High-pressure stabilisation of $R = Y$ member of $R_2CuTiO_6$ double perovskite series

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ABSTRACT

Double perovskite oxides of the $A_2B'B'O_6$ type with Jahn-Teller active $Cu_2^+$ as the $B'$ constituent have gained considerable research interest in recent years. For fundamental studies, the rare earth element ($R$) based systems such as $R_2CuTiO_6$ form an intriguing research platform as they allow systematic chemical-pressure studies by simply controlling the size of the $R$ constituent. However, for the $R_2CuTiO_6$ compounds conventional ambient-pressure high-temperature synthesis yields an orthorhombic ($Pnma$) double perovskite structure for the largest $R$ constituents (La-Gd) only, while the compounds with the smaller $R$s adopt a hexagonal structure. Here we demonstrate a hexagonal-to-perovskite structure conversion for the $R = Y$ compound achieved through a high-pressure (HP) high-temperature treatment at 4 GPa and 1000 °C. Structural details of the thus stabilized new double perovskite phase of $Y_2CuTiO_6$ are addressed through a combined DFT simulation and Rietveld refinement study, revealing signs towards the rare layered-type ordering of the $B$-site ($Cu$ and $Ti$) cations. Similar to the previously reported $R_2CuTiO_6$ perovskite phases with $R =$ La, Pr, and Nd, the $R = Y$ member is found paramagnetic throughout the measured temperature range of 5–300 K. From UV–vis absorption measurements the optical bandgap is estimated to be ca 3.4 eV.

Keywords:
Double perovskite
High-pressure conversion
Chemical pressure
Cation ordering

1. Introduction

Perovskites of the structure formula $ABO_3$ present one of the fundamental inorganic crystal structures for multi-metal oxides [1]. The structure can be described as a cubic lattice of corner-sharing $BO_6$ octahedra, with the $A$-site cation placed in the 12-coordinated void in the middle. Each one of the crystallographic sites tolerates a wide variety of elemental combinations and substitutions, allowing an impressively wide scope of chemical variation within the material group. When one of the cationic sites is occupied by two different elements in a 1:1 ratio, the term double perovskite is used [2–4]. Especially for the $A_2B'B'O_6$ type double perovskites, exciting properties can be achieved, such as room-temperature half-metallicity and magnetoresistance in $Sr_2FeMoO_6$ [5,6]; magnetically frustrated, spin-liquid-like ground states in $Sr_2CuTe_2W_1_3O_{10}$ [7–9]; spin glass and ferrimagnetism in $Pb_2NiReO_6$ [10]; and simultaneous electronic and ionic conductivity in $Sr_2MgMoO_6$ [11].

Many of the aforementioned attractive properties of $A_2B'B'O_6$ type double perovskites require that the two different $B$-site metal species, $B'$ and $B''$, are ordered. However, the ordering is not always complete. The degree of ordering is expressed by the parameter $S = 2g_0 - 1$, where $g_0$ annotates the fraction of $B$ cations with correct site occupancy. Thus $S = 1$ when all cations are in their annotated sites ($g_0 = 1$), and $S = 0$ when half of each $B$ species are misplaced ($g_0 = 1/2$). Also, the way the cations are ordered is of importance. For the $A_2B'B'O_6$ compounds various ordering patterns exist (Fig. 1); among these, the rock salt (RS) pattern, where the $B'$ and $B''$ cations alternate along all three crystallographic directions, is the most common, followed by the so-called layered ordering and columnar ordering patterns [12–14].

The appearance of chemical order requires sufficient incentive. The most potent driving forces for RS-type ordering are differences in size (bond strain) and/or charge (Coulombic repulsion, i.e. Madelung energy) between the cations of the ordered site [15]. Often cited minimum differences are $\Delta g > 2$ and $\Delta r > 5–17%$ [13], although the cooperative nature of the ordering incentives makes it impossible to set universal limits. Other types of ordering are extremely rare, as they induce anisotropy at the ordered site. Thus, atomic anisotropy (e.g. Jahn-Teller active species) is an additional requirement for the appearance of layered, columnar, or other ordering [13–18]. In practice, order is often hindered by limits set by thermodynamics and kinetics: while a prerequisite for diffusion, extreme temperatures simultaneously promote entropy-driven disorder.
The stability range of the perovskite structure regarding its constituents elements (ions) is commonly evaluated using the Goldschmidt tolerance parameter ($t$) [23] calculated from Shannon ionic radii [25], as follows:

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

where $r_A$, $r_B$, and $r_O$ are the ionic radii of A, B, and O, respectively. For an ideal perovskite, $t = 1$. Moderate mismatches of the ionic radii can be accommodated with structural distortions such as tilting of the BO$_6$ octahedra; the different tilting patterns are described by the Glazer notation [26]. However, severe radius mismatches destabilize the perovskite structure, instead promoting the formation of various non-perovskite structures; especially the well-known hexagonal structure [27]. Interestingly, high-pressure (HP) treatment can promote the formation of the perovskite phase [28] – both when the A-site ion is too large (as the larger A (s- or f-block) cations are generally more compressible than the smaller B (transition metal) cation [27,29,30]), and when the A ion is too small – as the dense perovskite phase is generally promoted under high pressure. Various perovskite compounds that require extreme pressure to form have been known for decades: single perovskite examples include BaMnO$_3$ [28], RmMoO$_3$ (R = Sc, Y, Dy–Lu), SrMnO$_3$ [31], BaVO$_3$ [29] and PbVO$_3$ [32], while double (and even triple) perovskite examples include Ba$_2$CoSbO$_6$, Ba$_2$ZnTeO$_6$ [30], Ba$_3$NiO$_6$ [33,34], Ba$_2$YIr$_2$O$_6$ [35], Pb$_2$FeMoO$_6$ [36], Ba$_2$CuTeO$_6$ [37] and Sr$_2$CuIrO$_6$ [38]. Double perovskites with a well-ordered B-site have also been prepared under high pressure [10].

Both aliovalent and isostructural substitution effects have been widely employed to control the formation and properties of double perovskite oxides [39,40]. The rare earth elements (R) provide a convenient system for investigating the limit for perovskite formability as a function of A-site radius, owing to their similar chemical behaviour [41]. In the series RmMoO$_3$ [31], the influence of the size of the A-site ion on phase preference is clearly demonstrated: a gradual transition from orthorhombic perovskite to hexagonal polymorph takes place when the larger Dy$^{3+}$ is replaced by smaller R$^{3+}$ ions, Ho$^{3+}$ and Er$^{3+}$. It is therefore reasonable to suppose that HP high-temperature treatment of hexagonal members of the R$_2$B’BO$_6$ family could introduce a similar hexagonal-to-orthorhombic phase transition as seen for RmMoO$_3$.

Among the R$_2$B’BO$_6$ perovskites, the R$_2$CuTiO$_6$ series is of special interest. The Cu$^{2+}$–d$^9$–Ti$^{4+}$–d$^1$ system presents a unique combination of a strongly Jahn-Teller active species known to promote B-site ordering (Cu(II)), and a species completely lacking d-electrons (Ti$^{4+}$); these characteristics have been considered important prognostics for exotic magnetic states if chemical order of the B-site can be achieved [7–9, 42–45]. So far signs of interesting dielectric properties, such as dielectric relaxation, that could be influenced by the presence of ordering have been reported for some R$_2$CuTiO$_6$ compounds [46–48]. However, previous investigations of the R$_2$CuTiO$_6$ series indicate that conventional ambient-pressure (AP) high-temperature synthesis yields the orthorhombic (Pnrn) double perovskite structure for the largest R constituents only, while the compounds with the smaller Rs adopt a hexagonal structure. Apparently, the transition from the orthorhombic perovskite to hexagonal structure takes place between Gd and Tb [47–51]. R$_2$CuTiO$_6$ with R = La, Pr, Nd, and Sm–Gd have been prepared in orthorhombic perovskite structure under ambient pressure [46,47,52–56], while the phases with R = (Y, Tb–Lu) have adopted the hexagonal structure [47, 49–51,56].

In this work, we demonstrate a hexagonal- to perovskite structure conversion for Y$_2$CuTiO$_6$ achieved through a HP treatment at 4 GPa and 1000 °C. Structural investigations through a combined DFT simulation and Rietveld refinement for this newly synthesized double perovskite phase reveal positive signs towards the layered-type ordering of the B-site Cu and Ti cations. The samples are moreover characterized with basic magnetic and UV–vis absorption measurements.

2. Experimental

2.1. Sample synthesis

The AP sample of the hexagonal (P62cm) Y$_2$CuTiO$_6$ phase [47,49,51,56] was synthesized through a sol-gel route from Y$_2$O$_3$ (Research Chemicals, 99,99%) and CuO (Aldrich, 99,99%) dissolved separately in small amounts of concentrated nitric acid and diluted to 2 mol/L. Next, citric acid was added to both solutions with a 1:3 ratio to metal cations. The solutions were separately stirred under gentle heating for 30–60 min until a significant portion of water was evaporated, and finally combined. Then, finely ground TiO$_2$ (AlfaAesar 99.9%) powder was added and water evaporation by heating was continued until a slightly viscous solution was obtained. Ethylene glycol was added (ethylene glycol vs. citric acid ratio 1:1), and water was further evaporated until a thick gel formed. The gel was dried and calcined at 140 °C overnight in air, forming a grey powder which was then crushed and calcined at 600 °C overnight. The powder was ground in ethanol using a mortar and pestle, dried, and pressed into pellets using isostatic pressing at room temperature. Finally, the pellets were calcined at 1250 °C for 24 h in air.

The HP sample was prepared using a cubic anvil geometry press. In this setup, a powder precursor of ca. 100 mg is loaded into a gold capsule, and placed inside an electrically insulating boronitride sleeve including caps; an outer graphite sleeve functions as a resistance heater. Then this assembly is placed inside a pyrophyllite cube, which works as a pressure-transferring medium, and steel and molybdenum discs are added above and below the sleeve assembly to connect the graphite to the current-carrying anvils. The sample was heated to 1000 °C for 15 min under a pressure of 4 GPa.
2.2. Characterisation

Phase purity and crystal structure were investigated using X-ray diffraction (XRD) on a PANalytical X'Pert PRO diffractometer, using Cu Kα radiation (λ = 1.54 Å). Crystal structure parameters were determined by Rietveld refinement, using FullProf software [57,58] and WinPlotr interface [59].

Optical absorption properties were measured with UV-vis-NIR spectroscopy over 185–1400 nm range on a Shimadzu UV-2600 spectrometer with ISR-2600 Plus integrating sphere attachment, using diffuse reflectance mode. The sample powder was mounted on a glass plate by dispersion with ethanol and subsequently drying before measurement. The optical bandgap \( E_g \) was estimated using the Tauc plot method [60] making use of the Kubelka-Munk transform [61] as detailed by [62]. For a solid and opaque sample, the energy dependent absorption coefficient \( \alpha \) normally used in the Tauc formula is replaced by the Kubelka-Munk function which transforms the reflectance spectrum to the corresponding absorption spectrum by taking the ratio of the absorption coefficient \( K \) and the scattering coefficient \( S \). The combined Kubelka-Munk-Tauc formula is formed as:

\[
B(h\nu - E_g) = (a_i h\nu)^{1/\gamma} = \left( \frac{K}{S} h\nu \right)^{1/\gamma} = \left( \frac{(1 - R_{\infty})^2}{2R_{\infty}} h\nu \right)^{1/\gamma}
\]

where \( h \) is the Planck constant, \( \nu \) is the photon’s frequency, \( B \) is a constant, and the reflectance \( R_{\infty} = (R_{\text{sample}} / R_{\text{banded}}) \). The factor \( \gamma \) is chosen according to the type of bandgap, e.g. \( \gamma = \frac{1}{2} \) for a direct and \( \gamma = 2 \) for an indirect bandgap. Thus, the bandgap \( E_g \) is found as the zero point of the extrapolated linear fit at the optical absorption edge.

Magnetic behaviour was investigated using a Quantum Design MPMS XL magnetometer. The measurements were performed on ca. 50 mg of sample packed into a sample holder consisting of nonmagnetic materials (paper and plastic). The temperature range was scanned with 2 K pre-field cooled and once zero-field cooled, and the molar amount of sample (\( \text{mg/mol} \)) as \( \chi = M/(Bn) \). The effective magnetic moment \( \mu_{\text{eff}} \) was calculated as:

\[
\mu_{\text{eff}} = \sqrt{3k_B N_A} \sqrt{\chi} \approx 2.828 \sqrt{\chi}
\]

where \( N_A \) is Avogadro’s constant, \( k \) is Boltzmann’s constant, \( \mu_B \) is Bohr’s magneton, and \( T \) is temperature.

2.3. Computational structure modelling

The atomic coordinates of the crystal structure were determined by a combination of Rietveld refinement and structural simulation by density-functional theory (DFT) calculations. Spin-polarized DFT calculations were performed on Crystal 17 software using the PBE0 hybrid density functional method and Gaussian-type basis sets. The Monkhorst-Pack type K-mesh for sampling the reciprocal space [63] was set to \( 6 \times 6 \times 6 \) for the RS-AFM structure with spins alternating along the c-axis, and \( 4 \times 6 \times 6 \) (longest axis first) for the four other structures. The tightened tolerance factors (TOLINTEGR) for evaluating the coulomb and exchange integrals were 8, 8, 8, 16, and the basis sets used were taken from literature [64,65].

The computed model followed a three-step protocol: first, the unit cell parameters were determined by Rietveld refinement. Second, these structures were entered into the DFT software, where the unit cell parameters were kept constant, while the atomic coordinates were allowed to be changed without symmetry restrictions. Finally, the DFT simulated atomic coordinates were fed back into the Rietveld refined models (including symmetry group) and compared to the experimental XRD data using FullProf. In this step, the atomic coordinates of oxygen were kept fixed, as were the symmetry-locked coordinates of the B-site, while the peak fit parameters and atomic coordinates of the A-site were re-refined to find the best fit.

Three possibilities for B-site ordering were considered: layered order, RS-order, and disorder; also partial ordering was investigated. As the DFT software can only handle ordered structures, an RS-ordered structure was taken as the closest approximation of a completely disordered phase. Further, the software cannot handle paramagnetic spin behaviour (as the calculations simulate 0K conditions), forcing a choice between completely omitting the magnetic influence or fixing it to either FM or AFM ordering. Five alternative combinations of spin ordering and chemical ordering of the B-site were thus considered; layered-order FM, layered-order AFM, RS-ordered FM, and two alternate RS-ordered AFM (alternating the spin orientation either within or between the ab-planes).

The validity of the final structure model was additionally verified by bond valence sum (BVS) calculation, which evaluates the expected valence of an atom based on its chemical bonds [66]. The valence of each atom \( (V) \) is calculated as:

\[
V = \sum v_i \cdot \exp \left( \frac{R_i - R_{\text{b}}}{b} \right)
\]

where \( v_i \) is the valence of each bond, \( R_i \) is the measured bond length, \( R_{\text{b}} \) is the bond length corresponding to a single bond (with bond valence equal) between the atom pair, and \( b \) is an empirical parameter. The values for \( R \) and \( b \) are found in literature to be \( R_1 = 1.679 \) and \( b_1 = 0.36 \) for the Cu\(^{2+}\)O\(^{2-}\) bond, and \( R_2 = 1.815 \) and \( b_2 = 0.37 \) for the Ti\(^{4+}\)O\(^{2-}\) bond [67].

3. Results and Discussion

The ambient-pressure synthesis yielded essentially phase-pure samples as characterized by XRD. Rietveld refinement (Fig. 2, top) converged on hexagonal space group P63cm (a = b = 6.19 Å, c = 11.52 Å), in agreement with previous reports [47-49,51]. No evidence of B-site order was found; this can be deduced from the absence of a [110] peak (which in this case would be expected around 18.25°), as this peak is only allowed by symmetry if the B-site is ordered. However, a low degree of ordering cannot be ruled out by the absence of a discernible [110] peak.

The HP treatment visibly changed the crystal structure, transforming the samples from olive green to dark red-brown in colour. The heating time was optimized to 15 min; longer times at maximal temperature

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Fig. 2. Rietveld refinement results for the hexagonal AP sample (P63cm) and perovskite (partially layered ordering) HP sample (P21/3). Peak matches are shown as black vertical lines, and Rietveld fit curves in blue.
resulted in the appearance of unidentified spurious phases. XRD characterization confirmed the samples to be essentially phase pure. Initial evaluation with Le Bail fit, as well as more thorough Rietveld refinements, converged well on orthorhombic symmetry group $Pbnm$. The refined structure matches well the structures of related compounds in the $R_2$CuTiO$_6$ series (Table S1). A comparison of the unit cell volume (calculated from the observed lattice parameters) as a function of $A$-site ion radius (tolerance parameter) for the $R_2$CuTiO$_6$ compounds shows that the new member fits the trend well, as illustrated in Fig. 3, even though the observed unit cell volume falls slightly below the line extrapolated based on the AP-synthesized members of the $R_2$CuTiO$_6$ series.

Tentatively, the slightly decreased unit cell volume could be interpreted as an indication towards $B$-site cation order, as cation disorder has been found to increase the unit-cell volume in $A_xB_yB'_zO_{3z}$ perovskites, due to electrostatic repulsion between the highly charged $B'$ cations [2]. Conversely, reducing the lattice volume by external pressure could then make the ordered structure energetically more favourable compared to the disordered case. This has been shown e.g. for Sr$_2$FeReO$_6$, for which the HP-synthesized samples had $S \approx 1$, compared to $S \approx 0.5$ for the AP-synthesized samples [68]. Similarly, chemical pressure (smaller $R$ constituent) could promote the $B$-site cation ordering, although the effect may be weaker [69,70].

Due to the absence of ordering in the hexagonal precursor phase, the HP samples were not expected to present evidence of ordering. The most common $R$ type order can be determined from its effects on symmetry, which in turn affects the XRD pattern: the [001], [100], and [100] peaks were not expected to present evidence of ordering. The most ion radius (CN = 8). The top x-axis shows the correlated tolerance parameter. Legend: hexagonal samples with green ‘o’, perovskite samples with red ‘+’.

Here only representative samples are shown; full data set with references are shown in SI (Table S1).

![Fig. 3. Unit cell volume (per Z) of $R_2$CuTiO$_6$ compounds as a function of $R^{3+}$-ion radius (CN = 8). The top x-axis shows the correlated tolerance parameter. Legend: hexagonal samples with green ‘o’, perovskite samples with red ‘+’.

Fig. 3. Unit cell volume (per Z) of $R_2$CuTiO$_6$ compounds as a function of $R^{3+}$-ion radius (CN = 8). The top x-axis shows the correlated tolerance parameter. Legend: hexagonal samples with green ‘o’, perovskite samples with red ‘+’. Here only representative samples are shown; full data set with references are shown in SI (Table S1).](image-url)

near-identical lattice parameters and similar structural features such as the same Glazer [26] tilting scheme $ab\ c^*$ and displacement of the $A$-site cation, which combined with imprecise oxygen positions produce almost indiscernible XRD patterns. To improve the Rietveld-refined models, DFT simulations were undertaken to more closely investigate the competing structural alternatives and to find the theoretical optimal positions for the oxygen coordinates, as well as to evaluate the total energy for each structural option. Unfortunately, the DFT software cannot handle a disordered model, so only the layered and RS ordered cases could be compared. Comparison of the DFT calculated structures indicates that the RS-ordering would be slightly more energetically favourable than the layered ordering (Table S2). We assume that the energy for a perfectly disordered structure cannot be lower than the RS ordered energy, and thus we interpret from the DFT data that both disorder and partial layered order are energetically possible for our compound.

Returning the DFT-adjusted structures to a new round of Rietveld fitting, we find support for the possibility of a partially layer-ordered $B$-site. The structure that best matches the XRD data (Fig. 2, bottom) shows partial ordering of $S \approx 15\%$, with repeated refinements of the $B$-site occupation factors giving slightly varying results. This model fits the XRD data slightly better than both the perfectly disordered and the perfectly layered structure models, although the difference is small. Comparing the DFT-adjusted structures to the initial Rietveld-refined structures, the main difference is adjustments of the oxygen sites. All versions of DFT shifted the equatorial oxygen positions closer to the Ti-site, in accordance with expectations as Ti$^{4+}$ is smaller than Cu$^{2+}$. The shifted oxygen positions did not result in any significant changes in bond angles or octahedral tilting patterns; however, the new oxygen sites fit the $P21/c$ symmetry significantly better than the $Pbnm$ symmetry. In the $Pbnm$ symmetry the equatorial oxygen sites are forced to split, which results in a worse fit to XRD data and difficulty in converging the post-DFT Rietveld refinement. Thus, we conclude that the $P21/c$ model (Table 1) with partial layered ordering of the B-site is the best match to the structure of our HP Y$_2$CuTiO$_6$ perovskite sample.

The $P21/c$ symmetry group differs from the symmetry group for an $ab\ c^*$-tilted perovskite suggested by literature, i.e. $P21/m$ [71]. We tried fitting the DFT-adjusted coordinates to $P21/m$, but found it not to fit the atomic positions and ordering pattern in our model. A possible explanation is the close relatedness of the present structure to the disordered $Pbnm$ model, with the preferred tilting pattern, atomic displacements, and direction of local layering being influenced by local disorder. For this reason, we also chose to retain the setting (including 90° angles) of the $Pbnm$ model in defining our $P21/c$ model.

The BVS values calculated for the aforementioned $P21/c$ structure support the adjusted oxygen coordinates calculated by DFT. The values for the three Rietveld-modified DFT-calculated structures fall close to the expected values for the cations: ~2.9 for Y$^{3+}$, 2.4–2.6 for Cu$^{2+}$, and 3.2–3.5 for Ti$^{4+}$. It is worth noting that the BVS values for Ti and Cu are expected to be a bit shifted away from their ideal values due to the HP synthesis and the (partial) disorder of the $B$-site.

**Table 1**

Final crystallographic parameters determined for HP Y$_2$CuTiO$_6$ perovskite: monoclinic $P21/c$ with $a = 7.457288$ Å, $b = 5.296503$ Å, and $c = 5.730494$ Å; $\beta = 90°$ (fixed by choice of setting). The refinement converged with R-factors $R_p = 17.1$; $R_{wp} = 21.1$; $R_{exp} = 14.57$; and global $\chi^2 = 2.10$ (conventional).

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3.1. Electromagnetic properties

Due to software limitations, only locked spin ordering patterns (FM or AFM) could be considered for the DFT calculation. The calculated total energies indicate that regardless of crystallographic ordering regime, the AFM spin ordering is more energetically favourable than FM ordering, although the energy differences are small (per formula unit, 1 meV for RS-order and 28 meV for layered order; see Table S2). A preference for AFM spin order is in line with the expectations for a perovskite compound with Cu$^{2+}$ in adjacent B-sites, as the FM coupling between two Cu$^{2+}$ ions is only predicted to occur when the B-site is perfectly RS-ordered with Cu$^{2+}$ alternating with a diamagnetic d$^0$-species such as Ti$^{4+}$. When two magnetic ions are bridged by a diamagnetic ion, the magnetic superexchange can become ferromagnetic [72,73].

Experimentally the compound is measured to be paramagnetic, with an effective magnetic moment ($\mu_{\text{eff}}$) of 1.34 $\mu_B$. This value is lower than the theoretical magnetic moment of Cu$^{2+}$ (1.73 $\mu_B$), the reason of which is not fully understood. Tentatively, we assume that it could be a consequence of the HP treatment. Similarly low $\mu_{\text{eff}}$ values have been reported for Cu$^{2+}$ in HP synthesized and subsequently oxygen depleted LaCuO$_3$ samples [74], and also in copper (II) complexes upon pressure application [75].

The magnetic susceptibility shows no magnetic transitions for neither the field-cooled nor the zero-field-cooled scan (Fig. 4). For an AFM compound, a sharp drop in the susceptibility should be noted at the lower end of the temperature range. Plotting the inverse of the molar susceptibility (1/$\chi$) as a function of temperature, we get a Curie-Weiss plot in which we see that the data approximately follow a straight line (Fig. 4, inset), which is typical for paramagnetic behaviour. However, the extrapolation of the higher-temperature (ca. 150–300 K) linear range of the Curie-Weiss plot yields a negative value for the Curie-Weiss temperature ($T_{\text{CW}}$), which implies AFM behaviour. Different interpretations of the linear range place the value of $T_{\text{CW}}$ between –77 and –89 K. There is thus a possibility that AFM ordering might appear at temperatures lower than the measured range, i.e. <5 K. Compared to other orthorhombic $R_2$CuTiO$_6$ perovskites, paramagnetic behaviour fits the trend. Previous studies have found negative $T_{\text{CW}}$ values for both hexagonal $Y_2$CuTiO$_6$ and the orthorhombic $R = \text{La, Pr, Nd}$ members of the series, despite all four being measured paramagnetic [47,53,54]. All of the studied orthorhombic samples expressed disorder at the B-site. This absence of permanent magnetic order can be explained by the disrupted crystallographic ordering in combination with thermal effects. Although the paramagnetic case could not be simulated by DFT, we note that the DFT-estimated energy difference for FM vs. AFM in the layered case is of the same order of magnitude as the thermal energy at room temperature.

The AP synthesized (hexagonal) sample pellets were olive green in colour, corresponding with a peak in optical reflectivity around 550 nm (ca. 2.2 eV). After HP treatment the samples turned red-brown, corresponding to increased reflectivity for wavelengths >600 nm (ca. 1.9 eV and lower energies). Optical reflectivity of each sample is plotted in Fig. 5. From the Tauc plot, shown in Fig. 6, the optical bandgap was estimated to be direct ($\gamma = \frac{1}{2}$), and extrapolating from the absorption edge around 4.5 eV the bandgap energy was estimated to 3.58 eV for the unpressed sample, and remained almost unchanged at 3.42 eV after pressing. This is comparable to the electronic bandgaps calculated by DFT, which gave values in the range of 3.1–3.3 eV for the perovskite structures with AFM spin ordering. For the FM ordered models, the DFT calculations showed different energies for the spin channels, in accordance with expectations for a compound where one spin channel is localized and participatory in the FM order and the other is itinerant or semi-itinerant. While the layered B-site ordered models produce comparable bandgap energies between the FM and AFM models, and a relatively small energy split (2.8 and 3.15 eV, respectively), the RS ordered FM model presents a significant energy difference between the channels (5.0 and 3.1 eV); that is, the RS/FM ordered model calculates to a spin-selective semiconductor. Such half-
metallic behaviour has been previously found in perovskites with highly R5-ordered B-site, e.g. Sr2FeMoO6 [5,6,14,39].

4. Conclusions

The R = Y member of the R2CuTiO6 series has been converted to perovskite structure under high pressure, thus extending the series to a smaller R constituent than has been presented before. Structural analysis combining Rietveld refinement and DFT simulations converges on P12/c symmetry, with indications of partial layered order of the B-site. Comparison of unit cell parameters shows a good fit to the linear trend of unit cell volume as a function of R5+-ion radius within the perovskite R2CuTiO6 members.

To our knowledge, signs of layered ordering in the R2CuTiO6 series have not previously been presented. This could be due to the extreme similarity of the X-ray diffraction data between the layered and the disordered structures. We only find the partially layered-order solution when combining our structural refinement with DFT simulations. A weakness of DFT is its inability to consider disordered structures, which somewhat undermines the DFT prediction that supports layered ordering. However, a second evaluation of the DFT prediction by Rietveld refinement of its output structure is confirmative of the partially layered order model.

Similar to other perovskite members of the series, Y2CuTiO6 is paramagnetic in the measured temperature range of 5–300 K. Curie-Weiss fitting of the measured magnetic data gives a clearly negative Weiss temperature of $T_{CW} = -77$ K, indicating a preference for AFM spin ordering in the case that magnetic ordering might appear at lower temperatures than reached here. With a disordered or partially layered-order B-site, paramagnetic or antiferromagnetic ordering is unsurprising, as, according to Goodenough-Kanamori-Anderson rules [72,73], ferromagnetic exchange is predicted only when the B-site is RS ordered.

The indication of partial layered ordering of the B-site raises the question whether the rock-salt ordering predicted to support FM exchange is still feasible. On this concern, more robust evidence is needed before a definite preference of layered order over rock salt order can be declared for this compound. Comparing to literature, the charge difference of 2 combined with a size difference of 17% could provide sufficient incentive for Cu$^{2+}$ and Ti$^{4+}$ to order in a rock salt pattern. As the incentives for ordering are sensitive to multiple parameters, it cannot be ruled out that a higher pressure or a different A-site species might enable rock salt ordering of another R2CuTiO6 compound.

Due to their similar chemical behaviour and small differences in ionic radii, the R2CuTiO6 series offers a good opportunity for exploring the limits of HP treatment as a means of pressure-induced phase transformation when the A cation is undersized. Furthermore, substitution of Y$^{3+}$ with Ho$^{3+}$, which is of near-identical size and forms a similar hexagonal AP structure as our sample [50], could add interesting magnetic interactions via the A-site $d_{3}^{2}$-occupation. The much smaller Yb$^{3+}$ ion is a similarly promising candidate due to noteworthy chemical similarity with Y$^{3+}$ [56].

CRediT authorship contribution statement

**Linda Sederholm:** Conceptualization, Investigation, Visualization, Writing – original draft. **Taneli Tiitinen:** Conceptualization, Investigation, Writing – review & editing. **Maarit Karpinnen:** Conceptualization, Supervision, Writing – review & editing.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jssc.2022.123646.

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