

THEORETICAL MODIFICATIONS OF SCANDIUM OXYCHLORIDE IN EXTREME CONDITIONS AS AN EXAMPLE OF RARE EARTH COMPOUNDS

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Abstract: *Theoretical modifications of ScOCl at extreme thermodynamic conditions have been identified and are studied as an example of rare earth element (RRE) compounds. Global optimizations with empirical potentials and local optimizations on the ab initio level were performed, leading to the identification of four new structure candidates on the energy landscape that are expected to be relevant under extreme conditions. The structural, as well as electronic properties of these polymorphs, have been investigated and compared with the modifications of the structure under standard conditions. Such theoretical explorations are very important since literature data regarding ScOCl is rather scarce, although ScOCl and the rare-earth elements (REEs) in general have a wide range of applications; for example, scandium is used in solid oxide fuel cells and could be used for potential future applications in photocatalysis or electronic devices, while oxyhalides of transition metals and REEs exhibit interesting magnetic and electronic properties.*

Keywords: ScOCl, Scandium oxychloride, *Ab initio*, DFT, high temperature, ScClO, structure prediction

1. Introduction

The rare-earth elements (REEs) share many comparable chemical and physical properties due to their similar electron configuration; in particular, the atoms of the REEs have the same number of electrons in the outer valence shell (e.g. Sc-3d¹4s², Y-4d¹5s² and La-5d¹6s²). Unlike Sc and Y, La and the lanthanides (Ce-Lu) have an additional 4f orbital that fills up before the 5d¹6s² shell. The most common and stable oxidation state of the REEs is +3, however, other oxidation states may occur, such as +2 (in case of Sm, Eu, and Yb) and +4 (in case of Ce, Pr and Tb) [1,2]. Hence, these chemical elements are highly electropositive and mostly form ionic compounds. Another similarity among the REEs is the so-called lanthanide contraction, where the ionic radius of the rare earth cations decreases (except for Sc and Y) with an increasing atomic number [2]. For example, the cation radius decreases approximately by one-fourth from La³⁺ to Lu³⁺ [2, 3]. Thus, it follows that chemical similarities, in particular the oxidation states and the ionic radii of the REEs, permit easy replacement of one REE by another one in various crystal structures. Besides resulting in very similar crystal structures for the REE compounds, this leads to the occurrence of numerous REEs within a single mineral, with a broad dispersion of the REEs in the earth's upper continental crust [4]. In particular, this suggests that if an REE compound is observed with a particular crystal structure for one REE, one can expect that this structure should also be feasible in an analogous compound with another REE. As commonly observed in the literature, the REEs can be divided into two distinct groups: (i) heavy rare-earth elements (HREEs) consisting of Gd to Lu including Y along with Sc, and (ii) light rare-earth elements (LREEs) consisting of La to Eu. The REEs are not found in their pure state in nature, but rather occur in a wide spectrum of about 250 different minerals species, such as carbonates, silicates, oxides, fluorides, phosphates, borates, arsenates, sulfates, vanadates and tantalates, and others [5, 6]. Some examples of minerals and their associated chemical composition are given in Table 1. [5, 6, 7]

Table 1. Selected minerals and their composition of the rare-earth elements (REEs).

Rare-earth mineral type	Chemical composition
Oxides	Cerianite $(Ce^{4+}, Th^{4+})O_2$
	Loparite $(Ce, Na, Ca)(Ti, Nb)O_3$
	Hibonite $(Ca, Ce)(Al, Ti, Mg)_{12}O_{19}$
Phosphates	Monazite $(Ce, La, Nd, Th)PO_4$
	Xenotime $(Y, Th, U, Dy, Yb, Er, Gd)PO_4$
	Pretulite $Sc(PO_4)$
Carbonates	Bastnaesite $(Ce, La)(CO_3)F$
	Synchysite $Ca(Ce, La)(CO_3)_2F$
	Lanthanite $(Ca, La)_2(CO_3)_3 \cdot 8H_2O$
Silicates	Jervisite $(Na, Ca, Fe^{2+})(Sc, Mg, Fe^{2+})Si_2O_6$
	Bazzite $Be_3(Sc, Al)_2Si_6O_{18}$
	Stillwellite $CeBSiO_5$
Fluorides	Fluocerite $(Ce, La)F_3$
	Gagarinite $NaCaY(F, Cl)_6$
	Tveitite $(Y, Na)_6Ca_6Ca_6(Ca, Na)F_{42}$
Borates	Braitschite $(Ca, Na)_7CeB_{22}O_{43} \cdot 7H_2O$
Sulfates	Chukhrovite $Ca_3(Y, Ce)(AlF_6)_2(SO_4)(OH)_6$
Arsenates	Chernovite $Y(AsO_4)$
Tantalates	Polycrase $(Y, Ca, Ce, U, Th)(Ti, Nb, Ta)_2O_6$
	Formanite $YTaO_4$
Vanadates	Yttrium vanadate YVO_4

The REEs form tens of thousands of compounds due to their high affinity toward oxygen and other chemical elements such as nitrogen, carbon, hydrogen, fluoride, and many other non-metals, including some metals, such as Be, Mg, Tc, Re and Mn [8]. Oxides of the REEs make the largest group of inorganic compounds with the typically stable R_2O_3 (R = rare earth element) stoichiometry (e.g. Sc_2O_3 , Y_2O_3 , etc...) [8]. Furthermore, since some lanthanoids have additional valence states (see above) other stoichiometries may occur too (e.g. Tb_4O_7 or EuO). [8]. At room temperature, all RREs form sesquioxides and they can exist in 5 different crystal structures [9]. These oxides are mostly used as a refractory material. Nevertheless, some oxides can be used for other applications; for example, Y_2O_3 can be added to the ZrO_2 host lattice in order to stabilize the cubic form of the ZrO_2 ceramics [10]. In the cases of Ce, Pr, and Tb, tetravalent or nearly tetravalent compounds may form (e.g., Tb_4O_7 Pr_6O_{11} or CeO_2) [11]. For instance, CeO_2 is used as a catalytic converter for environmentally unfriendly exhaust gases in the automotive industry [12].

In almost all REE compounds, NaCl-type structures have been shown to exist with typical RO (R= rare earth element) stoichiometry. A typical stable representative of such a structure is binary EuO [13]. Other NaCl-type structures of the REE compounds can be stabilized by adding carbon and/or nitrogen [14]. On top of that, the REEs can form high-order chemical compounds with other metal oxides, leading to the formation of perovskite and garnet structures [15]. Chemical compounds with the perovskite structure (e.g., $LaGaO_3$) can be used as superconductors, insulators, catalysts, or magnets. [15] Furthermore, garnet structures (e.g., $Y_3Fe_5O_{12}$) are much more complex compounds than perovskites and such compounds can find their application as electrical insulators, as well as materials with magnetic properties [16]. Hydrides of the REEs usually form nonstoichiometric chemical compounds which can crystallize in different crystal structures [17]. Regarding the halides (iodine, chlorine, bromine and fluorine) there are three major stoichiometries in the respective REE compounds, known as trihalides, tetrahalides and reduced halides [18]. Besides that, REEs can also form numerous intermetallic compounds, which nowadays play an important role in the development of materials for magnetic and electrical applications [19]. For instance, $LaNi_5$ is the main constituent in the Ni-metal hydride (Ni-MH) rechargeable batteries [20]. A so-called neodymium permanent

magnet composed of Nd, Fe, and B to form the $\text{Nd}_2\text{Fe}_{14}\text{B}$ tetragonal crystal structure is one of the strongest magnets known today [21].

Scandium (Sc) with the atomic number $Z=21$ is the first transition chemical element located in group 3 of the periodic table of elements, and it is classified as a rare earth element. Even though scandium, a lightweight chemical element, and by its nature, very similar to aluminum, has a high melting point and low toxicity, it is still commonly regarded as a non-essential element [22]. Up to now, the most important use of scandium is as an alloying element in aluminum-based alloys, since this leads to an increase in material strength including ductility and improves fatigue properties by forming very fine, coherent intermetallic Al_3Sc precipitates in the microstructure [23]. Nowadays scandium is also 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 [24]. However, we note that oxyhalides of transition metals and REEs exhibit interesting magnetic and electronic properties [25, 26], and thus analogous compounds of scandium might show potential for future applications in photocatalysis or electronic devices. One possible candidate in this regard is scandium oxychloride; however, there are not many studies about ScOCl available in the literature. Recently we have investigated the energy landscape of ScOCl at standard conditions using a multi-methodological approach [27], and in the current study, we will focus on the theoretical modifications that are specifically expected to be capable of existence in extreme environments. Here, we note that it is known from the literature that lanthanide oxyfluorides, oxychlorides, oxybromides, and oxyiodides provide a great diversity of structure types and accessible polymorphs, especially as metastable phases. [28] Such metastable structures can be accessed through e.g. quenching of structures accessed by application of temperature and/or pressure. [27-33]

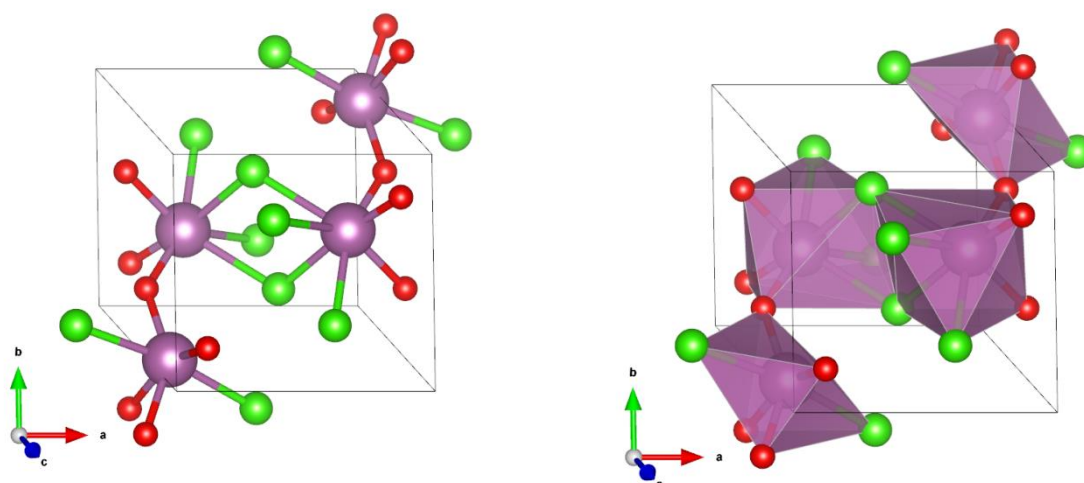


Figure 1. Visualization of the scandium oxychloride modification ScOCl-et-1 in space group $P-1$ (no. 2), presented with and without coordination polyhedra. Purple, green and red spheres denote Sc, Cl and O atoms, respectively.

2. Computational details

A search for structure candidates that might exist in extreme conditions has been performed for the ScOCl system, via the exploration of the energetically higher-lying minima on the energy landscape of ScOCl . [29-32] The general approach of finding structure candidates has been successfully applied previously [27] and consists of a combination of global optimization on the empirical level, and local optimization on the *ab initio* level, [34-36] but where we now focus on local minima with moderately high energies and/or high densities. Global Optimization (GO) of the energy landscape in the ScOCl system was performed using simulated annealing [37] combined with periodic stochastic minimizations, implemented in the G42+ code [38], where an empirical two-body potential consisting of Lennard-Jones and exponentially damped Coulomb terms were employed. [39,40] The

structure candidates obtained were analyzed using the SFND,[41] RGS, [42] and CMPZ [43] algorithms implemented in the KPLOT software. [44] Finally, promising structure candidates in the appropriate energy range were locally optimized on the *ab initio* level. The *ab initio* calculations and minimizations were performed using the CRYSTAL17 program, [45,46] employing analytical gradients with respect to atom positions and cell parameters. [47-49] Density functional theory (DFT) calculations were performed, using the local density approximation (LDA) with the correlation functional by Perdew and Zunger (PZ). [50] All-electron basis sets (AEBS) were used; for scandium, an Sc_864-11G*_harrison_2006 basis set as in refs. [51,52], for oxygen, a modified O_8-411_towler_1994 basis set as in refs. [53-55], and for chlorine, a Cl_86-311G_apra_1993 all-electron basis set as in refs. [56], respectively.

3. Results and Discussion

3.1. Candidates for modifications at extreme conditions

At standard conditions, the thermodynamically stable modification of scandium oxychloride (α -ScOCl) is found in the orthorhombic crystal structure with *Pmmm* (no. 59) space group at ambient conditions. [57-61] The equilibrium structure of ScOCl consists of layers of edge-connected ScO₄Cl₂ 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 addition, several other modifications (β -, γ -, and δ -ScOCl) are expected to be capable of existing as metastable phases under standard conditions, exhibiting space groups *P4/nmm*, *P42/m* and *C2/m*, respectively. [27] In this study, however, the focus is on possible modifications of ScOCl under extreme conditions. As a result of global optimization with their energies after *ab initio* relaxations, the four most relevant structure candidates on the EL at extreme conditions were identified. Their structural information, atom-atom distances, and computed total energies are presented in Table 1.

Table 1. Modification, space group, unit cell parameters (Å), atomic positions, bond lengths and computed total energies (E_h) for the predicted ScOCl structures at extreme conditions, labeled "ScOCl-extreme-type" (ScOCl-*et*-1, ScOCl-*et*-2, ScOCl-*et*-3, ScOCl-*et*-4, in short). The DFT calculations were performed using the LDA-PZ functional.

Modification and space group	Cell parameters (Å) and atomic positions	Bond length (Å)	Total energy (E _h)
ScOCl- <i>et</i> -1 <i>P</i> -1 (no. 2)	$a = 6.08, b = 5.57, c = 6.23,$ $\alpha = 109.06, \beta = 73.02, \gamma =$ 90.84 Sc 0.2400 0.4292 0.3012 Sc 0.0469 0.0462 0.7571 O 0.8988 0.7934 0.9286 O 0.0270 0.2649 0.5314 Cl 0.3625 0.7495 0.0750 Cl 0.4309 0.7761 0.5770	Sc-O 1 x 1.9530 Sc-O 1 x 2.0758 Sc-O 1 x 2.1357 Sc-Cl 1 x 2.5919 Sc-Cl 1 x 2.6389 Sc-Cl 1 x 2.7219 Sc-Cl 1 x 2.7501 Mean: 2.4096 Sc-O 1 x 1.9916 Sc-O 1 x 2.0790 Sc-O 1 x 2.1676 Sc-O 1 x 2.2020 Sc-Cl 1 x 2.5243 Sc-Cl 1 x 2.5389 Mean: 2.2506	-2584.9237
ScOCl- <i>et</i> -2 <i>Imma</i> (no.74)	$a = 3.95, b = 5.04, c =$ 11.05	Sc-O 2 x 1.9971 Sc-O 1 x 1.9962	-2584.9205

	Sc 1/2 1/4 0.1457 O 0 1/4 0.1737 Cl 1/2 1/4 0.9039	Sc-Cl 2 x 2.5814 Sc-Cl 1 x 2.6730 Mean: 2.3043	
ScOCl- <i>et</i> -3 <i>Pnma</i> (no. 62)	$a = 9.16, b = 3.69, c = 5.90$ Sc 0.5735 1/4 0.8203 O 0.0828 3/4 0.5581 Cl 0.6491 3/4 0.4586	Sc-O 2 x 1.9806 Sc-O 1 x 2.0053 Sc-Cl 2 x 2.9037 Sc-Cl 1 x 2.6689 Sc-Cl 1 x 2.6200 Mean: 2.4375	-2584.9161
ScOCl- <i>et</i> -4 <i>Imma</i> (no. 74)	$a = 5.02, b = 6.21, c = 10.76$ Sc 0 1/4 0.5952 O 0 0 1/2 Cl 0 1/4 0.8422	Sc-O 2 x 1.8603 Sc-Cl 2 x 2.5982 Sc-Cl 1 x 2.6569 Mean: 2.3148	-2584.8509

The ScOCl-*et*-1 modification has the lowest energy but the least symmetry of the candidates expected to be relevant in extreme environments (Table 1). ScOCl-*et*-1 crystallizes in the triclinic lattice with space group *P-1* (no. 2) and cell parameters $a = 6.08 \text{ \AA}$, $b = 5.57 \text{ \AA}$, $c = 6.23 \text{ \AA}$, $\alpha = 109.06^\circ$, $\beta = 73.02^\circ$, $\gamma = 90.84^\circ$. The ScOCl-*et*-1 has a complex structure comprised of 6-fold coordination (strongly distorted octahedra which are corner connected) and 7-fold coordination (forming edge-connected polyhedra) of Sc atoms by Cl and O atoms, within the structure (Figure 1). In particular, the coordination of the scandium atom by oxygen atoms in the distorted octahedra is four (Sc-O 1 x 1.9916 \AA , Sc-O 1 x 2.0790 \AA , Sc-O 1 x 2.1676 \AA , Sc-O 1 x 2.2020 \AA) while the coordination of the scandium atom by chlorine atoms is two (Sc-Cl 1 x 2.5243 \AA , Sc-Cl 1 x 2.5389 \AA). In the case of the 7-corner polyhedra, scandium atoms are surrounded by three oxygen atoms (Sc-O 1 x 1.9530 \AA , Sc-O 1 x 2.0758 \AA , Sc-O 1 x 2.1357 \AA), and four chlorine atoms (Sc-Cl 1 x 2.5919 \AA , Sc-Cl 1 x 2.6389 \AA , Sc-Cl 1 x 2.7219 \AA , Sc-Cl 1 x 2.7501 \AA). The mean cation-anion distance in the octahedra is 2.2506 \AA , while the 7-corner polyhedra have a slightly larger average cation-anion distance of 2.4096 \AA (Table 1).

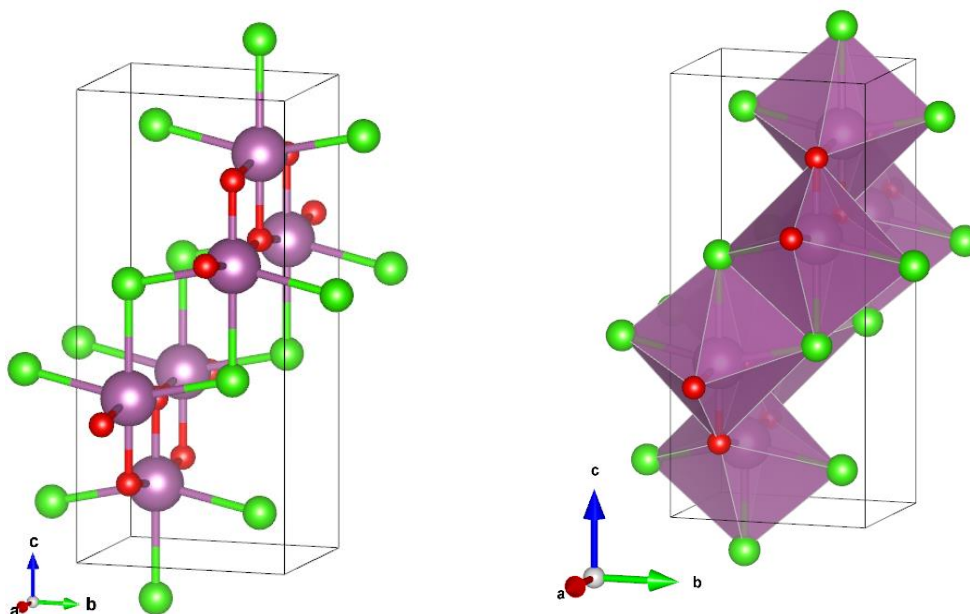


Figure 2. Visualization of the scandium oxychloride modification ScOCl-*et*-2 in space group *Imma* (no. 74), presented with and without coordination polyhedra. Purple, green and red spheres denote Sc, Cl and O atoms, respectively.

Figure 2 shows the ScOCl-*et-2* phase that might be relevant at high temperatures (Tables 1 and 2). Although this structure has higher energy than ScOCl-*et-1*, it crystallizes with a higher (orthorhombic) symmetry, *Imma* (no. 74) space group with $a = 3.95 \text{ \AA}$, $b = 5.04 \text{ \AA}$ and $c = 11.05 \text{ \AA}$. In the ScOCl-*et-2* structure, we find a 6-fold coordination (CN=6) of Sc atoms by Cl and O atoms, forming corner and edge-connected octahedra (Figure 2). In these approximate octahedra, the scandium atoms have 3 oxygen atoms (CN=3, Sc-O 2 x 1.9971 \AA , Sc-O 1 x 1.9962 \AA), and three chlorine atoms (CN=3, Sc-Cl 2 x 2.5814 \AA , Sc-Cl 1 x 2.6730 \AA) as first neighbors, with a mean cation-anion distance of 2.3043 \AA (Table 1). If we compare this structure to the ScOCl-*et-1* modification, we note that the 6-fold coordination in the latter case is a highly deformed octahedral environment with CN = 4+2, while the ScOCl-*et-2* phase exhibits ordered octahedra with coordination CN = 3+3. We note that the ScOCl-*et-2* modification shows some similarity with the anatase structure in TiO₂ [62,63] and anatase was recently found in the ternary TiOS system [64].

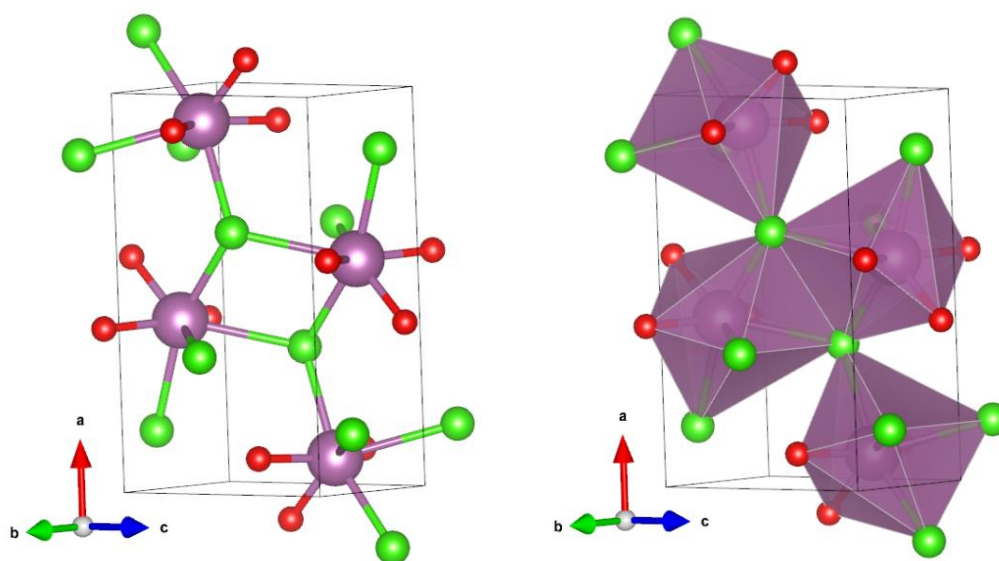


Figure 3. Visualization of the scandium oxychloride modification ScOCl-*et-3* in space group *Pnma* (no. 62), presented with and without coordination polyhedra. Purple, green and red spheres denote Sc, Cl and O atoms, respectively.

The ScOCl-*et-3* modification crystallizes in the orthorhombic lattice with *Pnma* (no. 62) space group and cell parameters $a = 9.16 \text{ \AA}$, $b = 3.69 \text{ \AA}$ and $c = 5.90 \text{ \AA}$. ScOCl-*et-3* shows a 7-fold coordination (CN=7) of Sc atoms by Cl and O atoms, forming corner and edge-connected polyhedra within the structure (Figure 3). Furthermore, the scandium atoms have three oxygen atoms (Sc-O 2 x 1.9806 \AA , Sc-O 1 x 2.0053 \AA) and four chlorine atoms (CN=4, Sc-Cl 2 x 2.9037 \AA , Sc-Cl 1 x 2.6689 \AA , Sc-Cl 1 x 2.6200 \AA) as neighbors, with a mean cation-anion distance of 2.4375 \AA (Table 1). When comparing the structures of ScOCl-*et-3* and ScOCl-*et-1*, we note similar coordination polyhedra where the Sc atoms are surrounded by 3 O atoms and 4 Cl atoms (CN= 3+4). Moreover, an orthorhombic *Pnma* structure has been synthesized as a metastable variant under elevated temperature and pressure conditions for lanthanide oxyfluorides [65,66], which indicates that the analogous ScOCl-*et-3* modification might be synthetically accessible.

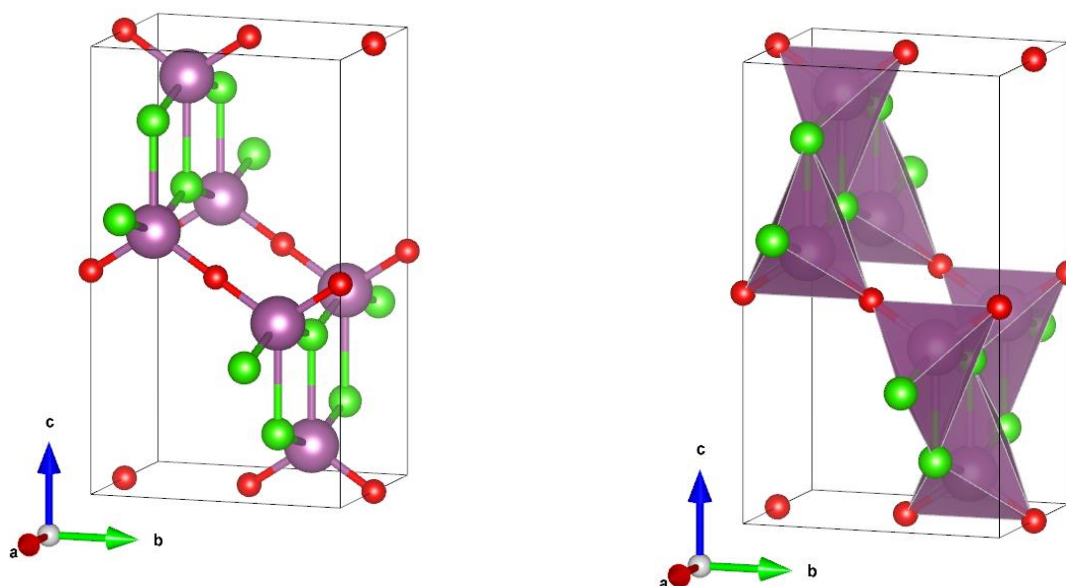


Figure 4. Visualization of the scandium oxychloride modification appearing ScOCl-*et-4* in space group *Imma* (no. 74), presented with and without coordination polyhedra. Purple, green and red spheres denote Sc, Cl and O atoms, respectively.

Finally, we present the ScOCl-*et-4* structure (Figure 4). Interestingly, this structure is also found in space group *Imma* (no. 74), like the ScOCl-*et-2* modification. However, these structures significantly differ both energetically and structurally (Tables 1 and 2, Figures 2 and 4). The unit cell parameters of ScOCl-*et-2* are $a = 3.95 \text{ \AA}$, $b = 5.04 \text{ \AA}$ and $c = 11.05 \text{ \AA}$, while those of ScOCl-*et-4* are $a = 5.02 \text{ \AA}$, $b = 6.21 \text{ \AA}$ and $c = 10.76 \text{ \AA}$, respectively, and the atom positions are also quite different. In addition, the ScOCl-*et-4* structure shows a unique 5-fold coordination of the Sc atoms by O and Cl atoms, forming monocapped tetrahedra (Sc-O 2 x 1.8603 \AA , Sc-Cl 2 x 2.5982 \AA , Sc-Cl 1 x 2.6569 \AA) and a mean cation-anion distance of 2.3148 \AA . Since analogous metastable orthorhombic structures have been stabilized under extreme conditions for several Ln-oxyfluorides (except for Ce, Pm, and Tm) [65,66], and have also been observed as a result of deviations from the 1:1:1 stoichiometry in F-rich oxyfluorides [67,68], it might well be possible to synthesize yet another orthorhombic metastable modification at extreme conditions, in this case for ScOCl.

3.2. Band gap calculations

Table 2. Compared total energies and band gap values for the experimentally known and the predicted ScOCl structures, at standard and extreme conditions. The DFT calculations were performed using the LDA-PZ functional.

Theoretical model	Total energy (E _h)	Band gap (eV)	Theoretical model	Total energy (E _h)	Band gap (eV)
α -ScOCl (FeOCl type)	-2584.9514	4.40	ScOCl- <i>et-1</i>	-2584.9237	3.84
β -ScOCl (PbClF type)	-2584.9480	4.36	ScOCl- <i>et-2</i> (anatase-like)	-2584.9205	4.47
γ -ScOCl	-2584.9420	4.58	ScOCl- <i>et-3</i>	-2584.9161	4.69
δ -ScOCl	-2584.9351	4.63	ScOCl- <i>et-4</i>	-2584.8509	4.60

In order to explore the potential of the ScOCl system for applications, the electronic properties and size of the band gap of the predicted theoretical modifications of ScOCl under extreme conditions were investigated and compared to the modifications found at standard conditions (Table 2). The DFT calculations were performed using the same LDA-PZ functional as in the structural relaxations. The computed band gap of 4.40 eV for the α -ScOCl modification is in agreement with previous theoretical work (GGA 4.06 eV, GGA+U 6.00 eV, HSE06 6.26 eV [69]). We note that this is the first band gap calculation of all other ScOCl phases, showing a great diversity among the proposed modifications and highlighting the possibilities for fine-tuning electronic properties in the ScOCl system. Especially important is the ScOCl-*et*-1 modification which shows a band gap of only 3.84 eV, i.e., a reduction of about 15% compared to the α -ScOCl phase, which could dramatically change the electronic properties of ScOCl material.

4. Conclusion

We have explored the possibility of the existence of scandium oxychloride modifications under extreme conditions, using global optimization with empirical potentials and local optimization on the *ab initio* level. The four structure candidates on the energy landscape expected to be most relevant in extreme conditions were identified. Among these, the ScOCl-*et*-1 modification has the lowest energy but also the lowest symmetry, crystallizing in a triclinic space group, while the other 3 phases exhibit an orthorhombic symmetry, where especially ScOCl-*et*-2 and ScOCl-*et*-4 show very regular octahedral and monocapped tetrahedral coordination polyhedra around the scandium atoms.

Moreover, the size of the band gap was computed for all predicted ScOCl structures, including the band gaps for those modifications found at standard conditions in earlier work. The results show that there is a great diversity in the electronic properties of ScOCl, with particularly interesting ones for the hypothetical modifications expected to be important under extreme conditions. The discovery of these new modifications for extreme conditions and their eventual synthesis might have possible applications in solid oxide fuel cells, photocatalysis, or electronic devices.

Acknowledgments

This research was financially supported by the Ministry of Education, Science, and Technological Development of the Republic of Serbia (Grant No. 1702201). The authors thank Prof. R. Dovesi, Prof. K. Doll, and Crystal Solutions for software support.

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