Experimental report

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Proposal:	**5-14-261**	**Council:**	10/2016
Title:	Pathways of Cation and Anion Diffusion in BaLiF3 Single Crystals		
Research area:	Chemistry		

This proposal is a new proposal

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Samples: BaLiF3

Instrument	Requested days	Allocated days	From	To
D9	8	5	20/01/2017	25/01/2017

Abstract:

We intend to determine the nature of ionic conductivity and the pathways of thermally induced diffusion in the inverse cubic perovskite BaLiF3. To this end, single-crystal neutron diffractometry at high temperature followed by careful analysis of the Debye-Waller factors including anharmonic contributions is necessary. Reconstruction of the scattering-length density using the maximum-entropy method (MEM) and derivation of probability-density functions (PDFs) allows mapping of the actual ion pathways. The associated effective one-particle potentials (OPPs) give access to the energy barriers for migration. Comparing these results to powder neutron diffraction, high-temperature NMR investigations (Prof. Wilken-ing, Graz), and quantum-chemical computations (Prof. Bredow, Bonn), we hope to acquire a fundamental understanding of mobility in potential two-ion conductors and lay a foundation for further experiments with mixed anion sets.

Experimental Report

Pathways of Cation and Anion Diffusion in $BaLiF_3$ Single Crystals

Fluoride perovskites have stirred considerable interest because of their possible application in semiconductors, lithography, optoelectronics, and chemosensorics. Using neutron diffractometry at elevated temperatures, we try to map diffusion pathways of the mobile species in single crystals of the inverse cubic perovskite $\mathrm{BaLiF_3}$ (see Fig. 1). Additionally, we aim to investigate a possible interplay of the two mobile species present, $\mathrm{Li^+}$ and $\mathrm{F^-}$. Careful evaluation of Debye–Waller factors (DWFs) including anharmonic contributions should allow for the modelling of probability-density functions (PDFs) and one-particle potentials (OPPs)—if ion mobility is high enough.

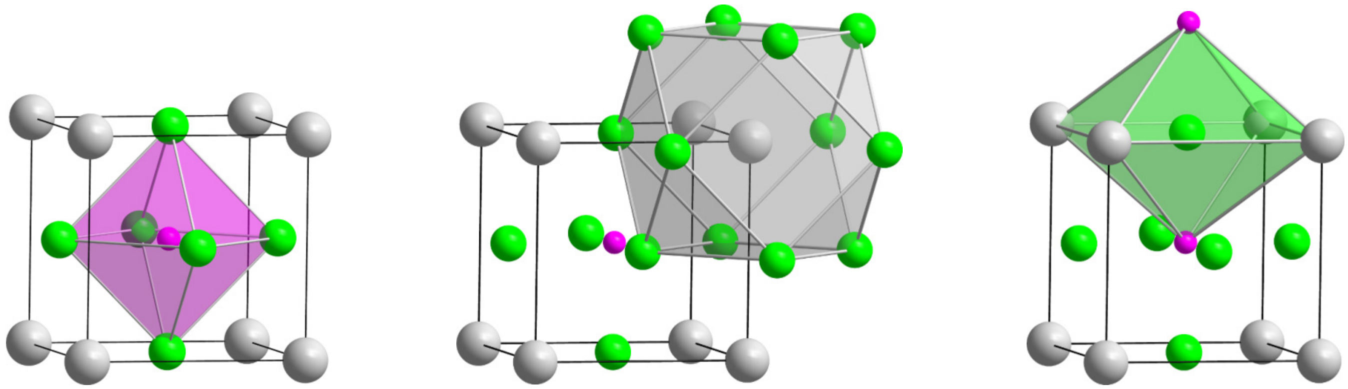

Fig. 1. Coordination polyhedra around lithium (left), barium (center), and fluoride ion (right) in the inverse cubic perovskite $\mathrm{BaLiF_3}$ (gray: $\mathrm{Ba^{2+}}$, pink: $\mathrm{Li^+}$, green: $\mathrm{F^-}$; ions with arbitrary radii, unit cell in black).

Diffraction data of a high-quality {100}-cut crystal measuring 0.5 × 0.5 × 0.5 $\mathrm{mm^3}$ were acquired at room temperature (r.t.), 400, 550, and 640 °C. (Unfortunately, the target temperature of 700 °C could not be stabilized because of the oven malfunctioning.) After verification of mergeability of some representative low-angle reflections, a data set with a redundancy of *ca.* 4.2–4.4 (286–364 reflections) was collected at each temperature. Absorption was corrected for using Gaussian integration over a grid of 32 × 32 × 32 voxels. Structures were solved with Superflip[1] using a charge-flipping algorithm and refined with Jana2006[2] against F_o^2 data—merged and weighted *via* the instability factor—using the full-matrix least-squares algorithm. Extinction was corrected for during refinement using the Shelxl model.[3]

At first, all atoms were refined anisotropically when a significant lack of scattering-length density at the fluoride position relative to the cation positions became obvious. For the refinement against r.t. data, the quality increased dramatically from $S = 2.21$, $R_1 = 0.0236$, $wR_2 = 0.0894$ to $S = 1.18$, $R_1 = 0.0146$, $wR_2 = 0.0470$ when substitution of fluoride against oxide ions according to the following defect equation was permitted (constrained for electroneutrality):[4]

$$2\ \mathrm{F_F^{\times}} + \mathrm{H_2O} = \mathrm{O_F'} + V_\mathrm{F}^{\bullet} + 2\ \mathrm{HF}$$

The same holds for the higher temperatures. All refinements led to compositions $\mathrm{BaLi(F_{3-\mathit{x}}O_{\mathit{x}}\square_{\mathit{x}})}$ with $x \leq 0.1$ (slightly decreasing with temperature). As the composition should be temperature-invariant, it was fixed at $\mathrm{BaLiF_{2.810}O_{0.095}}$, the average of the refined values.

As is expected, all displacement parameters increase with rising temperature. This effect is slightly more pronounced for the anions (see Fig. 2). For the displacement parameters, anharmonic terms of the fourth (D_{ijkl}) and sixth order (F_{ijklmn}) were tested. For reasons of site symmetry, the parameters of the third and fifth order have to be zero and only four D_{ijkl} and six F_{ijklmn} are allowed. Insignificant contributions ($< 3\sigma$) were set to zero and excluded from refinement. Interestingly, lithium ions show no anharmonicity at all, implying that they are immobile in the studied temperature range. The fluoride ions exhibit small anharmonic effects that manifest in a single significant D_{ijkl} or F_{ijklmn} at 400 °C and above.

Fig. 2. Structure of $BaLiF_{3-x}O_x$ at r.t. (left) and 640 °C (right). Ellipsoids for 90% probability (for color key, *cf.* Fig. 1).

Overlays of structure pictures and PDF maps show that the anion probability-density distribution is flattened within the barium–anion planes and constitutes lobes, which stretch roughly towards adjacent anion positions and become visible at lower density values (see Fig. 3). This merely hints at a pathway avoiding the vicinity of cation positions, while the anharmonicity of displacement is so small that an analysis of the OPP yields activation barriers for anion migration above 2 eV. These are at odds with literature values of 0.7–0.9 eV from NMR and conductivity studies,[5] which means that, in the single crystal and at the temperatures monitored, migration is not abundant enough to trace diffusion pathways and establish activation barriers *via* the PDF/OPP formalism.

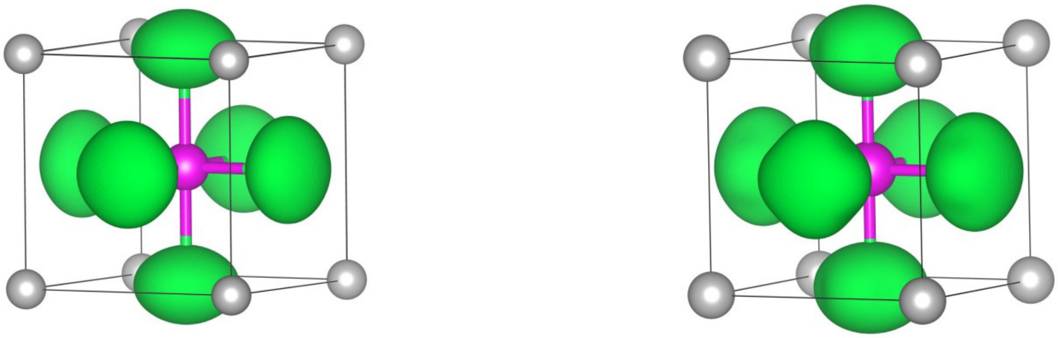

Fig. 3. Detail of the structure of $BaLiF_{3-x}O_x$ at 400 °C (left) and 640 °C (right) with isosurface plot of anion PDF. Ellipsoids of 90% probability; PDF isovalue: 10^{-4} Å^{-3} (for color key, *cf.* Fig. 1).

However, the experiments have yielded high-quality structure models at elevated temperatures. Because of the model's accuracy and reliability, they are ideal starting points for modern topological methods: we used procrystal-void analysis,[6] VORONOI–DIRICHLET partitioning,[7] and natural-tiling analysis[8] to find the most probable ion diffusion pathways. Results show that Li^+ is part of the immobile framework as it lacks viable pathways between crystallographic positions. The anions, on the other hand, are mobile along bent pathways between adjacent positions. Analyses of bond-valence energy landscapes (BVEL)[9] suggest an associated energy barrier of *ca.* 0.6 eV.

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