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Electronic Supplementary Information

Mismatch in cation size causes rapid anion dynamics in solid electrolytes: the role of the Arrhenius pre-factor

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XRPD patterns



Fig. S1 a) X-ray powder patterns of high-energy ball milled CaF_2 , BaF_2 and $Ba_{1-x}Ca_xF_2$ mixtures with compositions of x = 0.2, 0.3, 0.4, 0.5 and 0.8. The samples were prepared in a planetary mill using a ZrO_2 vial set; the rotational speed was 600 rpm, the milling time was set to 10 h. After 100 h of milling, the sample with x = 0.5 does not reveal any residual nanocrystalline CaF_2 indicating almost complete mixing of the fluorides, which is in contrast to the mixture treated for only 10 h (see red arrows). In Ba-rich mixtures orthorhombic BaF_2 , see the pattern of $Ba_{0.8}Ca_{0.2}$, is visible.

Crystallite sizes

Average crystallite sizes were calculated by evaluating the width of the reflections in the X-ray powder patterns with the equation introduced by Scherrer:

$$\langle d \rangle = \frac{K \ \lambda \ 360^{\circ}}{2 \ \pi \ \beta_{1/2} \cos \theta}$$

Here, the shape factor *K* is 0.94 as is usually used to approximate spherical crystallites; λ denotes the X-ray wavelength, $\beta_{1/2}$ represents the broadening of the respective reflection peak at half maximum and θ is the Bragg angle. We used Cu K_a radiation with a wavelength of 1.5406 Å.

Table S1: Average crystallite sizes of all high-energy ball milled $Ba_{1-x}Ca_xF_2$ mixtures estimated via the equation introduced by Scherrer, the error is ± 2 nm

x	$D_{\rm p}({\rm nm})$
0	43
0.2	17
0.3	15
0.4	14
0.5 (10 h)	10
0.5 (100 h)	10
0.8	10
1	22

¹⁹F MAS NMR spectra of Ba_{1-x}Ca_xF₂:

In Fig. S2 ¹⁹F MAS NMR spectra of the mixed $Ba_{1-x}Ca_xF_2$ samples are shown. Deconvolution of the spectra was carried out with Gaussians (see green lines). The chemical shift for $[Ba]_4$ compared to pure nanocrystalline BaF_2 is different for each composition. The NMR line showing up at 175 ppm (marked by the red dots in Fig. S2) originates from small fractions of orthorhombic BaF_2 in the sample. The presence of this phase can also be seen through X-ray diffraction (see Fig. S1). Note that the second signal for orthorhombic BaF_2 shows up at 103 ppm and is, therefore, overlapping with other signals, as it is indicated by the dashed red lines in Fig. S2. The asterisks mark spinning sidebands.



Fig. S2: a) ¹⁹F MAS NMR spectra of Ba_{0.8}Ca_{0.2}F₂ and Ba_{0.9}Ca_{0.1}F₂ recorded at 470.4 MHz and a spinning frequency of 60 kHz. The spectrum shown at the bottom refers to a stochiometric mixture of BaF₂ and CaF₂ to highlight the initial δ_{iso} values of the starting materials, 58 ppm (CaF₂) and 152 ppm (BaF₂), respectively.