

REScO₃ Substrates—Purveyors of Strain Engineering

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The thermodynamic and crystallographic background for the development of substrate crystals that are suitable for the epitaxial deposition of biaxially strained functional perovskite layers is reviewed. In such strained layers the elastic energy delivers an additional contribution to the Gibbs free energy, which allows the tuning of physical properties and phase transition temperatures to desired values. For some oxide systems metastable phases can even be accessed. Rare-earth scandates, REScO₃, are well suited as substrate crystals because they combine mechanical and chemical stability in the epitaxy process with an adjustable range of pseudo-cubic lattice parameters in the 3.95 to 4.02 Å range. To further tune the lattice parameters, chemical substitution for the RE or Sc is possible.

electric, magnetic, or elastic fields. The energetic contribution of a homogeneous elastic field is proportional to the biscal product of elastic stress σ and elastic strain ϵ . Both are tensors of rank 2, and for strained bodies their product must be added as a contribution to G in Equation (1).^[2] To obtain significant contributions to G , usually strains of order $\epsilon = 10^{-3}$ to $\approx 3 \times 10^{-2}$ are required, which are not straightforward to be reached by external tension or compression, particularly in brittle materials.

An elegant way to impart such strains is through *strain engineering* by the epitaxial growth of single crystalline layers

1. Introduction

In his seminal paper “On the equilibrium of heterogeneous substances,”^[1] J. W. Gibbs pointed out that in thermodynamic equilibrium either the entropy is maximum (for constant energy) or the energy is minimum (for constant entropy). These conditions are expressed nowadays as the condition that the Gibbs free energy must have a minimum. Usually this Gibbs energy is described by

$$G = H - TS = U + pV - TS \quad (1)$$

as a function of pressure p and temperature T . Here H is enthalpy, S is entropy, and U is internal energy. Gibbs recognized^[1]; however, other potential contributions to G , such as energies of

on substrates that are “almost” (but not completely) lattice matched. For conventional semiconductors this method has become widely utilized to enhance mobility and make transistors with higher performance.^[3] For ferroelectric materials (e.g., BaTiO₃) strain engineering can be employed to raise the phase transition of the unwanted paraelectric state by several hundred Kelvin.^[4] Even more exciting is the prospect of using strain engineering to stabilize phases that are normally metastable, that is, to access the properties of phases that were previously “hidden.” Examples include stabilizing a ferroelectric polymorph of SrTiO₃ (which in the absence of strain is not ferroelectric at any temperature) at room temperature,^[16] stabilizing a simultaneously ferromagnetic and ferroelectric polymorph of EuTiO₃ (the strongest known multiferroic^[5]), and stabilizing an emergent polarization vortex phase exhibiting negative capacitance.^[6]

Substrate crystals for strain engineering should fulfil the following requirements:

- 1) The available substrate assortment should cover a wide range of lattice parameters to enable the growth of epitaxial thin films with a broad choice of strain states (sign and magnitude).
- 2) Substrates should be chemically and crystallographically compatible with the thin films to be grown upon them, during deposition and thereafter (this means that perovskites are prospective candidates, because many oxide thin films of interest are perovskites too).
- 3) Substrate crystals should not undergo disruptive phase transitions between their melting point and room temperature.
- 4) To pave the way for an integration of elements into silicon-based electronic devices, the corresponding substrate materials should be stable in contact with silicon.

Back in 1957 Geller reported room-temperature crystallographic data for a series of perovskite type compounds with orthorhombic

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DOI: 10.1002/crat.201900111

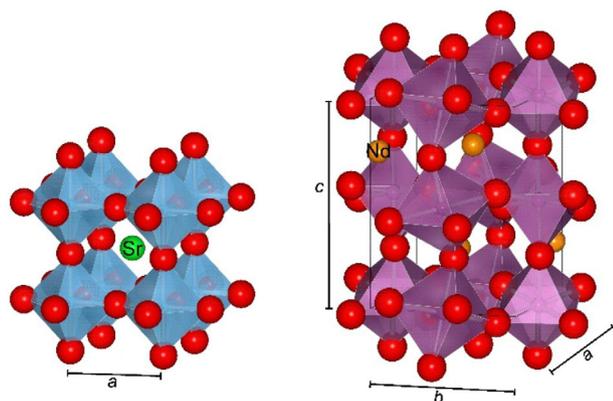


Figure 1. Left: One (cubic) unit cell of SrTiO_3 ^[12] contains 1 formula unit. Right: One (orthorhombic) unit cell of NdScO_3 ^[13] contains four formula units.

symmetry and chemical formula REScO_3 (RE = Gd, Nd, Pr, La, and Y).^[7] Most of these compounds were shown to melt congruently at high temperature, $T_f > 2000$ °C.^[8] Using a thermodynamic approach the oxides of a few chemical elements including scandium and most of the rare-earth (RE) elements were identified to fulfil condition 4.^[9] Thus, it would appear that rare-earth scandates satisfy the important criteria for use as substrates for strain engineering of oxide perovskite thin films.

A significant share of the development of growth technologies for REScO_3 single crystals for substrate applications was done at the author's home institution, the Leibniz Institute for Crystal Growth in Berlin, Germany. This paper reviews these efforts and presents subsequent results on related substrate crystals that go beyond pure REScO_3 compounds to extend the range of lattice constants available for the strain engineering of perovskite thin films.

2. Pure REScO_3

For the rare-earth elements from RE = La to Tm, plus Y, compounds of the type REScO_3 are known to exist. Of these, high pressure synthesis is required to form phase-pure powders of ErScO_3 , TmScO_3 , and YScO_3 .^[10] The rare-earth scandates melt congruently for RE = La...Dy, but HoScO_3 decomposes upon heating in the solid phase to a bixbyite type $(\text{Ho,Sc})_2\text{O}_3$ solid solution prior to melting.^[8,11] The same is true for YScO_3 .^[8,11] Because the other REScO_3 are in equilibrium with the melt, crystal growth by the Czochralski method seemed feasible—except for the very high melting LaScO_3 ($T_f = 2390$ °C^[8]) and CeScO_3 . Melting points T_f for the other REScO_3 are lower, but still above 2000 °C (e.g., DyScO_3 ; $T_f = 2100$ °C^[8]).

All REScO_3 crystallize in the GdFeO_3 structure type that is usually described as a distorted perovskite. **Figure 1** compares the crystal structure of the ideal (cubic, space group $Pm\bar{3}m$, #221) perovskite SrTiO_3 with that of NdScO_3 (orthorhombic, space group $Pbnm$, #62). In both structures the smaller cations Ti^{4+} or Sc^{3+} , respectively, are octahedrally coordinated to oxygen, but the octahedra are tilted and distorted in the scandates, resulting in lower symmetry. The lattice parameter in the c -direction is doubled,

whereas a and b are scaled by a factor $\approx \sqrt{2}$. Consequently, the REScO_3 unit cell contains four formula units.

In the setting of **Figure 1** (right) the lattice parameters a and b are similar, and correspond to $\sqrt{2}$ times the “pseudocubic” lattice parameter a_{pc} of the structure; $c \approx 2 a_{pc}$.^[13] Even if a single parameter a_{pc} is not able to describe the complex strain relations in an epitaxial layer, it is suitable for a first approximation. Other descriptions are the pseudocubic lattice parameters that span the (110) substrate surface, i.e., $\frac{1}{2}\sqrt{a^2 + b^2}$ and $\frac{1}{2}c$ ^[14] or $a_{pc} = \sqrt[3]{\frac{1}{4}abc}$.^[15] In an alternative setting the space group #62 is $Pnma$, and one has $a \approx c$, with the long axis being the b -axis.

The structural similarity of the REScO_3 makes them ideal substrates for the epitaxy of perovskite type oxides such as SrTiO_3 and BaTiO_3 . Haeni et al.^[16] could deposit unrelaxed SrTiO_3 (100) layers on the (110) surface of DyScO_3 that are tensile strained by almost 1% for films as thick as 35 nm.^[17] As the lattice mismatch between the thin film and the underlying substrate increases, the thickness of the unrelaxed film that can be formed decreases. For high strains (beyond roughly 3×10^{-3} , depending upon the specific material and growth conditions), film relaxation occurs immediately through the introduction of defects, for example, dislocations or cracks.^[21] Depending on the elastic stiffness of the layer, the elastic energy contribution to the Gibbs energy amounts to several 100 kJ mol^{-1} , which can shift, for example, ferroelectric transition temperatures by hundreds of Kelvins. In recent years REScO_3 substrates have become commercially available, for example, from CrysTec, Berlin, Germany.^[18]

The accessible pure REScO_3 compounds offer a_{pc} ranging from 3.95 (DyScO_3 ,^[19]) to 4.02 Å (PrScO_3 ,^[20]). This range matches well with values that are desired for strain engineering of important ferroelectric and multiferroic materials like $(\text{Ba,Sr})\text{TiO}_3$ or BiFeO_3 .^[21] Nevertheless, two problems remain unsolved: 1) The accessible REScO_3 offer stepwise a_{pc} “jumps” from REScO_3 to $\text{RE}'\text{ScO}_3$ as the RE constituent is changed. Additionally, PmScO_3 crystals were never grown because promethium is radioactive, which makes this material practically useless. Hence, a more gradual fine-tuning of a_{pc} is desirable. 2) The “largest” REScO_3 with RE = La, Ce have not yet been grown with substrate quality, because their melting points are extremely high, that is, too high for iridium crucibles, thus precluding crystal growth by the Czochralski method. Isostructural LaLuO_3 with $a_{pc} = 4.17$ Å, however, melts at 2120 °C congruently and good crystals can be grown.^[22]

3. Mixed Crystals $(\text{RE,RE}')\text{ScO}_3$

Both of the issues mentioned above can possibly be solved by the growth of solid solutions between appropriate components. The first encouraging results were obtained with $(\text{Nd,Sm})\text{ScO}_3$ (as a substitute for PmScO_3) and $(\text{Sm,Gd})\text{ScO}_3$ (as a substitute for EuScO_3).^[23] For both systems the rare-earth components are the next nearest neighbors in the RE series on either side of the RE of interest, with consequently very similar structural and thermodynamic properties.

As expected, both systems form solid solutions over the whole concentration range. Differential thermal analysis (DTA) studies

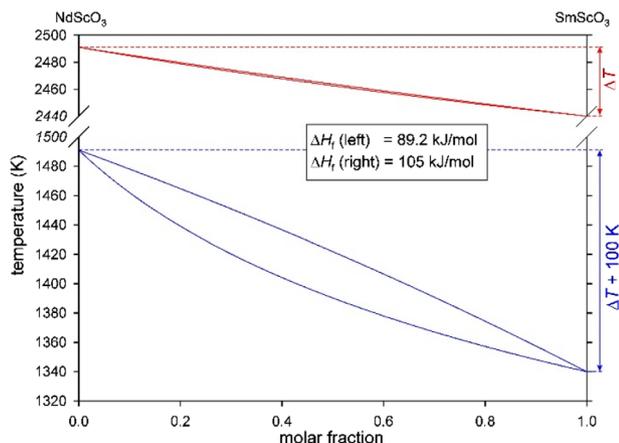


Figure 2. Top: Pseudobinary phase diagram of the $\text{SmScO}_3\text{--NbScO}_3$ system as previously published in Figure 4 of ref. [23]. Bottom: Hypothetical phase diagram that is obtained if T_f (left) is lowered by 1000 K, and T_f (right) is lowered by 1100 K.

Table 1. Thermodynamic data for some perovskites. Accurate data for the upper 4 compounds are from FactSage databases.[25] The data for the REScO_3 compounds are estimated values from our own DTA measurements.[23,26]

Formula	ΔH_f kJ mol ⁻¹	ΔS_f J (mol·K) ⁻¹	T_f K	Space group
CaTiO_3	106.64	47.76	2233	$Pm\bar{3}m$ at T_f
SmAlO_3	81.41	34.31	2373	$R\bar{3}c$ at T_f [27]
GdAlO_3	77.40	33.05	2342	$Pbnm$ [28]
KMgF_3	85.66	63.323	1353	$Pm\bar{3}m$
NdScO_3	89	36	2491	$Pbnm$ [14]
SmScO_3	105	43	2440	$Pbnm$ [14]
GdScO_3	85	35	2423	$Pbnm$ [14]
DyScO_3	89	38	2370	$Pbnm$ [14]

of mixtures between pure REScO_3 reveal almost ideal behavior of the mixed crystal systems. Moreover, the two-phase liquid+solid field of both pseudobinary phase diagrams is extremely narrow, of the order of 2 K only (Figure 2 top). This is beneficial for crystal growth, because segregation during crystal growth is then marginal.

The almost ideal behavior of the $\text{REScO}_3\text{--RE'ScO}_3$ mixed crystal systems is certainly mainly due to the high chemical similarity of the components, and due to the very high liquidus temperatures where excess energies become often smaller. The narrow liquid + solid phase fields that were found not only in the two systems mentioned above, but also for (Tb,Gd)ScO₃ and (Tb,Dy)ScO₃[26] are very helpful for the growth of bulk crystals with low segregation. Nonetheless, the narrowness initially seemed a bit surprising, because in other systems with very similar components (e.g., alkali halides[24]) the span of the two-phase field is often wider.

Reasons for this different behavior are found in the numerical data of Table 1 and in the Schröder-van-Laar equations

$$x^{\text{sol}} = \frac{\exp(a) - 1}{\exp(a) - \exp(b)} \quad (2)$$

$$x^{\text{liq}} = \exp(b) x^{\text{sol}} \quad (3)$$

$$\text{where } a, b = \frac{\Delta H_f}{R} \left(\frac{1}{T} - \frac{1}{T_f} \right) \quad (4)$$

that describe for ideal systems the solidus and liquidus curves as functions of the heats of fusion ΔH_f and melting points T_f of both components. Equation (4) shows that ΔH_f is scaled by reciprocal temperature differences. Because $\Delta H_f = \Delta S_f \cdot T_f$, the entropy change during melting is more relevant than the enthalpy change.

Table 1 reports data for some perovskites with melting points between 1353 and 2491 K (1080 and 2218 °C, respectively). The first four data rows are compiled from a reliable reference; for the last 4 substances the accuracy of the melting points are approx. ± 20 K from our own DTA measurements. The ΔH_f values for the REScO_3 were estimated by comparing the melting peak areas with that of melting Al_2O_3 ($T_f = 2327$ K, $\Delta H_f = 118.41$ kJ mol⁻¹). It turns out that the ΔS_f are of the order of 33–43 J (mol·K)⁻¹ for perovskites that have comparatively low symmetry at T_f , but are significantly higher for the undistorted perovskites with cubic symmetry. Additionally it is known at least for the REScO_3 , that they show a significant degree of structural disorder, especially vacancies on the RE position.[14,19] The entropy gain during melting from the crystalline structure to the highly disordered melt is obviously less significant, if the crystal structure itself shows already some degree of disorder.

Another numerical effect influencing the width of the two-phase field results from the difference of inverse temperatures in Equation (4): If at very high T both melting points are similar, this difference will always be small; but this difference scales ΔH_f . From that stems a drastic effect which is demonstrated by the lower panel of Figure 2, where a hypothetical phase diagram was calculated with Equations (2)–(4) for identical ΔH_f , but with T_f that are lowered by 1000 K on the left side and by 1100 K on the right side; here the width of the two-phase field approaches a significant level of 30 K.

4. Related Perovskites

The (RE,RE')ScO₃ solid solutions that were described in the previous section allow fine-tuning of the lattice constants only in the range of the accessible rare-earth scandates, which end for large lattice constants with PrScO_3 . Lanthanum lutetate LaLuO_3 is another isostructural orthorhombic perovskite with a very large lattice constant $a_{\text{pc}} = 4.17$ Å and accessible $T_f = 2120$ °C.[22] It seemed interesting to check if LaLuO_3 forms solid solutions with LaScO_3 , and if substrate crystals can be grown.

The extremely high melting point of LaScO_3 ($T_f = 2390$ °C) is beyond the thermal limits that were accessible for DTA measurements, but for samples between pure LaLuO_3 and 59 mol% LaScO_3 melting peaks could be recorded.[29] The measurements proved that both end members form solid solutions in any arbitrary ratio, but in contrast to the (RE,RE')ScO₃ systems from the previous section, the two-phase field between solidus and liquidus is fairly wide (up to ≈ 50 K). This is an impediment to crystal growth because strong segregation must be expected. Fortunately, resulting from a small positive excess enthalpy of the solid

phase, an azeotrope exists at ≈ 8 mol% LaScO_3 , where the solidus and liquidus meet in one point. Consequently segregation vanishes at the azeotrope point and remains small in its vicinity. From a starting melt with 27.6% LaScO_3 a 75 mm long single crystal could be grown where the LaScO_3 content changed by segregation from 35.4% (top) to 31.1% (bottom). By X-ray diffraction studies of another crystal with 43% LaScO_3 a pseudocubic lattice constant $a_{\text{pc}} = 4.1224 \text{ \AA}$ was measured—nearly halfway between those of the end members.^[30]

The $\text{La}(\text{Lu},\text{Sc})\text{O}_3$ crystals mentioned above can only be grown in the region of large a_{pc} , close to LaLuO_3 , and the gap towards the REScO_3 is wide. It seemed worthwhile to check if partial substitution of Sc^{3+} by Lu^{3+} could result in crystals with lattice parameters that are somewhat higher than for “pure” rare-earth scandates. Unfortunately, pure lutetates RELuO_3 are not stable for many RE. In initial DTA studies it was revealed that, in contrast to some reports in the literature, the perovskite NdLuO_3 is only a metastable phase.^[31] Instead, a mixture of $(\text{Nd},\text{Lu})_2\text{O}_3$ solid solutions of the cubic “C-phase” (bixbyite structure) and the monoclinic “B-phase” is found. Nevertheless, further studies of the ternary system Nd_2O_3 - Lu_2O_3 - Sc_2O_3 revealed that a wide composition field around NdScO_3 exists, where the first phase to crystallize is the perovskite phase. This potential growth window can be used to access pseudo-cubic lattice parameters up to at least 4.031 \AA .^[32]

5. Conclusions

REScO_3 compounds with perovskite structures are useful substrates for the deposition of strained functional perovskite layers. “Strain engineering” of the film grown on such substrates introduces a third component to the Gibbs free energy G of the epitaxial layer: in addition to $T \cdot S$ and $p \cdot V$, the biscalar product of stress σ and elastic strain ϵ is present which enables unprecedented physical effects, see Equation (1).

Rare-earth scandates are extraordinary well suited for such substrate applications for several reasons:

- 1) They show high structural similarity and chemical stability towards potential epitaxial layers.
- 2) Crystals of good quality and with technically relevant dimensions can be grown directly from the melt, because no structural phase transitions occur between the melting point and room temperature.
- 3) The lattice constants of the substrates and hence the biaxial elastic strain of the thin film can be tuned by an appropriate choice of the RE element.

This paper shows that the development of a growth technology for REScO_3 single crystal substrates for the effective strain engineering of perovskite thin films is far from finished. Instead, the range of accessible lattice parameters can be extended by alloying them on the RE site as well as on the Sc site, which allows the development of substrate crystals with lattice constants well beyond the limits of the “pure” REScO_3 series. Further progress is expected by increasing the number of alloying components.

Acknowledgements

The authors express their gratitude to Reinhard Uecker and Peter Reiche who initiated the growth of rare-earth scandate crystals at IKZ two decades ago. Reinhard Uecker drove forward this development until his retirement. And last but not least: This work would not have been possible without the “golden hands” of our technicians Margitta Bernhagen, Mario Brützam, Isabelle Hanke, Martina Rabe, Elvira Thiede, Markus Stypa, and Andreas Tauchert, and without our students Julia Hidde, Michael Klupsch, and Tamino Hirsch.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

perovskites, rare-earth scandate, strain engineering, substrate crystals

Received: June 7, 2019

Published online: September 18, 2019

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