

## Toward the development of the strongest solid lewis acid

### Anion Substitution in $\beta$ -AlF<sub>3</sub>

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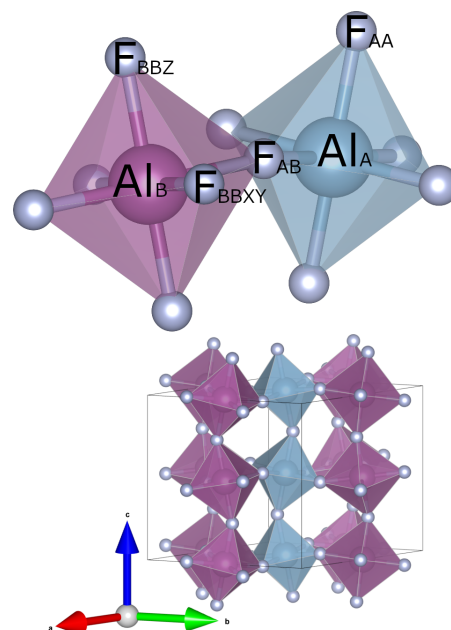
#### In Short

- Fluorine interactions
- Teflate chemistry
- Solid Lewis Super Acids
- Periodic DFT

AlF<sub>3</sub> ranks among the strongest solid Lewis acids available and performs well as catalyst for different organic reactions, especially those including a C-H activation step.[1] Its Lewis acidity is drastically raised if the surface and accessibility of the containing AlF<sub>6</sub>-octahedra is increased.[2] So called high-surface  $\beta$ -AlF<sub>3</sub> shows a higher Lewis-acidity than the widely used SbF<sub>5</sub>. The Lewis acidity can be increased even further if defects are incorporated in the AlF<sub>3</sub> structure that contain chloride (creating *Aluminum Chlorofluoride*, or short *ACF*), teflate anions or a mixture of both.[3] The structures of the resulting products are solid, but amorphous however, and mostly experimental data is available about this topic. We aim to model different possible unit cells of the  $\beta$ -phase of AlF<sub>3</sub> containing such defects and substituted groups to gain an insight in how different conformations of the amorphous structure could look like and how the very high Lewis acidity actually is created.

### Preliminary work

While the main structural motive in all phases of solid AlF<sub>3</sub> is the AlF<sub>6</sub>-octahedron (see Figure 1), the catalytically active sites are found in surface defects that contain aluminum cations with a coordination number below 6, so called *undercoordinated* Al-sites. It could also be shown that significant catalytic activity is only found in amorphous solids of these materials. To model this amorphicity, we will use in this proposal large supercells of  $\beta$ -AlF<sub>3</sub>, which is a metastable and less dense polymorph of AlF<sub>3</sub>. Our research aims to model super cells in which different anions are removed and replaced within the  $\beta$ -AlF<sub>3</sub> structure (replaced anions: Al<sub>n</sub>F<sub>3n+1</sub><sup>-</sup>, n = 0,1,2,3; inserted anions: Cl<sup>-</sup> for n = 0,1 and TeF<sub>5</sub>O<sup>-</sup> for n = 2,3) to simulate some of the interconverting conformations



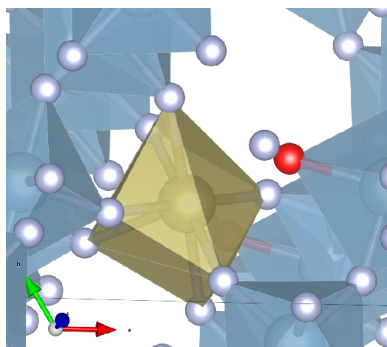
**Figure 1:** Calculated structure of  $\beta$ -AlF<sub>3</sub>. Top: symmetry-inequivalent aluminum centers with inequivalent fluorides. Bottom: Unit cell after full geometric optimization (space group 63, Cmcm). Aluminum centers B in purple, aluminum centers A in grey.

that represent the amorphicity with a high number of undercoordinated Al-sites.

From this main structure, a systematic approach can be derived to substitute anions. First, one single fluoride can be replaced with a single chloride (*monosubstitution*). Another approach has been carried out where a larger anion (AlF<sub>4</sub><sup>-</sup>) was cut out to leave more space for the larger Cl<sup>-</sup> compared to the F<sup>-</sup>. A similar workflow has been conducted for substitution with a teflate (TeF<sub>5</sub>O<sup>-</sup>) anion. The teflate mimics the electronic properties of a single fluoride, but with higher sterical demand, and are of particular interest since AlF<sub>3</sub> shows an even higher Lewis acidity than HS-AlF<sub>3</sub> or ACF if doped with low amounts of the teflate ion. However, due to the larger ionic radius, a bigger cavity has been cut out by removing an Al<sub>2</sub>F<sub>7</sub><sup>-</sup>-unit.

The results show that the teflate can react in different manners. For some of the modeled structures, the teflate occupies the cavity. The Te-O bond remains stable, however weakened, as the oxygen and at least one of the teflate-fluorides form bonds to surrounding, undercoordinated Al-cations. In another structure with different alignment of the inserted teflate group, the oxygen migrates away from the tellurium toward an adjacent aluminum, while the teflate replaces the oxygen with two

fluorides, creating a structure in which the tellurium has a coordination number of 7. This has been previously described by Seppelt in 1998, who stated that tellurium originating from teflates can adopt coordination numbers higher than 6 in fluoride-rich environments[4].



**Figure 2:** 3D-Visualization for substitution of  $Al_2F_7^-$ -unit with teflate. Close up after inserting teflate along Z-Axis of the unit cell (after md and optimization). The oxygen of the teflate has been exchanged with two fluorides from the environment.

## Project objectives

The presented preliminary studies give already various possible structural motives which can occur within a small energy range and can lead to the amorphicity of the material. Although periodic DFT calculations might not be an optimal way to represent or investigate an amorphous solid at first glance, the different structures, their energies and unit-cell data indicate a promising way to investigate the actual chemical equilibrium reaction happening inside the solid as well as the catalytic activity. The different, optimized unit cells can be interpreted as momentary snapshots of a dynamic compound with comparable energies. Analyzing bond distances and coordination number of inserted anions/metal centers during the MD and Bader charges of all different unit cells provides the possibility to gain averaged data that can be compared to experimental results.

The reaction behavior of the solid toward an anion substitution will be investigated depending on different parameters: first, the inserted anion, second, the shape of the cut out cavity by modeling a wide range of possible, inequivalent structures, and in the case of substituting with the teflate, also third, by the different orientations of the inserted teflate anion.

## Method

All calculations will be run with the *Vienna Ab Initio Software Package (VASP)*. We will use periodic DFT with the GGA-PBE exchange correlation functional. The DFT-D3 method developed with Becke-Johnson damping has been chosen for van der Waals-dispersion energy correction. The modeled supercells will be fully optimized to conduct ab-initio MD with Nosé-Hoover thermostat at 700 K. Preliminary calculations for ab-initio molecular dynamic simulations have shown that we need around 500 fs for equilibrating the system to the given temperature.

## More Information

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## Funding

DFG Sonderforschungsbereich (SFB) 1349

## DFG Subject Area

327-01