ELAND 2023: Energy Landscapes: Theory and Applications

# Structure prediction and complex energy landscapes exploration of rare-earth ternary compounds

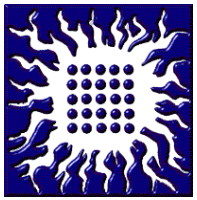
Dr. rer. nat. Dejan Zagorac

Laboratory for Theoretical Investigations of Materials (L-TIM),
Center of Excellence “CextremeLab”, Belgrade, Serbia
Department of Materials Science (170),
"Vinča" Institute of Nuclear Sciences, Belgrade, Serbia
University of Belgrade, Belgrade, Serbia

*08.06.2023, Porquerolles (France)*


FLEURS

# Who and where I am?


- Laboratory for Theoretical Investigations of Materials (L-TIM),
- Center of Excellence CEXTREME LAB
- Department of Materials Science (170),
- "Vinča" Institute of Nuclear Sciences, Belgrade, Serbia
- University of Belgrade, Belgrade, Serbia

# rare-earth elements (REEs)

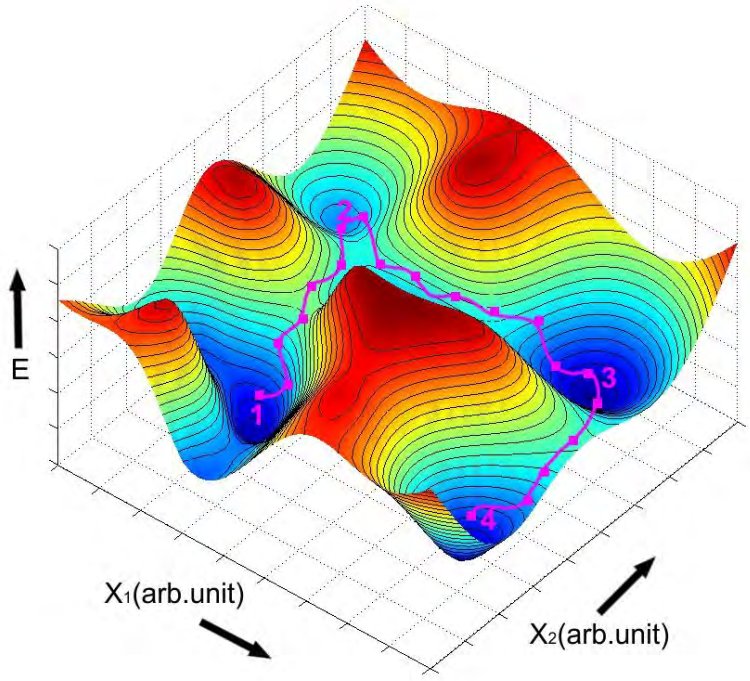
- Scandium, yttrium, and lanthanum plus the chemical elements from lanthanum to lutetium (the lanthanoids) comprise the rare-earth elements (REEs).
- Over the last two decades the REEs and their compounds, such as oxides, fluorides, selenides, etc., have been recognized as critical and strategic materials, 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 (chemical catalysis, glass additives, metal alloying elements, rechargeable batteries, cell phones, superconductors, ceramics, magnets for generators and motors, monitors and digital displays, etc)

# rare-earth elements (REEs)

- 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.
- Thus, identifying new REE compounds and modifications as feasible new materials is of great value.
- Although there are a few studies available regarding the oxyhalides of the REEs and their possible applications in various fields (e. g. scintillators), not much work has been done for ScOCl

# ScOCl

- 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.



# ScOCl

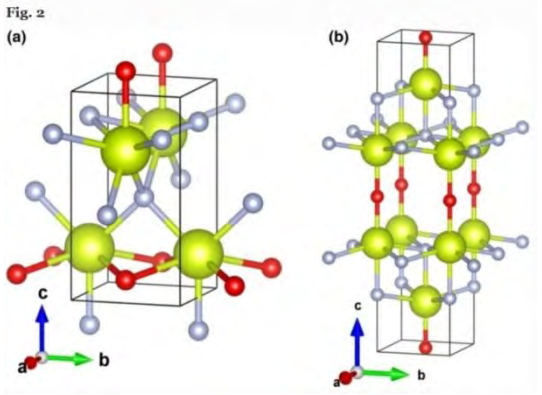
- In the first stage of the study, we performed global optimization of the energy landscape of the ScOCl system using simulated annealing as implemented in the G42+ code.
- In particular, the standard stochastic simulated annealing based on many random Monte Carlo walks on the energy landscape, was supplemented 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 ($\varepsilon$=0.3 eV/atom; $\sigma ij=(ri+rj)$, with effective radii ($r_{Sc}$=0.91 Å, $r_{O}$=1.45 Å, $r_{Cl}$=1.99 Å) and exponentially damped Coulomb terms ($\exp(-\mu r)qiqj/r$; $\mu$=0.1/Å; $q_{Sc}$= +3, $q_{O}$= -2, $q_{Cl}$= -1) were employed.

# Data Mining: ICSD database

- Reliable crystal structure data of high quality play an important part in optimizing the development of new materials which foster innovation in various areas.
- The Inorganic Crystal Structure Database (ICSD) is the world's largest database of fully evaluated and published crystal structure data, mostly obtained from experimental results.
- However, the purely experimental approach is no longer the only route to discover new compounds and structures.

# ICSD database

- At present, the ICSD database contains more than 250.000 crystal structures
- All important crystal structure data are available, including unit cell, space group, complete atomic parameters, etc.
- 80 % of the structures are allocated to about 9,000 structure types.
- Abstracts for a quick grasp of the article content are available.
- Simulation of Powder Diffraction Data
- Keywords to describe physical and chemical properties are provided.



# Classification and standardization of theoretical data in the ICSD

- In the past few decades, numerous computational methods for simulating and predicting structures of inorganic solids have emerged, creating large numbers of theoretical crystal data.
- In order to take account of these new developments the scope of the ICSD was extended in 2017 to include theoretical structures which are published in peer-reviewed journals.

[1] D. Zagorac, H. Müller, S. Ruehl, J. Zagorac and S. Rehme, J. Appl. Cryst. (2019) 52, 918-925.

# Classification and standardization of theoretical data in the ICSD

- The major problem of theoretical structures is that a huge amount of calculations exists in a broad variety of quality. We have developed **three major criteria** for the selection:

1. the structure **should be published** in a peer-reviewed journal
2. the structures **have a low** $E_{(tot)}$ (close to the equilibrium structure)
3. we choose the method which delivers data that are **closest to comparable experimental results**

- Theoretical crystal structures are clearly separated from experimental structures in the ICSD.

[1] D. Zagorac, H. Müller, S. Ruehl, J. Zagorac and S. Rehme, J. Appl. Cryst. (2019) 52, 918-925.

# Classification and standardization of theoretical data in the ICSD

- Furthermore we have categorized all theoretical structures by the following 13 methods used for the theoretical calculation listed below, with additional 3 theoretical category connected to the experiment

Table 2
Summary of theoretical categories in the ICSD.

| Theoretical category in the ICSD | References† |
|---|---|
| *Ab initio* optimization | Zagorac *et al.* (2014*a*); Mayo *et al.* (2016) |
| Empirical and semi-empirical potential | Fan *et al.* (2015); Yoo *et al.* (2016) |
| Geometric modelling | Zagorac *et al.* (2014*b*); George *et al.* (2015) |
| Monte Carlo simulation | Hao *et al.* (2014); Mena *et al.* (2016) |
| Molecular dynamics | Schmidt *et al.* (2015); Paściak *et al.* (2015) |
| Plane waves method | Weerasinghe *et al.* (2015); Goncharov *et al.* (2016) |
| FP(L) augmented plane-wave method (+lo) | Mukadam *et al.* (2016); Čebela *et al.* (2017) |
| Projector augmented wave method | Zurek & Yao (2015); Buckeridge *et al.* (2016) |
| Linear combination of atomic orbitals method | Zagorac *et al.* (2011); Larbi *et al.* (2016) |
| (FP) linear muffin-tin orbital (ASA) | Uba *et al.* (2016); Mishra & Ganguli (2016) |
| Hartree–Fock method | Shimazaki & Nakajima (2015); Zagorac *et al.* (2017*a*) |
| Density functional theory | Civalleri *et al.* (2007); Schönecker *et al.* (2015) |
| Hybrid functionals | Lee *et al.* (2015); Sluydts *et al.* (2017) |
| Predicted (non-existing) crystal structure | Doll *et al.* (2008); Luković *et al.* (2017) |
| Optimized (existing) crystal structure | Olsson *et al.* (2015); Erba *et al.* (2015) |
| Combination of theoretical and experimental structure | Retuerto *et al.* (2016); Cvijović-Alagić *et al.* (2019) |

† References to example theoretical structures found using that theoretical method and already searchable in the ICSD.

[1] D. Zagorac, H. Müller, S. Ruehl, J. Zagorac and S. Rehme, J. Appl. Cryst. (2019) 52, 918-925.

- Maybe one of the most important examples for the experimentalists is the use of the theoretical category: **predicted (non-existing) crystal structure**. As crystal structure predictions become more and more reliable, this category can be an excellent tool for synthesis planning
- **Optimized (or existing) crystal structures** are theoretically calculated structures of existing experimental crystal structures in the ICSD until the year of publication.
- If a **combination of theoretical and experimental data** exist in the manuscript they are highly valuable to all materials scientists with a great variety of possible applications, owing to the high precision of the published data.

# Upgrade of the theoretical CIF file

- ICSD database now provides additional computational information used in the calculation of the respective theoretical crystal structures.
- This computational information provides **details about the code, search algorithm, method, basis set information and technical details of the calculation** (e.g. cutoff energy, K-point mesh etc.), providing information on reproducibility and quality of computations.
- In addition, comments on the tolerances in energy, forces etc. used in calculations (which are similar to the experimental structure criteria R factors, etc.) have been provided.

# ScOCl

- The *ab initio* calculations were performed using the CRYSTAL17 program, based on linear combinations of atomic orbitals (LCAO). Full structural relaxation was performed without symmetry restrictions.
- 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).
- Moreover, the hybrid PBE0 exchange correlation functional has been used. 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.

[1] D. Zagorac, J. Zagorac, M. Fonović, M. Pejić, J. C. Schön, Z. Anorg. Allg. Chem. 2022, 648, e202200198.

# ScOCl

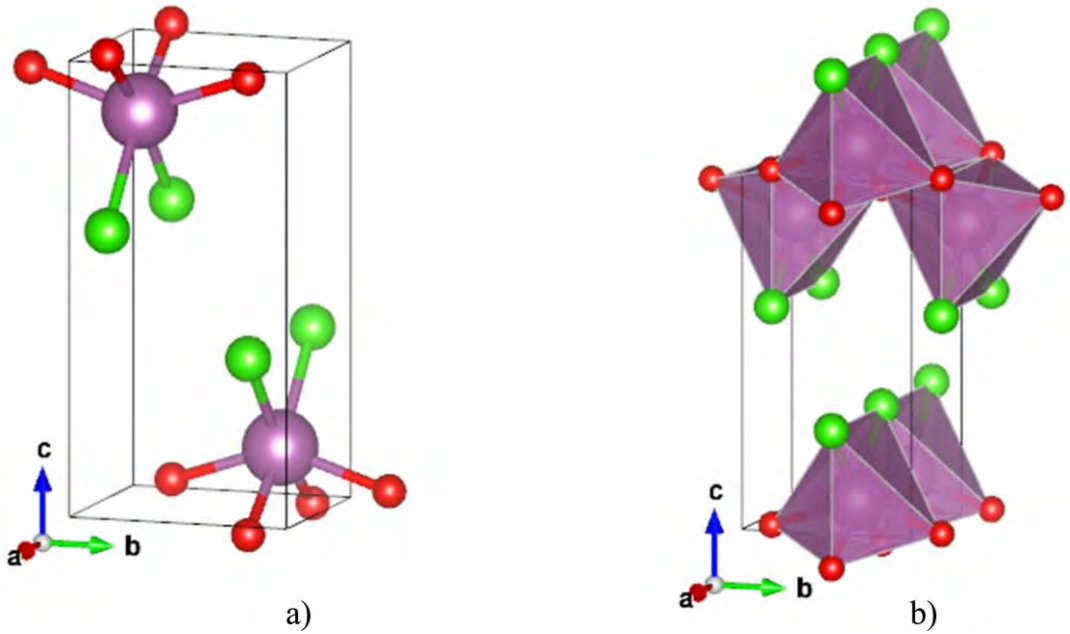
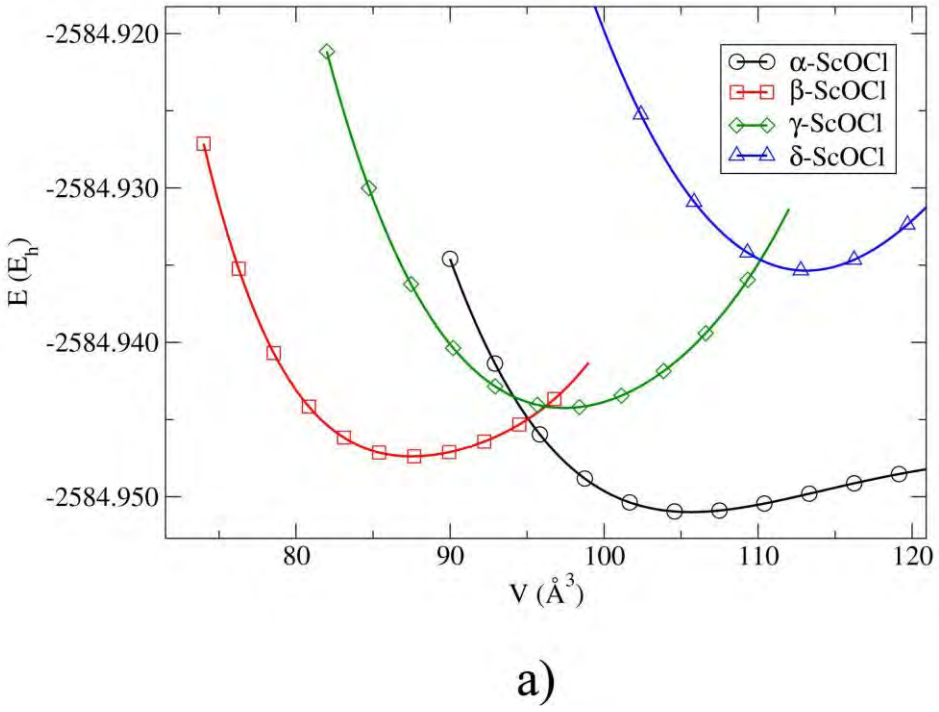


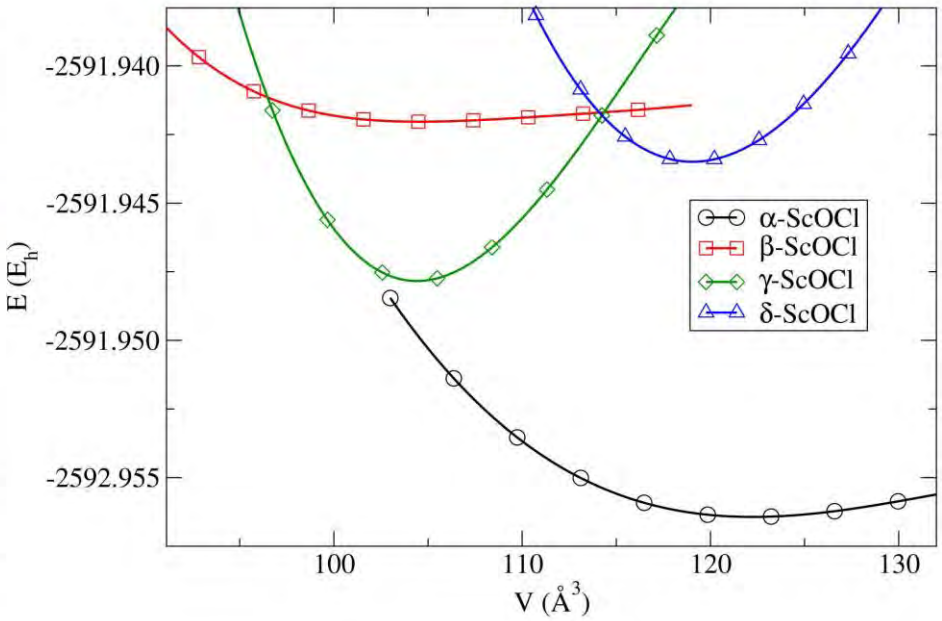

Figure : Like all other 3d transition-metal oxyhalides, ScOCl crystallizes in the orthorhombic crystal system and *Pmmn* (no. 59) space group, as reported in Refs. [1-3]. This structure has been classified as α-ScOCl and was found as the lowest energy minimum after global optimization using empirical potentials and local optimization using LDA-PZ and hybrid PBE0 functionals.

[1] L. Jongen, G. Meyer, Acta Crystallogr. Sect. E 2005, 61, i153-i154.[2] W. Li, N. Miao, J. Zhou, Z. Sun, J. Mater. Chem. C 2021, 9, 547–554.[3] E. Garcia, J. D. Corbett, J. E. Ford, W. J. Vary, Inorg. Chem. 1985, 24, 494–498.

# ScOCl




a)

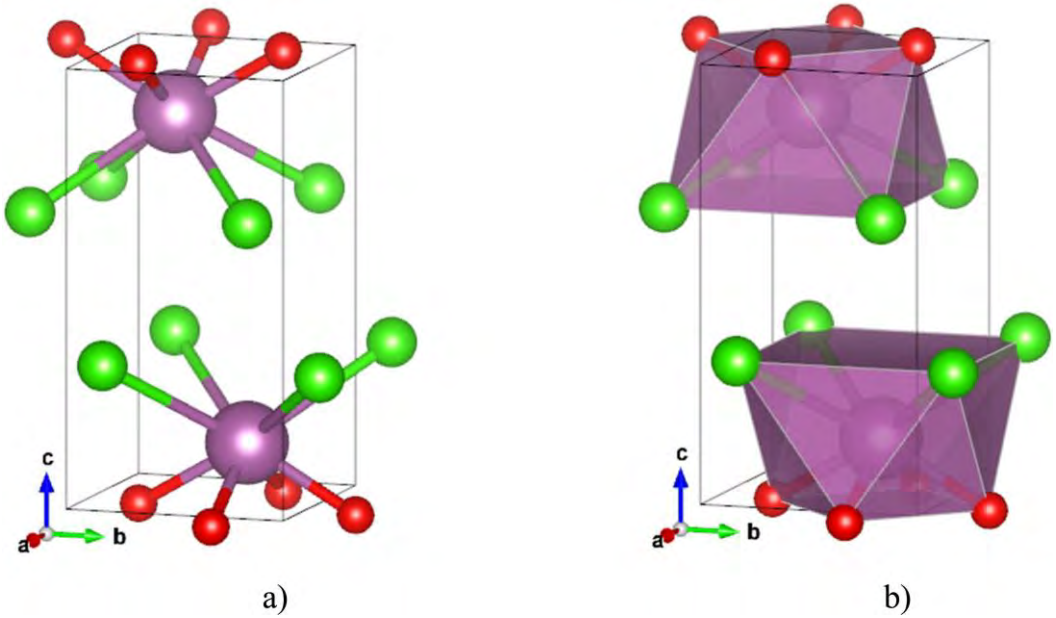



b)

- 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 (Eh).

[1] D. Zagorac, J. Zagorac, M. Fonović, M. Pejić, J. C. Schön, Z. Anorg. Allg. Chem. 2022, 648, e202200198.

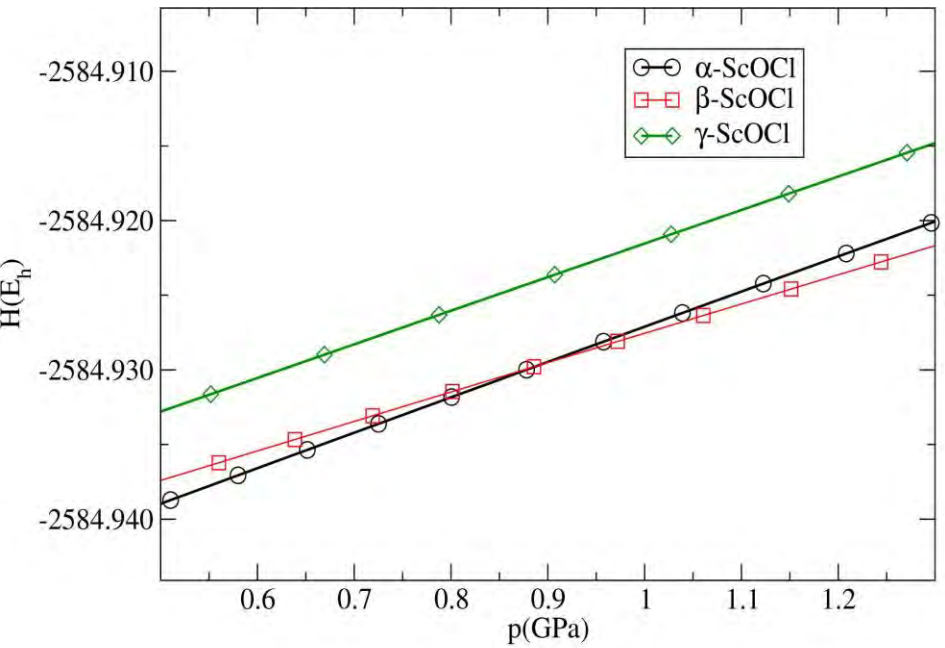
# ScOCl



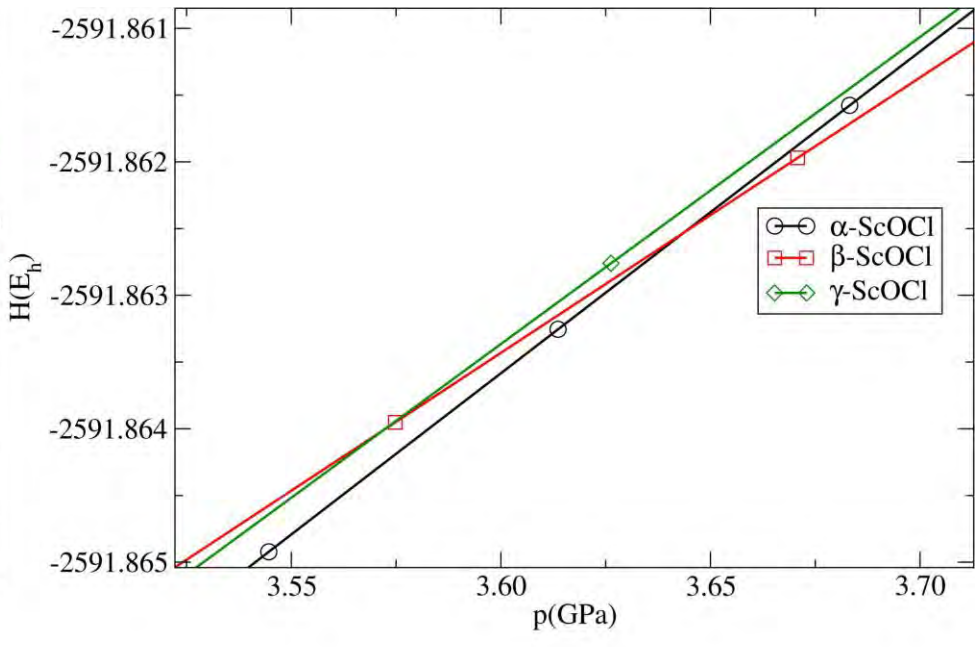

- Visualization of the predicted β-ScOCl high-pressure modification shown with and without polyhedral. The beta phase appears in *P4/nmm* ( no. 129) as high pressure modification.

[1] D. Zagorac, J. Zagorac, M. Fonović, M. Pejić, J. C. Schön, Z. Anorg. Allg. Chem. 2022, 648, e202200198.

# ScOCl




a)

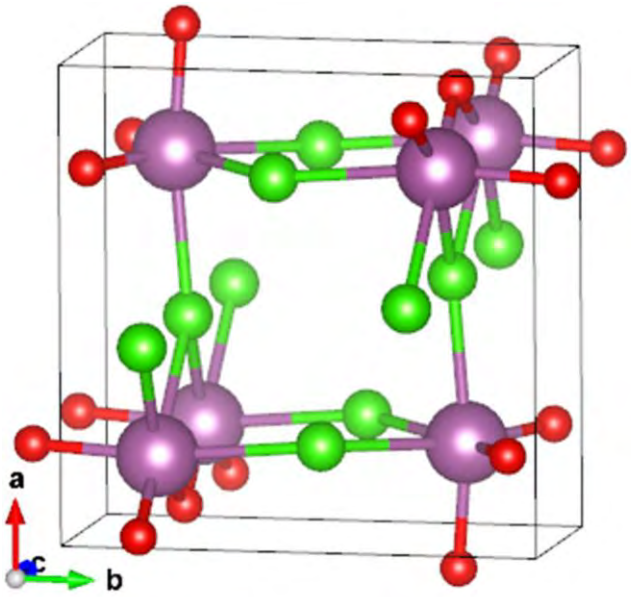



b)

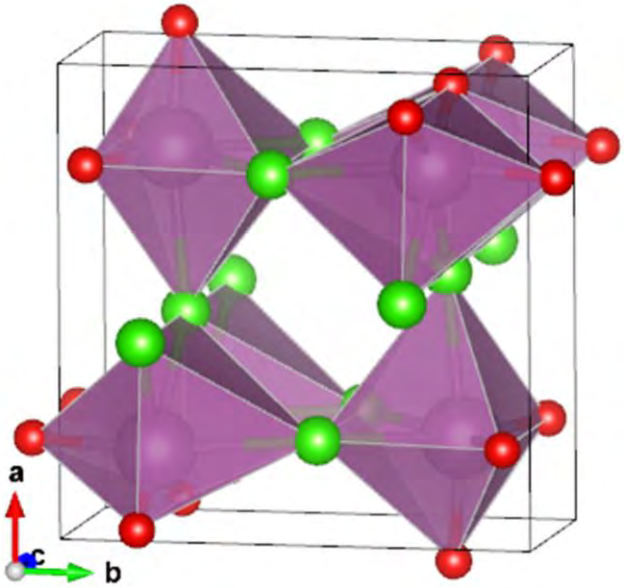
- Calculated H(p) curves for the most relevant predicted structures of ScOCl using the a) LDA and b) PBE0 level of theory. Energies per formula unit are given in Hartree (Eh).

[1] D. Zagorac, J. Zagorac, M. Fonović, M. Pejić, J. C. Schön, Z. Anorg. Allg. Chem. 2022, 648, e202200198.

# ScOCl




a)

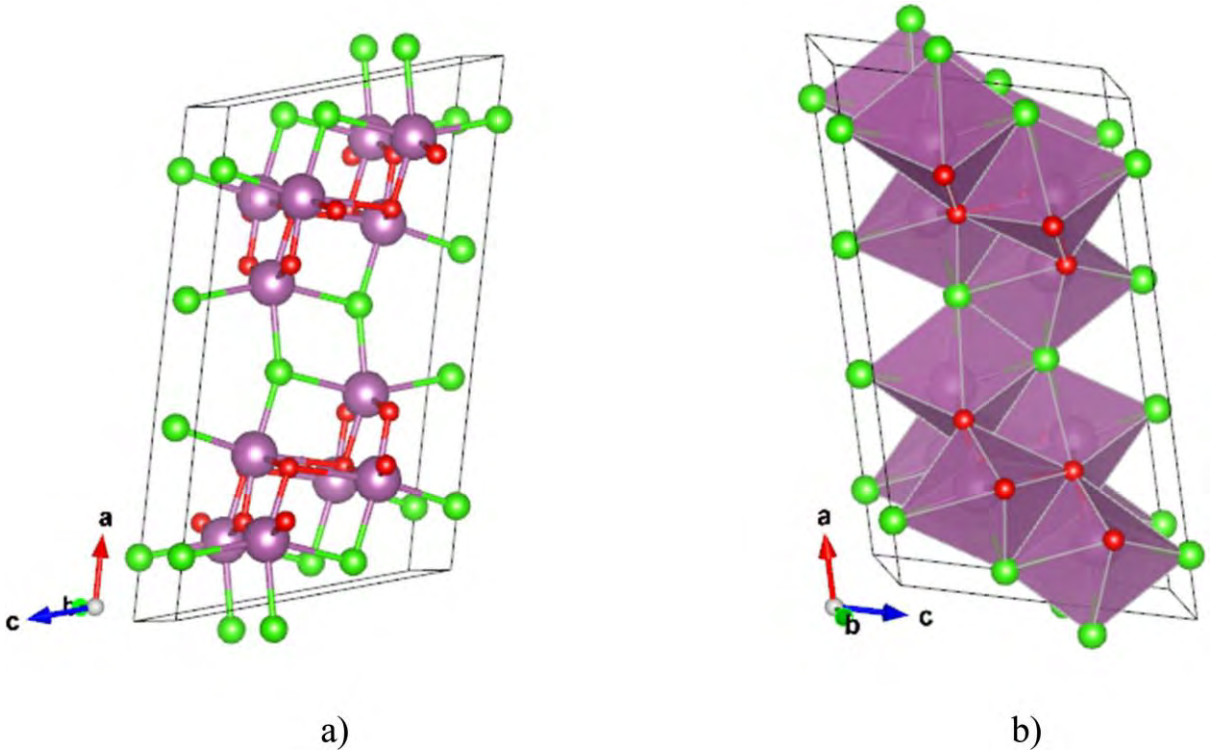



b)

- Visualization of the predicted γ-ScOCl modification shown with and without polyhedral. The gamma phase appears in *P42/m* ( no. 84) as metastable modification.

[1] D. Zagorac, J. Zagorac, M. Fonović, M. Pejić, J. C. Schön, Z. Anorg. Allg. Chem. 2022, 648, e202200198.

# ScOCl

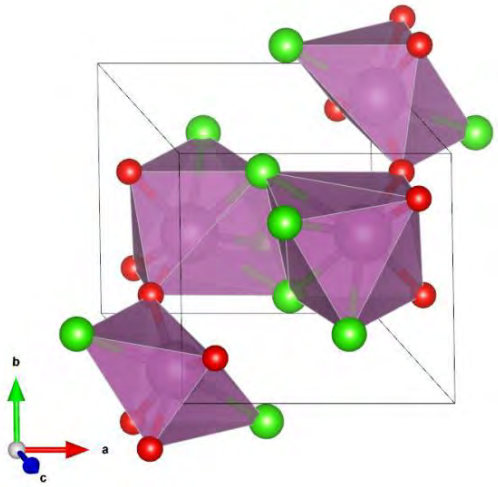


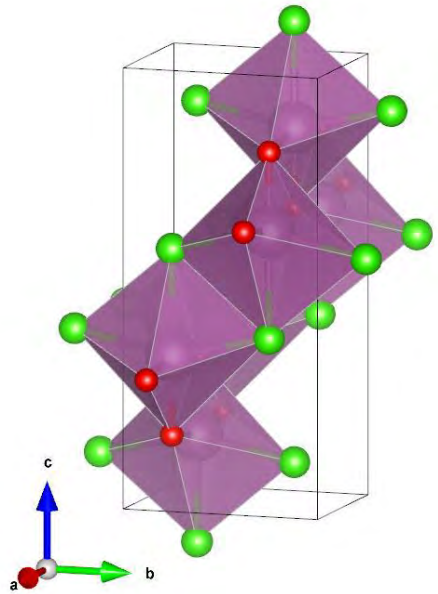

a) b)

- Visualization of the predicted δ-ScOCl modification shown with and without polyhedra. The sigma phase appears in *C2/m* ( no. 12) as HT modification.

[1] D. Zagorac, J. Zagorac, M. Fonović, M. Pejić, J. C. Schön, Z. Anorg. Allg. Chem. 2022, 648, e202200198.

# ScOCl-Extreme




- Visualization of the scandium oxychloride modification ScOCl-et-1 in space group *P-1* (no. 2), and ScOCl-et-2 in space group *Imma* (no. 74), in the extreme conditions. Purple, green and red spheres denote Sc, Cl and O atoms, respectively.

[1] D. Zagorac, M. Fonović, J. Zagorac, M. Pejić, J. C. Schön, Journal of Innovative Materials in Extreme Conditions 2022, 3, 19-29.

# LaFSe

- The ternary lanthanum and lanthanoid fluoride selenides have been investigated for a number of years since they either have technological importance as semiconductors or as host materials for luminescence applications.
- With the availability of computational crystal-structure prediction and theoretical calculations of physical properties, the structural diversity of the La/F/Se system can be explored in search of new compounds or polymorphs with many intriguing physical properties.
- In this study, we have focused on the system LaFSe using global optimization methods and *ab initio* energy minimizations to identify promising (metastable) polymorphs in addition to the two already known modifications combined with experimental methods.

[1] Buyer C, Grossholz H, Wolf S, Zagorac D, Zagorac J, Schön JC, et al. Crystal-Structure Prediction and Experimental Investigation of the Polymorphic Lanthanum Fluoride Selenides LaFSe and La2F4Se. Crystal Growth & Design 2022;22:7133-42.

# LaFSe

- GO: combination of the well-known simulated annealing algorithm with periodic stochastic minimizations, as implemented in the G42+ code
- A fast computable robust empirical two-body potential consisting of Lennard-Jones and exponentially damped Coulomb terms was employed to perform the global searches with a reasonable computational effort
- LO: The *ab initio* calculations were performed using the CRYSTAL17 code based on LCAO.
- DFT: LDA-PZ, GGA-PBE functional
- In addition, the hybrid HSE06 and the B3LYP functionals
- Electronic Band-Structure Calculations

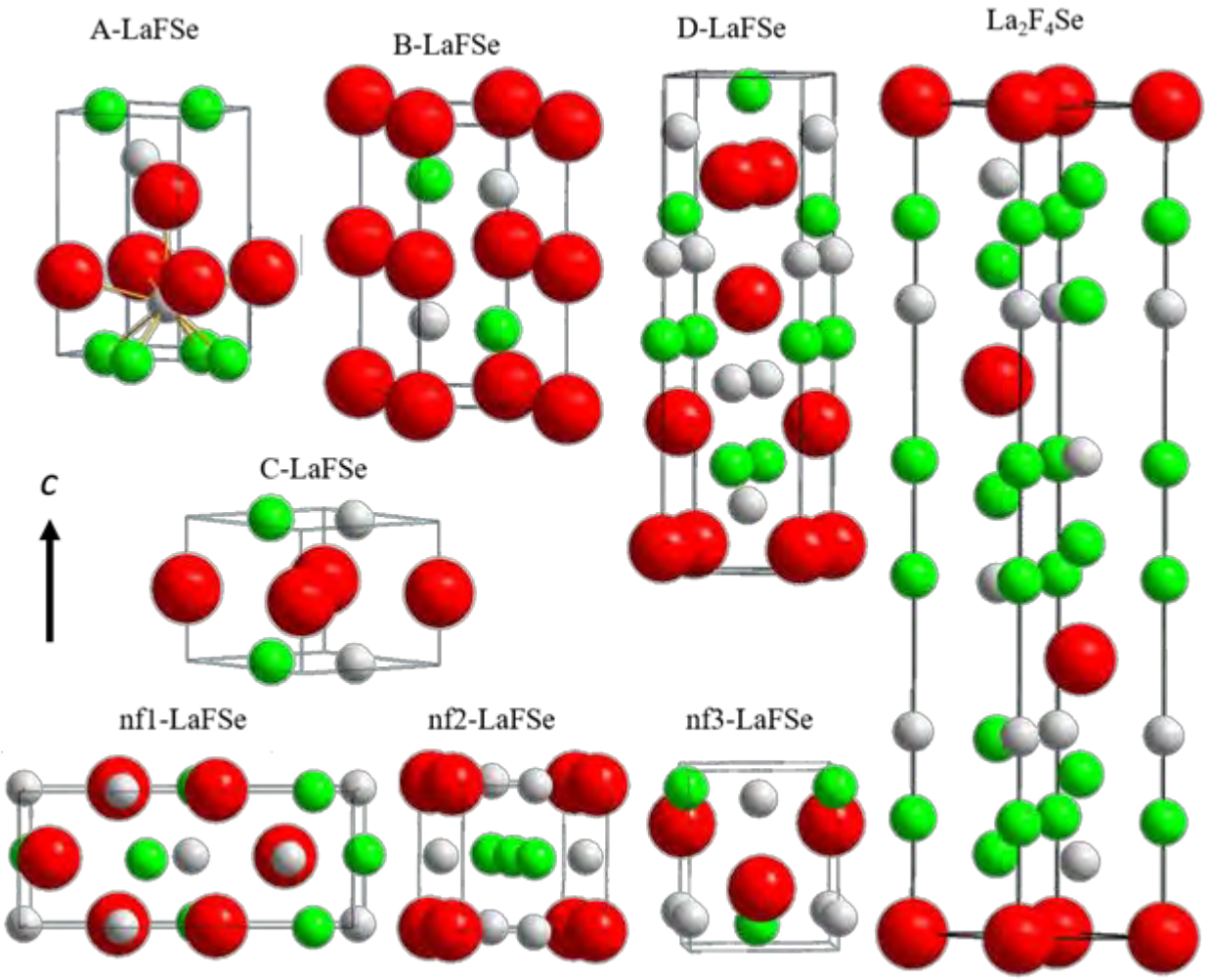
[1] Buyer C, Grossholz H, Wolf S, Zagorac D, Zagorac J, Schön JC, et al. Crystal-Structure Prediction and Experimental Investigation of the Polymorphic Lanthanum Fluoride Selenides LaFSe and La2F4Se. Crystal Growth & Design 2022;22:7133-42.

# LaFSe

- Lanthanum fluoride selenides (A-LaFSe, B-LaFSe and La2F4Se) have been synthesized through high-temperature experiments from an appropriate La/LaF3/Se mixture and characterized using single-crystal as well as powder X-ray diffractometry and UV/Vis diffuse reflectance spectroscopy.
- A-type LaFSe crystallizes in the tetragonal space group *P4/nmm* with a = 413.79(3) pm, c = 715.24(5) pm, and Z = 2 with the PbFCl-type structure;
- B-type LaFSe in the hexagonal space group *P63/mmc* with a = 421.602(2) pm, c = 818.163(7) pm, and Z = 2 with the CeHSe-type structure;
- and La2F4Se in the trigonal space group $R\bar{3}m$ with a = 417.86(2) pm, c = 2326.78(9) pm, and Z = 3 in the Ce2F4Se-type structure, respectively.

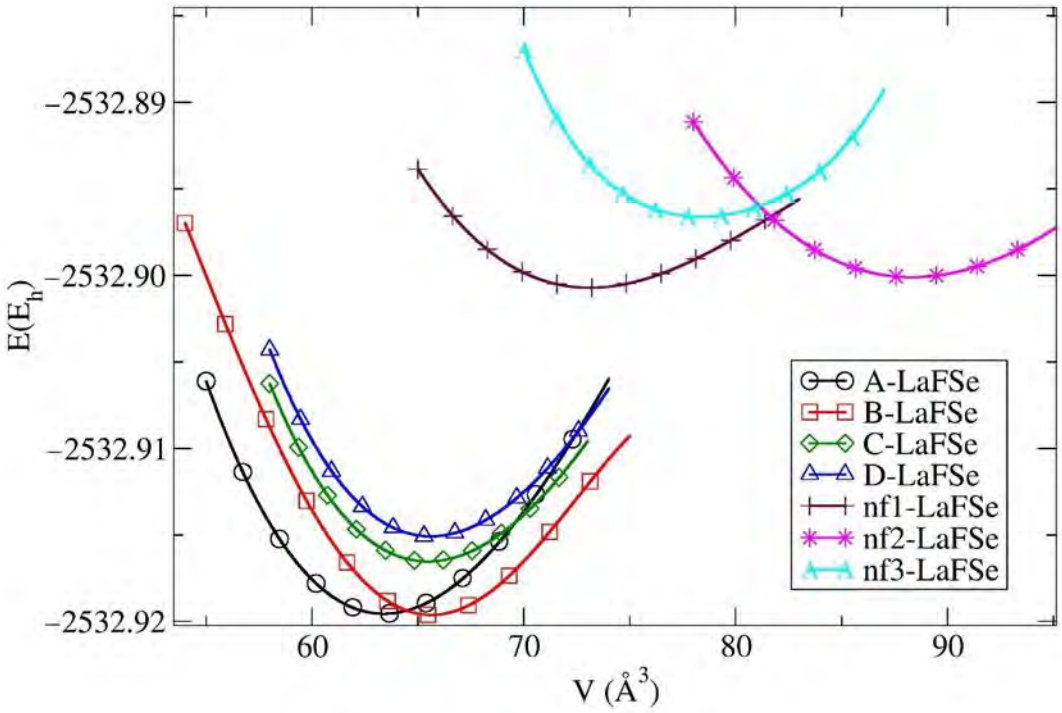
[1] Buyer C, Grossholz H, Wolf S, Zagorac D, Zagorac J, Schön JC, et al. Crystal-Structure Prediction and Experimental Investigation of the Polymorphic Lanthanum Fluoride Selenides LaFSe and La2F4Se. Crystal Growth & Design 2022;22:7133-42.

# LaFSe




[1] Buyer C, Grossholz H, Wolf S, Zagorac D, Zagorac J, Schön JC, et al. Crystal-Structure Prediction and Experimental Investigation of the Polymorphic Lanthanum Fluoride Selenides LaFSe and La2F4Se. Crystal Growth & Design 2022;22:7133-42.

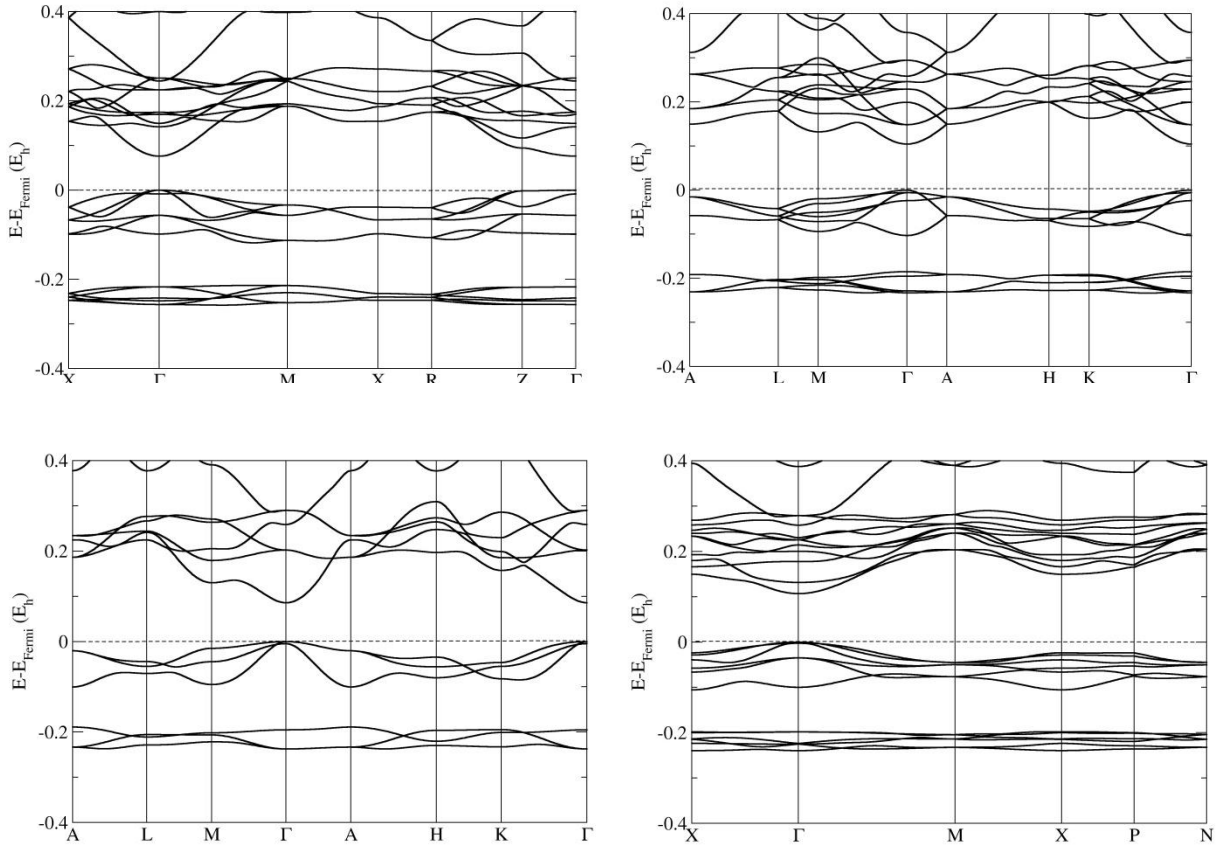
# LaFSe




- Figure. Energy vs. volume curves, E(V), for the most relevant structure candidates computed in the LaFSe system using the GGA-PBE functional. Energies per formula unit are given in Hartree (Eh).

[1] Buyer C, Grossholz H, Wolf S, Zagorac D, Zagorac J, Schön JC, et al. Crystal-Structure Prediction and Experimental Investigation of the Polymorphic Lanthanum Fluoride Selenides LaFSe and La2F4Se. Crystal Growth & Design 2022;22:7133-42.

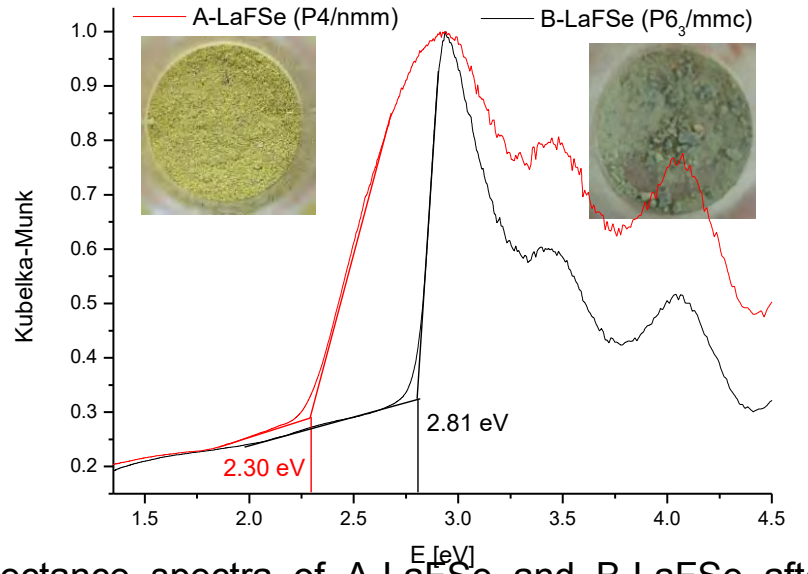
# LaFSe




- Electronic band structures for the A-, B-, C-, and D-LaFSe modifications performed using a hybrid HSE06 functional.

[1] Buyer C, Grossholz H, Wolf S, Zagorac D, Zagorac J, Schön JC, et al. Crystal-Structure Prediction and Experimental Investigation of the Polymorphic Lanthanum Fluoride Selenides LaFSe and La2F4Se. Crystal Growth & Design 2022;22:7133-42.

# LaFSe




- Figure. Diffuse reflectance spectra of A-LaFSe and B-LaFSe after applying a Kubelka-Munk transformation together with the color of the measured samples.

| | A-LaFSe | B-LaFSe | C-LaFSe | D-LaFSe | nf1-LaFSe | nf2-LaFSe | nf3-LaFSe |
|---|---|---|---|---|---|---|---|
| Exp. (UV/Vis) | 2.30 | 2.81 | n/a | n/a | n/a | n/a | n/a |
| LDA-PZ | 1.13 | 1.69 | 1.31 | 1.77 | 2.19 | 1.78 | 3.03 |
| Theo. (LDA)[71] | 1.03 | 1.73 | n/a | n/a | n/a | n/a | n/a |
| GGA-PBE | 1.27 | 1.98 | 1.52 | 1.90 | 2.40 | 2.08 | 3.26 |
| HSE06 | 2.07 | 2.84 | 2.33 | 2.80 | 3.25 | 2.94 | 4.22 |
| B3LYP | 2.66 | 3.38 | 2.85 | 3.21 | 3.61 | 3.36 | 4.59 |

[1] Arai, T.; Iimura, S.; Hosono, H. Doping Induced Polymorph and Carrier Polarity Changes in LaSeF. Chem. Mater. 2018, 30, 597

# Conclusion

- *Rare-earth ternary compounds and especially scandium oxychloride (ScOCl) and Lanthanum fluoride selenide (LaFSe) have recently become of interest as an advanced material with various possible applications e.g. in solid oxide fuel cells, photocatalysis, and electronic devices, as are oxyhalides of various transition metals.*
- *In the case of ScOCl, a multi-methodological approach has been used for structure prediction and energy landscape exploration, while final structure optimization has been accomplished 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.*

# Conclusion

- *A successful synthesis of these novel ScOCl modifications would have the potential for extending the scientific, technological and industrial applications of ScOCl.*
- *Finally, the energy landscape of LaFSe has been investigated using global optimization and synthesized through high-temperature experiments and characterized using single-crystal as well as powder X-ray diffractometry and UV/Vis diffuse reflectance spectroscopy.*
- *All were calculated using four different functionals (LDA−PZ, GGA−PBE, B3LYP, and HSE06)*
- *The results of the calculations concur with the experimentally observed structures and predict additional, so far unknown LaFSe polymorphs, showing great promise for tuning the band gap for semiconductor applications.*

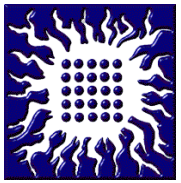
# Thanks to:

Ass. Prof. Dr. J. Zagorac,
Prof. Dr. J.C. Schön,
Prof. Dr. T. Schleid,
Doc. Dr. Sc. M. Fonović,
C. Buyer
M. Pejić,
T. Škundrić,
D. Jovanović,

and my friends and colleagues from experimental group.

University of Belgrade, Belgrade, Serbia

Serbian Ministry of Education, Science and Technological Development, Serbia



Vinča Institute of Nuclear Sciences, Belgrade, Serbia


Center of Excellence “CextremeLab”, Belgrade, Serbia

Laboratory for Theoretical Investigations of Materials (L-TIM)

And thank to you all!

# Thank you for your attention☺


**65th Birthday of Prof. Dr. J. Christian Schön –** Invitation to contribute to a **Special Issue of Journal of Innovative Materials in Extreme Conditions (*abbr. JIMEC*)**

-We kindly ask you to indicate your participation by **July 1st, 2023**
-Please submit your contribution by October 1st, 2023.
-It is my pleasure to announce that the Guest Editors for this special issue are: **Prof. Dr. Peter Salamon**, San Diego State University, USA, **Prof. Dr. David Wales**, University of Cambridge, UK, and **Prof. Dr. Karl Heinz Hoffmann**, TU Chemnitz, Germany.

*Open for submission, Volume 4, special issues planned to have it published in December 2023.*

Notice: JIMEC is an open access journal which means that all content is **freely available** without charge and there are **no article processing charges**. .

More information at: http://jimec.edu.rs/