

Rapid communication

Oriented growth of $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ Ruddlesden–Popper phases in chemical solution deposited thin films

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Abstract

Oriented thin films of perovskite-related $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ Ruddlesden–Popper phases ($n = 1, 2, 3$) were grown on (001) single-crystalline SrTiO_3 substrates. Preparation of the films was carried out by wet chemical deposition from metalorganic Sr–Ti solutions (rich in Sr) and subsequent conversion into the crystalline state by thermal treatment in air atmosphere at a maximum temperature of 700 °C. Solutions were prepared by a modified Pechini method. The films were investigated by wide-angle X-ray scattering and high-resolution transmission electron microscopy. The phase content of powders prepared from the dried solutions and annealed under similar conditions differed from that present in the films, i.e. only polycrystalline SrTiO_3 was detected together with oxides of Ti and Sr.

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1. Introduction

The rapid development of thin film deposition methods in the last decades nowadays allows synthesizing a variety of functional materials in the form of thin films and multilayers. The functionality of oxide materials in general is diversified, covering dielectric, ferro- and piezoelectric as well as magnetic properties. Among oxide materials, SrTiO_3 (STO) crystallizing in the perovskite-type of structure is of special interest due to its superior dielectric properties (paraelectric up to low temperatures; with high dielectric constant of good tunability [1]) and its chemical and structural stability in a wide temperature range [2,3].

From reports in the literature it is known, that in STO crystals, exposed to reducing or oxidizing conditions at elevated temperatures, the near-surface structure can change significantly [4–6]. In particular, the formation of crystallographic shear phases (belonging to the $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ Ruddlesden–Popper (RP) homologous series [7–9]; see Fig. 1 for structure models) is observed,

which is induced by accommodation of long-range order lattice distortions formed in consequence of local deviations from STO chemical composition. Furthermore, the authors of the present report recently discovered a reversible tunability of surface-structural distortions in a single-crystalline STO plate under the influence of an external electric field [10,11]. It was interpreted in terms of electromigration of SrO ion complexes and thus reversible formation of RP phases in near-surface regions of the STO crystal.

Beside these surface-structural effects, which are also important considering the interpretation of macroscopic properties of STO, the RP phases itself are of great fundamental and technological interest. The prospect of “engineering” the properties of the constituent STO layers by varying the index n has stimulated synthesis as well as investigation and theoretical estimation of dielectric properties of several members of the $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ RP series. The single crystal growth of members of the RP series is difficult. Only STO ($n = \infty$) melts congruently whereas the growth of Sr_2TiO_4 ($n = 1$) and $\text{Sr}_3\text{Ti}_2\text{O}_7$ ($n = 2$) is complicated by phase transitions and decompositions [12]. Applying conventional ceramic processing techniques, single-phase (polycrystalline) Sr_2TiO_4

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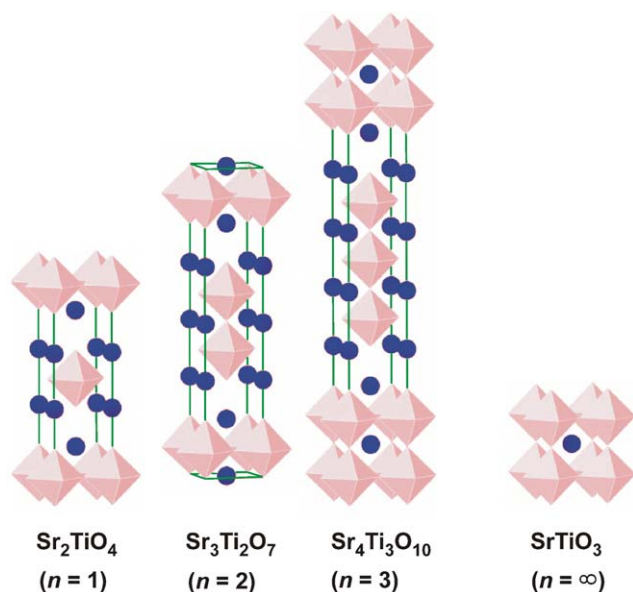


Fig. 1. Schematic drawing of the unit cell of the $n = 1$ (Sr_2TiO_4 , tetragonal, $a \approx 3.9 \text{ \AA}$, $c \approx 12.6 \text{ \AA}$), $n = 2$ ($\text{Sr}_3\text{Ti}_2\text{O}_7$, tetragonal, $a \approx 3.9 \text{ \AA}$, $c \approx 20.4 \text{ \AA}$), $n = 3$ ($\text{Sr}_4\text{Ti}_3\text{O}_{10}$, tetragonal, $a \approx 3.9 \text{ \AA}$, $c \approx 28.1 \text{ \AA}$) and $n = \infty$ (SrTiO_3 , cubic, $a \approx 3.9 \text{ \AA}$) members of the $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ RP homologous series. Black spheres represent Sr atoms, while Ti atoms are located in the center of the oxygen octahedra (gray color).

[7,13–16], $\text{Sr}_3\text{Ti}_2\text{O}_7$ [8,13–16] and $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ ($n = 3$) [14] could be formed. Through the use of a preliminary mechanical activation, the sintering temperature (usually above 1400°C) could be reduced substantially [17,18]. A sol–gel method for the preparation of ultra-fine single-phase powders of the first three members of the RP series is reported as well [19]. Previous attempts to synthesize intermediate members ($3 < n < \infty$) of the series were not successful [13], what has been explained by lattice energy calculations [20–22] evincing that there is no driving force to form single-phase samples with intermediate n .

The epitaxial growth of thin films of the first five members of the RP series on STO substrates was achieved by molecular beam epitaxy (MBE) [23]. Sr_2TiO_4 , $\text{Sr}_3\text{Ti}_2\text{O}_7$ and $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ films were found to be nearly single-phase, while $\text{Sr}_5\text{Ti}_4\text{O}_{13}$ and $\text{Sr}_6\text{Ti}_5\text{O}_{16}$ films exhibited antiphase boundaries and intergrowth defects.

To our knowledge, up to now no single crystal structure analysis of other members of the RP homologous series than STO (cubic, space group $Pm\bar{3}m$; see [24], for example) is reported. Non-final members of the series are described in frames of tetragonal symmetry (space group $I4/mmm$) on base of powder diffraction investigations [7–9].

In principle, wet chemical deposition methods should be particularly suitable for the preparation of thin films of multicomponent perovskite-like thin films, especially of such with varying stoichiometry (as it is the case in the RP homologous series). Thus, in the presented work we have used a modified Pechini method [25,26] to prepare the RP films. The preparation of STO films with this method has already been accomplished [27–30] but to our knowledge it

is the first time that films of low- n RP phases are deposited wet chemically.

2. Experimental

2.1. Solution preparation and film deposition

The preparation of the Sr–Ti solutions was based on the modified Pechini method developed by Zanetti et al. [27] for the preparation of STO films. First, citric acid (Aldrich, concentration $\geq 99.5\%$) was dissolved in distilled H_2O and titanium isopropoxide (tyzor organic titanate, Aldrich) was added to the citric acid solution. The resulting Ti citric acid solution was heated up to a temperature of 70°C and SrCO_3 (Aldrich, $99.9+\%$) was added. After the solution became clear (i.e. after complete dissolution of the salt), ethylene glycol (Aldrich, ACS reagent) was added and the solution was heated up to a temperature of $80\text{--}90^\circ\text{C}$ to boil off some excess water. The molar ratio of Sr to Ti ions was fixed at 2:1. Two different molar ratios of citric acid to metals were chosen, i.e. 1:1 (deposition solution for sample F1) and 3:2 (deposition solution for sample F2). The mass ratio of citric acid to ethylene glycol was 3:2. The viscosity of the polymeric solution was adjusted to 25 mPas by adding water to the solution.

Dip coating of single-crystalline (001) STO substrates (Crystec, one-side polished) was performed at a constant withdrawal speed of 0.56 cm/min using a dc-micrometer drive (Physik Instrumente). Afterwards, the wet films were dried in a conventional lab furnace (2 h duration at a temperature of 150°C) in air atmosphere. As-prepared samples were annealed in a tubular furnace in air atmosphere following the temperature regime shown in Fig. 2. The temperatures of annealing (400°C for pyrolysis of residual organic components and 700°C for crystallization) were chosen considering the results of STO formation in thin films deposited by the modified Pechini method [28–30].

For preparation of the powder sample, a small amount of the polymeric solution (molar ratio of citric acid to Ti and Sr metals is the same as for film F1, i.e. equal to 1:1) was poured into a Petri dish and dried for the duration of 24 h at a temperature of 150°C . The powder was sequentially annealed in air atmosphere by a procedure similar to this used for the preparation of the films (Fig. 2) but with prolonged duration of both stages of annealing (5 h at every temperature level). Furthermore, another powder sample was prepared by pulverization of the STO substrate.

2.2. Characterization

The crystalline phase contents of the films (deposited at the polished side of the STO substrate) and powders were investigated by means of wide angle X-ray scattering (WAXS) at ambient conditions after every stage of annealing. The diffraction patterns were recorded using

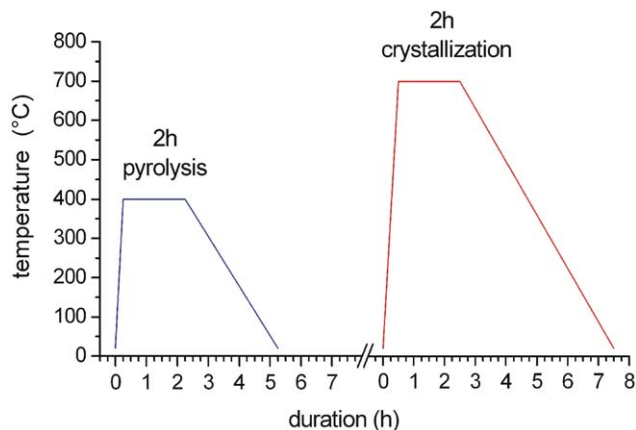


Fig. 2. Annealing procedure of the wet deposited films including pyrolysis of residual organic compounds (400 °C) and crystallization (700 °C).

an X-ray diffractometer URD-6 (Seifert FPM) with a scintillation detector. The $\text{CuK}\alpha$ radiation, monochromatized by a secondary Johansson-type graphite-monochromator, was used. Measurements were carried out in symmetrically coupled ω - 2θ scan mode, where ω is the angle of incidence and 2θ is the detection angle. Additionally, the WAXS patterns of prepared powder samples, mixed with a Si reference powder (Standard reference Material 640b of NIST), were recorded. The data obtained in these measurements were used as a standard for refinement of the unit cell parameters of the crystalline phases found in the powders. The WAXS patterns obtained were analyzed using reference data of Powder Diffraction File 2 (PDF2) [31].

Thin foils of the cross-section of the films were prepared for high-resolution transmission electron microscopy (HRTEM) by a standard technique involving cutting-off the appropriate pieces, mechanical grinding, mechanical dimpling and etching by 7 keV Ar^+ ion bombardment to perforation. The samples prepared were examined in a Philips CM30 transmission electron microscope operated at 300 kV. According to investigations of the cross-section of the samples, the thickness of the films was of about 200 nm.

The molar ratio of Sr to Ti atoms in the dried powders was determined by means of wavelength-dispersive X-ray fluorescence analysis (WDX) using an X-ray fluorescence spectrometer ARL ADVANT'X⁺ (Thermo). The fluorescence data of the analyzed powders were recorded in Helium atmosphere. The intensities of the maxima of characteristic energy lines were registered by an Ar-methane-flow detector for low energies up to 8 keV and by a scintillation detector for higher energies. For detecting the whole energy range, several crystals (LiF, PET, TIAP) were used. The atom-concentrations were calculated using the computer program UNIQUANT [32] based on the algorithm described in [33].

The viscosity of the polymeric solutions was measured at a temperature of 23 °C with a falling ball viscometer (Gilmont Instruments).

3. Results and discussions

3.1. Films

Fig. 3 presents the WAXS patterns of two different single-layered films after each stage of annealing. Strongest reflections in the diffraction patterns arise from the (001)-oriented STO substrate as can be gathered from the WAXS pattern of an uncoated substrate shown in Fig. 3 for comparison. After annealing at a temperature of 400 °C, additional reflections occurred in the diffraction patterns which can be attributed to polycrystalline STO, SrO or SrCO_3 . The (local) growth of Sr-rich phases coheres with the adjustment of a Sr excess during preparation of the deposition solutions, which is also confirmed by WDX

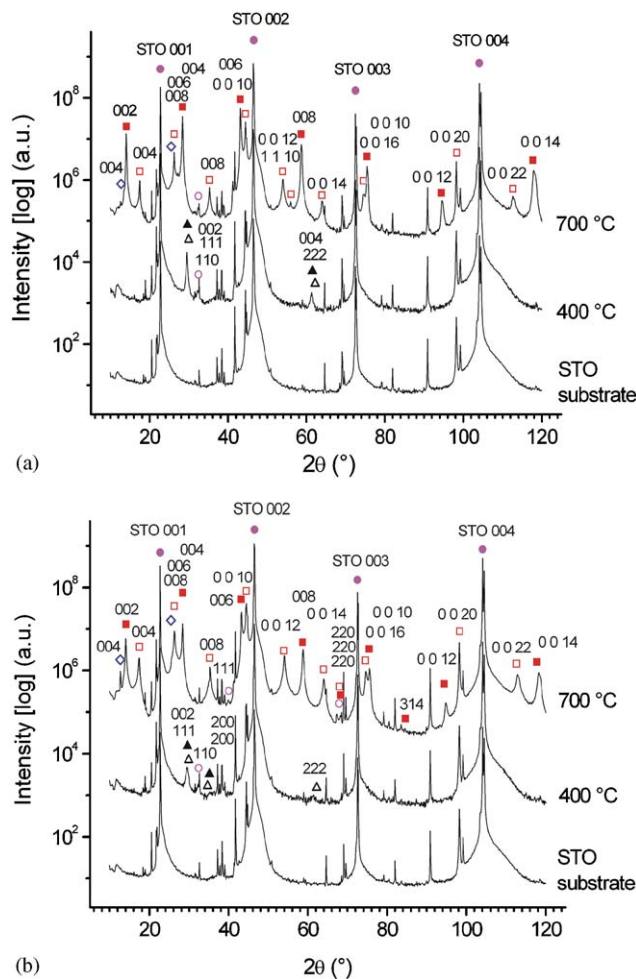


Fig. 3. Intensity versus diffraction angle (ω - 2θ WAXS scans) of the single-layered films on STO substrate recorded from samples F1 (a) and F2 (b) after subsequent annealing in air (2h duration) at the temperatures indicated. The WAXS pattern of the uncoated STO substrate is shown for comparison ((●) and (○)—substrate and polycrystalline SrTiO_3 , respectively (space group $Pm\bar{3}m$, PDF2 code 35-0734); (△) SrO (space group $Fm\bar{3}m$, PDF2 06-0520); (▲) SrCO_3 (space group $Pm\bar{c}n$, PDF2 05-0418); (■) Sr_2TiO_4 $n = 1$ RP phase (space group $I4/mmm$, PDF2 39-1471); (□) $\text{Sr}_3\text{Ti}_2\text{O}_7$ $n = 2$ RP phase (space group $I4/mmm$, PDF2 39-1471); (◇) $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ $n = 3$ RP phase (space group $I4/mmm$, PDF2 76-0741)).

Table 1

Unit cell parameter c of the tetragonal RP phases with different n as determined from WAXS patterns (Fig. 3)

Sample	c (Å)	n
F1	12.582(2)	1
F2	12.571(2)	1
F1	20.363(3)	2
F2	20.350(5)	2
F1	27.84(5)	3
F2	27.83(5)	3

The e.s.d. of the parameters are given in brackets.

analysis of powders prepared from the solutions (see below).

After annealing at a temperature of 700 °C, a multitude of additional reflections with considerably high intensities were detected in the diffraction patterns. Almost all of these were identified as $00l$ -reflections of the Sr_2TiO_4 ($n = 1$), $\text{Sr}_3\text{Ti}_2\text{O}_7$ ($n = 2$) and $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ ($n = 3$) RP phases. From the indexing of the reflections the conclusion can be drawn, that the crystallographic c -axis of the identified RP phases in the film is oriented perpendicular to the (001) surface of the STO substrate. Presumably STO is epitaxially, at least textured, grown in the films annealed at a temperature of 700 °C as well, which cannot be gathered directly from the diffraction patterns due to the overlap with STO substrate reflections and the X-ray geometry used. The occurrence of (less distinct) reflections in the WAXS patterns, which belong to RP phases and exhibit mixed indices, could be attributed to possible defects in the films.

The c lattice parameters of the RP phases grown (Table 1) were calculated by means of [34] on the basis of the central angle-positions of the reflections observed using the lattice parameter of STO substrate ($a = 3.905$ Å) as an internal standard. As it is seen, for both films deposited, they are similar and in excellent agreement with unit cell parameters of the corresponding phases known from the literature [7–9,13–16,23].

Furthermore, the existence of RP phases in the samples is also confirmed by HRTEM analysis. As an example, Fig. 4 shows a HRTEM image of a well-ordered crystal region of the Sr_2TiO_4 ($n = 1$) RP phase.

To clearly distinguish whether RP phases are formed in the films or in surface regions of the underlying STO substrate (what can occur with annealing in oxidizing atmosphere [4,5]), WAXS patterns of uncoated STO substrates annealed at temperatures of 700 and 900 °C in air (similar to the procedure shown in Fig. 2) were recorded, too. Since they exhibited no further reflections it can be stated that RP phases were solely formed in the films.

The relative intensities of Sr_2TiO_4 and $\text{Sr}_3\text{Ti}_2\text{O}_7$ reflections are different in diffraction patterns recorded from the F1 and F2 films annealed at a temperature of 700 °C (Fig. 3). It indicates that a different volume

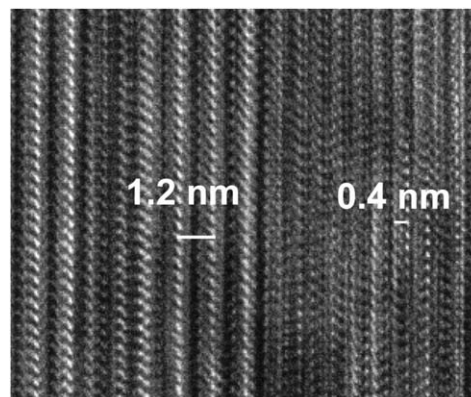


Fig. 4. Cross-sectional HRTEM image of the sample F1. Periodical spacings corresponding to STO substrate (right) and Sr_2TiO_4 $n = 1$ RP phase region (left) are marked.

fraction of these phases must be present; in particular in the film F1 the volume fraction of Sr_2TiO_4 (compared to $\text{Sr}_3\text{Ti}_2\text{O}_7$) is expected to be higher than in the film F2. The WDX analysis of dried solution powders revealed, that in the two deposition solutions (prepared with different citric acid to metals molar ratios) also the molar ratio of Sr to Ti atoms differs slightly: the Sr:Ti molar ratio of the deposition solution for the film F1 is 66:33 while for the solution used for preparation of the film F2 it is 63:36. Thus, the stoichiometry in the film F1 exactly corresponds to that of the $n = 1$ RP phase Sr_2TiO_4 . The volume fraction of Sr_2TiO_4 in the film is higher indeed, but it is not pure, as could be expected from the Sr:Ti molar ratio. Otherwise, from lattice energy calculations it is known, that the $n = 2$ RP phase $\text{Sr}_3\text{Ti}_2\text{O}_7$ is the thermodynamically most stable member of the series [20,21]. Hence the formation of RP phases, especially in thin films seems to be governed by rather complex mechanisms and further studies thereto would be interesting.

3.2. Powders

Fig. 5 presents the WAXS patterns of a powder prepared from a polymeric solution with 1:1 molar ratio of citric acid to Sr and Ti (as in film F1) after each stage of annealing (5 h duration at 400 and 700 °C in air atmosphere). As it is seen from comparison with results obtained for films (Fig. 3), the phase content of films and powders differs considerably. A significant diffraction volume of polycrystalline STO ($a = 3.9096(8)$ Å according to calculations by means of [34]) is formed in the powder after annealing at 400 °C yet. Similar to films after thermal treatment at 400 °C, reflections of SrCO_3 and a Sr oxide (SrO_2 in difference to SrO in films) were observed in the WAXS patterns of the powder. Annealing at a higher temperature of 700 °C, resulted in an increase of STO ($a = 3.9061(2)$ Å) reflection intensities. As distinct from films, no reflections of RP phases were detected in the powder annealed at

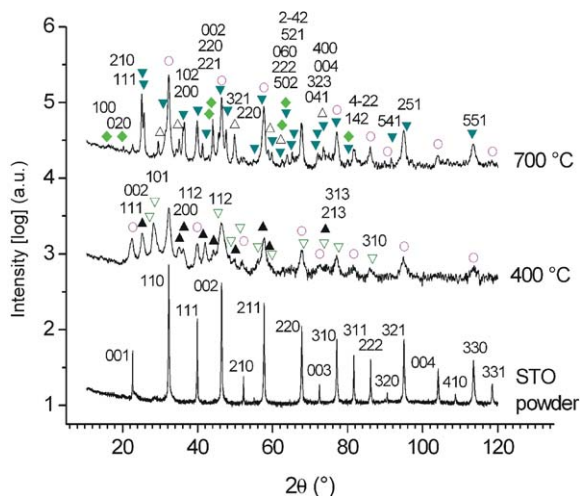


Fig. 5. Intensity versus diffraction angle (ω - 2θ WAXS scans) of a powder (prepared by drying the deposition solution of film F1) after subsequent annealing in air (5 h duration) at the temperatures indicated. For comparison at bottom a ω - 2θ WAXS pattern of a pulverized STO substrate ($a = 3.9047(5)$ Å according to calculations by means of the program [34]) is shown. The WAXS patterns are corrected for $\text{CuK}\alpha_2$ (∇) SrO_2 (space group $I4/mmm$, PDF2 73-1740); (\blacktriangledown) TiO_2 (space group $Pbca$, PDF2 29-1360); (\blacklozenge) TiO (space group $A2/m$, PDF2 72-0020). Other symbols and data (for polycrystalline SrTiO_3 , SrO and SrCO_3) are the same as in Fig. 3.

700 °C whereas SrCO_3 , SrO and different Ti oxides were observed. As it is known (for example, [8,9,15]), polycrystalline RP powders can be prepared by conventional solid state reaction technique using considerably higher annealing temperatures of about 1200–1500 °C in air atmosphere. However, in [19] the preparation of phase-pure RP powders at low temperatures between 700 and 900 °C, starting from sol-gel-derived strontium titanate gels of varying cation stoichiometry is reported. Unfortunately no detailed description of the annealing procedure is given in [19], therefore a comparison of both wet chemical powder preparation routes with regard to the formation of RP phases is difficult.

Thus, beside kinetic effects that we consider to influence the phase formation of RP phases, also the (001)-oriented STO single-crystal substrate is considered to be of importance for the oriented growth of $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$, $n = 1, \dots, 3$ RP phases in the films after annealing at 700 °C in air atmosphere.

4. Conclusion

Thin films of $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{3n+1}$ RP phases ($n = 1, \dots, 3$) were grown oriented on (001) single-crystalline SrTiO_3 (STO) substrates via wet chemical deposition from Sr-rich metalorganic Sr–Ti solutions and subsequent annealing in air atmosphere at a maximum temperature of 700 °C. The volume fraction of different RP phases present in the films varied according to stoichiometry of anions in the deposition solutions. The phase content of powders

prepared from the dried solutions and annealed under similar conditions differed from that, present in the films, beside STO and oxides of Ti and Sr (also SrCO_3) no RP phases were formed.

Considering the results on the phase content and chemical composition of the films and powders, it is obvious that the formation of RP phases is governed by a complex mechanism. Beside thermodynamic effects, also kinetic and substrate effects are considered to play an important role during preparation and structural evolution of the RP phases in the solution-prepared films and powders.

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