Czochralski growth and characterization of perovskite-type (La,Nd)(Lu,Sc)O₃ single crystals with a pseudocubic lattice parameter of about 4.09 Å

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ABSTRACT

(La,Nd)(Lu,Sc)O₃ solid solution single crystals with liquidus temperatures of about 2170 °C were grown by the Czochralski method to provide perovskite substrates with a pseudocubic lattice parameter of 4.086 Å for epitaxial purposes. We achieved single crystals with diameters up to 17 mm and total lengths up to 50 mm. Relatively high crystalline quality was confirmed by rocking curve measurements and by energy dispersive Laue mapping. Despite the complex composition, a good chemical homogeneity on the macroscale and nanoscale was verified by micro X-ray fluorescence elemental mapping and transmission electron microscopy. Only minor segregation along the pulling direction was found by chemical analyses using inductively coupled plasma atomic emission spectroscopy. Epitaxial La-doped BaSnO₃ films grown on these substrates exhibited a mobility of 181 cm² V⁻¹ s⁻¹ at room temperature.

1. Introduction

Strain-engineering in perovskite oxide thin films has become a widely used approach to deliberately tune and greatly enhance the functional properties of materials, e.g. shifting the Curie temperature of ferroelectric materials [1,2] or increasing piezoelectric coefficients [3]. Specifically, Choi et al. [4] could increase the Curie temperature of the ferroelectric-to-paraelectric transition of BaTiO₃ by nearly 500 °C by imparting 1.7% biaxial strain through commensurate growth on a DyScO₃ substrate. Depending on the epitaxial layer, the choice of appropriate rare-earth (RE) scandate substrate allows the elastic strain to be adjusted stepwise, by the choice of proper RE ion. Additionally, strain-engineering in perovskite oxide films also ‘activates’ properties that are not present in the unstrained ground state of the material [2]. Examples include turning on ferroelectricity in SrTiO₃ [5] (a material that in its unstrained state is not ferroelectric at any temperature) as well as turning on both ferroelectricity and ferromagnetism in EuTiO₃ (a material that in its unstrained state is a paraelectric and antiferromagnetic insulator) to make it the strongest multiferroic material known [6,7].

The literal foundation for strain-engineering of various perovskite oxide

films was and still is the availability of high-quality single crystal substrates with the perovskite structure and a particular lattice parameter. Czochralski-grown high-quality rare-earth (RE) scandate REScO₃ (RE = Dy - Pr) substrate crystals addressed this requirement with pseudocubic lattice parameters in the 3.95–4.02 Å range [8–11]. The upper limit of 4.02 Å (for PrScO₃) is given by the constraint that not all possible RE scandates can be grown in iridium crucibles by the Czochralski method because of the very high melting points of CeScO₃ and LaScO₃, the latter being 2390 °C [12]. One way to exceed this limit by about 0.01 Å is the growth of NdLu_{1-x}Sc_xO₃ mixed crystals, as demonstrated by Hirsch et al. [13]. In the last few years, the discovery of the promising properties of perovskite materials like BaSnO₃ [14–16] with lattice parameters well above 4 Å (4.116 Å for BaSnO₃) has triggered the development of novel substrates to address the current lattice parameter gap in the 4.03–4.18 Å range [17–20]. Uecker et al. [20] demonstrated solid solution crystals of (LaLuO₃)_{1-x}(LaScO₃)_x with $x = 0.265\text{--}0.43$, yielding the first substrates in the 4.122–4.145 Å range. To minimize the liquidus temperature and segregation as well as to access slightly lower lattice parameters at the same time, we expanded the ternary system La₂O₃ – Sc₂O₃ – Lu₂O₃ to a quaternary system, i.e. Nd₂O₃ was added. In this paper we demonstrate the successful Czochralski growth of

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(La,Nd)(Lu,Sc)O₃ solid solution substrate crystals. The structural quality, chemical homogeneity and the basic properties of a La_{0.557}Nd_{0.394}Sc_{0.589}Lu_{0.459}O₃ crystal are evaluated. The pseudocubic lattice parameter of this specific substrate crystal is about 4.086 Å, which is shown to enable the epitaxial growth of compressively strained thin films of BaSnO₃; it should also permit the growth of other perovskites of contemporary interest with relatively large lattice parameters.

2. Material and methods

2.1. Bulk single crystal growth

Melt compositions with liquidus temperatures of about 2170 °C were used for the Czochralski experiments. The starting materials were prepared from dried and mixed powders of La₂O₃ (25 mol%, 4 N5 purity), Lu₂O₃ (29.25 mol%, 5 N purity), Nd₂O₃ (25.75 mol%, 4 N purity) and Sc₂O₃ (20 mol%, 4 N purity). Prior to weighing and mixing, the individual powders were tempered for 15 h at temperatures between 850 °C and 1200 °C (850 °C for Lu₂O₃, 1000 °C for La₂O₃ and Sc₂O₃, 1200 °C for Nd₂O₃). The mixed powders were next pressed into cylindrical bars by cold isostatic pressing at 2000 bar in order to optimize the crucible filling process. The crystal growth experiments were performed using a conventional RF-heated Czochralski setup equipped with a crucible balance. Experiments were done with automatic diameter control under an atmosphere of 99.999% pure argon at atmospheric pressure. Iridium crucibles (about 40 mm in diameter and height) embedded in ZrO₂ and Al₂O₃ insulation were used. An actively heated iridium afterheater was placed on top of the crucible. Crystal growth occurred at a rate of 0.5 mm h⁻¹ and a rotation rate of 10 rpm. Due to the lack of a seed crystal, an iridium rod was used to initiate crystal growth. Shortly after initiating growth, necking was applied and a small diameter (5 to 7 mm) was kept for a length of about 14 mm to grow out potential subgrains or twins. Following this, the diameter was broadened to about 17–18 mm for the remainder of the 25 mm long cylindrical section and completed by a relative short end cone with a length of about 7 mm.

2.2. Chemical and structural analyses

Rocking curve X-ray diffraction (XRD) measurements were performed on a mechanically rough-polished cross section prepared from the center of the cylindrical part of the grown crystal with the large (~17 mm) diameter using a high-resolution diffractometer (Bruker D8) with Cu Kα₁ radiation (λ = 1.5406 Å). 200 Bragg peaks were used for the evaluation of the crystalline quality. For all scans, the collimated beam had a divergence of about 20" and the measurement spot covered an approx. 10 mm length at the surface of the sample. The spot width depended on the size of the primary beam aperture. Aperture widths of 0.1 and 1.2 mm were used.

For single crystal X-ray diffraction investigations, a sliced section of the crystal (shortly behind the seed) was crushed into small fragments. One fragment with dimensions 132 × 150 × 161 μm³ was selected. The specimen was glued to the tip of a 50 μm glass fiber and a full sphere of data was collected on a Bruker D8 Venture diffractometer up to a resolution of ~37 pm. For a full description of the instrumentation and experiment, refer to Table 1. The chemical composition of the same section and of sections prepared from the large-diameter (~17 mm) part of the crystal were measured using an inductively coupled plasma-optical emission spectrometer (ICP-OES) IRIS Interpid HRDuo. The samples were dissolved by microwave digestion in a mixture of HNO₃ and H₂O₂ (220 °C, 20 min). The spectrometer was calibrated with synthetic solution standards. Standard deviations (σ) for La, Nd, Lu and Sc (from analyses conducted three to five times) were in the range of 0.1–0.2, 0.06–0.12, 0.06–0.26 and 0.05–0.09 wt%, respectively.

Micro X-ray fluorescence (μ-XRF) elemental mapping and energy dispersive Laue mapping (EDLM) [21] were carried out under low vacuum conditions (below 1 mbar) using a Bruker M4 TORNADO spectrometer to (1) investigate the chemical homogeneity of a mechanically polished cross section prepared from the large-diameter part (~17 mm diameter, about

half way to the beginning of the end cone) and (2) to assess the microstructure. EDLM is suitable for the qualitative detection of subgrains mis-oriented from each other by as little as 40" to 100" for chemo-mechanically polished samples. Analysis of nearly the full sample area was achieved at a step size between spot measurements of 17 μm. A surface area of 18.6 × 20.4 mm² was scanned "on the fly" by moving the sample stage continuously (the mapped area was larger than the sample). The measurement time per point was set to 10 ms and all spots were measured four times to increase the counting statistics, i.e. four passes of the scans were performed. The principles of the XRD surface mapping technique, the measurement procedure and the measurement setup are described elsewhere [21]. To maximize the intensity of the Bragg Peaks (i.e. to perform high sensitivity EDLM mappings) the Rh X-ray source was operated at a voltage of 50 kV and the tube current was set to 600 μA. μ-XRF investigations at ambient pressure using a custom stepper motor driven sample-stage (see Section 3.2, Fig. 6) allowed point spectra to be measured as a function of sample orientation. To perform this measurement a spectrum was recorded, the sample was rotated by ten degrees and another spectrum was recorded. This procedure was repeated until 360° were covered, i.e. 36 spectra were taken. These spectra measured at different sample orientations were used to calculate the minimum spectrum, which is free of Bragg peaks. Additionally, it was helpful to select crystal orientations suitable for high-intensity high-sensitivity EDLM mapping under the conditions described above. For determination of the chemical homogeneity of the cross section, the spectrometer was calibrated using a standard section of the grown crystal that had been measured by ICP-OES.

(1 0 1)-oriented substrates with dimensions 10 mm × 10 mm were cut from the lower half of the boule (closest to the tail of the crystal) and chemo-mechanically polished (by CrysTec GmbH) to provide a surface that is ready for epitaxial overgrowth. These substrates were analyzed by EDLM mapping and XRD rocking curves prior to growing epitaxial BaSnO₃ films on them. The XRD was performed using a Panalytical Empyrean with a PreFix hybrid 2 × Ge 220 monochromator on the incident beam side and a triple axis/rocking curve attachment (2 × Ge 220) on the diffracted beam side. A 2 mm incident mask and 0.5° slit were used, which illuminated a region on the substrate about 6 mm by 1.3 mm in area. Rocking curves of the 202 (La,Nd)(Lu,Sc)O₃ substrate peaks were measured in a triple-axis geometry. For the EDLM mapping of the substrates, a step size of 25 μm was used and a total surface area of 33.2 × 22.6 mm² was scanned (six substrates were measured and displayed in one map). The measurement time per point was set to 10 ms and all spots were measured eight times.

2.3. Optical spectroscopy

A La_{0.55}Nd_{0.40}Sc_{0.58}Lu_{0.47}O₃ solid-solution sample and for comparison a neodymium-free La_{0.947}Lu_{0.676}Sc_{0.377}O₃ solid-solution crystal (both perovskites crystallize in the same space group, *Pnma* (62)) [20] were investigated in transmission by optical spectroscopy using a Perkin-Elmer Lambda 19 spectrometer from 200 to 3000 nm. The thicknesses of the samples were about 0.5 mm.

2.4. Transmission electron microscopy

The structural quality and the homogeneity of the La_{0.557}Nd_{0.394}Lu_{0.459}Sc_{0.589}O₃ solid solution sample was investigated on the nanometer scale by (scanning) transmission electron microscopy (STEM) using a FEI-Titan 80-300 operated at 300 kV. STEM high angle annular dark field (STEM-HAADF) imaging was performed with a semi-convergence angle of the electron probe of 9.0 mrad and with an inner acceptance semi-angle of the annular detector (Fischione model 3000) of 35 mrad. STEM-HAADF image simulations were performed using a frozen phonon multi-slice approach with conditions for the electron probe and detector corresponding to those used in the STEM imaging of the sample. The specimen for the TEM measurement was prepared solely by wedge polishing following the procedure of Voyles et al. [22] to

avoid artifacts due to ion-milling. The piece for the TEM specimen preparation was taken from the middle of the large-diameter part immediately adjacent to the sample on which chemical analysis was performed using ICP-OES.

3. Results and discussion

3.1. Czochralski growth of solid solutions

Solid-solution crystals with diameters up to 17 mm and total lengths up to 50 mm were grown by the Czochralski technique. The grown crystals were found to be transparent (water-clear) and had violet coloration in direct sunlight (Fig. 1a). Artificially produced light by standard tubular fluorescence lamps changed the crystal coloration to distinct grey-green (Fig. 1b). This optical effect is discussed in detail in Section 3.5.

Fig. 1. Czochralski grown single crystal shown in (a) direct sunlight and (b) in artificially produced light from standard tubular fluorescence lamps.

3.2. Segregation and crystal quality

ICP-OES measurements revealed a solid solution composition of $\text{La}_{0.557}\text{Nd}_{0.394}\text{Sc}_{0.589}\text{Lu}_{0.459}\text{O}_3$ close to the seed end of the crystal. Due to segregation, the chemical composition slightly changes along the growth direction of the boule. The La and Sc concentrations were observed to decrease, and the Nd and Lu concentrations increase along the direction from the seed to the tail of the crystal. A composition of $\text{La}_{0.551}\text{Nd}_{0.400}\text{Sc}_{0.575}\text{Lu}_{0.473}\text{O}_3$ was determined immediately behind the shoulder (start of the large-diameter part) and $\text{La}_{0.545}\text{Nd}_{0.406}\text{Sc}_{0.561}\text{Lu}_{0.488}\text{O}_3$ for the central part of the crystal. The results show, that the composition shift along the growth axis is very low, but it should be kept in mind if ultrafine tuning of the lattice parameters is required. In contrast, the chemical homogeneity of a (1 0 0)-oriented cross section (cut at about 5° off from the pulling direction) is relatively high. In Fig. 2a–e, the results of high intensity elemental maps are shown to visualize the distribution of the elements across the entire surface. A quantitative μ -XRF line scan (Fig. 3) over the cross section revealed small radial variations. In the central part of the crystal we found a slight depletion of Sc and La accompanied by an increase of the Lu and Nd content by about 0.3 and 0.1 at% from the average composition, respectively. At the rim of the crystal the Sc content is approximately 0.3 at% higher and accordingly the Lu content lower compared to the average values. In overall low standard deviations were determined for La, Nd, Lu and Sc, which are 0.113, 0.102, 0.115 and 0.169 at%, respectively. Under the applied Czochralski growth conditions, where a slight segregation takes place, a relatively homogeneous distribution of the constituents (perpendicular to the pulling direction) can be only achieved for a flat or slightly convex growth interface.

The mixed crystal contains four metal ions, but their concentration is obviously subject to restriction, which reduces the degrees of freedom. For all three crystal compositions mentioned in the previous paragraph, one finds for the concentration ratio z $([\text{Lu}] + [\text{Sc}])/([\text{La}] + [\text{Nd}]) = 1.102\text{--}1.103 \approx \text{const}$. This restriction agrees with the crystal structure data given in Table 2 which show that only 14% of the A cations are potentially occupied by Lu^{3+} or Sc^{3+} , and only 8% of the B cations are potentially occupied by La^{3+} or Nd^{3+} . Hence, the crystal

Fig. 2. Elemental maps measured at high beam current (600 μA) of (a) Nd, (b) La, (c) Lu and (d) Sc across the entire area of the cross-sectional piece from the large-diameter part of the crystal. Good homogeneity is observed. (e) Superimposed color-coded intensity plot of all measured elements and (f) of several Bragg Peaks (F1–F3). The red dotted line indicates the position of the rocking curve measurements (see Fig. 7 for rocking curves). For better visibility, the position of a subgrain region is marked in blue. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Quantitative line scan measured across the mechanically polished cross-sectional piece (from rim to rim as shown by the yellow line on the image in the inset). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

can be described as (lanthanum, neodymium)(lutetate, scandate) – rather than a (lanthanum, neodymium, lutetium, scandium) oxide. The parameter z is slightly larger than unity, in analogy to pure REScO_3 single crystals, where also a slight Sc excess is observed [23]. The description as $(\text{La}, \text{Nd})(\text{Lu}, \text{Sc})\text{O}_3$ offers the possibility to display all crystal composition in a square diagram, in analogy to a “reciprocal salt pair,” which is done in Fig. 4. Three of the four corners correspond almost (irrespective of the small non-stoichiometry) to well-known distorted perovskite compounds (“P phase”) with congruent melting behaviour. The upper right corner corresponds to neodymium lutetate (NdLuO_3), which exists only as a metastable phase [24]. Of the four pseudobinary rim systems in Fig. 4, only the right rim $\text{NdLuO}_3 - \text{NdScO}_3$ was investigated so far, and from this study [13] it is known that the high-temperature X phase crystallizes first from melts with the composition NdLuO_3 , up to ca. 40% NdScO_3 . The blue dashed boundary of this phase should extend (not necessarily straight) towards the top rim of the phase diagram, but its position there can only be guessed to be closer to the LaLuO_3 corner, because this perovskite has the lower liquidus.

The starting composition for crystal growth is outside the projection plane of Fig. 4 ($z = 0.9704$), but is nevertheless displayed in the diagram by a cross. Now the segregation process can be understood well: from this melt material with the “red circle” composition crystallizes first, shifting the composition of the residual melt in the opposite direction. Seen in this way it is obvious that the composition of the growth front moves toward the top right of Fig. 4 as crystallization occurs.

In order to assess whether the good chemical homogeneity of the crystals established by μ -XRF elemental mapping on a tens of micrometer scale also holds on a nanometer scale, we performed TEM measurements. Using TEM dark field imaging (see Fig. 5a) and STEM-HAADF imaging (the intensity is proportional to the mean atomic number density within the probed volume) we have not observed any indications for chemical inhomogeneities like e.g. inclusions or significant fluctuations of the crystal composition within an investigated specimen volume of approximately $1 \times 100 \times 0.1 \mu\text{m}^3$ (length $\times$ width $\times$ thickness of the investigated region along the electron transparent edge of the wedge shaped TEM specimen). The horizontal stripe-like contrast apparent in Fig. 5a are so-called thickness fringes related to the increasing thickness of the TEM specimen in the direction perpendicular to the edge of the wedge-shaped specimen. Even when examined on an atomic level by comparing the STEM-HAADF intensity of atomic columns in the experiment on the same quantitative intensity scale [25] with an image simulation of a $\text{La}_{0.545}\text{Nd}_{0.406}\text{Sc}_{0.561}\text{Lu}_{0.488}\text{O}_3$ crystal, we find very close agreement

(see Fig. 5c and d) The image simulation shown in Fig. 5d is based on a supercell with an orthorhombic $Pnma$ crystal structure as obtained by X-ray diffraction (see next paragraph) and a composition of $\text{La}_{0.545}\text{Nd}_{0.406}\text{Sc}_{0.561}\text{Lu}_{0.488}\text{O}_3$, as determined by ICP-OES, with cations randomly distributed on their respective sites. For a supercell thickness of 17 nm, corresponding to $21 \times [0\ 1\ 0]$ orthorhombic lattice parameters (or 42 pseudocubic perovskite unit cells), the simulation reproduces the mean intensity of the experimental STEM-HAADF image as well as the fluctuation/distribution of the STEM-HAADF intensity of the atomic columns. The significantly darker atomic columns seen in Fig. 5c and d are attributed to columns having a high Sc content (Sc has atomic number $Z = 21$, much smaller than that of Lu, La and Nd)).

To evaluate the microstructure of the crystal, EDLM measurements were made. Superimposed color-coded Bragg Peak intensity maps (Fig. 2f) revealed a relatively high homogeneity in intensity over nearly the entire area of the mechanically polished surface. Minor differences in Bragg peak intensities are related to slight differences in planarity and surface quality, which often occurs for mechanically polished samples. At the very periphery of the crystal a subgrain is identified in one minor region (marked in blue in Fig. 2f). The hallmark of a subgrain with a different orientation is a significant deviation in the intensity and/or energy of the Bragg peaks. In Fig. 6 the measured sum spectra for area A3 is compared with the sum spectra of areas A1 and A2 and for a spectrum that is free of Bragg peaks. Since the spectra taken for A1 and A2 are identical (intensities and intensity ratios are the same) an intense mosaicity can be excluded for the main part of the crystal. It is worth mentioning that the maps show a very slight difference in contrast in close proximity to the subgrain (area A3) towards the lower left end of area A2. In this region located at the crystal periphery, a minor mosaicity cannot be excluded.

X-ray rocking curve measurements (see Fig. 2f for the measurement location) on the mechanically polished samples show a full width at half maximum (FWHM) value of 115 arc sec (Fig. 7). These rocking curves are significantly broadened compared to the true FWHM of these crystals due to the damage inflicted by the coarse mechanical polishing. An improved, epitaxial grade polish, reduces this FWHM significantly as discussed below.

By studying the EDLM plots and rocking curve measurements performed on the chemo-mechanically polished $10\text{ mm} \times 10\text{ mm}$ substrates (see Figs. 8 and 9) it becomes obvious that the crystal contains subgrains in certain regions within the second half of the boule. This is visible by local intensity variations in the EDLM plots and by the observation of satellite peaks in the rocking curves, respectively. The FWHM values observed on the substrates following an epitaxial grade polish (by CrysTec GmbH) ranged from 40 to 120 arc sec. As for all surface-sensitive X-ray diffraction techniques, the detection limit of such defects depends on the quality of the surface.

3.3. Crystallographic data obtained by X-ray diffraction

The integrated data were analyzed using XPREP [26] and $|E \cdot E - 1|$ statistics. As the latter suggested the presence of an inversion center, $Pnma$ (62) was indicated as the most likely space group. In this space group, 46 weak but significant systematic absence violations were observed. The measurement was repeated at an accelerating voltage of 30 kV from the X-ray tube to avoid the emission of $\lambda/2$ -radiation. The measuring time was increased to compensate for the loss of X-ray flux. Similar intensities were observed for the main reflections while all but two of the systematic absence violations disappeared. This confirmed our suspicions that these reflections were caused by the $\lambda/2$ -effect [27]. The remaining two reflections are most probably caused by other phenomena, such as involving multiple diffraction (Renninger effect) [26,27]. The finding that the crystal studied belongs to space group $Pnma$ (62) is further corroborated by the TEM measurements shown above. The dark lines in Fig. 5b corresponding to systematic absences are the so-called Gjønnes-Moodie lines. They occur in the

Table 1
Instrumentation, experiment and refinement results.

Instrumentation	Bruker D8 Venture
Geometry	Kappa
Detector	CMOS-PHOTON100
Radiation	Mo K_{α}
Wavelength	71.073 pm
Tube voltage	50 kV
Tube current	30 mA
Monochromator	“Triumph” (primary, graphite, focusing)
Temperature	29.150 °C
Crystallite size	$0.132 \times 0.150 \times 0.161 \text{ nm}^3$
Max. 2θ	144.8
Resolution	$\sim 37 \text{ pm}$
Total number of Reflections	107901
Symmetry forbidden	4766
Unique reflections	2848
Space group	$Pnma$ (#62)
Lattice parameter a, b, c	$587.56(2) \times 816.97(2) \times 568.53(2) \text{ pm}^3$
R_{int}	5.19 %
R_{sigma}	1.12 %
R1	1.52 %
wR2	3.86 %
R1 (after merging for Fourier)	1.72 %
GooF	1.073
Highest peak	2.36 e/pm^6
Deepest hole	-2.58 e/pm^6

disks of the kinematically forbidden reflections $h00$ and $00l$ for odd h and l in the $[0\ 1\ 0]$ zone axis convergent beam electron diffraction pattern and correspond to the 2_1 screw axes of the $Pnma$ ($P\ 2_1/n\ 2_1/m\ 2_1/a$) space group.

With the space group determined, the structure was solved using intrinsic phasing (SHELXT [26]). The metal atoms were modelled on the 4a and one 4c site, while constraining the combined occupancy of all metals to unity for each site. The combined occupancy from both sites for each cation species (La, Nd, Sc and Lu) was constrained to the respective values determined by elemental analysis (ICP-OES). As a starting point, a larger amount of lanthanum and neodymium was assumed to be present on the 4c site (corresponding to the A-cation site of the ABO_3 perovskite lattice) and conversely for scandium and lutetium on the 4a site (corresponding to the B-cation site of the ABO_3 perovskite lattice). This is justified due to the larger ionic radii of lanthanum and neodymium, which is consistent with the longer metal-oxygen distances found around the 4c site (Table 3). Similarly, a rough bond valence sum analysis suggested this to be the most favorable of the possible arrangements.

The refinement (SHELXL-2014/7 [26]) converged to $R1 = 0.0152$

Table 2
Atomic parameters.

Name	Species	Wyckoff	x	y	z	$U_{\text{eq}} / \text{\AA}^2$	sof
B	La Nd Lu Sc	4a	0	0	0	0.00847(1)	0.03172(8) 0.04932(8) 0.35951(8) 0.54549(8)
A	La Nd Lu Sc	4c	0.05103(2)	0.25	0.48675(2)	0.00549(1)	0.52552(8) 0.34502(8) 0.09945(8) 0.04373(8)
O1	O	4c	0.45494(13)	0.25	0.61129(13)	0.01162(8)	1
O2	O	8d	0.30185(9)	0.44140(7)	0.19669(8)	0.01245(6)	1

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B	0.00749(1)	0.00941(1)	0.00850(1)	0	-0.00111(1)	0
A	0.00538(1)	0.00527(1)	0.00581(1)	-0.00031(1)	-0.00001(1)	0.00042(1)
O1	0.01344(1)	0.00732(1)	0.01411(1)	0	-0.00339(1)	0
O2	0.01028(1)	0.01648(1)	0.01059(1)	-0.00210(1)	-0.00358(1)	0.00243(1)

Fig. 4. Phase relation and segregation during the crystallization of (La,Nd)(Lu,Sc)O₃ mixed crystals.

Fig. 5. TEM images of a $\text{La}_{0.545}\text{Nd}_{0.406}\text{Sc}_{0.561}\text{Lu}_{0.488}\text{O}_3$ crystal taken along the $[0\ 1\ 0]$ projection: (a) dark-field TEM, (b) electron diffraction, (c) experimental and (d) simulated STEM HAADF images, respectively, shown on the same quantitative intensity scale.

Fig. 6. A comparison of X-ray fluorescence sum spectra measured over the 9.3 to 15.2 keV energy range for the three different areas (A1–A3) marked on the inset (EDLM plot). Three relevant Bragg peaks are marked for microstructure mapping analysis (F1–F3). The minimum spectrum is free of Bragg peaks and it shows only Lu peaks at 9.843 (L_{g5}), 10.143 (L_{g1}), 10.458 (L_{g2}), 10.511 (L_{g3}) and 10.843 (L_{g4}) keV. The minimum spectrum was calculated by measuring the crystal at different crystallographic orientations using an automated rotating sample stage (shown in the inset).

and $wR2 = 0.0386$ (Table 1). A preferred occupation of the 4c site by neodymium and lanthanum and conversely the 4a site by scandium and lutetium was retained by the completed refinement. Atomic parameters and site occupation factors are shown in Table 2. These findings are in good agreement with models for the archetype of this class of perovskite, $GdFeO_3$, where the smaller iron is occupying the 4a site, in octahedral coordination and the larger gadolinium ion the 4c site. An investigation into a possible under-occupation of the 4c site like the one found in $La_{0.94}ScO_{2.91}$ or $Nd_{0.967}ScO_{2.951}$ as was shown in [23,28] was deemed infeasible, due to the already high amount of substitutional disorder.

The coordination environment of the lanthanide atoms on the B site is octahedral as is apparent in Fig. 10. This coordination polyhedron has inversion symmetry, with the metals occupying the exact center of the octahedron and all opposing oxygen atoms forming a perfectly straight axis with the center. The three major axes of the octahedron are canted with respect to each other. The coordination environment for the metal on the A site (4c) is markedly larger than the 4a site. The metals on this site coordinate eight oxygen atoms as their nearest neighbors. Other than the mirror plane contained, the eleven-sided coordination polyhedron is rather irregular.

The determined unit cell parameters of $La_{0.557}Nd_{0.394}Sc_{0.589}Lu_{0.459}O_3$ are $a = 5.8756(2)$ Å, $b = 8.1697(2)$ Å and $c = 5.6853(2)$ Å. This corresponds to a pseudocubic lattice parameter of 4.086 Å.

Fig. 7. X-ray diffraction rocking curves of 2 0 0 peaks investigated for a mechanically polished cross section. The scans were performed with different primary beam apertures (0.1 and 1.2 mm).

3.4. Suitability as a substrate for $BaSnO_3$

To assess the suitability of $(La,Nd)(Sc,Lu)O_3$ as a substrate for the epitaxial growth of $BaSnO_3$ films, thin films of La-doped $BaSnO_3$ were grown by molecular-beam epitaxy (MBE) on the 10 mm × 10 mm polished substrates shown in Figs. 8 and 9. The orientation of these substrates is (1 0 1) using the $Pnma$ standard setting of space group #62 used throughout this manuscript (these substrates are (1 1 0) oriented

Fig. 8. (a) Superimposed color-coded intensity plots of all measured elements and (b) of several Bragg Peaks (F1,F3,F4,F6) measured on 6 randomly selected 10 mm × 10 mm substrates obtained from the lower half of the boule (closest to the tail of the crystal). Please note: due to relatively low Bragg peaks intensities, not all mosaic features might be visible.

Fig. 9. XRD rocking curves of the 202 peak measured at the three positions indicated on each of the six (La,Nd)(Sc,Lu)O₃ substrates studied. Although the rocking curve peaks are relatively narrow, they do exhibit structure consistent with the presence of low-angle grain boundaries that are inhomogeneously distributed across the substrate.

Table 3
Distances to nearest oxygen atoms from B (4a) and A (4c) metal-site.

Vector	Distance / pm	Vector	Distance / pm
B - O2	223.50(5)	A - O2	235.40(8)
	223.50(5)		238.25(5)
	225.06(5)		238.25(5)
	225.06(5)		247.66(8)
	225.45(2)		270.86(5)
	225.45(2)		270.86(5)
			292.03(6)
			292.03(6)

Fig. 10. Crystal structure of the title compound (left) showing the orthorhombic distorted ABO₃ perovskite structure. A cutout of the pseudocubic cell is shown at the right side.

using the *Pbnm* non-standard setting of space group #62 that dominates the thin-film growth literature). Details of the MBE growth are given elsewhere [29]. In brief, the substrate was held at a temperature of 880 °C and simultaneously exposed to molecular beams of lanthanum, barium, tin oxide (SnO is the dominant species) and ozone (~10% ozone plus 90% oxygen). The barium flux was 4.0×10^{13} atoms/(cm²·s) and the tin oxide flux was 7.5×10^{13} molecules/(cm²·s). Epitaxy was readily achieved in an ozone background pressure of 1.0×10^{-6} Torr. Note that tin oxide is supplied in excess under these

adsorption-controlled conditions where excess tin oxide is desorbed and thermodynamics is used to form a single-phase BaSnO₃ film.

Having achieved epitaxial growth, we moved on to measure the mobility of La-doped BaSnO₃ grown on (1 0 1) (La,Nd)(Sc,Lu)O₃ substrates. Mobility is a far more sensitive measure of film quality than structural characterization. We chose MBE because our growth process has achieved BaSnO₃ films with the highest mobility of all thin film growth methods to date. The highest mobility that we have achieved on commercial substrates, none of which are well lattice matched to BaSnO₃, is 183 cm²/(V·s) at room temperature at a mobile electron concentration of 1.2×10^{20} cm⁻³ [29]. This film was grown on a (1 0 1) DyScO₃ substrate.

The large lattice mismatch to commercially available substrates results in huge densities of threading dislocations, about $\sim 10^{11}$ cm⁻², in the aforementioned La-doped BaSnO₃ films grown on DyScO₃. The much closer lattice match of La_{0.557}Nd_{0.394}Sc_{0.589}Lu_{0.459}O₃ to BaSnO₃ (−0.7% rather than −4.2% on DyScO₃) made us hopeful that we could achieve higher mobilities on this new substrate by reducing the density of threading dislocations.

The heterostructure that we used to evaluate the mobility consisted of a 180 nm thick undoped BaSnO₃ layer grown on a bare (1 0 1) (La,Nd)(Sc,Lu)O₃ substrate followed by a 180 nm thick La-doped BaSnO₃ film (total film thickness is 360 nm). This heterostructure for mobility measurement is analogous to that used in our prior work. Unlike DyScO₃, for which substrate termination recipes have been developed that provide atomically smooth surfaces with known termination [30], no recipes have yet been developed for (La,Nd)(Sc,Lu)O₃. So, we grew directly on the chemo-mechanically polished surface supplied by CrysTec GmbH.

Hall effect measurements revealed that at room temperature the La-doped BaSnO₃ film grown on (1 0 1) (La,Nd)(Sc,Lu)O₃ had a mobility of 181 cm²/(V·s) at a mobile electron concentration of 1.1×10^{20} cm⁻³. XRD measurements made on the same film on which this mobility was measured are shown in Fig. 11. The $\theta - 2\theta$ scan, Fig. 11a, shows that the film is phase pure. A close-up of the 0 0 2 BaSnO₃ peak (Fig. 11b) shows clear thickness fringes, indicating that the BaSnO₃ film is of constant thickness. The out-of-plane lattice constant of the BaSnO₃ film is 4.135 ± 0.0015 Å, consistent with it being commensurately strained by −0.7% by the underlying substrate. Rocking curves of the 0 0 2

Fig. 11. X-ray diffraction scans of a 180 nm thick La-doped BaSnO₃ film grown on a 180 nm thick undoped BaSnO₃ layer grown on a (1 0 1)-oriented (La,Nd)(Sc,Lu)O₃ substrate prepared from the lower half of the boule (closest to the tail of the crystal). (a) $\theta - 2\theta$ scan demonstrating the BaSnO₃ to be phase pure, (b) a close-up of the 0 0 2 BaSnO₃ peak shows clear thickness fringes indicative of the growth of a smooth film, (c) overlaid rocking curves of the 0 0 2 film and underlying 2 0 2 substrate peak, and (d) ϕ -scans of the 1 0 1 peaks of the BaSnO₃ film and 2 0 0 and 0 0 2 peaks of the (La,Nd)(Sc,Lu)O₃ substrate show that the film grows epitaxially with the expected cube-on-pseudocube epitaxial orientation relationship. This film exhibited a mobility 181 cm²/(V·s) at a mobile electron concentration of 1.1×10^{20} cm⁻³ at room temperature.

BaSnO₃ and 2 0 2 substrate peaks are overlaid in Fig. 11c. The film and substrate have relatively narrow rocking curves with FWHM of 95 arc sec and 42 arc sec, respectively. Although these rocking curves are fairly narrow, the peak shape of both rocking curves show deviations from an ideal peak. Rocking curves taken from multiple substrates cut from the same (La,Nd)(Sc,Lu)O₃ single crystal all show significant deviations from ideal XRD peak shape. These rocking curves are overlaid in Fig. 9 and indicate the presence of subgrain boundaries, as discussed in Section 3.2. ϕ -scans of the 1 0 1 peaks of the BaSnO₃ film and 2 0 0 and 0 0 2 peaks of the (La,Nd)(Sc,Lu)O₃ substrate show that the film grows epitaxially with the expected cube-on-pseudocube epitaxial orientation relationship: (0 0 1) BaSnO₃ || (1 0 1) (La,Nd)(Sc,Lu)O₃ and [1 0 0] BaSnO₃ || [0 1 0] (La,Nd)(Sc,Lu)O₃ (Fig. 11d).

3.5. Optical properties

The optical transmission spectra are shown in Fig. 12. The spectrum of the La_{0.947}Lu_{0.676}Sc_{0.377}O₃ crystal shows a high transparency and no absorption peaks over the entire wavelength range. Between 295 and 375 nm there is a decrease in absorption, which changes at lower wavelengths into what appears to be the band gap absorption. In contrast,

the La_{0.55}Nd_{0.40}Sc_{0.58}Lu_{0.47}O₃ crystal has many spectral lines, which match the absorption lines of the Nd³⁺ ion (see Fig. 12). The good transparency over a large wavelength range and the high concentration of Nd³⁺ incorporated without phase change or loss in crystal quality suggests that Nd-doped (LaLuO₃)_{1-x}(LaScO₃)_x solid solution could be an interesting solid-state laser material.

The Nd³⁺ absorption lines explain why this crystal shows a version of the Alexandrite effect, which can be seen in Fig. 12. In (Nd,Lu)(Sc,Lu)O₃, the color appears to change from purple to green when the light source is changed from the sun to a fluorescent tube (see Fig. 1), but when the crystal is observed under incandescent light it also appears purple. The effect here is different from the one observed in Alexandrite, where a color difference is observed between daylight and incandescent light. This is called the type 1 Alexandrite effect by Liu et al. [31] and occurs in materials which, like Alexandrite, have two transmission bands in the visible spectrum. Then the power distribution of the light source determines the observed color. (Nd,Lu)(Sc,Lu)O₃ shows a type 2 Alexandrite effect, which occurs in materials with many absorption peaks in the visible spectrum. A different color is observed under fluorescent light because the emission spectrum of such lamps is dominated by fairly sharp peaks. If such a peak overlaps with an

Fig. 12. (a) Transmission spectra of $\text{La}_{0.947}\text{Lu}_{0.676}\text{Sc}_{0.377}\text{O}_3$ and of $\text{La}_{0.55}\text{Nd}_{0.40}\text{Sc}_{0.58}\text{Lu}_{0.47}\text{O}_3$ with wafer thicknesses of 0.496 and 0.527 mm, respectively. The neodymium-free crystal is transparent over the almost the entire wavelength range whereas the $\text{La}_{0.55}\text{Nd}_{0.40}\text{Sc}_{0.58}\text{Lu}_{0.47}\text{O}_3$ crystal shows the characteristic Nd^{3+} peaks. (b) Close-up of the 200–1000 nm range.

absorption line of the material, the color change is dramatic.

4. Conclusion and outlook

The Czochralski method is suitable for growing perovskite-type $(\text{La,Nd})(\text{Lu,Sc})\text{O}_3$ single crystals with diameters up to 17 mm and total lengths up to 50 mm. The pseudocubic unit cell parameters of the specific $\text{La}_{0.557}\text{Nd}_{0.394}\text{Sc}_{0.589}\text{Lu}_{0.459}\text{O}_3$ composition grown is 4.086 Å. Investigations of segregation revealed a very low composition shift along the growth axis and a remarkably high chemical homogeneity of a (1 0 0) oriented cross section, that indicates a flat or slightly convex interface shape during growth. Overall, in terms of structure, lattice parameters, structural quality and chemical homogeneity at the macroscale and nanoscale the novel solid-solution substrate single crystals should be appropriate to enable the growth of slightly compressive strained high-quality epitaxial films of PbZrO_3 , $\text{PbZr}_{1-y}\text{Ti}_y\text{O}_3$, LaInO_3 , and other perovskites of interest in this relatively large lattice parameter range where there has been a dearth of available single-crystal perovskite substrates. In terms of further improvements regarding the current crystal growth process for $(\text{La,Nd})(\text{Lu,Sc})\text{O}_3$ single crystals, the next steps should be focused on the elimination of subgrains.

For the case of epitaxial La-doped BaSnO_3 films grown on these substrates, initial experiments achieved a mobility of $181 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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