**Mixed cation effect in the metastable anion conductor $Ba_{1-x}Ca_xF_2$ ($0 \leqslant x \leqslant 1$)**
**Correlating long-range ion transport with local structures revealed by ultrafast $^{19}F$ MAS NMR**

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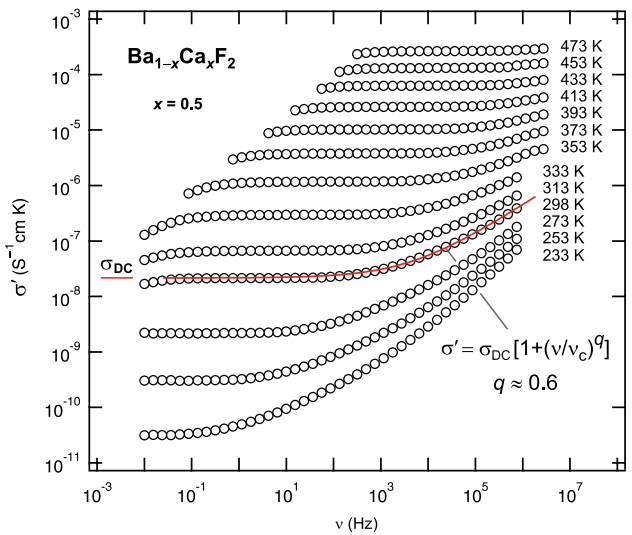
S1




S2

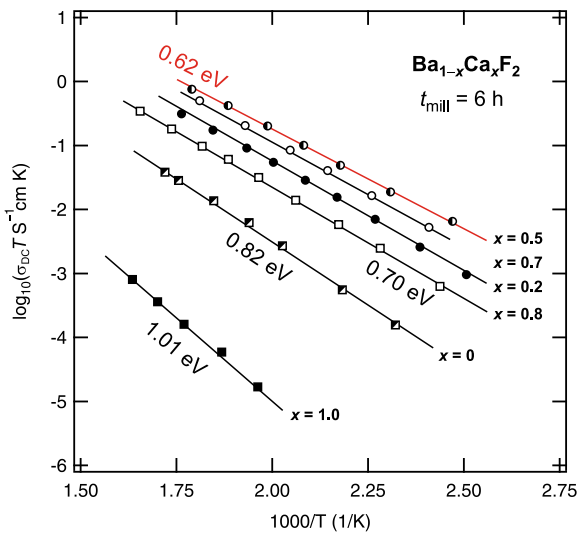



Fig. S1: Conductivity isotherms (first run, beginning from 233 K) obtained with the Novocontrol impedance analyzer. As an example, the impedance spectra of a sample with the composition $x = 0.5$ are shown. The red line represents a fit according to a power-law behaviour of the real part of the complex conductivity. Note that at low frequencies and high temperatures electrode polarization affects the dc-plateaus.

Fig. S2: Arrhenius plot of the dc-conductivities read out from the corresponding plateaus of the isotherms shown in Fig. S1. Activation energies range from ca. 1 eV to approximately 0.6 eV depending on the composition $x$. $\sigma_{DC}T(x)$ (determined at $T = 554$ K) and $E_a(x)$ are shown in Fig. 2.

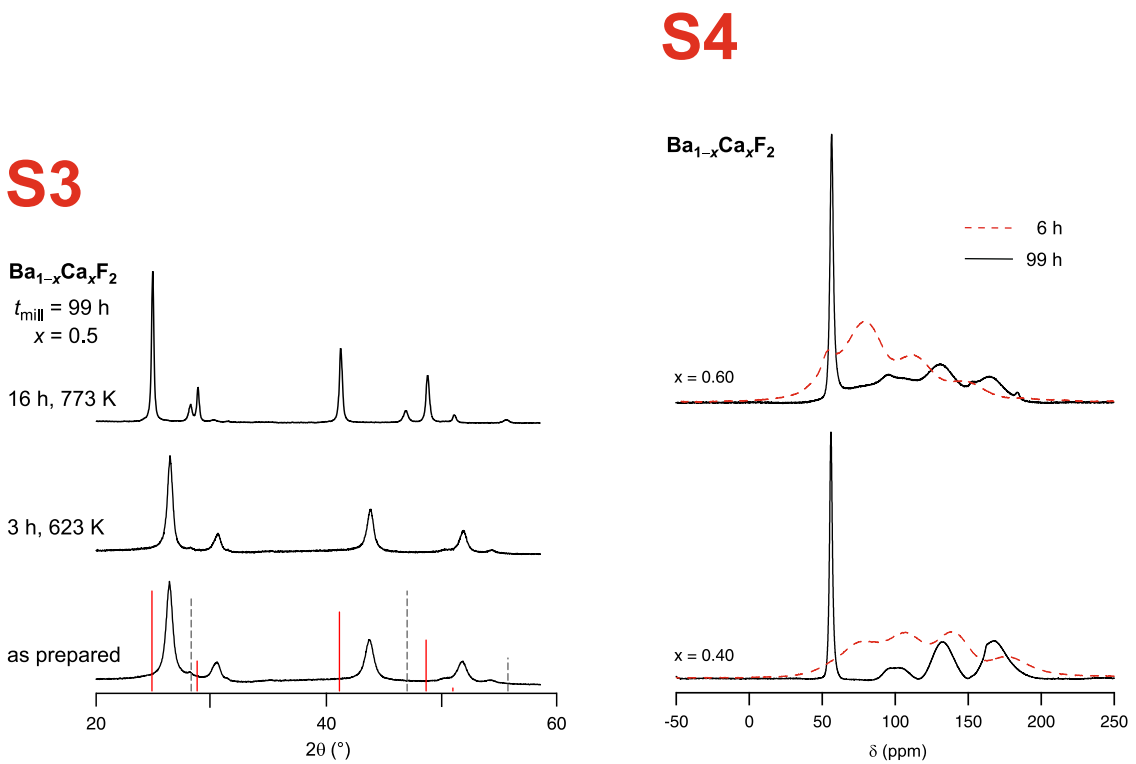



Fig. S3: XRPDs of $Ba_{1-x}Ca_xF_2$ ($x = 0.5$) showing the metastability of the mixed fluoride prepared by high-energy ball milling. Annealing for 3 h at 623 K does not lead to any significant changes. The small change in XRD peak widths might indicate grain growth and/or structural relaxation. Decomposotion is clearly observed after annealing the metastable sample(s) for 16 h at 773 K.

Fig. S2: $^{19}F$ MAS NMR spectra of $Ba_{1-x}Ca_xF_2$ ($x = 0.4$ and $x = 0.6$) prepared by high-energy ball milling of $CaF_2$ and $BaF_2$ for six and 99 h, repeectively. The broad NMR lines represent the mixed sites in the ternary fluoride as discussed in the text.