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Computational discovery of new modifications in scandium oxychloride (ScOCl) using a multi-methodological approach

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Dedicated to Professor Thomas Schleid on the occasion of his 65th birthday

Scandium oxychloride (ScOCl) has recently become of interest as an advanced material with possible applications in solid oxide fuel cells, photocatalysis, and electronic devices, as are oxyhalides of various transition metals. In the present study, crystal structure prediction has been utilized to fully investigate the energy landscape of ScOCl. A multi-methodological approach has been used consisting of a combination of two search methods, where the final structure optimization has

been performed on *ab initio* level using DFT-LDA and hybrid PBE0 functionals. The experimentally observed α -ScOCl phase has been found as well as several additional structure candidates at high pressures and/or temperatures. A successful synthesis of these novel ScOCl modifications would have the potential for extending the scientific, technological and industrial applications of ScOCl.

1. Introduction

Scandium, yttrium, and lanthanum plus the chemical elements from lanthanum to lutetium (the lanthanoids) comprise the rare-earth elements (REEs). Over the last two decades the rare-earth elements and their compounds, such as oxides, fluorides, selenides, etc.,^[1–7] have been recognized as critical and strategic materials, as they play a vital role in the development of modern technological applications, such as electronics, manufacturing, military, medical science, energy conversion and storage, and a variety of other areas.^[8,9] These include chemical catalysis (e.g., for air pollution control in vehicle exhaust systems), polishing of high-quality optical glass (including glass additives), metal alloying elements, rechargeable batteries, cell phones, superconductors, components of various ceramics systems, magnets for generators and motors, monitors and digital displays, and many other applications.^[8–10] Quite gener-

ally, the incorporation of REE-based materials in workpieces has resulted in outstanding improvements in the performance of these applications. Even though the REEs are relatively abundant (average concentration ranges from 130 mg/g to 240 mg/g) in the Earth's upper continental crust, the extraction, processing, and separation of the REEs minerals is costly, time-consuming, and requires high energy consumption.^[8–10] Thus, identifying new REE compounds and modifications as feasible new materials is of great value.

Scandium is used in solid oxide fuel cells as a stabilizing agent for zirconia-based electrolyte materials in order to improve performance and/or reduce the operating temperature of the fuel cell.^[11] For example, for hydrogen storage purposes, a new aluminum-based alloy, $\text{ScAl}_{0.8}\text{Mg}_{0.2}$, has recently been developed.^[12] The most important chemical compounds of scandium are oxygen-containing compounds, i.e., oxides (e.g. Sc_2O_3), hydroxides (e.g. $\text{Sc}(\text{OH})_3$), complex halides (e.g. ScX_3 ; X=Cl, Br, I, F) and lastly oxyhalides (e.g. ScOX ; X=Cl, Br, I, F) as well as complex compounds.^[8,13–23] Oxyhalides belong to a class of chemical compounds where oxygen and halogen atoms are linked to another chemical element in form of O^{2-} and X^{1-} anions.^[24–26] Concerning applications, oxyhalides of transition metals exhibit interesting magnetic and electronic properties,^[27,28] and could be used for potential future applications in photocatalysis or electronic devices.

Although there are a few studies available regarding the oxyhalides of the REEs and their possible applications in various fields (e.g. scintillators),^[29–32] not much work has been done for ScOCl. It is known that there are a few possible methods for the synthesis of the REEs oxyhalides including scandium oxyhalide. The so-called ammonium halogenide route is one of the best known, and it is based on the solid-state reaction of ammonium halide with REEs, as reported in Ref. [33]. Other ways include the wet chemical synthesis method, described in Ref. [34], and utilizing chemical transport, discussed in Refs. [35] and [36]. Like all other 3d transition-metal oxyhalides, ScOCl crystallizes in the

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orthorhombic crystal system and *Pmmn* (no. 59) space group, as reported in Refs. [37–40]. In the Ref. [41], the authors demonstrated that the structure of ScOCl consists of layers of edge-connected ScO_4Cl_2 octahedra where all O–Cl and O–O edges are shared with neighboring octahedra. The oxygen anions reside within ScOCl layers while the Cl anions of each layer point outwards, resulting in van der Waals type interactions between layers. In this study, we investigate the energy landscape of ScOCl, with the goal of identifying alternative modifications that might be stable or metastable at high pressures and/or temperatures and amenable to synthesis, and also open new insights into the structural features of ScOCl compounds.

2. Computational Details

To perform structure prediction and gain insight into the structural stability of the possible phases existing in the ScOCl system, a multi-methodological approach has been used consisting of a combination of global optimization on the empirical level, data mining, and local optimization on the *ab initio* level.^[42–44] In the first stage of the study, we performed global optimization of the energy landscape of the ScOCl system using simulated annealing^[45] as implemented in the G42+ code.^[46] In particular, the standard stochastic simulated annealing based on many random Monte Carlo walks on the energy landscape, was supplemented by periodic stochastic quenches (i.e. random walks with temperature $T=0$ K) of length 3000 steps each, resulting in 250 local minima along every simulated annealing trajectory. A fast computable robust empirical two-body potential consisting of Lennard-Jones terms ($\epsilon=0.3$ eV/atom; $\sigma_{ij}=(r_i+r_j)$, with effective radii ($r_{\text{Sc}}=0.91$ Å, $r_{\text{O}}=1.45$ Å, $r_{\text{Cl}}=1.99$ Å) and exponentially damped Coulomb terms ($\exp(-\mu r)q_iq_j/r$; $\mu=0.1/\text{Å}$; $q_{\text{Sc}}=+3$, $q_{\text{O}}=-2$, $q_{\text{Cl}}=-1$) were employed to perform the global searches with a reasonable computational effort.^[47–49]

In the second stage, we performed data mining-based explorations of the ICSD database,^[50,51] to find possible structure candidates in the ScOCl system via analogy to known crystallographic structures.^[52] A well-known KDD (knowledge discovery in databases) process, which involves selection, preprocessing, transformation, and interpretation/evaluation (or post-processing) has been used. In order to identify a sufficiently large number of structure candidates for the ScOCl system, we have extracted unique structure types with the general formula ABX that occur among more than 250.000 crystal structures in the ICSD database. In total, more than 5.000 structure candidates have been identified using global optimization and data mining. The symmetries of the identified structures were determined using the SFND,^[53] and RGS^[54] algorithms, while duplicate structures were discarded using the CMPZ^[55] algorithm; all three algorithms are implemented in the KPLOTT code.^[56] We note that most of the thousands of different

structure candidates found on the energy landscape of ScOCl show low symmetry; however, this presence of a vast number of low-symmetry minimum configurations is actually quite common since they often represent distortions or defect variants of the few high symmetry modifications present as minima on the energy landscape. Nevertheless, the α - and β -phases showing high symmetry were identified as low-energy minima on the landscape; both these modifications appeared several times as local minima during the global optimizations, and both modifications were also found as part of the data-mining-based searches. On the other hand, the γ - and δ -modifications were only found using global optimization, together with many distorted variants (e.g. many distorted versions of the γ -ScOCl modification appeared in the monoclinic space group *P2/m* (no. 10), while alternatives to the ideal δ -ScOCl modification appeared in the triclinic *P-1* (no. 2) space group). Finally, each promising structure candidate was subjected to local optimization on the *ab initio* level.

The *ab initio* calculations were performed using the CRYSTAL17 program, based on linear combinations of atomic orbitals (LCAO).^[57,58] Full structural relaxation was performed without symmetry restrictions. The local optimizations employed analytical gradients with respect to the atom positions,^[59] and the cell parameters,^[60] and a local optimization routine.^[61] Density functional theory (DFT) calculations were performed in the present study, using the local density approximation (LDA) with the correlation functional by Perdew and Zunger (PZ).^[62] Moreover, the hybrid PBE0 exchange-correlation functional has been used. The PBE0 functional mixes the Perdew–Burke–Ernzerhof (PBE) exchange energy and Hartree–Fock exchange energy in a 3:1 ratio, along with the full PBE correlation energy.^[63,64] Our previous studies showed that it is reasonable to choose several different *ab initio* methods, to gain better insight into the quantitative validity of the results.^[65–67] All-electron basis sets (AEBS) based on Gaussian-type orbitals (GTO) were used. In the case of scandium, an Sc_864-11G*_harrison_2006 basis set was used as in refs. [68,69]. For oxygen, a modified O_8-411_towler_1994 basis set was used as in refs. [70–72], and for chlorine, a Cl_86-311G_apra_1993 all-electron basis set as in refs. [69,73], respectively.

3. Results and Discussion

The only experimentally observed structure of scandium oxochloride (ScOCl) crystallizes in the orthorhombic crystal system with the *Pmmn* (no. 59) space group, as reported in Refs. [37–40]. This structure has been classified as α -ScOCl and was found as the lowest energy minimum after global optimization using empirical potentials and local optimization using LDA-PZ and hybrid PBE0 functionals. Furthermore, three so far unknown ScOCl modifications have been predicted as other promising low-energy candidates. These four most relevant structure candidates obtained from global optimization and data mining-based searches, with their energies after local *ab initio* relaxations, are presented in Table 1, while their structural

¹For access to the freely available G42+ code, please contact the author (J. C. Schön) directly.

Table 1. Calculated total and relative energies of the most promising ScOCl modifications after local optimization on *ab initio* level, using LDA-PZ and hybrid PBE0 functionals. The total energy, E_{tot} , per formula unit is given in Hartree (E_h). The relative energy, E_{rel} , i.e., the energy relative to the one of the optimized α -ScOCl modification, is given in kJ/mol.

	α -ScOCl E_{tot} (E_h)	E_{rel} (kJ/mol)	β -ScOCl E_{tot} (E_h)	E_{rel} (kJ/mol)	γ -ScOCl E_{tot} (E_h)	E_{rel} (kJ/mol)	δ -ScOCl E_{tot} (E_h)	E_{rel} (kJ/mol)
LDA	-2584.9514	0	-2584.9480	8.9	-2584.9420	24.7	-2584.9351	42.8
PBE0	-2591.9561	0	-2591.9422	36.5	-2591.9480	21.3	-2591.9436	32.8

information, together with comparisons to previous reports, are listed in Table 2.

Next, we have computed the $E(V)$ and $H(p)$ curves. Figure 1 presents the energy versus volume curves, $E(V)$, on an *ab initio* level using the LDA and PBE0 functional of the most relevant structure candidates in the ScOCl system. The α -ScOCl modification is the energetically most favorable structure regardless of the functional employed and in agreement with previous theoretical and experimental observations. The β - and γ -ScOCl modifications are low-energy minima on the enthalpy landscape likely to be relevant for high pressures, while the δ -phase might be present at high temperatures. In order to further investigate the pressure-related phase transition, enthalpy vs pressure curves, $H(p)$, were computed using the LDA-PZ and hybrid PBE0 functional (Figure 2). The high-pressure phase transition from the $\alpha \rightarrow \beta$ phase is found to take place at approx. 1 GPa using LDA (and at ~ 3.7 GPa using PBE0), while

the γ -ScOCl phase remains thermodynamically metastable in the high-pressure region for both LDA and PBE0 calculations.

The structure of α -ScOCl is a typical layered structure of the FeOCl type.^[74,75] This structure type is usually described with double Fe–O layers that are sandwiched between layers with chlorine. In the distorted ScO_4Cl_2 octahedra, the Sc atoms are coordinated by four oxygen and two chlorine atoms (Figure 3a). Each Sc is bonded to two oxygen ions at a distance of 2.0534 Å and two others at a distance of 2.1184 Å. The Sc–Cl distances are 2.4874 Å (Table 3). By sharing O–O and O–Cl edges the slabs are formed and they are stacked along the *c* direction (Figure 3b). The slabs are connected with weak van der Waals interactions and thus one expects larger compressibility along the *c*-axis.

The predicted β -ScOCl modification is found in the PbClF structure type, also called the matlockite structure (Figure 4),^[76,77] in the tetragonal $P4/nmm$ (no. 129) space group (Table 1). According to our calculations, the β -phase in the

Table 2. Modification, space group, unit cell parameters (Å), and atomic positions for the predicted ScOCl structures after LDA and PBE0 local optimization.

Method	Modification, space group, unit cell parameters (Å) and atomic positions α -ScOCl (FeOCl type)	β -ScOCl (PbClF type)	γ -ScOCl	δ -ScOCl
LDA	<i>Pmmn</i> (no. 59) $a = 3.45$; $b = 3.90$; $c = 7.83$ Sc (1/4 3/4 0.1199) O (1/4 1/4 0.0372) Cl (1/4 1/4 0.6513)	<i>P4/nmm</i> (no. 129) $a = 3.55$; $c = 6.93$ Sc (3/4 3/4 0.1508) O (1/4 3/4 0) Cl (3/4 3/4 0.6479)	<i>P42/m</i> (no. 84) $a = 7.60$; $c = 3.43$ Sc (0.1941 0.2034 0) O (0.7882 0.0584 0) Cl (0.4521 0.2214 1/2)	<i>C2/m</i> (no. 12) $a = 14.22$; $b = 3.92$; $c = 8.16$; $\beta = 106.23$ Sc (0.1275 0 0.6954) Sc (0.2063 0 0.3056) O (0.8364 1/2 0.2901) O (0.2382 1/2 0.3591) Cl (0.8755 0 0.9959) Cl (0.9481 0 0.6346)
PBE0	<i>Pmmn</i> (no. 59) $a = 3.52$; $b = 3.94$; $c = 8.81$ Sc (1/4 3/4 0.1075) O (1/4 1/4 0.0328) Cl (1/4 1/4 0.6878)	<i>P4/nmm</i> (no. 129) $a = 3.58$; $c = 8.08$ Sc (3/4 3/4 0.1295) O (1/4 3/4 0) Cl (3/4 3/4 0.6878)	<i>-P42/m</i> (no. 84) $a = 7.76$; $c = 3.47$ Sc (0.8075 0.7984 0) O (0.2097 0.9420 0) Cl (0.5496 0.7801 1/2)	<i>-C2/m</i> (no. 12) $a = 15.50$; $b = 3.95$; $c = 8.12$; $\beta = 106.76$ Sc (0.8762 0 0.3034) Sc (0.7770 0 0.6641) O (0.1527 1/2 0.6960) O (0.2436 1/2 0.6107) Cl (0.1449 0 0.0163) Cl (0.0524 0 0.3556)
Experiment/ theory in literature	<i>Pmmn</i> (no. 59) $a = 3.47$; $b = 3.96$; $c = 8.27$ (EXP ^a) $a = 3.44$; $b = 3.96$; $c = 8.18$ (EXP ^b) $a = 3.45$; $b = 3.95$; $c = 8.12$ (GGA ^c) $a = 3.67$; $b = 4.23$; $c = 8.18$ (GGA + U ^c)	n.a.	n.a.	n.a.

^a Ref. [39], ^b Ref. [41], ^c Ref [38].

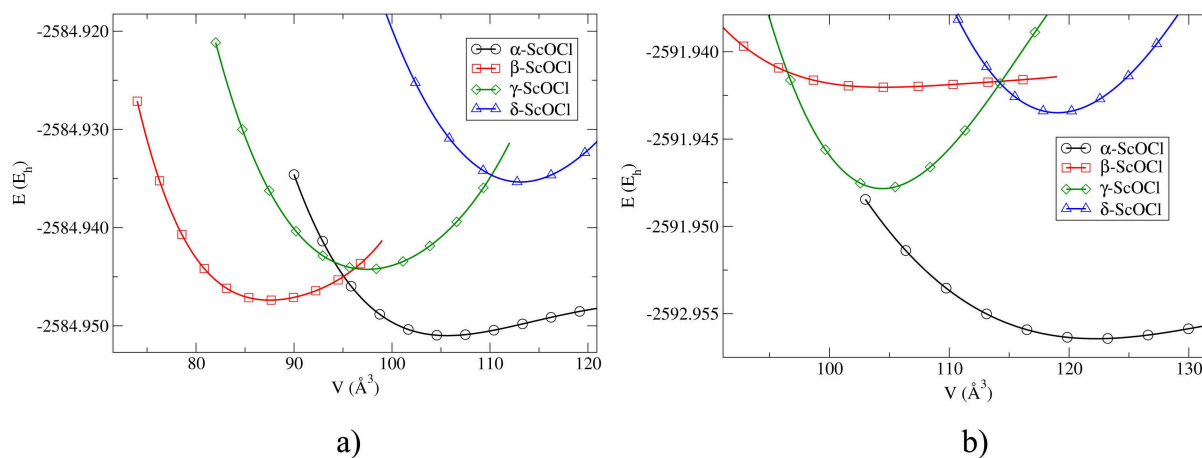


Figure 1. Calculated $E(V)$ curves for the most relevant predicted structures of ScOCl using the a) LDA and b) PBE0 level of theory. Energies per formula unit are given in Hartree (E_h).

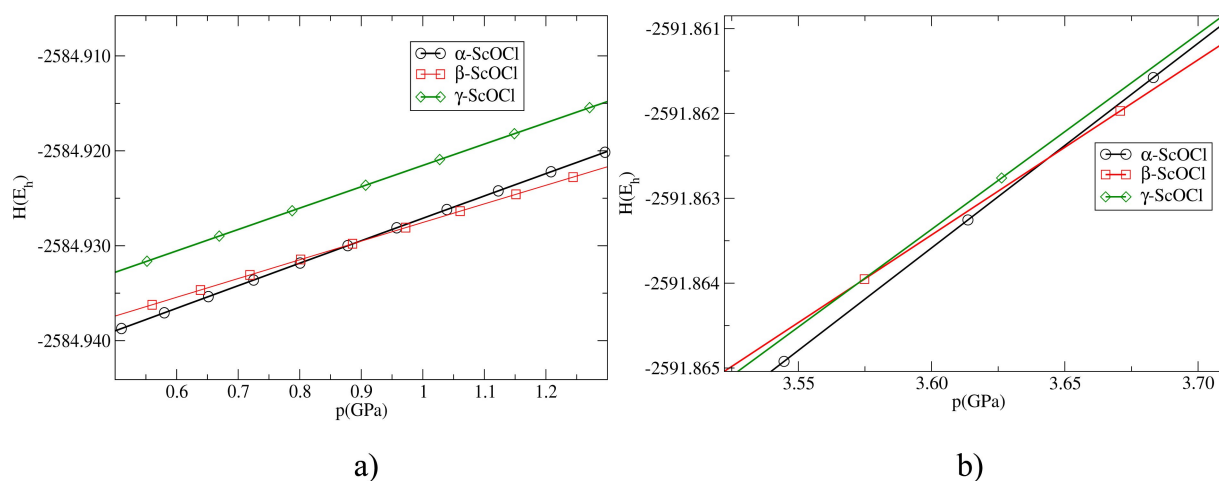


Figure 2. Calculated $H(p)$ curves for the most relevant predicted structures of ScOCl expected at high pressures. Calculations were performed using the LDA (a) and PBE0 (b) level of theory. Energies per formula unit are given in Hartree (E_h).

Table 3. Summary of calculated distances for the most relevant scandium oxychloride modification. Distances are given in units of Angstrom (\AA).

Modification	α -ScOCl	β -ScOCl	γ -ScOCl	δ -ScOCl 1 st polyhedra	2 nd polyhedra
Sc-O	2×2.0534 2×2.1184	4×2.06114	2×2.0014 1×1.9937	2×2.0323 1×1.8892 1×2.6287	2×2.0219 1×2.0787
Sc-Cl	2×2.4874	4×2.8741	2×2.6082 1×2.6255	1×2.3777 1×2.4099	1×2.4592 1×2.5327 1×2.6062
Average	2.2198	2.4678	2.3064	2.2283	2.2868

scandium oxychloride system should be the thermodynamically preferred modification at high pressures (exceeding one GPa) and low temperatures. We note that this structure type has also been observed in the related LaOCl compound,^[78,79] and recently in many other complex compounds,^[7,80–83] which

suggests that this prediction is quite reasonable from the chemical point of view. Synthetically, the β -phase should be accessible from the α -phase via a first order phase transition when applying high pressures, possibly together with moderately elevated temperatures. However, we note that our

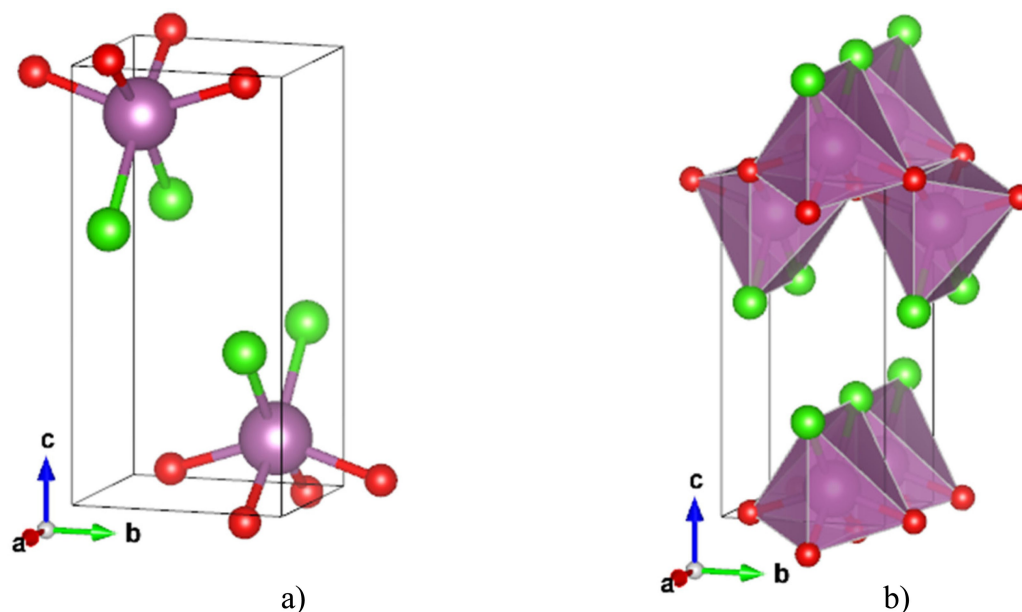


Figure 3. Visualization of the experimentally and theoretically found structure of the α -ScOCl modification presented with and without coordination polyhedra about scandium atoms. Dark purple balls correspond to Sc atoms, light green balls to Cl atoms, and light red balls correspond to oxygen atoms, respectively.

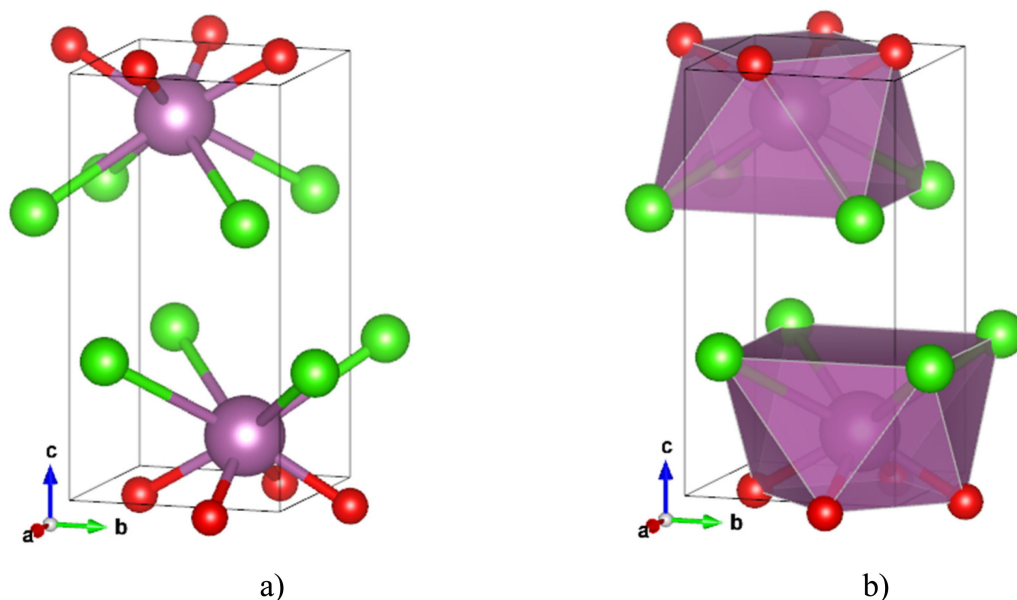


Figure 4. Visualization of the predicted β -ScOCl high-pressure modification shown with and without polyhedra. For notation, c.f. Figure 2.

calculations show that a competing (metastable) modification, γ -ScOCl, might be capable of existence at elevated pressures; this phase might be observed as a side or intermediary product when applying high pressures, e.g., via the sequence " α -ScOCl (stable at standard conditions) \rightarrow γ -ScOCl (metastable) \rightarrow β -ScOCl (stable at high pressures)". This transition might be facilitated by applying moderately high temperatures, in addition to the high pressures.

Scandium cations in the β -phase are surrounded by four oxygen and four chlorine anions forming ScO_4Cl_4 polyhedra. Each Sc atom is bonded to four oxygen ions at the same distance of 2.06114 Å. The Sc–Cl distances are 2.8741 Å (Table 3). β -ScOCl is again a layered structure, where - similar to the α -ScOCl structure - layers with oxygen are sandwiched between layers with chlorine with the slabs stacked along the c direction. However, in β -ScOCl, the coordination of Sc is increased to 8 (CN=8, Figure 4b), compared to the six-fold

coordination of the α - phase, as expected for a high-pressure modification.

The structure of the newly predicted γ -ScOCl modification is shown in Figure 5. Interestingly, the γ -phase is also a tetragonal form of scandium oxychloride exhibiting the $P42/m$ (no. 84) space group (Table 1), making it similar to the β -phase in this regard. However, the coordination polyhedra around the scandium atoms are deformed octahedra connected via edges and corners, thus resembling a distorted rutile or magnesium fluoride structure as far as the arrangement of the octahedra is concerned.^[84–86] Inside the octahedra, scandium is coordinated by three oxygen and three chlorine atoms. Thermodynamically, the γ -ScOCl modification is metastable with respect to the α and β phase, at low and high pressures, respectively. According to the $E(V)$ curves, the γ -ScOCl modification is metastable (at low temperatures) with respect to the α - and β -phases, at low and high pressures, respectively. However, we note that our calculations with the hybrid PBE0 functional show that the γ -ScOCl modification is actually more favorable than the beta phase at pressures below 3.5 GPa (Figure 2b). This fact might be exploited to access the γ -modification experimentally when starting in the beta phase: β -ScOCl (stable at high pressures) \rightarrow γ -ScOCl (metastable) \rightarrow α -ScOCl (stable at low pressures). It appears to be quite feasible that upon lowering the pressure, the (thermodynamically metastable) γ -phase might appear first as an intermediary modification before the thermodynamically stable α -phase finally takes over at low pressures. As far as the energy differences between the γ - and the α -modifications for the two functionals employed are concerned (c.f. table 1), these correspond to about 700–800 K, suggesting that using moderate temperatures when reducing the pressure could be helpful in obtaining the γ -phase.

The δ -ScOCl modification is shown in Figure 6. Regarding the δ -modification, the energy difference to the α -phase

corresponds to a temperature of about 1000–1500 K. Thus, accessing the δ -phase will most likely require quite high temperatures of several thousand Kelvin, which is not easy to create in actual synthesis conditions. However, we note that the δ -ScOCl appears to be the least symmetric one of all the promising structure candidates exhibiting the monoclinic $C2/m$ (no. 12) space group. We also remark that an unknown crystalline compound, which had recently been observed during the synthesis of ScOCl nanoparticles via scandium functionalization of carbon aerogels, was indexed in a primitive monoclinic unit cell ($a=10.80$ Å, $b=5.97$ Å, $c=4.97$ Å, $\beta=95.31^\circ$),^[41] suggesting that additional low-symmetry phases of ScOCl such as the proposed δ -ScOCl modification might be accessible via similar synthesis routes.

The predicted structure of the δ -ScOCl type consist of two types of deformed coordination octahedra with different types of bonds in the structure. In the first type, scandium is coordinated by four oxygen and two chlorine atoms, while in the second type the coordination polyhedron consists of three oxygen and three chlorine atoms. All these octahedra are connected via shared faces and corners. Compared to the structures of α -ScOCl and γ -ScOCl, which also exhibit octahedral coordination of the scandium atoms, the structure of δ -ScOCl appears to lie between the α - and the γ -phase: δ -ScOCl inherits the layer-like building block aspect from the α -modification, while the corner connection between the blocks resembles the corner connection between the strings of edge-connected octahedra in the γ -modification. A summary of calculated distances for the most relevant ScOCl modifications is shown in Table 3.

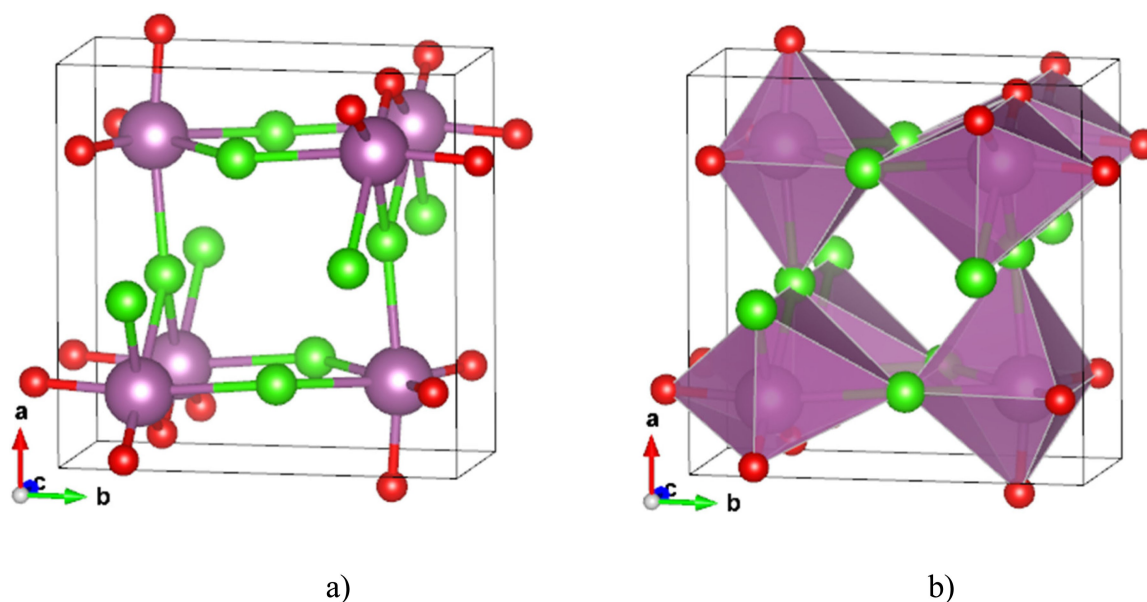


Figure 5. Visualization of the predicted γ -ScOCl modification shown with and without polyhedra. For notation, c.f. Figure 2.

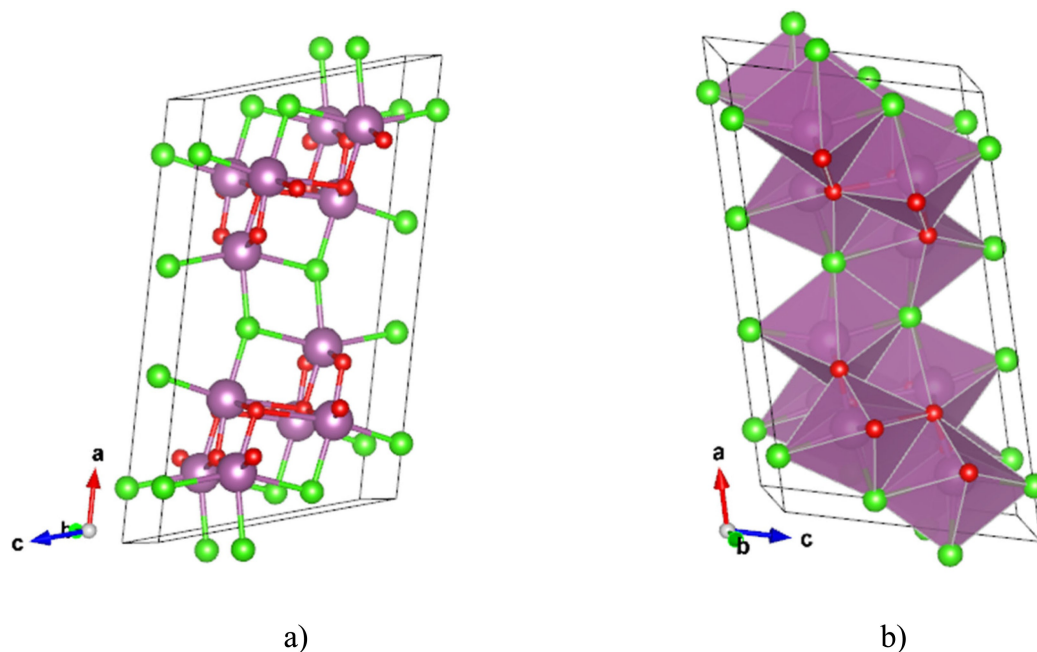


Figure 6. Visualization of the predicted δ -ScOCl modification shown with and without polyhedra. For notation, c.f. Figure 2.

3. Conclusions

Scandium-based materials are used in solid oxide fuel cells as a stabilizing agent for electrolyte materials, while oxyhalides of various transition metals show improved magnetic and electronic properties which could be used for potential future applications in photocatalysis or electronic devices. We performed a structure prediction study in order to fully investigate the energy landscape of the scandium oxychloride system. A multi-methodological approach has been used consisting of a combination of global optimization using empirical potentials, data mining over the ICSD database, and local optimization on the *ab initio* level. Our study has found the synthesized α -ScOCl phase as the global minimum at standard pressure, in agreement with the experiment. Moreover, the present study has generated a variety of structure candidates some of which appear to be promising candidates for an alternative new ScOCl modification at high pressures and/or temperatures. Further investigations of their structural, physical, and chemical properties, together with, e.g., high-pressure synthesis experiments, should yield new insights for advanced technological applications of ScOCl.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Scandium oxychloride · ScOCl · DFT · Structure prediction

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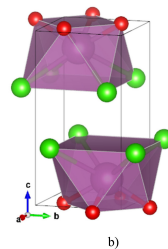
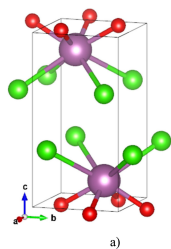
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1 – 10

**Computational discovery of new
modifications in scandium oxychloride (ScOCl) using a multi-methodological approach**
