LaSrNiRuO_4 . The differing reactivity of slow-cooled and quenched samples suggests there is an additional method that can be used to control the progress of topochemical reactions, which we investigate further here.

EXPERIMENTAL SECTION

Synthesis of LaSrNiRuO_6

Samples of LaSrNiRuO_6 were prepared via a citrate gel method. Suitable stoichiometric ratios of La_2O_3 (99.999%), SrCO_3 (99.99%), Ni powder (99.996%), and RuO_2 (99.99% dried at $800\text{ }^\circ\text{C}$) were dissolved in a minimum quantity of 6 M nitric acid. Then, 3 mol equivalents of citric acid and 5 mL of analar ethylene glycol were added, and the solution was heated with constant stirring. The gels thus formed were subsequently ground into a fine powder, placed in an alumina crucible, and heated at $1\text{ }^\circ\text{C min}^{-1}$ to $900\text{ }^\circ\text{C}$ in air. The powders were then reground, pressed into 13 mm pellets, and then heated at $1100\text{ }^\circ\text{C}$ in air for two periods of 24 h. At the end of the final heating period, samples were either cooled to room temperature at a rate of $4\text{ }^\circ\text{C min}^{-1}$ (subsequently referred to as slow-cooled samples) or removed from the furnace and rapidly transferred to a dry-ice-cooled alumina crucible and allowed to rapidly cool (subsequently referred to as quenched samples).

Reduction of LaSrNiRuO_6 to LaSrNiRuO_4

Samples of LaSrNiRuO_6 were reduced by reacting with 4 mol equivalents of CaH_2 at $360\text{ }^\circ\text{C}$ in a “venting” apparatus described previously.¹⁴ After the reaction, calcium-containing phases were removed from samples by washing with a 0.05 M solution of NH_4Cl in methanol and then a further $4 \times 80\text{ mL}$ aliquots of clean methanol before being dried under vacuum.

Characterization

Laboratory X-ray powder diffraction data were collected from samples contained in gastight sample holders using a PANalytical X'Pert diffractometer incorporating an X'celerator position sensitive detector (monochromatic $\text{Cu K}\alpha_1$ radiation). High-resolution synchrotron X-ray powder diffraction (SXRDP) data were collected using the I11 instrument at the Diamond Light Source Ltd. Diffraction patterns were collected using Si-calibrated X-rays with an approximate wavelength of 0.825 \AA from samples sealed in 0.3 mm diameter borosilicate glass capillaries. Rietveld refinements were performed using TOPAS Academic (V6).¹⁵ Thermogravimetric measurements were performed by heating powder samples at a rate of $5\text{ }^\circ\text{C min}^{-1}$ under a 10% H_2 in N_2 atmosphere, using a Mettler Toledo MX1 thermogravimetric microbalance. Scanning electron microscopy (SEM) images were collected using a Thermo Fisher Quanta FEG

250 microscope at 10 kV. The particle-size analysis was performed in DigitalMicrograph.

RESULTS AND DISCUSSION

Reactivity of LaSrNiRuO_6 with CaH_2

Two separate samples of LaSrNiRuO_6 , one prepared by a slow-cooled method and one by a quenched method, were ground together with 4 mol equivalents of CaH_2 and then heated at $360\text{ }^\circ\text{C}$ for three periods of 48 h, with intermediate regrinding. X-ray powder diffraction data (Figure 2) indicated that the

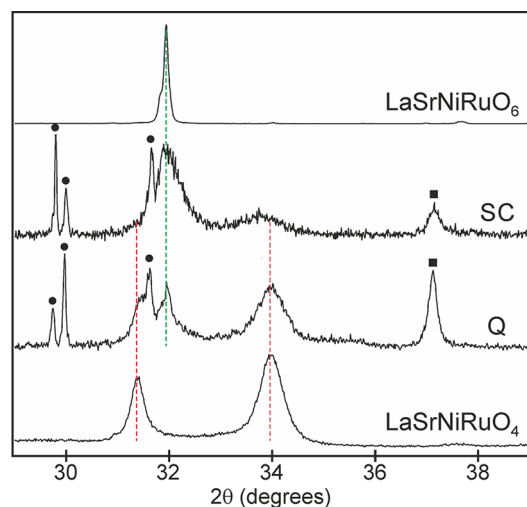


Figure 2. X-ray powder diffraction data collected from the products of reaction between slow-cooled (SC) and quenched (Q) LaSrNiRuO_6 and CaH_2 after three periods of heating at $360\text{ }^\circ\text{C}$. Analogous data collected from LaSrNiRuO_6 and LaSrNiRuO_4 are plotted for comparison. Solid circles indicate peak positions of CaH_2 , and solid squares indicate peak positions of CaO .

products of both reactions were mixtures of pseudocubic LaSrNiRuO_{6-x} , pseudotetragonal LaSrNiRuO_{4+x} , CaH_2 , and CaO . The ratio of $\text{LaSrNiRuO}_{6-x}/\text{LaSrNiRuO}_{4+x}$ in the samples can be crudely quantified by comparing the area of the overlapping 200/020/112 reflections ($2\theta \approx 32^\circ$) of LaSrNiRuO_{6-x} with that of the 112 reflection ($2\theta \approx 34^\circ$) of LaSrNiRuO_{4+x} and normalizing for their relative multiplicities. This analysis reveals a $\text{LaSrNiRuO}_{6-x}/\text{LaSrNiRuO}_{4+x}$ ratio of 74(1):26(1) for the slow-cooled sample and 29(1):71(1) for the quenched sample, demonstrating that the quenched sample reacted faster and further than the slow-cooled sample.

Two further heating periods of 48 h at $360\text{ }^\circ\text{C}$ converted the quenched sample completely into LaSrNiRuO_4 . In contrast, further heating of the slow-cooled sample at $360\text{ }^\circ\text{C}$ led to no further reaction, with the ratio of $\text{LaSrNiRuO}_{6-x}/\text{LaSrNiRuO}_{4+x}$ remaining unchanged. Raising the temperature of reaction to $370\text{ }^\circ\text{C}$ led to sample decomposition via nontopochemical reactions, and the formation of poorly crystalline Ni, Ru, La_2O_3 , and SrO. These results demonstrate that there is a significant difference in the reactivity of the slow-cooled and quenched samples with CaH_2 . Furthermore, in contrast to quenched samples, there appear to be no conditions under which a slow-cooled sample of LaSrNiRuO_6 can be converted into a phase-pure sample of LaSrNiRuO_4 by reduction with CaH_2 .

Structural Characterization of Slow-Cooled and Quenched LaSrNiRuO₆

X-ray powder diffraction patterns collected from both slow-cooled and quenched samples of LaSrNiRuO₆ prior to reduction could be readily indexed using the monoclinic unit cell reported for the phase.¹⁶ Refinement of a model based on the reported structure of LaSrNiRuO₆ (space group $P2_1/n$)¹⁶ against these diffraction data proceeded smoothly. The detailed results of the structural refinement (Table S1 in the Supporting Information) reveal the structures of the slow-cooled and quenched samples of LaSrNiRuO₆ are indistinguishable. Furthermore, thermogravimetric analysis (Figure S1, Supporting Information) indicated both quenched and slow-cooled samples were oxygen-stoichiometric. Combined, these observations indicate that the slow-cooled and quenched samples of LaSrNiRuO₆ are extremely similar with respect to their bulk crystal structures and chemical compositions, so these features are unlikely to be the origin of their differing reactivity.

Microstructural Characterization of Slow-Cooled and Quenched LaSrNiRuO₆

Although the refined structures of the slow-cooled and quenched samples are indistinguishable, direct comparison of the X-ray powder diffraction data collected from the two samples reveals all the diffraction peaks in the data set from the quenched sample are significantly broader than the corresponding features from the slow-cooled sample, as can be seen in Figure 3a,b and a plot of the diffraction peak full-width at half-maximum (fwhm) against 2θ shown in Figure 3c. Separation of the fwhm 2θ -dependence into contributions from crystal domain size and lattice strain (described in detail in the Supporting Information) reveals that the quenched sample has a smaller average particle/domain size (quenched:

122.7(2) nm; slow-cooled: 142.6(3) nm) and a lattice strain which is 30% higher than the slow-cooled sample.

To further examine the microstructure of the samples, we measured the average particle size of slow-cooled and quenched samples of LaSrNiRuO₆ via the analysis of SEM images, as described in detail in the Supporting Information. This analysis yielded values of 184(3) nm and 214(5) nm for the particle sizes of quenched and slow-cooled samples, respectively. These values are about 50% larger than those extracted from the SXR data, suggesting that the particles of LaSrNiRuO₆ contain multiple crystalline domains. In addition, close inspection of the particle-size distributions revealed that a significant fraction of the particles in the slow-cooled sample have diameters greater than 400 nm (~13%), while there are almost no particles of this size in the quenched sample (<4%).

This microstructural analysis of LaSrNiRuO₆ clearly shows that the quenched sample contains smaller, more strained crystal domains than the slow-cooled sample. We propose it is this microstructural difference, rather than some compositional difference, which is responsible for the differing reactivity of slow-cooled and quenched samples of LaSrNiRuO₆, as described below.

The role of the postsynthesis cooling rate in defining the crystalline domain size and lattice strain of LaSrNiRuO₆ samples appears to be related to the structural phase transition this material exhibits at around 400 °C,¹⁶ in which the arrangement of cooperatively tilted NiO₆ and RuO₆ octahedra changes from a high-temperature scheme described as $a^-a^-a^-$ in Glazer notation (space group $R-3$),^{17,18} to an $a^-a^-c^+$ twisting pattern at low temperature (space group $P2_1/n$). To further investigate this behavior, we performed a series of quenching experiments, in which pellets of LaSrNiRuO₆ were heated to 1100 °C (the synthesis temperature) and then slow-cooled to the “quenching temperature” indicated in Figure 4 and held

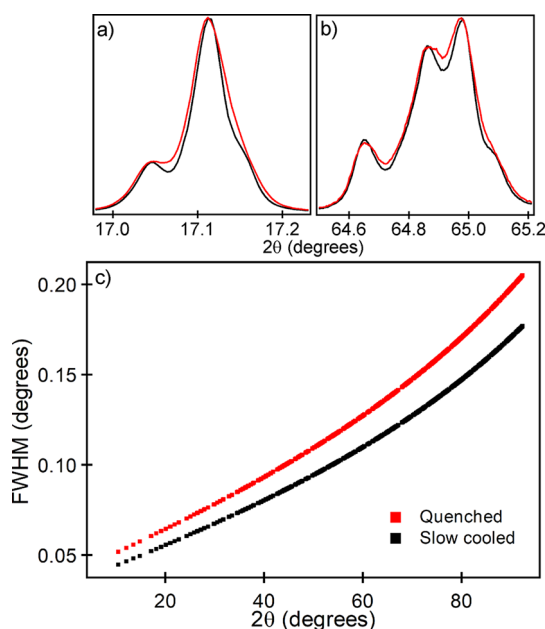


Figure 3. Plot of selected regions of the SXR data from quenched (red) and slow-cooled (black) samples of LaSrNiRuO₆ at (a) $2\theta \approx 17.1^\circ$ and (b) $2\theta \approx 64.9^\circ$. (c) A plot of fwhm against 2θ of SXR diffraction peaks collected from slow-cooled and quenched samples of LaSrNiRuO₆.

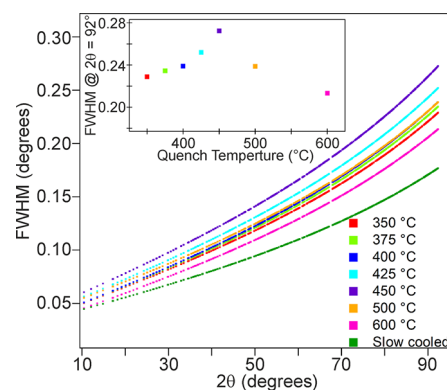


Figure 4. Plot of fwhm against 2θ of SXR data collected from samples of LaSrNiRuO₆ quench from different temperatures. Inset shows the fwhm of the diffraction peak at $2\theta = 92^\circ$ as a function of quenching temperature.

there for 2 h. The samples were then thermally quenched by rapidly removing them from the furnace and transferring them to a dry-ice-cooled alumina crucible. SXR data collected from these samples, after they had been ground into powder, were fit by the $P2_1/n$ symmetry model of LaSrNiRuO₆ to yield lattice parameters indistinguishable from the other samples of LaSrNiRuO₆ prepared in this study. Figure 4 shows a plot of the SXR diffraction peak fwhm as a function of 2θ for the different quenched samples, with the inset showing the fwhm

of the diffraction peak at $2\theta = 92^\circ$ for samples as a function of quenching temperature. These data show that rapidly quenching from 450°C yields samples with the broadest diffraction peaks and that all samples quenched in the range $350 < T/^\circ\text{C} < 600$ have significantly broadened diffraction peaks compared to a slow-cooled sample.

The influence of quenching on the microstructure of samples can be rationalized by noting there is no group/subgroup relation between the $R-3$ space group of the high-temperature phase and the $P2_1/n$ space group of the low-temperature phase, and as a consequence, there is no preference for any of the six possible orientations of the monoclinic cell axes of the low-temperature phase with respect to the rhombohedral cell axes of the high-temperature phase. Described in terms of crystal structure, one of the three a^- out-of-phase tilts becomes a c^+ in-phase tilt at the phase transition. This in-phase tilt could be aligned along either the x -, y -, or z -axes of the aristotype perovskite framework and be either “clockwise” or “anticlockwise” in sense, giving six equivalent possibilities. Thus, when the structural symmetry of the LaSrNiRuO_6 framework is lowered throughout the sample on cooling, a patchwork of small domains of the monoclinic phase is formed, each with a different cell axis orientation (orientation/sense of the c^+ tilt) compared to its neighbors, as shown in Figure 5.

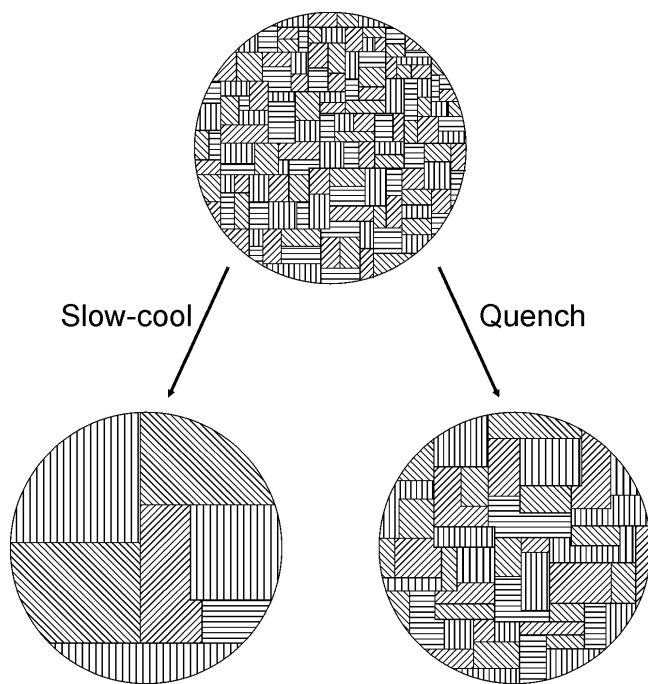


Figure 5. Schematic illustrating domain growth in LaSrNiRuO_6 . On cooling below the structural phase transition, a patchwork of small domains forms (top). These domains grow at different rates dependent on the cooling rate of the sample.

This patchwork of domains is energetically unfavorable. First, this is because the interfaces between domains are energetically expensive, as there are discontinuities in the cooperative tilts of the NiO_6 and RuO_6 units. A second unfavorable feature comes from the mismatch in the unit cell distortions of the low- and high-temperature phases. This arises because, relative to the aristotype, $a^0a^0a^0$ undistorted $Fm-3m$ symmetry phase of LaSrNiRuO_6 , the $R-3$ high-

temperature phase has a unit cell that is expanded along one of the $[111]$ directions. However, the low-temperature $P2_1/n$ phase has a unit cell that is expanded along $[110]$ and contracted along $[1-10]$. Thus, conversion from the $R-3$ phase to the $P2_1/n$ phase leads to a change in the shape or aspect ratio of the underlying perovskite framework. However, the presence of large numbers of small domains hampers this aspect ratio change, and as a result, the crystal domains formed are under considerable strain.

To lower the free energy of the system, some of the crystal domains will grow, at the expense of others over time, to relieve the lattice strain and minimize the area of the interfaces between domains. However, domain growth has a significant activation energy, and as a result, the rate of domain growth is temperature-dependent, dropping to zero below some “freezing” temperature. Quenched samples cool quickly, so they spend little time in the “domain growth temperature window”, which has the phase transition as its upper limit and the domain freezing temperature as its lower limit. As a result, samples quenched from temperatures just above the phase transition temperature only undergo modest domain growth as shown in Figure 5. In contrast, slow-cooled samples spend far longer at temperatures where domain growth can occur and as a result undergo extensive domain growth. Thus, if a sintered pellet of LaSrNiRuO_6 is either quenched or slow-cooled, a polycrystalline pellet with either small, highly strained domains or larger, less strained domains will be formed. When these pellets are then ground to powder, they will tend to fracture along the boundaries between domains, so the quenched pellet will be ground into a powder with smaller average particle/domain size and higher lattice strain than the slow-cooled pellet, accounting for the observed difference in microstructure between slow-cooled and quenched samples.

Structural Phase Transition of LaSrNiRuO_6

To further investigate the influence of sample quenching, SXRD data were collected as a function of temperature from a slow-cooled sample of LaSrNiRuO_6 and a sample quenched from 375°C , which were heated at $12^\circ\text{C min}^{-1}$ from 100 to 950°C and then cooled at the same rate back to 100°C . Each data set collected was fitted by structural models describing the $P2_1/n$ and $R-3$ phases of LaSrNiRuO_6 to determine the fraction of each phase in the sample at a given temperature.

The data in Figure 6 show that on heating, the slow-cooled and quenched samples begin transforming from $P2_1/n$ to $R-3$ symmetry at 350 and 315°C , respectively. However, this phase transition spans a wide temperature range, with complete conversion to the $R-3$ phase not achieved until 760 and 730°C for the slow-cooled and quenched samples, respectively, with a two-phase mixture existing between these temperatures. Data collected on cooling show the phase transition exhibits significant thermal hysteresis, with the reverse $R-3$ to $P2_1/n$ transition not beginning until 605 and 680°C for the slow-cooled and quenched samples, respectively, and complete conversion back to the $P2_1/n$ phase not achieved until 325 and 315°C , respectively.

The broad two-phase region observed and the large thermal hysteresis exhibited by the $P2_1/n$ -to- $R-3$ phase transition is consistent with the presence of a large energetic barrier (“activation energy”), which needs to be overcome during the structural change. The smaller thermal hysteresis observed for the quenched sample, compared to the slow-cooled sample, suggests that samples with smaller domain sizes and larger

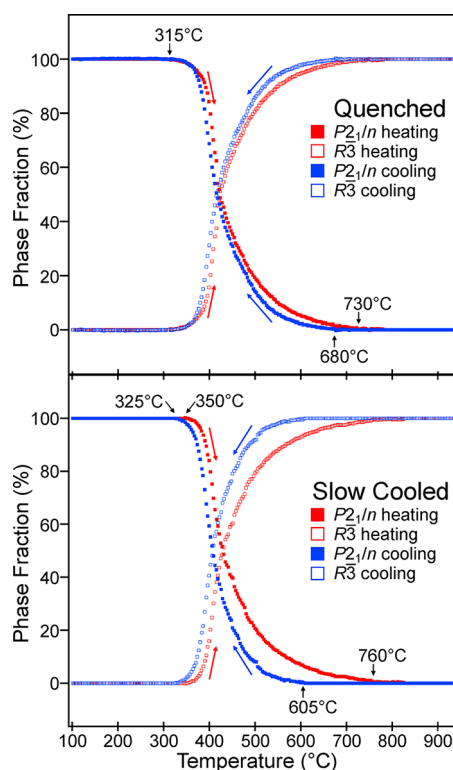


Figure 6. Plot of phase fraction against temperature for the structural phase transition of slow-cooled and quenched samples of LaSrNiRuO_6 determined by variable temperature SXR D data. Indicated temperatures mark the beginning and end of the phase heating and cooling.

lattice strain have a smaller $P2_1/n$ -to- $R-3$ phase-transition energy barrier. In addition, the lower onset temperature for the phase transition of the quenched sample suggests that the enhanced crystal strain and/or smaller domain size could destabilize the $P2_1/n$ phase with respect to the $R-3$ phase, leading to lower phase transition onset temperature.

It should be noted that a comparison of the SXR D data collected at 100 °C before and after the heating/cooling cycle shown in Figure 6 reveals that these data are identical, indicating the microstructural differences between the slow-cooled and quenched samples are preserved through this heating cycle. In contrast, SXR D data collected after annealing the quenched sample at 360 °C (the temperature of the reduction reaction) for 2 days revealed a slight sharpening of the diffraction peaks due to a decrease in lattice strain but no observable change in domain size.

The extensive two-phase region and thermal hysteresis exhibited by LaSrNiRuO_6 at the $P2_1/n$ to $R-3$ phase transition is consistent with a large activation energy associated with the changes in the cooperative tilting of the MO_6 units necessary to change from an $a^-a^-a^-$ to an $a^-a^-c^+$ tilting pattern or to move a domain wall between differently oriented $a^-a^-c^+$ domains and further suggests that the structural change at the phase transition is kinetically slow. It is likely that this large activation energy enhances the effect of sample quenching on the microstructure of LaSrNiRuO_6 .

Influence of the Microstructure on the Rate and Extent of Reduction

The differing phase-transition behavior observed for quenched and slow-cooled samples of LaSrNiRuO_6 suggests a mecha-

nism by which the microstructure of samples can influence the rate and extent of the reduction reaction that forms LaSrNiRuO_4 . Diffraction data collected during the reduction of LaSrNiRuO_6 (Figure 2) reveal that the only Ni/Ru phases observable during the reaction are pseudocubic LaSrNiRuO_{6-x} and pseudotetragonal LaSrNiRuO_{4+x} with no evidence for intermediate “ LaSrNiRuO_5 ” type phases. This indicates that LaSrNiRuO_6 and LaSrNiRuO_4 are close to being “line phases” and that LaSrNiRuO_6 is converted directly into LaSrNiRuO_4 without forming an appreciable concentration of material with an intermediate oxygen stoichiometry. Thus, we would expect that as oxygen is deintercalated from a particle/domain of LaSrNiRuO_6 , a layer of LaSrNiRuO_4 will form at the particle/domain surface, demarcated by a relatively sharp interface from the unreduced LaSrNiRuO_6 in the rest of the particle/domain, as shown in Figure 7a.

Thin film studies of the reduction of $\text{SrFeO}_{3-\delta}$ to SrFeO_2 ^{19,20} and LaNiO_3 to LaNiO_2 ²¹ reveal that the infinite-layer phases synthesized by reduction of perovskite hosts tend to form with their c -axis aligned perpendicular to the particle/domain surface, rather than parallel to it. Thus, we would expect that as oxygen is deintercalated from a particle/domain of LaSrNiRuO_6 , a layer of LaSrNiRuO_4 will form at the particle/domain surface aligned with its c -axis perpendicular to the particle/domain surface, as shown in Figure 5.

The reduction of LaSrNiRuO_6 ($a = 5.575 \text{ \AA}$, $b = 5.542 \text{ \AA}$, $c = 7.848 \text{ \AA}$, $\beta = 90.0^\circ$)¹⁶ to LaSrNiRuO_4 ($a = 5.652 \text{ \AA}$, $b = 5.652 \text{ \AA}$, $c = 6.915 \text{ \AA}$, $\beta = 90.5^\circ$)¹³ leads to a dramatic change to the lattice parameters of the material: a contraction of the c -axis of $\sim 11.9\%$ and an expansion in the area of the ab -plane of $\sim 3.3\%$ resulting in a decrease in cell volume of $\sim 9.1\%$. Therefore, even with a c -axis aligned region of LaSrNiRuO_4 (Figure 7a), there will be a very large, energetically unfavorable lattice strain present at the interface between the regions of LaSrNiRuO_4 and LaSrNiRuO_6 due to the large mismatch in lattice parameters of the two phases.

We propose that this large interfacial lattice strain is the origin of the microstructure-dependent reactivity of LaSrNiRuO_6 , because as a particle/domain of LaSrNiRuO_6 is reduced to LaSrNiRuO_4 , the large lattice strain that is established at the reaction interface opposes the reduction of LaSrNiRuO_6 and thus appears to add to the activation energy of the reduction reaction. Small particles/domains of $\text{LaSrNiRuO}_6/\text{LaSrNiRuO}_4$ are more flexible than larger particles/domains, and this enhanced plasticity results in a smaller interfacial strain contribution to the activation energy of the reduction reaction. As a result, small domains/particles will have a lower activation energy for reduction than larger domains/particles, as illustrated in Figure 7b.

As noted above, particles/domains of LaSrNiRuO_6 that have high lattice strains, due to rapid quenching, are less stable than less strained domains. This destabilization of LaSrNiRuO_6 via lattice strain will also act to reduce the apparent activation energy of the LaSrNiRuO_6 -to- LaSrNiRuO_4 reduction reaction (just as it does for the $P2_1/n$ -to- $R-3$ phase transition) as illustrated in Figure 7b.

Given that the activation energy of the LaSrNiRuO_6 -to- LaSrNiRuO_4 reaction is strongly affected by particle/domain size and lattice strain, we can separate the reduction-activation energy into two parts: an “intrinsic” activation energy arising from the chemical transformation (i.e., the reduction-activation energy of an unstrained macroscopic single crystal) and a “microstructural” contribution that lowers the activation

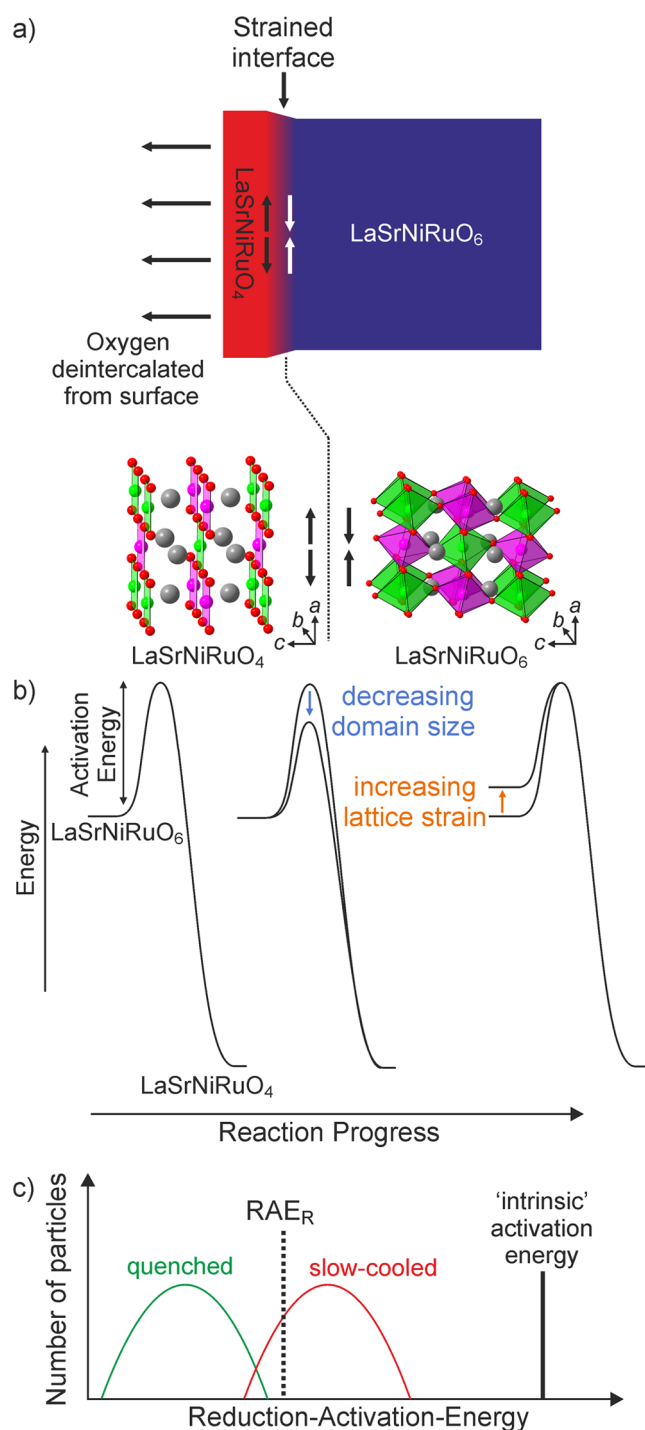


Figure 7. (a) Schematic diagram of the interface between LaSrNiRuO_{6-x} (blue) and LaSrNiRuO_{4+x} (red) formed during the reduction of a crystalline domain. (b) Schematic diagram showing how particle/domain size and lattice strain can lower the reduction-activation energy. (c) Schematic diagram showing how the influence of microstructural effects on the reduction-activation energy can lead to the observed differences in the reactivity of quenched and slow-cooled samples of LaSrNiRuO_6 .

energy by the processes described above. Any powder sample of LaSrNiRuO_6 contains a population of powder grains with a range of particle/domain sizes and lattice strains that will lower the reduction-activation energy by different amounts. The reduction-activation energy of a powder sample will therefore

span a range of values dependent on the distribution of particle/domain sizes and lattice strains of particles within sample. Figure 7c shows a schematic of the range of reduction-activation energies for a slow-cooled and a quenched sample of LaSrNiRuO_6 , with the quenched sample exhibiting a smaller average reduction-activation energy due to its smaller average particle/domain size and higher average lattice strain.

At a given reduction temperature, T_R , there is a set amount of thermal energy available, and thus, there is maximum value of activation energy, RAE_R , which can be overcome at this temperature. The differing reactivity of slow-cooled and quenched samples of LaSrNiRuO_6 is consistent with the situation shown in Figure 7c. The large lattice strain and small particle/domain size of the quenched sample lower the reduction-activation energy of all particles in the sample below the RAE_R at 360°C , allowing complete and rapid conversion to LaSrNiRuO_4 . In contrast, the smaller lattice strain and larger particle/domain size of the slow-cooled sample lead to a smaller lowering of the reduction-activation energy, so only a fraction of the particles in the sample have reduction-activation-energies below the RAE_R at 360°C , so only partial reduction of the sample occurs.

In many topochemical reactions, a lack of reactivity can be overcome by simply raising the reaction temperature. However, in the case of the LaSrNiRuO_6 -to- LaSrNiRuO_4 reaction, raising the reaction temperature leads to the onset of nontopochemical decomposition reactions. Thus, we can see that in the absence of “microstructural activation” it is not possible to prepare single-phase samples of LaSrNiRuO_4 via reduction of LaSrNiRuO_6 .

This situation highlights a general requirement of topochemical transformations: that there is a significant difference in the reaction rate (and therefore activation energy) between the desired topochemical process (e.g., anion deintercalation) and competing nontopochemical processes (e.g., structural rearrangement/decomposition). There are many cases, such as the LaSrNiRuO_6 -to- LaSrNiRuO_4 transformation, where the difference in rate/activation energy is insufficient to allow the preparation of single-phased samples of the topochemically manipulated product phase. Fortunately, in the LaSrNiRuO_6 -to- LaSrNiRuO_4 case, there is a convenient structural phase transition that allows the microstructure of the material to be manipulated to “activate” the topochemical reaction, but there are many instances where this type of activation is not possible. There are however other methods of achieving analogous activations of topochemical processes. For example, the “hard-soft” reaction sequence developed by Attfield^{22,23}—in which a “host” phase is prepared in a high-temperature, high-pressure reaction, quenched to ambient conditions, and then further transformed by a topochemical reaction—would be expected to benefit from enhanced reactivity due to the increased lattice strain present in the metastable host phase at ambient pressure. More generally, strain can be applied to “host” structures by depositing them as thin films on to substrates with slight lattice mismatches. Indeed, it is generally observed that thin films react faster and at lower temperatures than bulk powder samples,^{20,21,24–27} providing further support for the microstructural activation of solid-state topochemical reactions.

This microstructural activation of anion-focused topochemical reactions mirrors the extensive observations of microstructural effects in cation intercalation/deintercalation reactions, where it is observed that particle size^{28–32} and the buildup of lattice strain^{33,34} during intercalation/deintercala-

tion processes can affect not only the rates and extents of chemical conversion but also the pathways adopted.

CONCLUSIONS

The enhanced reactivity of quenched samples of LaSrNiRuO_6 , compared to analogous slow-cooled samples, can be attributed to the presence of a structural phase transition at $T \approx 400$ °C, which manipulates the microstructure of the double perovskite oxide so that quenched powder samples of LaSrNiRuO_6 have smaller average particle/domain sizes and higher lattice strains than slow-cooled samples. These microstructural features act to lower the activation energy of the topochemical reduction reaction that converts LaSrNiRuO_6 into LaSrNiRuO_4 , allowing the rapid reduction of quenched samples of LaSrNiRuO_6 at 360 °C but not slow-cooled samples. The sensitivity of the progress of the reduction reaction to the thermal history of the LaSrNiRuO_6 sample indicates that topochemical reduction reactions can be microstructurally activated, potentially expanding the range of solid phases that can be prepared by this type of process.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsorginorgau.1c00030>.

Complete description of the chemical, structural, and microstructural characterization of quenched and slow-cooled LaSrNiRuO_6 . Details of SEM particle-size analysis (PDF)

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The manuscript was written through contributions of all authors.

Notes

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