High-pressure evolution of novel $R_2CuTiO_6$ ($R = \text{Tb} – \text{Lu}$) perovskite phases

Linda Sederholm$^a$, Edmondo Gilioli$^b$, Davide Delmonte$^b$, Ayako Yamamoto$^c$, Maarit Karppinen$^{a,*}$

$^a$ Department of Chemistry and Materials Science, Aalto University, FI-00076, Espoo, Finland
$^b$ Institute of Materials for Electronics and Magnetism, CNR, Parma, A 43124, Italy
$^c$ Graduate School of Engineering and Science, Shibaura Institute of Technology, Saitama, 337-8570, Japan

A B S T R A C T

Perovskite oxides of the $R_2CuTiO_6$ type with a trivalent rare earth element ($R$) at the A-cation site and co-occupancy of the B-cation site with the Jahn-Teller $d^9$ Cu$^{2+}$ and $d^0$ Ti$^{4+}$ transition metals, provides an interesting playground for various chemical and physical phenomena. However, conventional solid-state synthesis under ambient-pressure (AP) yields the perovskite structure only for the largest $R$ constituents from La to Gd; with the smaller rare earth elements (Y, Tb–Lu) a non-perovskite (hexagonal BaTiO$_3$-type) structure is formed. Here we demonstrate that through high-pressure (HP) high-temperature treatment, the hexagonal AP structure can be converted into a distorted (orthorhombic) perovskite structure for all the smaller $R$ constituents. The critical pressure needed for the conversion increases with decreasing $R^{3+}$ ion size, up to ca. 6 GPa for $R = \text{Lu}$. Moreover, a novel intermediate phase is found to form for most of the $R$ constituents when pressures lower than the critical pressure are applied. We have employed both X-ray diffraction and UV–vis spectroscopy analyses to systematically follow the phase formation schemes for the different $R$ constituents.

1. Introduction

The perovskite structure is one of the fundamental crystal structures for inorganic multi-metal oxides. In its simplest, ideal form, the perovskite formula $ABO_3$ denotes a cubic lattice of corner-sharing $BO_6$-octahedra of oxygen-bonded B-site metal cations, with the 12-coordinated central space occupied by a larger A-site metal cation. The structure is highly tolerant of chemical modifications on each of the crystallographic sites, readily accepting various co-occupancy schemes [1]. At the fixed-ratio occupancies of 1:1, 1:2 and 1:3 on one of the cationic sites, numerous interesting families of double, triple and quadruple perovskites with an intriguing property palette have been synthesized [2–4]. Especially for the so-called B-site double perovskites of the $AB'B''O_6$ formulae [5], several cationic ordering patterns are possible, and accordingly exciting properties such as ferrimagnetism and spin-glass like properties in $\text{Pb}_2\text{NiReO}_6$ [6] and $(\text{Ca},\text{Sr})_2\text{CoOsO}_6$ [7], and angle-dependant super-exchange in $(\text{Ba},\text{Sr})_2\text{Cu(W,Te)}O_6$ [8] have been realized.

For double perovskites exhibiting various degrees of cationic order [9–12], an ordering parameter has been introduced to describe the adherence to a given atomic ordering pattern, most commonly rock-salt, layered, or columnar order. Cationic order appears as a result of sufficient incentive from thermodynamical parameters, bond strain, and coulombic repulsion. In addition, special cases of electronic effects may incentivise certain patterns, such as Jahn-Teller distortion sometimes promoting layered or columnar ordering [9].

The range of possible elemental combinations that can crystallize into a perovskite structure is limited by geometrical factors that derive from elemental radii. Best known is the Goldschmidt tolerance factor [13], that uses Shannon ionic radii [14] to evaluate whether a perovskite might form by a formula derived from the geometrical structure of an ideal perovskite:

$$t = \frac{r_A + r_O}{\sqrt{2(r_B + r_O)}}$$

Here, $r_A$, $r_B$, and $r_O$ are the ionic radii of the A and B cations and oxygen anion, respectively; for a co-occupied site the weighted mean radius of the occupants is used. An ideal perovskite has $t = 1$ and a perfectly cubic symmetry, while $t > 1$ indicates an oversized A-site occupant which will generally tear apart the B–O-bonding network. Moderately undersized A-site occupants leading to $t < 1$ can be accommodated with various structural distortions, whereby the network of $BO_6$-octahedra often takes on various tilting patterns as described by Glazer’s notation [15]. Thus, the lower limit of the tolerance parameter is derived from geometrical limits set by the octahedral network and can be described via the octahedral factor $\mu = r_B/r_O$. Filip et al. [16] have given a detailed description of the various formability limits derived from factors concerning the $BO_6$-octahedron network. The combined
limitations result in an allowed range of phase formability for the perovskite phase, which we take to include also distorted versions of the ideal perovskite structure as long as the atomic interconnectivity remains intact.

Outside of the perovskite formability range, the most common structures taken on by the AB0₃ stoichiometries are various structures with hexagonal symmetry, where the A- and B-coordination polyhedra follow various stacking and connectivity patterns. Some of these stacking patterns express local similarities to the perovskite structure, for example the series of structures presented by Syono et al. [17] and by Vente & Battle [18] where the BO₆-octahedra within the unit cell are grouped into corner-sharing and edge- or face-sharing structural regions. Meanwhile, in the structure first described as “hexagonal BaTiO₃” [19] and later refined by YakeI et al. [20] for a series of RMnO₃ compounds, the cations possess reduced coordination numbers of CN(A)=7 and CN(B)=5, and the layers of corner-sharing BO₆ trigonal bipyramids are not connected. This same hexagonal structure with space group P6₃cm has since been reported for a long list of compounds [17,21–30]; in this article, we refer to this structure as “hexagonal” structure or phase.

High pressure can influence the practical formability of perovskites, as the perovskite structure is among the densest atomic packings available for metal oxides [17,23,29–33]. Thus, an originally “unsuitable” combination of t, μ, and Δμ can be stabilized under (ultra)-high-pressure conditions, by compressing the material to a state where the dense perovskite phase is promoted (and its formation can be aided by high temperature). If the internal strain is not too high for the interatomic bonds in the structure, the phase will survive pressure release in metastable condition [34,35]. In double perovskites, the high-pressure treatment can also influence the cationic ordering both negatively and positively, depending on how the ordering-determining factors are influenced by compression of the atomic distances [36].

Many studies into the high-pressure stabilization of the perovskite structure have focused on sample series with a rare-earth element (R) at the A-site. For example, series of RMnO₃ [23,37,38] and RmO₃ [34,35,39] perovskites have been formed using pressures up to 20 GPa; all of these are reported to form in the hexagonal phase at ambient pressure. An investigation of the reported high-pressure phase conversion studies performed on the MTO₃ system (M = s-, d-, or f-block element, T = transition metal) implies that the absolute limit of formability for perovskites, even when physically compressed, would be around t ≈ 0.8 [17,23,34,35,37–45].

Recently, we reported a successful high-pressure (4 GPa) conversion of hexagonal Y₂CuTiO₆ to an orthorhombic perovskite structure similar to the structure seen in the R₃CuTiO₆ system for the largest R constituents (La–Gd) after ambient-pressure synthesis [46]. The R₃CuTiO₆ system has been considered as an interesting model system for electronic/magnetic studies owing to its Jahn-Teller d⁴ Cu⁴⁺/d⁴ Ti⁴⁺ B-site metal configuration [8,24,25,47–54]. Also, it provides an ideal platform for investigations aimed at shedding more light on the perovskite structure tolerance limits under high pressures. In the present study, we explore the limits of the perovskite formability regarding the size of the R constituent and the applied pressure range for R = Tb–Lu in R₃CuTiO₆. We demonstrate a trend of rapidly increasing critical pressure needed for the hexagonal-to-perovskite phase conversion as the size of the R constituent is decreased. A new intermediate phase is observed to occur for Er–Lu between the perovskite and the hexagonal phase regions in the pressure – versus – R-size phase diagram. From the steep rise of the border between the hexagonal phase and perovskite with R = Lu we estimate the tolerance parameter value of t ≈ 0.813 to be a hard limit for the perovskite formation.

2. Experimental

2.1. Sample synthesis

The ambient-pressure (AP) samples were synthesized through conventional solid-state synthesis using starting materials TiO₂, CuO, Tb₂O₇, and R₂O₃ (R = La, Dy–Lu). Hygroscopic rare-earth oxides were pre-heated at 900 °C overnight before weighing to ensure dryness. Stoichiometric (by metal) amounts of the precursors were mixed for 1 h in an agate mortar and then annealed at 1000 °C for 24 h. This step was repeated until no changes in composition were detectable between heating cycles.

The high-pressure (HP) conversions were then carried out for the AP samples for the pressure range of 1–4 GPa using a cubic anvil geometry press (Riken-Seiki; at Aalto University, Finland), following the synthesis procedure of our earlier work for R = Y [46]. Due to calibration limits, the lowest pressure used for the high-pressure treatment was 1 GPa. The AP precursor powder was loaded into a gold capsule, which was assembled into an electrically insulating boronitride sleeve, then into an outer graphite sleeve that functions as an electrical resistance heater, and finally into a pyrophyllite gasket that acts as a solid-state pressure-transfer medium. A portion of ca. 150 mg of the AP precursor was loaded into the gold capsule. The samples were pressed to their target pressure (reached within an hour), then heated to 1000 °C for 40–60 min before quenching and release of pressure. The heating/cooling rate was restricted to maximum 200 °C/min. Synthesis temperature was programmed by calibration (using a NIST standard thermocouple) to electrical load scale, measured in percentile of maximum load capacity of the electric heating system. Active cooling was provided by water flow through the axial anvils at 100–150 ml/min.

The HP treatment at 6 GPa was performed on a multi-anvil press (Rockland Research Corporation, Tecnoprecisa srl 1kton oleodynamic press; at IMEM-CNR in Parma, Italy). The setup consists of an outer set of 6 wedges in cubic geometry, enclosing an inner set of 8 tungsten carbide ISO G2 anvils in octahedral geometry. A similar gasket assembly was used as for the lower-pressure setup: the sample powder was encapsulated in either gold or platinum foil, and then loaded into an assembly of an electrically insulating MgO sleeve inserted into a larger graphite sleeve, all inserted into an octahedral gasket made of magnesium oxide doped with chromium oxide. The assembly included a thermocouple of standard NIST-S for in-situ temperature control, with the thermocouple wire pair connection placed at the surface of the metallic sample capsule. The samples were pressed slowly (overnight) to their target pressure, then heated at 50 °C/min to 900 °C, kept at this temperature for 45 min, and finally cooled at 100 °C/min before releasing the pressure slowly.

2.2. Sample characterization

The phase purity for the AP precursor powders and the phase composition of the HP samples were assessed by powder X-ray diffraction (XRD; PANalytical X’Pert PRO diffractometer; Cu Kα1 radiation, λ = 1.54 Å). Sample mounting was done by ethanol dispersion of the sample powder on a silicon substrate, let dry before analysis. Rietveld refinements were carried out using FullProf [55,56] software with WinPlotr [57] interface. Choice of starting point unit cell parameters was assisted by SuPdS software [58].

Optical absorption properties were investigated using diffuse reflectance mode on a UV–vis-NIR spectrophotometer over the range 185–1400 nm (Shimadzu UV-2600 spectrometer equipped with ISR-2600 Plus integrating sphere attachment). Sample mounting was identical as for XRD analysis. The obtained absorption spectra were used for calculating an estimate for the optical bandgap (Eg) using the Kubelka-Munk transform [59,60] and Tauc plot [61], as previously described in our earlier publication [46].

3. Results and discussion

The XRD patterns for the AP powders confirmed the phase-pure formation of all the intended ambient-pressure precursor phases; the patterns for R = Tb–Lu matched perfectly to the previous entries in the
ICDD and COD databases [25] with non-centrosymmetric space group $P6_3\text{cm}$ and the same atomic pattern, which we refer to as “hexagonal” phase (Fig. 1a); the same structure was concluded for our ambient-pressure $Y_2\text{CuTiO}_6$ sample presented in Ref. [46]. The pattern for $La_2\text{CuTiO}_6$, synthesized for comparison, matched with references in the database with space group $Pnma$ [62,63].

All the samples treated under high pressure were found to be converted to a similar orthorhombic perovskite structure as previously seen for the HP-treated $Y_2\text{CuTiO}_6$ in our previous study [46]. However, the pressure needed for the conversion was found to increase with decreasing $R^{3+}$ ionic radius, see Fig. 2. Also, for $R = Lu$, this conversion was not complete even using 6 GPa (the highest pressure reached in this study). From Fig. 2, it can be seen that the perovskite phase is obtained in phase-pure form e.g. for $R = Dy$ at 1 GPa, for $R = Ho$ at 2 GPa and for $R = Yb$ at 4 GPa. The $La_2\text{CuTiO}_6$ sample pressed at 4 GPa for comparison remained structurally unchanged.

For several of the $R$ constituents, an unidentified intermediate phase was found to form as a side-product at pressures below the critical pressure needed for the complete perovskite-phase formation. This was most evident for the $Lu_2\text{CuTiO}_6$ samples, as seen from the XRD patterns displayed in Fig. 3. The strongest diffraction peak suspected to belong to this intermediate phase is at $2\theta = 29.5^\circ$; however, this peak is close to the (110) peak of the hexagonal phase, and thus difficult to quantify. Therefore, we used the “stand-alone” peak appearing at $2\theta \approx 27.65^\circ$ to roughly estimate the relative amounts of the intermediate phase in the different HP samples. The results are visualized in the “pressure versus $R$ size” phase diagram in Fig. 2. For $R = Lu$, the portion of the intermediate phase first increases with applied pressure up to 3 GPa and then decreases, such that in the 6 GPa sample only traces of this unknown intermediate phase are seen and the orthorhombic perovskite phase dominates. Among the other $R$ constituents, the intermediate phase is barely visible in the $R = Ho$ samples, and clearly seen for the $R = Er$ (1.7 GPa), $R = Tm$ (2–2.5 GPa) and $R = Yb$ (2.5–3.5 GPa) samples. The full-range XRD patterns for all samples are shown in SI.

Unfortunately, we have not yet been able to match the diffraction peaks of the intermediate phase (even for the $R = Lu$ 3 GPa sample) with any structure model. However, similarities in some peak positions, particularly for the strongest peak at $2\theta \approx 33.5^\circ$, lead us to believe that a matching phase could be found within the series of differently stacked hexagonal structures presented in Refs. [17,18]. Another interesting candidate is the garnet structure reported by Sawamoto et al. to form in the border region of the phase conversion seen for RInO$_3$ ($R = Eu, Gd, Dy$) [39]. We have initiated a follow-up study aiming at obtaining the intermediate phase in single-phase form, which could then allow its structure determination. Since the phase fraction was the largest for the intermediate phase in combination with notable peak broadening for $Lu_2\text{CuTiO}_6$ samples at pressures below the critical pressure, we plan to scan the pressure axis for $Lu$-site constituents towards partially substituted Sc-for-$Lu$ samples.

The targeted orthorhombic perovskite phase (for all the $R$ constituents) was identified to express the same structural features as previously found for the HP sample of $Y_2\text{CuTiO}_6$ [46]. As with the $Y_2\text{CuTiO}_6$ sample, several B-site ordering patterns and thereto connected space groups were evaluated using Rietveld refinement to determine the best-fitting structural model. However, the presence of the unidentified intermediate phase in combination with notable peak broadening for several samples caused complications for the Rietveld refinements. While the unit cell parameters converged well, peak shape fitting proved challenging – and in some cases impossible – due to various degrees of asymmetry in the peak shape. Irregularities in sample surface level, caused by the sample fixation technique, are difficult to account for mathematically in the modelling of the peak shape. In addition, we noted increasing peak broadening with decreasing size of the $R^{3+}$ ion,
adding to the complexity of the peak shapes especially for the smallest R-ion samples. Internal strain caused by the release of pressure after phase formation could explain this trend.

While being able to exclude the structure model with rock-salt type ordering for all samples, we found roughly equal fits for the disordered Pnma model (Fig. 1b) and the P21/c model with partial layered order at the B site. The P21/c models converged to very different levels of B-site order, with no clear trend among the samples, despite the symmetrizing action of the pressure on the crystal structure. For Dy2CuTiO6, for which the best Rietveld refinement convergence was obtained, both the HP samples investigated presented a strong preference for layered-site order in the P21/c models, but the Pnma models converged with equally good fitness parameters and no conclusion on order could thus be made. The results of these refinements are presented in Table 1 and Table 2. The two cases that produced the next-best Rietveld refinement results, namely Tb2CuTiO6 and Ho2CuTiO6, both converged toward dominant B-site disorder for all samples and ordering models (see data in SI).

Since no conclusive evidence for the presence of B-site ordering could be found, we choose to report the unit cell data for the rest of the sample series obtained by the Pnma structure model in Table 3. The detailed list of calculated unit cell parameters and Rietveld refinement parameters can be found in SI. Plotting the unit cell parameters (a, b, c, and volume) as a function of R3+ ion radius, we notice an approximately linear trend among the HP-prepared perovskite phases, that differs in angle to the corresponding trend among the R2CuTiO6 perovskite phases with the largest R constituents (La–Gd) synthesized under ambient pressure. Since all samples prepared under high pressure fit the same structure model, with the same tiltting pattern of the octahedral network, it is unsurprising that an increase in A-site R3+ ion size results in a corresponding stretching of the unit cell parameters a, b, and c (as visualized in Fig. 4). Meanwhile, for the AP-synthesized R = La–Gd phases the structure changes as the R3+ ion increases in size. Although the structure and Pnma space group remain the same as for the Tb–Lu samples, the tilting gradually decreases for Gd–Nd [28]. Pr3+CuTiO4 has been reported in both orthorhombic [24] and monoclinic symmetry [67]. In La2CuTiO4 the tilting is reduced to 12° in all directions [62]. Changes in tilting are connected with unequal stretching and contraction for the a, b, and c axes, explaining how a contracts as b and c stretch between R = Gd and R = La [23]. Finally, from the data in Table 3 and Fig. 4, some small deviations from the linearity can be observed, with R = Tb and Yb being slightly smaller than the linearity would predict and R = Ho slightly larger. These slight deviations can be explained by the somewhat broad XRD peaks (typical for HP samples), leading to inaccuracies in lattice parameter determination. Also, we note that the R3+ ion radii are understood to be imprecise as they are taken from Shannon’s listed ionic radii, without accounting for high-pressure effects nor the asymmetric coordination environment in the distorted perovskite structure.

We also like to mention the difference in XRD data quality between the perovskite samples synthesized at different pressures, with peak sharpness appearing to decrease with increasing pressure. This is evident for example for Ho2CuTiO6 where e.g. the (212) and (230) peaks (at ca. 48.00°) are merged for the 4 GPa samples, but increasingly clearly distinguishable for the 3 and 2 GPa samples (Fig. 5).

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Unit cell parameters for Dy3CuTiO6 treated at 4 GPa, refined in space group Pnma. a = 7.47512(3) Å, b = 7.47561(4) Å, c = 5.32178(3) Å; R_p = 2.55, R_wp = 4.18, and R_brass = 6.68.</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>y</td>
</tr>
<tr>
<td>Dy</td>
<td>0.57526(17)</td>
</tr>
<tr>
<td>Cu</td>
<td>0</td>
</tr>
<tr>
<td>Ti</td>
<td>0</td>
</tr>
<tr>
<td>O1</td>
<td>-0.0373(16)</td>
</tr>
<tr>
<td>O2</td>
<td>0.1882(13)</td>
</tr>
</tbody>
</table>

Table 2 | Unit cell parameters for Dy2CuTiO6 treated at 4 GPa, refined in space group P21/c. a = 7.47560(4) Å, b = 5.32178(3) Å, c = 5.74123(3) Å; β = 90.005(3)°; R_p = 2.56, R_wp = 4.25, and R_brass = 7.06. |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>y</td>
</tr>
<tr>
<td>Dy</td>
<td>0.25100</td>
</tr>
<tr>
<td>Cu</td>
<td>0</td>
</tr>
<tr>
<td>Ti</td>
<td>0</td>
</tr>
<tr>
<td>O1</td>
<td>0.22923</td>
</tr>
<tr>
<td>O2</td>
<td>-0.0653</td>
</tr>
<tr>
<td>O3</td>
<td>0.44061</td>
</tr>
</tbody>
</table>

Table 3 | Summary of the unit cell parameters for the sample series, as refined in space group Pnma. A complete list of sample-specific unit cell and Rietveld refinement parameters can be found in SI. |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>R3+ ion</td>
<td>a (Å)</td>
</tr>
<tr>
<td>Tb</td>
<td>5.7474</td>
</tr>
<tr>
<td>Dy</td>
<td>5.7412</td>
</tr>
<tr>
<td>Y</td>
<td>5.7472</td>
</tr>
<tr>
<td>Ho</td>
<td>5.3013</td>
</tr>
<tr>
<td>Er</td>
<td>5.7225</td>
</tr>
<tr>
<td>Tm</td>
<td>5.7049</td>
</tr>
<tr>
<td>Yb</td>
<td>5.6915</td>
</tr>
<tr>
<td>Lu</td>
<td>5.6769</td>
</tr>
</tbody>
</table>

Fig. 4. Normalized unit cell parameters of perovskite R3+CuTiO6 samples plotted as a function of R3+ ion radius (as defined by Shannon for CN = 8). For comparison with previously reported structures, the values in the plot are normalized to single perovskite (Z = 1) values. Corresponding tolerance parameter values are shown at the top of the plot. Data for R = Gd–Pr are from Refs. [24,28,53,62,64–66].

The same trend is visible when comparing the Er3+CuTiO6 samples made at 2.5 and 4 GPa. The sample made at 1.7 GPa (the lowest pressure investigated for R = Er) presented an impurity phase associated with the border zone, and also broader peaks for the perovskite phase. We interpret that the sample is near the perovskite-forming minimum pressure, and this might affect the structure to make the peaks broader. In Tm2CuTiO6, the trend is less obvious; a small difference in peak separation is discernible between the (123) and (232) peaks (at ca. 60.50°), but the (212)/(230) peak pair is fused. The Yb2CuTiO6 sample series shows a presence of the intermediate phase across a wider pressure range, including the sample made at 3 GPa which nevertheless expresses
the sharpest separation between the (212)/(230) peaks (fused) and (040), and also between peaks (123) and (232).

We suggest that the blurring of the peaks for samples synthesized well above the critical pressure could come from unit cell strains appearing upon release of pressure. Octahedral tilting is known to be affected by high physical pressure. For example, with Ho$_2$CuTiO$_6$ the sample prepared at 4 GPa might crystallize with a different octahedral tilting pattern than the one made at 2 GPa: upon release of pressure, the octahedral network might not be able to move freely to relax into the tilting pattern preferred at the lowest pressure at which distorted perovskite phase is able to form. This could be a source of internal strain, which can cause peak broadening as a result of local deformation and altering of the interplanar distances in the strained unit cells.

Finally, we present the UV–vis absorption spectra for the samples in Fig. 6 to illustrate the phase changes from the sample colour point of view. With increasing synthesis pressure, absorption spectra of the hexagonal samples start expressing changes: most notable is the overall broadening of the reflectance peak in the visible spectrum and lowering of its intensity maximum at ca. 550 nm. This trend is visible for all sample series where hexagonal phase was obtained at multiple pressures (all spectra are shown in SI). It also corresponds with visible changes in sample colour, from subtly different shades of forest green to slightly darker green nuances. As the XRD patterns clearly show that the phase remains unchanged between hexagonal samples prepared at different pressures, we interpret these changes in reflectance to be an effect of bond length compression caused by the high-pressure treatment.

The spectra undergo a clear transformation when the sample phase changes to orthorhombic perovskite. The peak maximum at 550 nm is extinguished and a new, much lower maximum appears towards the red end of the visible light spectrum range, marking the beginning of a reflectance plateau extending into the infrared spectrum. Comparing perovskite samples of the same composition, the differences between spectra are mostly limited to overall intensity variations between different scans. The overall intensity differences can be explained by the sample fixation method producing slightly different sample coverage of the sample holder.

Based on the absorption spectra, the novel intermediate phase in the $R = \text{Lu}$ 3 GPa sample is very evidently different from both the AP sample and the perovskite sample features (Fig. 6 c). In the visible spectrum range, this sample expresses a nearly flat region, slightly higher toward the blue end of the spectrum. The low-energy side absorption limit is also at much lower wavelength at ca. 850 nm (ca. 1.5 eV) than for either the hexagonal or perovskite phase (ca. 1000 nm, 1.3 eV).

Optical bandgaps calculated from the Kubelka-Munk-Tauc transformed UV–vis data showed roughly similar values for all samples, fluctuating between 3.3 and 3.5 eV with no detectable trends regarding...
the phase nor the R constituent. These values are comparable with the bandgap we have reported for Y2CuTiO6, for which bandgap calculations by DFT calculations (3.1–3.3 eV) agreed with the result given by the Kubelka-Munk-Tauc method (ca. 3.6 eV) [46]. Only the R = Lu 3 GPa sample, concluded also by XRD to present the largest amount of the unknown intermediate phase, expressed a lower bandgap value of ca. 3.0 eV. However, we point out that the precision of these calculations is limited by the imprecision in interpretation of the energy interval that is best representative of the linear range that marks the onset of the absorption edge. From the plotted data, the exact position of the correct linear range is challenging to determine, especially so for the Lu2CuTiO6 3 GPa sample. Thus, we must conclude that these bandgap values should be interpreted as rough estimates only.

4. Conclusions

We have investigated the applied pressure/phase transformation diagram for the R2CuTiO6 system in the applied pressure range up to 6 GPa for the rare earth element constituents from Tb to Lu. These R constituents are the ones for which conventional ambient-pressure synthesis yields the R2CuTiO6 mixed-metal oxide with the hexagonal non-perovskite structure, similarly to several other R-based hexagonal systems such as the RMnO3 manganites.

We employed both X-ray diffraction and UV–vis spectroscopy to systematically follow the pressure-driven phase transformations within the R2CuTiO6 system. With decreasing size of the R3+ ion, increasingly high pressures are required to convert the R2CuTiO6 compounds to the perovskite structure. For the smallest Lu, this critical pressure was found to be ca. 6 GPa. For all the R constituents investigated from Tb to Lu, the resultant R2CuTiO6 perovskite structure showed an orthorhombic distortion described by the space group Pnma.

As an exciting observation, a novel intermediate phase was found to form for most of the R constituents when pressures close to the critical pressure were applied. The relative amount and the pressure stability range of this previously unreported phase were the largest for the smallest R constituent, Lu. Nevertheless, despite considerable efforts the crystal structure of the intermediate phase remained undefined, although implications could be noticed for example to an intermediate phase previously seen for the RnO3 system. Further investigations with varied high-pressure treatment conditions are ongoing to learn more about this phase.

Another general observation was that the applied pressure beyond the critical perovskite-formation pressure tended to decrease the sharpness of XRD peaks. Tentatively, we explain this as the consequence of unit cell strains appearing upon the release of applied pressure.

Finally, it should be emphasized that the present results and conclusions for the R2CuTiO6 compounds should be rather straightforwardly transferable to many other interesting perovskite systems based on different rare earth elements (or alternatively e.g. different alkaline earth elements) as the A-site constituents, to provide further understanding on the pressure-driven structural transformations in these systems.

CRediT authorship contribution statement

Linda Sederholm: Writing – original draft, Visualization, Methodology, Investigation, Conceptualization. Edmondo Gilioli: Resources, Methodology. Davide Delmonte: Resources, Methodology. Ayako Yamamoto: Validation, Methodology. Maarit Karpipinen: Writing – review & editing, Supervision, Resources, Funding acquisition, Conceptualization.

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.

Data availability

Data will be made available on request.

Acknowledgements

We acknowledge the funding from the Finnish Cultural Foundation (Project THERMOF), and the use of the RawMattERS Finland Infra-structure (RAMI) at Aalto University. LS thanks Emil Aaltonen Foundation and Fortum and Neste Foundation for the travel grants that enabled the mobility necessary for this work.

Appendix A. Supplementary data

Supplementary data to this article can be found at https://doi.org/10.1016/j.solidstatesciences.2024.107514.

References
