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.

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 is de-
symmetry and chemical formula REScO$_3$ (RE = Gd, Nd, Pr, La, and Y). Most of these compounds were shown to melt congruently at high temperature, $T_f > 2000 \, ^{\circ}\text{C}$. 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. 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 Tb, 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$_3$. The rare-earth scandates melt congruently for RE = La…Dy, but HoScO$_3$ decomposes upon heating in the solid phase to a bixbyite type (Ho,Sc)$_2$O$_3$ solid solution prior to melting. The same is true for YScO$_3$. 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$_3$ $(T_f = 2390 \, ^{\circ}\text{C})$ and CeScO$_3$, Melting points $T_f$ for the other REScO$_3$ are lower, but still above 2000 $^{\circ}\text{C}$ (e.g., DyScO$_3$: $T_f = 2100 \, ^{\circ}\text{C}$).

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\overline{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; $c \approx 2 \times a_{pc}$. 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 $\frac{1}{2}\sqrt{a^2 + c^2}$ or $a_{pc} = \frac{1}{4}\sqrt{abc}$. 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$_3$. Haen et al. 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. 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 $3 \times 10^{-3}$, depending upon the specific material and growth conditions), film relaxation occurs immediately through the introduction of defects, for example, dislocations or cracks. Depending on the elastic stiffness of the specific material and growth conditions), film relaxation occurs immediately through the introduction of defects, for example, dislocations or cracks. Additionally, 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 Kelvin. In recent years REScO$_3$ substrates have become commercially available, for example, from CrysTec, Berlin, Germany.

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 (Ba,Sr)TiO$_3$ or BiFeO$_3$. Nevertheless, two problems remain unsolved: 1) The accessible REScO$_3$ offer stepwise $a_{pc}$ “jumps” from REScO$_3$ to RE’ScO$_3$ as the RE constituent is changed. Additionally, PrMnScO$_3$ 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 $^{\circ}\text{C}$ congruent and good crystals can be grown.

3. Mixed Crystals (RE,RE’)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 (Nd,Sm)ScO$_3$ (as a substitute for PmScO$_3$) and (Sm,Gd)ScO$_3$ (as a substitute for EuScO$_3$). 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 offer solid solutions over the whole concentration range. Differential thermal analysis (DTA) studies
of mixtures between pure REScO₃ 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 REScO₃–RE′ScO₃ 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., alkalihalides[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

\[ x_{\text{sol}} = \frac{\exp(a) - 1}{\exp(a) - \exp(b)} \]  

(2)

\[ x_{\text{mol}} = \exp(b) x_{\text{sol}} \]  

(3)

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

that describe for ideal systems the solidus and liquidus curves as functions of the heats of fusion \( \Delta H_f \) and melting points \( T_f \) of both components. Equation (4) shows that \( \Delta H_f \) 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 \( \Delta H_f \) values for the REScO₃ were estimated by comparing the melting peak areas with that of melting Al₂O₃ (\( T_f = 2327 \) K, \( \Delta H_f = 118.41 \) kJ mol⁻¹). It turns out that the \( \Delta S_f \) 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 REScO₃, 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 \( \Delta H_f \). 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 \( \Delta H_f \), 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 \((\text{RE},\text{RE}')\text{ScO₃}\) 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 PrScO₃. Lanthanum lutetate LaLuO₃ is another isostructural orthorhombic perovskite with a very large lattice constant \( a_{\text{cpx}} = 4.17 \) Å and accessible \( T_f = 2120 \) °C.[22] It seemed interesting to check if LaLuO₃ forms solid solutions with LaScO₃, and if substrate crystals can be grown.

The extremely high melting point of LaScO₃ \( (T_f = 2390 \) °C) is beyond the thermal limits that were accessible for DTA measurements, but for samples between pure LaLuO₃ and 59 mol% LaScO₃ 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 \((\text{RE},\text{RE}')\text{ScO₃}\) 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 \( \approx 8 \text{ mol}\% \text{LaScO}_3 \), 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\% \text{LaScO}_3, a 75 mm long single crystal could be grown where the \text{LaScO}_3 content changed by segregation from 35.4\% (top) to 31.1\% (bottom). By X-ray diffraction studies of another crystal with 43\% \text{LaScO}_3 a pseudocubic lattice constant \( a_{pc} = 4.1224 \text{ Å} \) was measured—nearly halfway between those of the end members.\(^{[10]}\)

The \( \text{La(Lu,Sc)}_3 \) crystals mentioned above can only be grown in the region of large \( a_{pc} \), close to \( \text{LaLuO}_3 \), and the gap towards the \( \text{REScO}_3 \) is wide. It seemed worthwhile to check if partial substitution of \( \text{Sc}^{3+} \) by \( \text{Lu}^{3+} \) could result in crystals with lattice parameters that are somewhat higher than for “pure” rare-earth scandates. Unfortunately, pure lutetates \( \text{RELuO}_3 \) are not stable for many RE. In initial DTA studies it was revealed that, in contrast to some reports in the literature, the perovskite \( \text{NdLuO}_3 \) is only a metastable phase.\(^{[31]}\) Instead, a mixture of \( (\text{Nd,Lu})_2\text{O}_3 \) solid solutions of the cubic “C-phase” (bixbyite structure) and the monoclinic “B-phase” is found. Nevertheless, further studies of the ternary system \( \text{Nd}_2\text{O}_3-\text{Lu}_2\text{O}_3-\text{Sc}_2\text{O}_3 \) revealed that a wide composition field around \( \text{NdScO}_3 \) 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 \( \text{Å} \).\(^{[32]}\)

5. Conclusions

\( \text{REScO}_3 \) 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 the products of stress \( \sigma \) and elastic strain \( \varepsilon \) 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 \( \text{REScO}_3 \) 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” \( \text{REScO}_3 \) series. Further progress is expected by increasing the number of alloying components.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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