# Experimental report

08/07/2022

|  |  |  |  |
|---|---|---|---|
| **Proposal:** | **EASY-907** | **Council:** | 10/2020 |

**Title:** Variable-temperature neutron diffraction on fluoride-ion conductors (Ba0.5Sr0.5SnF4)

**Research area:** Materials

**This proposal is a new proposal**

**Main proposer:** **Briseis MERCADIER**

**Experimental team:**

**Local contacts:** Emmanuelle SUARD

**Samples:** Ba0.5Sr0.5SnF4 tetragonal

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D2B | 12 | 12 | 30/06/2021 | 01/07/2021 |

## Abstract:

The development of all-solid-state fluoride ion batteries is limited by the lack of knowledge on fluoride ionic transport, primarily caused by the difficulty in describing the atomic structure at different length scales. We are currently investigating the structural features of the prototype BaSnF4 F-ion conductor by combining a large set of experimental data with computational methods. BaSnF4 crystallizes in two different polymorphs, namely the disordered (cubic, space group Fm-3m) and ordered (tetragonal, P4/nmm) structure. Both polymorphs can be obtained with 50% of the barium replaced by strontium (Ba0.5Sr0.5SnF4). The population of F-ions in interstitial sites, thought to be involved in the ionic conduction, is not visible using conventional means but could be seen if neutrons are used. Hence, we wish to measure on D2B the newly obtained tetragonal form of Ba0.5Sr0.5SnF4, at 298 K and at low-temperature (100 K). We expect to see an interstitial site for F-ions already demonstrated in isostructural PbSnF4, and compare results with the pure BaSnF4 tetragonal phase. High resolution data could help solve the structure and assign the different environments observed by 19F NMR.

# Experimental report: EASY-904 and EASY-907

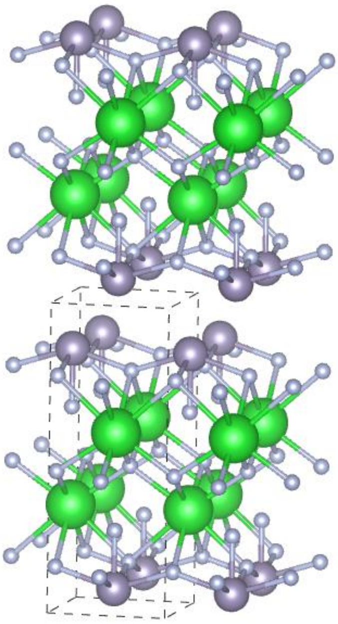
## I. Context

The most widespread electrochemical storage devices are lithium-ion batteries (LIB), in which lithium ions are used as charge carriers. Though these devices are well-developed, they rely heavily on the use of a resource with limited availability. It is therefore necessary to implement other complementary storage solutions.

On the other end of the electrochemical potential scale (+3.05 V vs SHE), fluoride ion appears to be an attractive option. Fluoride is the 13th most abundant element on earth,[2] and as a mobile anion with a single negative charge, it can be easily utilized in multi-electron redox reactions at the electrodes, yielding batteries with high theoretical energy densities. [3–5]

Most fluoride-ion batteries (FIB) are secondary, all-solid-state batteries (ASSB). Where, both electrodes and the electrolyte are solids. Electrolytes are selected based on several criteria. The most important ones are the ionic conductivity, electrochemical stability, and the absence of electronic conductivity.

The material possessing the highest F-ion conductivity is $PbSnF_4$, with a room-temperature (RT) conductivity above $10^{-3}$ S.cm$^{-1}$. $PbSnF_4$ structure is visualised on the right. $PbSnF_4$ ionic mobility has been studied, and linked to the presence of interstitial F-ions in the Sn-Sn interlayer.



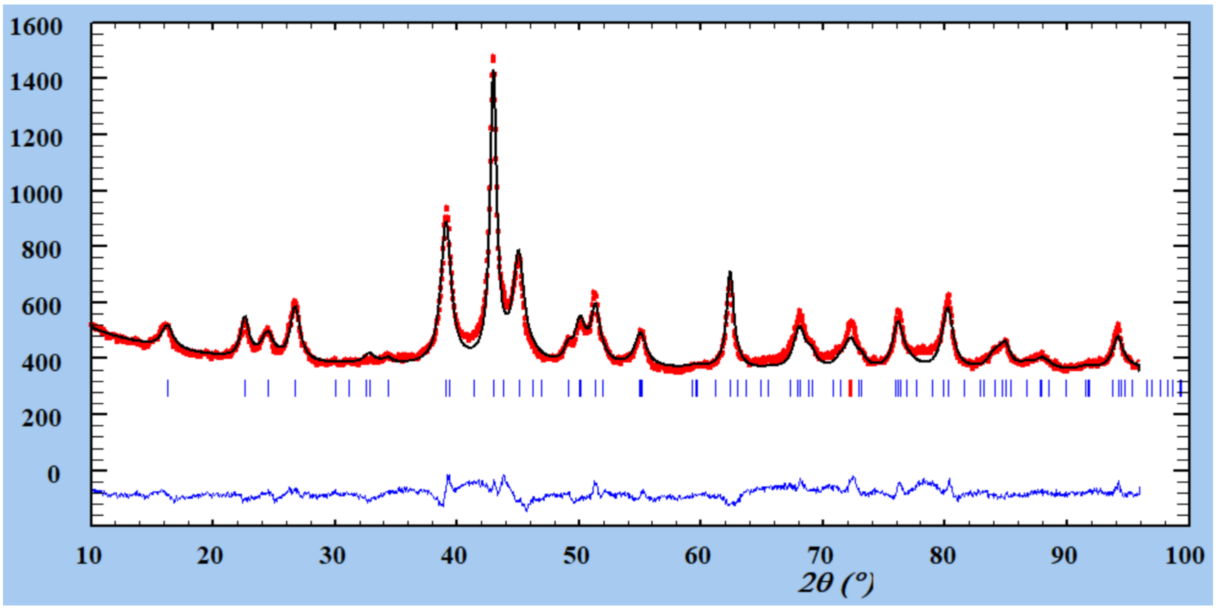
$PbSnF_4$ has several isomorphs, namely $BaSnF_4$ and $SrSnF_4$, as well as a solid solution, $Ba_{1-x}Sr_xSnF_4$. These isomorphs have not yet been studied as closely, and it is unknown whether the mechanism behind F-ion mobility is the same in all isomorphs or not. In order to verify that, two samples were sent for neutron measurement, which allows for better F-ion visualisation compared to regular X-ray diffraction, and should help characterizing the presence of possible interstitial anions. The samples were also measured both at room temperature and at 100 K, as a way to confirm the presence or absence of mobile interstitials.

## II. Experiments

The materials were synthetized and their purity was verified by regular XRD as well as Mössbauer spectroscopy.

The measured neutron diagrams were fitted first by full pattern matching, followed by a rietveld refinement, as implemented in the Fullprof software. To modelise the peaks, the Thompson-Cox Hastings function was used, as it takes microstructure into account. Gaussian and Lorentzian parameters accounting for paletet-shaped particles (size-model = 1) were refined, as these materials have 2D structure, leading to sheet-like particle growth (verified via SEM).

An example of such fit is presented below (Bragg R-factor: 8.87).



It was also attempted to fit the collected data with an added F-ion interstitial site. However, the fit did not improve after adding this interstitial, and the occupation of the site was negative, suggesting that it is not present in the structure.

The results of the measurements at 100 K were very similar, with seemingly no interstitial ions in the Sn-Sn layer.

It is however interesting to follow the trends of the cell parameters with temperature variations:

| Sample | a (Å) | c (Å) | c/a |
|---|---|---|---|
| $Ba_{1-x}Sr_xSnF_4$ | 4.2689 (4) | 11.4099 (18) | 2.673 |
| $Ba_{1-x}Sr_xSnF_4$ (100 K) | 4.2487 (4) | 11.382 (2) | 2.679 |
| $BaSnF_4$ | 4.3523 (4) | 11.281 (3) | 2.592 |
| $BaSnF_4$ (100 K) | 4.3333 (6) | 11.309 (6) | 2.910 |

The lowering of temperature is accompanied by a contraction along the a and b axis but an expansion along the c axis. However, the distances between 2 tin atoms stay the same (determined by Rietveld refinement). It suggests that this distance is the defining factor of the structure, and therefore is one parameter shrinks, as is expected when lowering the temperature, the other direction must expand to maintain it.

## Conclusions

The experiments did not provide definite proof on the presence or absence of the interstitial F-ions.

However, it allowed us to gain further insight of the material’s behaviour with varying temperature, highlighting the structural importance of the Sn-Sn distance. It also showed the absence of a phase transition at low-temperature. Further study via other means