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Supporting information for article:

The Inverse Perovskite BaLiF3: Single-Crystal Neutron Diffraction and Analyses of Potential Ion Pathways

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S1. X-ray diffraction

Data were collected using a "Bruker D8 VENTURE" diffractometer equipped with a goniometer in κ geometry, a "Bruker PHOTON II CPAD" detector, and a graphite-monochromated "Bruker IμS 3.0" Mo-K_α source ($\lambda = 0.71075$ Å). An analytical absorption correction using a multifaceted crystal model was performed using *SADABS* 2014/5 (Bruker, 2001). The structure was solved with *SUPERFLIP* (Palatinus & Chapuis, 2007) using a charge-flipping algorithm and refined with *JANA2006* (Petříček *et al.*, 2014) against F_o^2 data using the full-matrix Levenberg–Marquardt algorithm. A parameter to account for extinction of type I (isotropic, Lorentzian distribution) according to Becker and Coppens (1974) was employed. All ions were refined using ionic form factors with fixed occupations and anisotropic displacement parameters if symmetry permitted.

Further details of the crystal structure investigation may be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808-666; e-mail: crysdata@fiz-karlsruhe.de, on quoting the deposition number CSD-434518.

Table S1   Summary of X-ray diffraction at room temperature.

Crystal data	
Chemical formula	$BaLiF_{2.8}O_{0.1}$
M_r	199.1
Crystal system, space group	Cubic, $Pm\bar{3}m$
Temperature (K)	279 (2)
a (Å)	3.9970 (8)
V (Å^3)	63.86 (4)
Z	1
$F(000)$	85
Radiation type	Mo $K\alpha$
μ (mm^{-1})	15.35
Crystal size (mm)	$0.33 \times 0.21 \times 0.10$
Data collection	

Diffractometer	Bruker D8 VENTURE
Absorption correction	Numerical *SADABS* 2014/5 (Bruker, 2001)
T_{min}, T_{max}	0.020, 0.089
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2602, 34, 34
R_{int}	0.057
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.708
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.010, 0.023, 1.09
No. of reflections	34
No. of parameters	6
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.73, −0.50
Extinction coefficient	5300 (500)

Weighting scheme based on measured s.u.'s $w = 1/[\sigma^2(I) + (0.02044I)^2]$. Computer programs: Bruker *APEX2* (Bruker, 2012a), Bruker *SAINT* (Bruker, 2012b), *SUPERFLIP* (Palatinus & Chapuis, 2007), *JANA2006* (Petříček *et al.*, 2014), *VESTA* (Momma & Izumi, 2011).
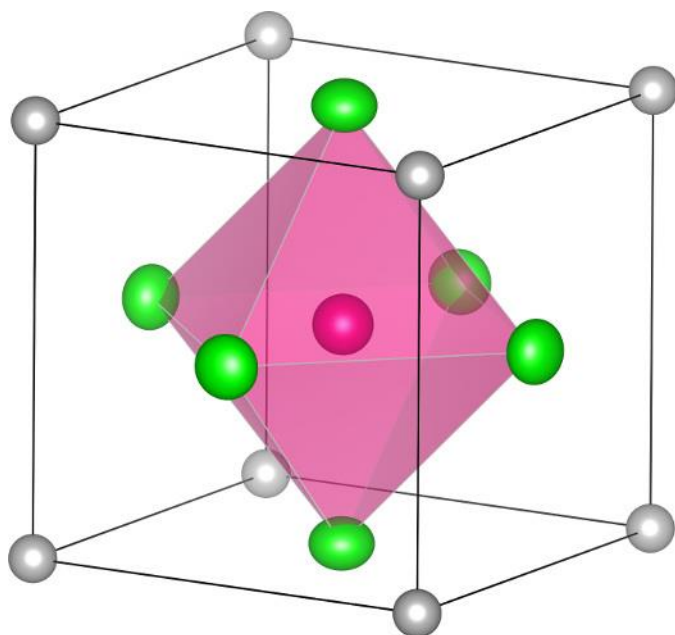
Figure S1 Crystal structure according to X-ray diffraction (grey: barium, pink: lithium, green: fluoride/oxide ions; ellipsoids of 90% probability; unit cell in black).

S2. Composition and anion content

To check the fit of measured and refined fluoride contents, test refinements of the occupancies were performed at every temperature point. Within an anisotropic-harmonic model of atomic displacement, the oxide and fluoride occupancies were constrained to yield compositions $BaLiF_{3-2x}O_x$. The results (see Table S2) were equal to the value from elemental analysis within no more than two s.u. so that the occupancy was finally fixed at the latter value.

Table S2 Refined fluoride occupancies and resulting compositions at different temperatures.

$\vartheta/°C$	$a[F1]$[a]	Composition
26.8	0.0581(3)	$BaLiF_{2.787(14)}O_{0.107(14)}$
412	0.0582(3)	$BaLiF_{2.795(17)}O_{0.103(17)}$
555	0.0591(5)	$BaLiF_{2.84(2)}O_{0.08(2)}$
636.2	0.0591(4)	$BaLiF_{2.83(2)}O_{0.08(2)}$
Average	0.0586(6)[b]	$BaLiF_{2.81(3)}O_{0.09(3)}$

[a] Occupancy of the fluoride ion with s.u. according to refinement. [b] Average over all temperatures with s.u. according to averaging statistics.

S3. MEM-reconstruction of SLD

Table S3   Relative weights λ_n for the generalised constraints of higher order n and unweighted/weighted final residuals R_F/wR_F for the data sets recorded at different temperatures.

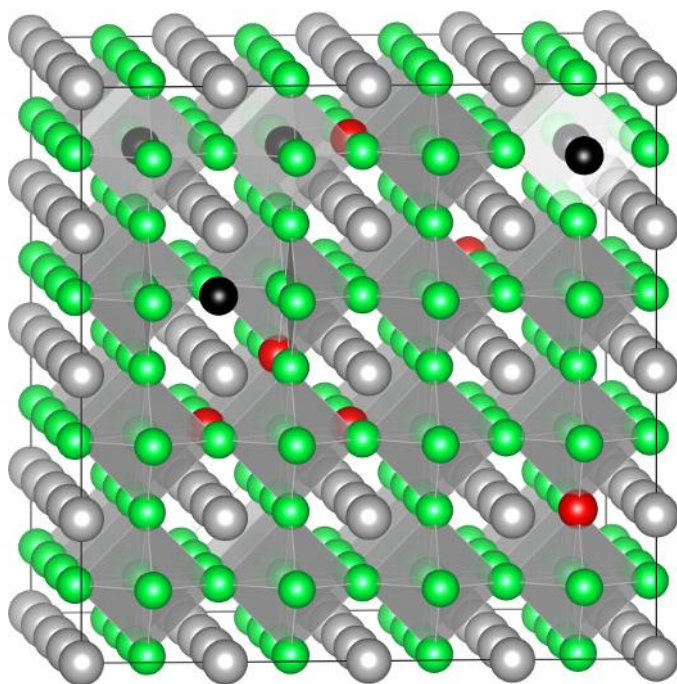| $\vartheta/°C$	λ_2	λ_4	λ_6	R_F	wR_F
26.8	0.75	0.25	0	0.0261	0.0268
412	0.5	0.5	0	0.0335	0.0319
555	0.4	0.4	0.2	0.0401	0.0374
636.2	0.3	0.3	0.4	0.0345	0.0324

S4. BVEL calculations

Figure S2 Representation of the ordered $4 \times 4 \times 4$ supercell for the evaluation of the BVEL (grey: barium, pink: lithium, green: fluoride, red: oxide ions, black: anion vacancy; ions with ionic radii; supercell boundaries in black).

References

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