Room-Temperature AFM Electric-Field-Induced Topotactic Transformation between Perovskite and Brownmillerite SrFeO$_x$ with Sub-Micrometer Spatial Resolution

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Reversible structural transformations between perovskite (PV) ABO$_{3-\delta}$ and brownmillerite (BM) ABO$_{2.5}$ ($A = \text{Ca}^{2+}, \text{Sr}^{2+}; B = \text{Fe}^{4+/3}, \text{Co}^{4+/3}$) oxides can be induced by topotactic oxygen exchange at moderate temperatures under reducing/oxidizing conditions. The combination of a large oxide-ion conductivity and a small free energy difference between the 4+/3+ oxidation states of many 3d transition metal ions enables these topotactic transformations. Herein, it is demonstrated that the electric field produced by a voltage-biased atomic force microscopy tip can induce such transformation between PV SrFeO$_{3-\delta}$ and BM SrFeO$_{2.5}$ at room temperature and with sub-micrometer spatial resolution. Interestingly, the structural transformation is kept after the electric field is removed, allowing a nonvolatile control of the local chemical, electrical, optical, and magnetic properties. Thus, the results presented in this paper open the door for the fabrication of stable ionic-based devices through the electric field patterning of different crystallographic phases.

1. Introduction

Oxygen-deficient (Ca,Sr)(Fe,Co)O$_{3-\delta}$ perovskites (PV) exhibit fast O$^2-$ ion mobility and electrical conductivity at high temperature, which make them very appealing for the development of memory devices,[1] and also of solid oxide fuel cells,[2,3] and oxygen separation membranes.[4,5] On many of these PV, a topotactic oxygen extraction rendering the brownmillerite (BM) (Ca,Sr)(Fe,Co)O$_{2.5}$, or the square-planar (Ca,Sr)(Fe,Co)O$_{2.0}$ can be induced via different chemical/electrochemical reactions,[1,6–11] and high temperature thermal treatments under oxygen/vacuum.[12–19]

But although topotactic transformations (TPt) have been shown to be a powerful tool to tune the properties of several oxides,[20] the need of either high temperatures or specific electrochemical-cell configurations, along with the lack of spatial control over the position and resolution of the transformation, limits its applications in many technologies requiring spatial sub-micrometer control.

In this work we demonstrate that the TPt between PV and BM phases of SrFeO$_x$ thin films can be induced locally with sub-micrometer spatial resolution at room temperature by the electric field created by an AFM tip. Accumulation regions of charged oxygen vacancies, $V_O^-$, transform spontaneously into the stable BM phase leading to large changes in the electronic and crystal structure of the original perovskite film. Our approach offers important advantages over the previously tested methods to induce the PV–BM transformation, for instance, i) the crystallographic transformation is achieved at room temperature; ii) the process is performed in ambient conditions, without any further modification of the surface of the film. This is an important
advantage over electrochemical methods which require the use of ionic liquids or other electrochemical media, particularly if an additional functionalization of the surface is pursued. Finally, iii) the sub-micrometer spatial control over the crystallographic transformation achieved with this method opens the door to the patterning of stable ionic-based devices with different functionalities.

2. Results and Discussion

Reversible topotactic transformation between the PV and BM phases of SrFeO$_{2.5}$ epitaxial thin films can be achieved by post-deposition thermal annealing under different oxygen pressures. In Figure 1, we show a detail of the X-ray diffraction pattern of a 50 nm thick film of BM SrFeO$_{2.5}$ on a (001) SrTiO$_3$ (STO) substrate. Postdeposition annealing at 500 °C and $P(O_2) = 300$ mTorr produces the complete transformation from the orthorhombic BM ($a_{pc} = 3.97$ Å) to the cubic PV phase ($a = 3.86$ Å). A subsequent annealing at the same temperature but under reduced oxygen pressure, $P(O_2) = 0.1$ mTorr, results in an oxygen loss from precise positions (topotactic transformation), and the recovery of the BM phase (see the structural model in Figure 1b and Figure S1 in the Supporting Information). We verified the occurrence of the transformation in films of SrFeO$_x$ deposited on SrTiO$_3$, LaAlO$_3$, NdAlO$_3$, and MgO, as a proof of the negligible role of the substrate in the PTt transformation. Additionally, X-ray reciprocal space mapping (not shown) demonstrated that the 50 nm films of SrFeO$_x$ on STO remain totally strained, in the BM and PV phases.

On the other hand, although oxygen mobility decreases very rapidly at low temperature, other authors reported that Co/Fe-based perovskites can undergo reversible TPt oxygen uptake to the BM phase at room temperature during electrochemical reactions.$^{[1,6,7,9,21]}$

Therefore, the charged nature of $V_{O}$ and their large mobility in the PV phase, should make them amenable to their control by a local electric field applied by a voltage-biased AFM tip, as it was shown in other 3d oxides.$^{[22–25]}$ We hypothesize that the small free energy difference between the PV and BM phases in SrFeO$_{x}$ could lead to the spontaneous rearrangement of the vacancies accumulated by the electric field in a region of the PV film, leading to the local transformation into the BM phase.$^{[26]}$

Figure 2a shows a scheme of this process, in which a negative voltage-biased AFM tip scanning a film of SrFeO$_{3.5}$ induces an accumulation region of positively charged $V_{O}$. The optical microscope images of Figure 2b (reflected light) indeed show a clear change in color of an area of the PV SrFeO$_{3.5}$ film recorded under a $-10$ V biased AFM tip. In this case the darkest accumulation area is consistent with a larger optical bandgap (insulating, no reflecting light), while the surrounding film, not affected by the electric field, remains metallic (intense reflection of light). The change in color is observable in regions scanned above $-4.5$ V, and becomes more intense above $-7$–$8$ V.

The local electrical conductivity was probed by conductive-AFM. After scanning different portions of the film (of either $10 \times 10$ $\mu$m$^2$ or $5 \times 5$ $\mu$m$^2$) with a negative biased AFM tip, the local conductivity between the tip and the sample was measured. The results, as shown in Figure 2c, demonstrate a drastic reduction of the electrical conductivity of the regions were $V_{O}$ are accumulated by the electric field. This is consistent with the smaller optical reflectance observed in the images and suggests the transformation from conducting SrFeO$_{3.0}$ PV to insulating SrFeO$_{2.5}$ BM.

The evolution of the room temperature Raman spectra for different voltages is shown in Figure 3a. These experiments were performed on a film deposited on LSAT, to avoid the large background signal from STO.$^{[27]}$ The appearance of the peaks at $\approx 331$, $\approx 430$, and $\approx 625$ cm$^{-1}$ in the pristine regions of the film are characteristic of a tetragonal or orthorhombic PV, of composition SrFeO$_{x}$, $x = 2.7$–$2.9$.$^{[28]}$ The intensity of these peaks decreases gradually and shows a blue-shift in the regions scanned with an increasing voltage, at the same time that a broad maximum with a shoulder at $\approx 710$ cm$^{-1}$ characteristic of the stretching modes of FeO$_4$ tetrahedra in the BM phase$^{[29]}$, develops (see Figure S2 in the Supporting Information for further details). The comparison with the Raman spectrum of a BM SrFeO$_{2.5}$ film shown in the same figure suggests the full transformation of the PV into BM above $\approx -9$ V.

The microstructural transformation was corroborated through a comparative scanning transmission electron microscopy (STEM) analysis of two cross-section lamellae; a first
specimen extracted from the as-grown area of the sample, and a second specimen extracted from the squared area previously scanned under $-10$ V. The as-grown sample evidences a PV pseudo-cubic structure; Figure 3b). This is highlighted by the fast Fourier transform (FFT) of the film; Figure 3c), where the main in-plane and out-of-plane periodicities can be indexed as

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**Figure 2.** AFM electric-field-induced local topotactic transformation. a) Applying an electrical voltage between the AFM tip and the PV SrFeO$_{3-\delta}$ film in contact mode produces a large electric field in the region underneath the tip, accumulating $V_{OC}$. b) Optical image (taken with the AFM camera, reflected light) of different regions of the film after scanning with $-10$ V (left). The triangular shadow on the top of the image corresponds to the AFM cantilever. The picture at the right shows different regions scanned with increasing voltages, from $-4.5$ to $-10$ V, at $-0.5$ V steps. The areas scanned with the electric field change their color with respect to the conductive PV film background, consistent with a decrease in conductivity. The scale bar is 25 $\mu$m long in both images. c) Local electrical conductivity probed by conductive AFM. The portions of the film previously scanned with the voltage-biased AFM tip become electrically insulating. The conductivity measurements were performed on a SrFeO$_x$ film deposited on a (001) MgO substrate, to avoid any possible contribution from oxygen vacancies that could be formed in the STO substrate.

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**Figure 3.** Structural characterization of the regions scanned by the voltage-biased AFM tip. a) Room temperature Raman spectra ($\lambda = 532.19$ nm) of the PV film after scanning different regions with an increasing voltage. The spectra were displaced vertically for clarity. The Raman spectrum of the substrate (LSAT) and a BM film are also shown for comparison. The peaks characteristic of the PV and BM phases are indicated by vertical dashed lines. The peaks of the PV practically disappear in the regions scanned at the higher voltages, and the broad peak at $\approx 710$ cm$^{-1}$ characteristic of the BM appears. Panels (b) and (c) show the STEM and Fourier transform of a pristine area of the film, showing the microstructure of the PV film. In panels (d) and (e), we show the same microstructural analysis of a lamella extracted from an region scanned at $-10$ V, showing the characteristic morphology and superstructure spots of the BM phase.
the (001) and (010) reflections of a PV structure. A quantitative analysis of the lattice parameter performed by geometrical phase analysis (GPA)[10] (see Figure S3 in the Supporting Information) demonstrates that the film is fully strained, in spite of the presence of sparse structural defects (for instance, stacking faults such as the one clearly visible in the STEM image). The out-of-plane lattice parameter averages 3.83(4) Å, which nicely agrees with the PV lattice parameter deduced from XRD. After the AFM scan at −10 V, a full transformation of the film has occurred at microscopic level (Figure 3d). A superstructure characteristic of the BM phase is formed throughout the film increasing the out-of-plane lattice parameter of the original PV structure. This is also reflected in the FFT as an extra spot labeled (001)BM in Figure 3e.[31] As in the parent PV phase, GPA evidences that the film remains strained, and the out-of-plane lattice parameters has expanded up to 3.99(3) Å.

The transformation was additionally characterized through the change in the oxidation state of Fe by synchrotron X-ray absorption spectroscopy (XAS) around the Fe K and L2,3-edges, and the O K-edge, inside and outside an area scanned with a voltage-biased AFM tip (Figure 4). An energy shift of at the Fe K-edge to lower energies in the scanned region indicates a lower Fe valence (Figure 4a). According to a calibration curve performed using stoichiometric iron oxides with different oxidation states, the edge displacement increases linearly with the oxidation state (OS) of Fe: \( E(\text{Fe}) = E_0 + 4.1 \times \text{OS} \)[12] For the oxidation states we have used a Fe foil to extract the \( E_0 = 7112 \text{ eV} \). Based on the XAS spectra, we obtained a valence of Fe \( \approx +3.78 \) in the pristine region of the film, and Fe \( \approx +3.07 \) in the \((150 \times 300 \mu \text{m}^2)\) area scanned by the −10 V biased AFM tip. These values correspond to chemical compositions of SrFe\(^{2+}\)O\(_{2.85}\) and SrFe\(^{3+}\)O\(_{2.54}\), respectively, in agreement with the chemical formula for oxygen deficient PV and BM, respectively.[28] X-ray photoemission spectroscopy (XPS) measurements around Fe 2s energy (see Figure S4 in the Supporting Information), led to similar oxidations states: SrFe\(^{2+}\)O\(_{2.85}\) and SrFe\(^{3+}\)O\(_{2.54}\) for the pristine and electric-field-scanned region, respectively.

In Figure 4b, we show the XAS spectra of SrFeO\(_3\) around the Fe L2,3-edge, for the pristine PV film and for a region scanned at −10 V. The isotropic spectra have been obtained as an average of left and right circular polarized light, normalized to maximum intensity of the L1-edge. The spectra consist of two multiplets \((L_1 \text{ and } L_2)\) at 710 and 722 eV, which are separated by the spin–orbit splitting of the Fe 2p core hole. The peak at the low energy side of the L1-edge is characteristic of a lower oxidation state of Fe,[33] and it was associated in SrCoO\(_3\), to a reduction in the coordination of the transition-metal ion, from octahedral to tetrahedral. The increase of this feature in the region of SrFeO\(_{3.5}\) scanned with the −10 V biased AFM tip supports the occurrence of the PV to BM transformation in this area.

The XAS at the O K-edge is shown in Figure 4c. The peaks between \(528–532 \text{ eV}\) result from the transition from O:1s to O:2p states. Previous works demonstrated that PV SrFeO\(_{3.5}\) is a negative charge transfer system, meaning that the Fe\(^{4+}\)/\(^{3+}\) redox pair lies below the O:\(^{-}\)/O:\(^{2-}\) level.[34–37] In this situation, covalent mixing makes the electronic configuration of Fe\(^{4+}\)(d\(^4\)) closer to Fe\(^{3+}\)(d\(^3\)-L\(_0\)), and therefore important information about Fe\(_{3d}\) states can be obtained from the O K-edge adsorption spectrum.[33,38] The crystal field splitting produces the double peak at 530 and 532 eV, and its strong suppression after electric field scanning is consistent with an increasing population of tetrahedrally coordinated Fe, as the PV transforms into BM.[39]

Therefore, the microstructural and spectroscopic results discussed so far demonstrate that it is possible to achieve a local, stable topotactic PV-to-BM transformation in thin films of SrFeO\(_{3.5}\) by the direct action of an electric-field-biased AFM tip scanning the bare surface of the film.

This structural tunability is possible by a combination of small \(V_0\) formation energy in SrFeO\(_x\), and a very low free energy difference between the BM and PV phases at room temperature (=250 meV).[13] These are considerably smaller.

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**Figure 4.** Spectroscopic evidence of the local PV to BM transformation. a) Comparison of the Fe K-edge X-ray absorption on a pristine region of the film (green line), and on an area \((150 \times 300 \mu \text{m}^2)\) previously scanned by the −10 V biased AFM tip (orange line). The displacement of the absorption to lower energies in the electric field-scanned region indicates a lower formal charge of Fe (see the text). Panels (b) and (c) show the comparison between the Fe L2,3-edge and O K-edge X-ray absorption spectra taken on an area scanned with the −10 V biased AFM tip (orange line), and a pristine region of the film (green line). The vertical arrow in (b) marks a low energy feature in the 2p\(_{3/2}\) peak, characteristic of a lower Fe-oxidation state and tetrahedral coordination in this region (see the text). The spectra were displaced vertically for clarity.
than for Co or Mn oxides for instance,[44] putting SrFeO$_3$ in an optimal position to observe this kind of transformation.

An important result is that, given the considerably larger lattice parameter of the BM ($a_{pc} = 3.97$ Å) with respect to the PV ($a = 3.86$ Å), the crystallographic transformation induced by the AFM tip should be accompanied by a local expansion of the film. Taking the pseudocubic lattice parameters, the full transformation of a 50 nm thick film from PV to BM should increase its thickness by $\approx 1.2$–$1.3$ nm, perfectly detectable by AFM topography.

In Figure 5a, we show the local increase in height measured by AFM topography of PV SrFeO$_{3-x}$ films (50 nm thick) deposited on different substrates, after scanning several areas of $5 \times 5$ µm$^2$ with a voltage-biased AFM tip. The AFM images are shown in Figure 5b,c for films deposited on NAO (NdAlO$_3$) and STO, respectively.

Above a threshold voltage $\approx 2.5$–$3.5$ V, there is a local expansion of the film, reaching a plateau of $\approx 1.2$–$1.5$ nm between $\approx -4$ and $-6$ V (Figure 5a). Although the threshold voltage changes slightly for the films deposited on different substrates, probably reflecting the effect of epitaxial strain in oxygen mobility (NdAlO$_3$, LaAlO$_3$, and SrTiO$_3$ induce a strain on SrFeO$_{3-x}$ of $\approx 2.5$%, $\approx 1.8$%, and $\approx 1.1$%, respectively).[21] the local expansion induced by the voltage-biased AFM tip is observed irrespective of the substrate used to grow the SrFeO$_{3-x}$ PV film. Also, although SrTiO$_3$ is very susceptible to the creation of oxygen vacancies, NdAlO$_3$, LaAlO$_3$, or MgO are not.[40,41] Therefore, the observation of the PV–BM transformation in films of PV SrFeO$_{3-x}$ on these substrates discards any possible effect of oxygen exchange with the SrTiO$_3$ substrate.

Interestingly, increasing the voltage above $\approx 7$–$8$ V produces an even larger expansion of the film height, to a maximum of $\approx 4$ nm for the films on STO, and of $\approx 5$–$6$ nm for NAO and LAO. This suggests a transformation between different stable intermediate phases, with different oxygen content or microstructure, as previously suggested by other authors.[11,20,42,43] The observation of a larger Raman shift at high voltages also supports this picture (see Figure S2 in the Supporting Information).

The expansion observed at high voltages in Figure 5a is higher than calculated using the pseudocubic lattice parameters and will require instead $c = 4.20$ Å. The local spectroscopic probes discussed before discard the possibility of any material deposition from the tip or oxide segregations to explain the large expansion above $\approx 7$ V. Different tips (conductive and insulating) with different force constants were employed in different scanning modes (contact and noncontact) to discard any possible artifact from electromechanical coupling during the topography measurements.

Also, several areas of $10 \times 10$ µm$^2$ were scanned at $\approx 10$ V in thin films of PV of different thicknesses, and the local change in height increases linearly with the total film thickness (see Figure S5 in the Supporting Information). This confirms the intrinsic nature of the large local expansion observed above $\approx 7$ V.

The effect of any possible surface damage by the AFM tip was also verified. Scanning the films with different combinations of bias-voltage and applied force to the AFM tip, demonstrate that the local change from PV to BM is due to the drag of $V_{O}$ by the strong, local electric field, and not by an effect of the local pressure or surface damage (Figure S6 in the Supporting Information). Additionally, in order to discard any effect coming from the substrate, a bare STO substrate was scanned at $\approx 10$ V; no change of the surface topography was observed after this process.

Therefore, the large expansion observed at the higher voltages must be characteristic of an intrinsic microstructural or compositional change in the sample. One possibility is

Figure 5. Topographic effect of the AFM-induced PV to BM transformation. a) Height of the electric-field-scanned regions obtained from the AFM topography, for different applied voltages, and for films deposited on different substrates. The arrows mark the threshold voltage for the transformation. The pseudocubic lattice parameters compatible with such expansion are indicated in the right axis. These were calculated assuming a full transformation of the film. An incomplete transformation will result in even a larger lattice parameter of the BM lattice. Panels (b) and (c) show the AFM topography images of the PV SrFeO$_{3-x}$ thin films deposited on NdAlO$_3$ (NAO) and STO, respectively, after several squares ($5 \times 5$ µm$^2)$ have been recorded with an AFM tip biased at different voltages.
a change in the orientation of the oxygen vacancy channels (OVC) of the BM above a certain voltage. A lattice parameter as large as \( \approx 4.15 \) Å was reported in BM \( \text{SrFeO}_{2.5} \) after a change in the orientation of the OVC from horizontal to vertical.\(^{[44]}\) However, this does not seem to be the case in our films, as the STEM analysis shown in Figure 3b–e shows OVC parallel to the interface with the substrates in the \(-10\) V samples.

On the other hand, a large expansion of \( \approx 8\% \) of the unit cell was reported in \( \text{SrCoO}_{2.5} \), after \( \text{H}^+ \) absorption and bonding to the apical \( \text{O}^{2-} \) ions in tetrahedral layers of the BM, to form \( \text{HSrCoO}_{2.5} \).\(^{[1]}\) The dissociation of water from the ambient, in a process in which \( \text{HO}^- \) ions fill an oxygen vacancy site cannot be excluded in our case.\(^{[45]}\) Actually, we followed the evolution of the surface potential of the scanned regions through Kelvin probe AFM (Figure S7 in the Supporting Information). The observed decay of surface potential could be a result of surface electrochemical activity; ionic species formed from water dissociation at high electric field will produce an accumulation of charge which will decay with time.

In any case, a definitive conclusion about the precise nature of the high-voltage phase requires further microstructural and compositional investigation, beyond the objectives of this paper.

The BM phase formed by the voltage-biased AFM tip at room temperature are perfectly stable over time. Figure 6a–c shows the AFM topography images and line profiles of \( 10 \times 10 \) \( \mu \)m\(^2\) squares just after being recorded at \(-10\) V, and after 5 days under ambient conditions. The changes in topography are negligible during this time, demonstrating an excellent stability of the phases. We have followed some samples over 6 months and found similar results (Figure S8 in the Supporting Information).

On the other hand, annealing the sample at \( 300 \) °C in \( 300 \) mTorr of \( \text{O}_2 \) for 2 h is enough to redistribute the \( \text{V}_0 \) toward the surrounding conducting PV film, or through exchange with the atmosphere.\(^{[46]}\) This treatment erases the topographic height (Figure 6d), and recovers the original PV structure in the whole film, demonstrating the thermal reversibility of the effect.

3. Conclusions

The possibility to control the crystallographic transformation between the PV and BM phases of \( \text{SrFeO}_x \) at room temperature, using a voltage biased AFM tip acting directly on the bare surface of the PV film has been demonstrated. This transformation is accompanied by a local expansion of the film thickness and changes in the electrical conductivity, which are stable for months under usual ambient conditions. Given the large difference in the electrical conductivity of the PV and BM, as well as their different magnetic configuration,\(^{[47]}\) the local control over the TPt reported in this paper opens enormous possibilities to study, in a controlled way, magnetic exchange interactions at their interface, fabricate stable resistive memories,\(^{[48,49]}\) or ionic-conducting circuits, with sub-micrometer resolution.
(for example, see Figures S9 and S10 in the Supporting Information). Eliminating the use of ionic liquids or any other electrochemical bath to achieve the transformation at room temperature also offers important advantages over previously reported methods, in terms of undesired reactivity or postfunctionalization of the electric field transformed surfaces.

Finally, given the similarities between SrFeO$_3$ and other oxides, like CaFeO$_x$, (Ca,Sr)CoO$_x$, La$_{1−x}$Sr$_x$MnO$_3$, or VO$_2$, susceptible to large changes in their electric, magnetic and structural properties after oxygen manipulation, the method reported here offers a new approach to design new functional materials.

4. Experimental Section

Thin films of SrFeO$_{δ+ε}$ were deposited on single-crystal substrates of SrTiO$_3$ (STO), LaAlO$_3$ (LAO), NdAlO$_3$ (NAO), and MgO from a dense ceramic target by pulsed laser deposition (Nd:YAG Laser, λ = 266 nm, 5 Hz, fluence = 1.5 J cm$^{-2}$) at a temperature of 700 °C, and oxygen pressure of P(O$_2$) = 10 mTorr. After deposition, the samples were annealed at the growth temperature for 10 min at P(O$_2$) = 2 × 10$^{-6}$ Torr to obtain the BM, or at 300 mTorr for the PV. The samples were then rapidly cooled down to room temperature inside the PLD chamber under the same oxygen pressure, to keep the oxygen content.

AFM measurements were performed on a NX10 by Park Systems. All the AFM experiments were performed using electric force microscopy (EFM) mode that allows to apply a bias voltage at the AFM tip, which is electrically conductive (Pt-coated, ~25 nm tip radius). The surface electric potential of the sample was measured by the scanning Kelvin probe mode (SKPM).

High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) experiments were carried out in a probe corrected FEI Titan Low Base 60-300. This instrument is equipped with a high brightness field emission gun (X-FEG) and a CETCOR aberration corrector for the probe by CEOS. TEM lamellas for these experiments were prepared in a FEI Dual Beam Nova 200 in cryogenic conditions (~100 °C) to minimize local deoxygenation of the films due to local heating during the milling.

Synchrotron X-ray diffraction and X-ray absorption experiments on the Fe K-edge were performed at the BM25-SpLine beamline at ALBA synchrotron. The XRD patterns were obtained on a Six-Circle diffractometer in vertical geometry with incident light of wavelength 532.2 nm (1 mW, laser spot 100 µm × 50 µm). XAS spectra on the Fe K-edge were acquired by WiTec, working in near-backscattering geometry with incident light of wavelength 532.2 nm (1 mW, laser spot around 5 µm diameter, diffraction grating 1800 lines/mm).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

atomic force microscopy, thin films, topotactic reactions

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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