Mechanosynthesized nanocrystalline BaLiF$_3$: The impact of grain boundaries and structural disorder on ionic transport

Andre Düvel,$^{ab}$ Martin Wilkening,$^{sab}$ Reinhard Uecker,$^c$ Sebastian Wegner,$^d$ Vladimir Šepelák,$^{sbe}$ and Paul Heitjans$^{ab}$

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The mechanosynthesis of highly pure nanocrystalline BaLiF$_3$ is reported. The product with mean crystallite diameter of about 30 nm was prepared by joint high-energy ball-milling of the two binary fluorides LiF and BaF$_2$ at ambient temperature. Compared to coarse-grained BaLiF$_3$ with $\mu$m-sized crystallites, which is available via conventional solid-state synthesis at much higher temperatures, the mechanosynthesized product exhibits a drastic increase of ionic conductivity by several orders of magnitude. This is presumably due to structural disorder introduced during milling and to the presence of a large volume fraction of interfacial regions in the nanocrystalline form of BaLiF$_3$ providing fast diffusion pathways for the charge carriers. Starting from mechanosynthesized nanocrystalline BaLiF$_3$ it is possible to tune the transport parameters in a well defined way by subsequent annealing. Changes of the electrical response of mechanosynthesized BaLiF$_3$ during annealing are studied in situ by impedance spectroscopy. The results are compared with those of a structurally well-ordered single crystal which clearly shows extrinsic and intrinsic regions of ionic conduction.

I. Introduction

Fast-ion conductors play a crucial role in materials science.\textsuperscript{1–7} In particular, they are needed to develop sustainable energy storage systems, chemical sensors or advanced electrochromic devices.\textsuperscript{8–17} Currently, there are two main strategies to find (ceramic) materials showing high ionic conductivity. One is to synthesize new bulk materials with improved transport properties, the other is to modify the microstructure of known (single- or multi-phase) materials and, thus, to take advantage of nano-size and interface effects.\textsuperscript{18,19} In a simplified view nanocrystalline ion conductors can be regarded as structurally heterogeneous materials consisting of nm-sized crystallite grains and a large fraction of interfacial regions\textsuperscript{4} which in many cases dominate the overall ionic transport behaviour. The interfacial regions may also show structural disorder and can provide fast diffusion pathways for the ions.\textsuperscript{20} Recently, we observed a large increase of the Li ion conductivity of lithium tantalate, LiTaO$_3$, when the microcrystalline source material with a mean crystallite diameter in the $\mu$m range was high-energy ball-milled for several hours in a shaker mill in order to produce its nanocrystalline, structurally disordered but chemically identical counterpart.\textsuperscript{21} Subsequent annealing of the so obtained nanocrystalline sample allowed us to adjust the Li dc-conductivity in a controlled way. LiTaO$_3$ as well as nanocrystalline LiNbO$_3$ investigated before\textsuperscript{20,22–25} served as a model substance to study the influence of crystallite size and structural disorder on the ionic conductivity.

In the present paper we extend our investigations to a ternary Li containing fluoride viz. BaLiF$_3$. In particular, the paper is aimed at the fundamental question how and to which extent interfaces and grain boundaries affect the overall charge transport in ion conductors. BaLiF$_3$ turned out to be a suitable model system for this purpose. It is one of the rare examples and the only known ternary fluoride which crystallizes with the cubic inverse perovskite-type structure\textsuperscript{26–28} (space group Pm$\bar{3}$m, $a = 0.3996$ nm (polycrystalline powder, see ref. 26), $a = 0.3994(7)$ nm (single crystal, see ref. 29). Presumably, two mobile charge carriers, Li$^+$ and F$^-$, are present in BaLiF$_3$. This is in contrast to LiTaO$_3$ where Li cations dominate ionic conductivity.\textsuperscript{21} It is presently not clear whether one of the two is dominant; this is subject to future work in our laboratory. While nanocrystalline LiTaO$_3$ was prepared by reducing the particle size of coarse-grained lithium tantalate by ball milling (top-down approach, see ref. 21), phase pure nanocrystalline BaLiF$_3$ can be easily mechanosynthesized by high-energy ball milling a stoichiometric mixture of LiF and BaF$_2$ at ambient temperature as is shown here. Mechanosynthesis by high-energy ball-milling inducing a heterogeneous reaction has been used in recent years to produce quite a number of compounds not easily accessible by conventional routes (see, e.g., ref. 30–33). To our knowledge, the mechanosynthesis route has not been reported for BaLiF$_3$ in the literature so far. The mean crystallite size of the product obtained ranges from 11 to 30 nm. Let us note that...
in its single crystalline form BaLiF$_3$ is considered to be a promising window material in the ultra-violet and vacuum-ultra-violet region.\cite{26} Moreover, it is of interest as a potential laser-active medium when doped with suitable transition metals\cite{34,37} and discussed as possible candidate for quantum computing devices.\cite{38}

The ionic transport parameters and diffusion properties of as prepared and annealed mechanosynthesized BaLiF$_3$, which was characterized by X-ray diffraction, ultra-fast $^{19}$F MAS NMR spectroscopy as well as preliminary TEM micrographs, were investigated by impedance spectroscopy. The results are compared with those of a Czochralski grown BaLiF$_3$ single crystal, see, e.g., ref. 39, as well as with those of a microcrystalline powder sample. The latter was prepared by conventional solid-state synthesis\cite{40} and is characterized by a mean crystallite size with a diameter of about 0.8 $\mu$m.

II. Experiment

A Preparation of BaLiF$_3$

Nanocrystalline BaLiF$_3$ was prepared by high-energy ball milling of BaF$_2$ (99.99%, Sigma Aldrich) together with an equimolar amount of LiF (99.99%, Alfa Aesar) in a Fritsch Pulverisette 7 (premium line) planetary mill. The total mass of the mixture was about 2 g. A grinding beaker made of stabilized ZrO$_2$ with a volume of 45 mL was employed. The mixture was mechanically treated for times between 30 and 180 min using 140 milling balls (ZrO$_2$, 5 mm in diameter) at 600 rpm. One sample, which was prepared by milling of BaF$_2$ and LiF in an equimolar ratio for three hours, was annealed at 870 K for 24 h as well as 50 h in air.

Single crystalline BaLiF$_3$ was prepared by the following procedure. First, the starting materials of the crystal growth processes BaF$_2$ (crystal pieces) and LiF (GFT “optical grade”) were purified by a pre-treatment,\cite{34} i.e., the source materials were treated with HF at elevated temperatures. Afterwards they were mixed in the required ratio and subjected to a zone melting procedure under HF. Since BaLiF$_3$ melts incongruently at about 1100 K the composition of the starting melt has to deviate from the crystal composition. According to the peritectic point of the binary phase diagram BaF$_2$-LiF the chosen composition was Ba$_{0.86}$Li$_{1.14}$F$_{2.86}$. The crystal was grown in a platinum crucible by conventional Czochralski technique with RF-heating and automatic diameter control. In order to suppress oxidation of the melt the growth atmosphere consisted of an Ar-CF$_4$ mixture. The growth rate was 2 mm h$^{-1}$ and the rotation varied from 10 to 25 min$^{-1}$. The so obtained colorless crystal was 70 mm in length and 18 mm in diameter.

For comparison, polycrystalline BaLiF$_3$ was also prepared by conventional solid-state (high-temperature) synthesis following the procedure being described in detail in ref. 40. According to that preparation route an equimolar mixture of BaF$_2$ and LiF, which was initially mixed for 10 min in a planetary mill at 600 rpm, was heated for about two hours in nitrogen atmosphere at 620 K for drying purposes and then fired at 1020 K for 5 h. After that it was left to cool down to room temperature. It has to be mentioned that synthesizing BaLiF$_3$ via ceramic synthesis routes has some disadvantages compared to one-step mechanochemical preparation. In particular, vaporization of Li at high temperatures leads to less pure and non-stoichiometric products.

B XRD, impedance and NMR measurements

Sample characterization of the powders was carried out at room temperature using X-ray diffraction (XRD) with a Philips PW 1800 operating with Cu-K$_\alpha$ radiation at 40 kV. For the impedance spectroscopy measurements an HP 4192 A analyzer (frequency range 5 Hz to 13 MHz) connected to a home-built cell was employed. Conductivity jigs with a four terminal configuration were used. The powdered samples were pressed to cylindrical pellets (8 mm in diameter and 1 mm in thickness) at room temperature. If not stated otherwise this was done by applying an uniaxial pressure of about 1 GPa. Electrodes were applied either by Au sputtering or by subsequent pressing the uncoated pellet between Pt powder.

During the measurements the impedance samples were strictly kept under inert gas atmosphere by using a stream of dry nitrogen (99.999%). Temperatures ranged from 298 K to about 800 K.

$^{19}$F MAS (magic angle spinning) NMR spectra were acquired with a Bruker Avance III spectrometer operating at 471 MHz. The NMR spectra were recorded using a single excitation pulse at an ultra-fast spinning speed of $\nu_{\text{rot}}$ = 60 kHz with room-temperature bearing gas. The $\pi/2$ pulse length was about 2 $\mu$s.

III. Results and discussion

A Sample characterization by XRD and $^{19}$F MAS NMR

In Fig. 1 X-ray diffraction (XRD) powder patterns of equimolar mixtures of BaF$_2$ and LiF treated in the planetary mill for $t_{\text{milling}}$ = 30, 60 and 180 min, respectively, are shown. Already after 30 min of milling, the XRD powder pattern of BaLiF$_3$ with its inverse cubic perovskite structure (see Fig. 1) dominates the diffractogram. After milling the mixture for one hour the conversion of LiF and BaF$_2$ to BaLiF$_3$ seems to be close to 100% since there are no peaks visible pointing to residual LiF or BaF$_2$. The latter are highlighted in Fig. 1(a) by asterisks and filled circles, respectively. The XRD peak positions found for BaLiF$_3$ are in perfect agreement with those reported in the literature.\cite{41} For comparison, in Fig. 1 the XRD pattern of a sample prepared by conventional solid-state synthesis as well as that of mechanosynthesized BaLiF$_3$, which was annealed at 870 K for 24 h, are also shown.

In Fig. 2 magnifications of some of the XRD patterns displayed in Fig. 1 are shown in order to verify the phase purity of the mechanosynthesized products with respect to residual LiF and BaF$_2$. In contrast to the conventionally prepared sample where a small amount of residual BaF$_2$ is found, after 1 h of mechanical activation of the LiF: BaF$_2$ mixture, the XRD peaks of the two binary starting materials cannot be detected any longer. Furthermore, it can be clearly seen that BaLiF$_3$ ($Pm\bar{3}m$) is the only phase which is formed under the milling conditions described above. This is fully corroborated by $^{19}$F MAS NMR (vide infra).
Compared to the XRD peak widths of conventionally prepared BaLiF$_3$, those of the ball-milled product are broadened due to both much smaller crystallite sizes and effects of lattice strain $\varepsilon$. In a first approximation we have used the equation introduced by Scherrer\(^4\) (1) to determine the mean crystallite size $\langle d \rangle$, which is related to the broadening of the peak via

$$\langle d \rangle = \frac{K \cdot \lambda_{\text{XRD}} \cdot 360}{2 \pi \cdot \beta(0.1h)} \cdot \cos \theta \quad (1)$$

$\theta$ denotes the angle between the surface of the sample and the incident X-ray beam. $K = 0.89$ is chosen assuming a spherical shape of the crystallites. $\lambda_{\text{XRD}}$ is the average wavelength of the X-ray source. For a Cu anode $\lambda_{\text{XRD}}$ of the K$\alpha_1$ line equals 0.154 nm. In the case of Lorentzian-shaped XRD peaks, which is the case here, the width (fwhm, full width at half maximum) $\beta_{h(0.1h)}$ is given by $\beta_{h(0.1h)} = \beta_h - \beta_0$ taking into account instrumental broadening effects. $\beta_0$ is the measured peak width and $\beta_h$ is the width of a reference material such as microcrystalline CaF$_2$ or coarse-grained BaLiF$_3$ produced from BaLiF$_3$ single crystals. Expectedly, the mechano-synthesized BaLiF$_3$ samples show mean crystallite sizes in the nm-range. As an example, mechano-synthesized BaLiF$_3$ obtained after $t_{\text{mill}} = 180$ min is characterized by $\langle d \rangle \approx 30$ nm. Reducing the milling time leads to an increase of $\langle d \rangle$ (see Table 1). The sample which was prepared by solid-state synthesis at a much higher temperature has a crystallite size of 0.8 $\mu$m. Interestingly, the XRD peak widths of the mechano-synthesized material, which was additionally annealed at 870 K, are less broadened than those of the conventionally prepared one which was calcined at much higher $T$ (see Fig. 2(b) for comparisons). Most likely, this is due to a larger mean crystallite size indicating that the microstructure of a ball-milled powder favours grain growth. In order to quantify to which degree lattice strain $\varepsilon$ affects the $\langle d \rangle$ values listed in Table 1, we have analyzed the XRD patterns according to the procedure of Williamson and Hall.$^{43}$

$$\frac{\beta_{h(0.1h)} \cos \theta}{\lambda_{\text{XRD}}} = 4\varepsilon \frac{\sin \theta}{\lambda} + \frac{1}{\langle d \rangle} \quad (2)$$

Except for the mixture milled for 30 min, the values obtained by eqn (2) for $\langle d \rangle$ are twice as large as those estimated $via$ eqn (1), see Table 1. This indicates that the values obtained by the Scherrer equation should be regarded as a rough estimate for the crystalline size.

Apart from an almost negligible impurity, which might be identified with orthorhombic BaF$_2$ (chemical shifts $\delta$ amount to 102 and 176 ppm, see ref. 44) or another metastable intermediate, the phase purity of mechano-synthesized BaLiF$_3$ probed by X-ray powder diffraction is clearly confirmed by the room temperature $^{19}$F MAS NMR spectrum shown in Fig. 3. Orthorhombic BaF$_2$ is a known high pressure modification of BaF$_2$.\(^{45,46}\) In a previous study we have shown that it is formed to a small extent during mechanical treatment of cubic BaF$_2$ for 3 h in a planetary mill.\(^{44,47}\) Increasing the milling time to about 6 h increases the amount of orthorhombic BaF$_2$ formed. Thus, one might suppose that during the initial stages of milling an LiF:BaF$_2$ mixture, orthorhombic BaF$_2$ is formed first which transforms into BaLiF$_3$ shortly after.

In agreement with the crystal structure of BaLiF$_3$ a single and Lorentzian-shaped $^{19}$F NMR resonance line is observed under high-speed MAS conditions. It shows up at $\delta = 66$ ppm when referenced to C$_6$F$_6$. The measured chemical shift is identical to that recently reported in the literature for a powdered sample of BaLiF$_3$.\(^{48}\) Here, the same $\delta$-values are found for the other samples investigated within this study.

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Fig. 1 Left: X-ray powder diffraction patterns of nanocrystalline BaLiF$_3$ prepared by mechanical treatment of BaF$_2$ and LiF (molar ratio of 1 : 1) in a planetary mill at 600 rpm and for different milling times $t_{\text{mill}}$ (a) 30 min, (b) 60 min and (c) 180 min. (d) For comparison, the corresponding XRD pattern of conventionally prepared BaLiF$_3$ is shown, too. (e) XRD pattern of mechanosynthesized BaLiF$_3$ ($t_{\text{mill}}$) which was annealed at 870 K for 24 h. Right: Crystal structure of BaLiF$_3$ (space group $Pm\bar{3}n$). Large blue spheres denote Ba cations, orange and green spheres represent Li cations and F anions.
However, the NMR line width of the mechanically synthesized nanocrystalline product is by more than a factor of two larger than that of microcrystalline BaLiF$_3$. Since the spectra are recorded with the same spinning speed $n_{\text{rot}}$ of approximately 60 kHz, the larger line width can be attributed to a distribution of chemical shifts present in the mechanically prepared product. This clearly reflects microstructural disorder such as distortions of the F$^-$/Co octahedra or deviations from ideal bond lengths.

### B Impedance spectroscopy studies on structurally different forms of BaLiF$_3$

#### 1. Mechanosynthesized, nanocrystalline BaLiF$_3$

**a Basics.** Impedance spectroscopy is a simple but important method to study the electrical processes occurring in a system on applying an ac signal across the sample pellet. The technique is based on analyzing the electrical response of the system usually after a sinusoidal perturbation. The impedance is generally calculated as a function of the frequency of this perturbation. Conventionally, the output response, which comprises both resistive (real part) and reactive (imaginary part) components, is either displayed in a complex plane plot (Nyquist plot or Cole–Cole diagram) or in form of impedance spectra, i.e., the real part $\Re(\hat{Z}(\omega))$ is plotted vs. frequency. Here, $\omega = f2\pi$ denotes the angular frequency. In a Cole–Cole plot the negative imaginary part $\Delta_{\omega}$ of the impedance ($\omega$) is plotted vs. the real part $\Re(\hat{Z}(\omega))$ and appears in succeeding semicircles representing the contributions to the electrical properties due to the bulk material, grain boundary effects and, if there are any, interfacial polarization phenomena. The impedance $\hat{Z}(\omega)$ is given by

$$\hat{Z}(\omega) = Z' - iZ'' = R - \frac{i}{\omega C} \quad \text{and} \quad \frac{Z'}{Z''} = \frac{\epsilon'}{\epsilon} = \tan \delta \quad (3)$$

where $R$ and $C$ are the resistance and capacitance, respectively. $i = (-1)^{1/2}$ is the imaginary unit, $\epsilon'$ and $\epsilon''$ denote the real and imaginary parts of the complex dielectric permittivity, $\delta$ is the loss angle. The peaks of the different semicircles are characterized by their individual time constants according to the relation

$$\omega_{\text{max}} \tau = \omega_{\text{max}} RC = 1 \quad (4)$$

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**Fig. 2** Magnifications of the XRD powder patterns shown in Fig. 1. The XRD peaks of residual BaF$_2$ are indicated. After $t_{\text{mill}} = 60$ min the formation of BaLiF$_3$ is completed. The diffractogram of a sample treated for 180 min in the planetary mill verifies the phase purity of mechanosynthesized BaLiF$_3$. For comparison, the XRD diffractograms of the two coarse-grained samples are also shown. The peak at about 25° 2$\theta$, which is of very low intensity, reveals a very small amount of residual BaF$_2$ owing to weighing errors.

**Table 1** $\langle d \rangle$ and $\varepsilon$ values of BaLiF$_3$ prepared via different ways. The mean crystallite sizes were estimated via XRD peak broadening. The error of $\langle d \rangle$ is at least of the order of ±5 nm

<table>
<thead>
<tr>
<th>$t_{\text{mill}}$</th>
<th>$\langle d \rangle$ (eqn (1))</th>
<th>$\varepsilon$</th>
<th>$\langle d \rangle$ (eqn (2))</th>
</tr>
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<tbody>
<tr>
<td>30 min</td>
<td>50 nm</td>
<td>0.003</td>
<td>340 nm</td>
</tr>
<tr>
<td>60 min</td>
<td>40 nm</td>
<td>0.002</td>
<td>80 nm</td>
</tr>
<tr>
<td>180 min</td>
<td>30 nm</td>
<td>0.002</td>
<td>60 nm</td>
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However, the NMR line width of the mechanically synthesized nanocrystalline product is by more than a factor of two larger than that of microcrystalline BaLiF$_3$ (Fig. 3). Since the spectra are recorded with the same spinning speed $\nu_{\text{rot}}$ of approximately 60 kHz, the larger line width can be attributed to a distribution of chemical shifts present in the mechanically prepared product. This clearly reflects microstructural disorder such as distortions of the F$^-$ octahedra or deviations from ideal bond lengths.

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**Fig. 3** $^{19}$F MAS NMR spectra of 'single crystalline' (top) and mechanosynthesized (nanocrystalline) BaLiF$_3$ (bottom) which were recorded at a spinning speed of 60 kHz using ambient bearing gas pressure. A small piece of the single crystal was ground in an agate mortar for the MAS NMR measurements. The different line widths (fwhm) are 2.5 and 5.9 ppm, respectively. Inset: magnification of the NMR spectrum of nanocrystalline BaLiF$_3$. Most likely, the signal of very low intensity which shows up at about 103 ppm can be attributed to orthorhombic BaF$_2$. The emergence of a peak at about 5.9 ppm is most likely due to the formation of BaF$_2$.
Thus, the relaxation frequency is given by $f_\text{max} = 1/(2\pi RC)$. Alternatively, other representations, e.g., the complex modulus $M(\omega) = M' + iM''$ can be used to highlight a particular aspect of the electrical response of a sample. For example, the modulus representation is useful when measurements are affected by high capacitance effects, such as those due to inter-granular impedances and electrode polarization effects. $M(\omega)$ is related to the complex impedance via the equation

$$M' + iM'' = \omega C_0 Z$$

where $C_0 = (\varepsilon_0 A)/d$. $A$ and $d$ are area and thickness of the pellet and $\varepsilon_0$ is the permittivity of free space.

b Complex plane plots and impedance spectra. The first part of this section is concerned with nanocrystalline BaLiF$_3$ synthesized by high-energy ball milling (see above). We have started to characterize the sample by impedance spectroscopy measurements at temperatures $T > 385$ K. The temperature was continually increased in order to detect any changes of the electrical response of the sample. In Fig. 4(a) the complex impedance spectra of mechanosynthesized BaLiF$_3$ are shown which were measured at the temperatures indicated. Partly, the corresponding peak frequencies, i.e., the frequencies where the imaginary part passes through the maximum, are given.

As often observed for structurally disordered materials, the arcs of mechanically prepared BaLiF$_3$ can be described by depressed semicircles, i.e., the respective centers lie below the $Z'\cos\theta$ axis. In particular, this holds for low temperatures when the data of BaLiF$_3$ is regarded. These shifts clearly reveal that the curves are composed of a range of semicircular arcs pointing to a large distribution of relaxation frequencies being characteristic of the electrical response of the sample. With increasing temperature the shape of the arcs progressively become more semicircular and their centers shift towards the origin of the complex plane plot. Most likely, these observations are due to slight structural changes of the sample. At low frequencies spikes are clearly visible which originate from electrode polarization effects.

The same features also govern the corresponding impedance spectra which are shown in Fig. 4(b). At both low $T$ and low frequencies they clearly show a distinct dc-conductivity plateau. The dc-conductivity $\sigma_{dc}$ is identical to the value which can be determined from the corresponding resistance of the low-frequency intercept of the complex impedance arcs on the real axis. With increasing frequency the dispersive region of the impedance spectra shows up. Once again, the frequency dependence of $\sigma'$ changes with temperature. Up to frequencies of about $f = 1$ MHz the spectra can be roughly described by a power law behaviour according to $\sigma' = \sigma'_{dc} + A_0 f^s$ with $A_0$ being the dispersion parameter and $s$ the power law exponent usually ranging between 0 and 1. Here, $s$ turns out to be depending on temperature. It is approximately 0.63 at low and reaches 0.40 at high temperatures.

In Fig. 4(c) the temperature dependence of the dc-conductivity is shown in an Arrhenius representation according to

$$\sigma_{dc}T = \sigma_0 \exp(-E_a/(k_B T))$$

where $E_a$ denotes the activation energy and $k_B$ Boltzmann’s constant. $\sigma_0$ turns out to be 0.74(1) eV. Very similar results were obtained for a sample which was prepared by mechanical treatment of LiF and BaF$_2$ for $t_{mill} = 20$ h under the same preparation conditions. For that sample a mean crystallite diameter of about 11 nm can be estimated from XRD peak broadening (see section III A). For comparison with the $\sigma_{dc}T$ data, the temperature dependence of the so-called characteristic frequency $\omega_c$, being a measure of the onset of conductivity dispersion according to $\sigma' = \omega_c/(\omega_c - f)^s$ is shown in Fig. 4(c), too. $\omega_c(T)$ also follows Arrhenius behaviour with an activation energy being similar to that deduced from $\sigma_{dc}T$ (cf. Fig. 4(c)). Plotting $\sigma_{dc}T$ vs. $\omega_c$ in a log-log plot should result in a straight line with a slope of unity. This is only roughly fulfilled below 465 K. At higher $T$ deviations show up and the slope is reduced to about 0.8

![Fig. 4](image-url)

Fig. 4  (a) Cole–Cole plots of mechanosynthesized BaLiF$_3$ which was produced by joint milling of LiF and BaF$_2$ in a planetary mill for 3 h. The frequencies $f_{\text{max}}$ indicated follow Arrhenius behaviour. From the intercepts at low frequencies (marked exemplarily by two arrows) the resistance is obtained showing the same temperature dependence as the dc-conductivity (see Fig. 4(b)). (b) Corresponding impedance spectra of mechanosynthesized BaLiF$_3$, i.e., the real part of $\sigma$ is plotted vs. frequency $f = \omega/2\pi$. The dc-conductivities can be directly read out from the low-frequency plateau where $\sigma'$ is independent of frequency. Solid lines represent fits according to Jonscher’s power law: $\sigma' = \sigma'_{dc} + A_0 f^s$ (see text for further explanation). (c) Electrical dc-conductivity of mechanosynthesized nanocrystalline BaLiF$_3$ as a function of temperature (plotted as $\sigma_{dc}T$ vs. 1000/$T$). Solid lines represent fits according to an Arrhenius law. The activation energy turns out to be 0.74(1) eV characterizing long-range transport of the charge carriers in the ternary fluoride. For comparison, the electrical relaxation rate $\gamma_{\text{rel}}$ deduced from the $M''$ maxima and the characteristic frequency $\omega_c$ are also included.
indicating that the electrical relaxation behaviour depends on temperature. The fact that a linear relationship between \( \sigma_{dc} \) and \( \omega_c \) is not fully observed is also seen when the well-known temperature scaling of \( \sigma_{dc} \) or the modulus representation is used to characterize the conduction processes in mechanosynthesized BaLiF\(_3\). In order to obtain a conductivity master curve (see Fig. 5), \( \sigma_{dc} \) and \( \sigma_{dc} T \) are used to scale the conductivity spectra which collapse into a single curve if \( \sigma_{dc} \propto \omega_c \) holds. It can be seen from Fig. 5 that the scaled impedance spectra do not coincide. This is in agreement with the features observed when \( M'' \) is plotted vs. frequency for different temperatures (Fig. 6).

e Comparison with the modulus representation. The peak maxima of \( M''(\omega/2\pi) \) increase with increasing \( T \). This is accompanied by a reduction of the peak widths. Simultaneously, the asymmetry of the modulus curves, which shows a peak width of only 1.7 decades. Ideal Debye behaviour is obtained when \( \beta' = 1 \). This is in agreement with eqn (7) fits \( M''(\omega/2\pi) \) well except at large frequencies. However, this has negligible effect on the electrical relaxation rate \( 1/\tau_M \), which can be deduced from the peak maxima of \( M'' \) (see below). Moynihan et al. proposed

\[
M(\omega) = \left[ 1 - L(-d\phi/dt) \right] \quad \text{(8)}
\]

with \( \lim_{\omega \to \infty} M(\omega) = 1/\epsilon_\infty \), where \( L(x) \) is a Lorentzian function. Numerical simulations of \( M(\omega) \) for given \( \beta' \) values can be used to relate the full width at half maximum \( \Gamma \) of the \( M''(\omega) \)-curves with \( \beta' \). In Fig. 7 \( \beta' (1/T) \) of the \( M'' \)-curves of Fig. 6 is shown ranging from approximately 0.5 \((T \approx 400 K)\) to about 0.64 \((T \approx 530 K)\). Let us note that the use of \( M'' \) to analyze impedance data is often criticized because \( M'' \) represents a tangled combination of both the conductivity \( \sigma' \) and the permittivity \( \epsilon' \) which, in contrast to \( M'' \), can be measured directly. However, here the \( M'' \)-representation is just used to highlight changes of the electrical response of the samples during heat treatment and to compare these results with those obtained when \( \sigma' \) is analyzed directly. With this in mind we have additionally parameterized the \( M'' \) data of as prepared mechanosynthesized BaLiF\(_3\) on the frequency scale directly with Lorentzian-shaped fits according to

\[
M'' \propto \frac{\omega T}{1 + (\omega T)^{2n}} \quad \text{(9)}
\]

Once again, such an analysis, which is used here simply to illustrate the deviations from ideal Debye behaviour, yields temperature dependent stretching factors \( \beta = 1 - n_\phi \) ranging from 0.31 at about 385 K to ca. 0.5 when the temperature is raised to about 550 K (see Fig. 7). The peak maxima of Fig. 6 mark the crossover from long-range to short-range motions of the charge carriers. The frequencies \( f_{M,max} \) associated can be roughly transformed into electrical relaxation rates \( 1/\tau_M \) via \( f_{M,max} \approx 2\pi \tau_M = 1 \). The temperature dependence of \( 1/\tau_M \) obtained this way is shown in Fig. 7 together with that of \( 1/\tau_e \). Taking into account non-exponential KWW-correlation functions (eqn (7)), the rates obtained via eqn (9) slightly differ from those shown in Fig. 4(c) yielding an activation energy \((0.75(2) eV)\) which is very similar to that obtained when \( \sigma_{dc} T \) is analyzed \((0.74(2) eV)\) which is very similar to that obtained when \( \sigma_{dc} T \) is analyzed. The corresponding pre-exponential factor \( \tau_{\phi,0} \) of the underlying Arrhenius law

\[
\tau_M^{-1} = \tau_M^{-1,0} \exp(-E_{\phi,0}/k_B T) \quad \text{(10)}
\]

translates out to be about \( 2.2 \times 10^{13} \text{s}^{-1} \) and, thus, lies in the typical range of phonon frequencies.

The deviation from Debye behavior manifests itself also in the absolute widths of the modulus spectra. At low temperatures the peak width \( \Gamma \) is about 2.1 decades (on the frequency scale). The spectrum measured at the highest \( T \) (see Fig. 6) reveals a peak width of only 1.7 decades. Ideal
Debye response is characterized by a width of about 1.14 decades. As we will show below, such a behaviour is exactly found when structurally well-ordered, single crystalline BaLiF$_3$ is investigated by impedance spectroscopy.

**d Influence of annealing on $\sigma'$ and $M''$.** After the last measurement performed at 548 K the sample was let to cool down to room temperature. Then a second run of measurements was started. The corresponding modulus spectra are shown in Fig. 8. It can be seen that after annealing, the shape of $M''(\omega)$ turns out to be nearly independent of temperature. The peaks are all characterized by almost the same width which equals that of the spectrum measured at 548 K of the first run. Interestingly, the positions of the peak maxima did not change. Therefore, analyzing the data of the second run according to eqn (9) yields electrical relaxation rates $\tau_M^{-1}$ being very similar to those measured before (see Fig. 7). A third run of measurements did not lead to any further changes of the data. Obviously, the sample was brought into a stable structural state. The changes observed for the first and second run should also show up in the corresponding impedance spectra. For comparison, in Fig. 9(a) the spectra of the second run are compared with those displayed in Fig. 4(b). Note that the respective temperatures of the two runs slightly differ. Whereas at high temperatures the spectra coincide, a remarkable difference shows up at low $T$ when the dispersive regime is regarded. In contrast to the first run, the spectra of the sample exposed to 550 K, can be scaled such that an almost ideal master curve is obtained, i.e., the linear relationship $\sigma_{dc}T \propto \omega_e$ is more and more fulfilled. The spectra can be fitted with power laws characterized by $s \approx 0.4$ depending only slightly on $T$. This is in fair agreement with $\beta' \approx 0.64$ which can be very roughly related to $s$ via $\beta' = 1 - s$.\(^{25}\)

Expectedly, the scaling behaviour observed for $\sigma'$ holds also for the corresponding modulus spectra of the second run of measurements. The soft annealing process carried out at 550 K and under $N_2$ atmosphere does not influence the dc-plateaus. Instead, the thermally induced structural relaxation of the sample mainly affects short-range motions of the charge carriers rather than long-range transport parameters. This can be clearly illustrated when the ac-conductivity $\sigma'$ is read out at a frequency of 1 MHz and plotted as $\sigma' T$ vs. the inverse temperature (Fig. 9(c)). Before annealing at 550 K $\sigma'_{ac(1 \text{ MHz})} T$ exhibits non-Arrhenius behaviour. This is in contrast to the situation after the sample was exposed to 550 K. The data of the annealed sample follow an Arrhenius law with an

![Fig. 7](https://example.com/fig7.png)  \[\log_{10}(\tau_M) \text{ vs. } 1000/T(1/K)\]

**Fig. 7** Temperature dependence of (i) the most probable electrical relaxation time $\tau_M$ in nanocrystalline BaLiF$_3$ as obtained from eqn (9) and (ii) the stretching exponent $\beta'$ of the underlying KWW correlation function (eqn (7)) as well as $1 - n_\sigma$ obtained from eqn (9). The solid line shows a fit according to an Arrhenius relation, $\tau_M^{-1} = \tau_M^{0} \exp(-E_{a,M}/(k_BT))$, with $E_{a,M} = 0.75(2)$ eV and $\tau_M^{0} = 2.2 \times 10^{13}$ s$^{-1}$. Squares show the relaxation rates deduced from the complex modulus spectra of Fig. 8.

![Fig. 8](https://example.com/fig8.png)  \[\log_{10}(\tau_M) \text{ vs. } 1000/T(1/K)\]

**Fig. 8** Repetition of the complex modulus measurements shown in Fig. 6 after the sample was exposed to about 550 K. The curves were recorded at 423 K, 480 K, and 543 K (2nd run). For comparison, some of the curves of Fig. 6, whose peak height depends on $T$ are shown, too. The corresponding relaxation rates $\tau_M^{-1}$ are shown in Fig. 7.

![Fig. 9](https://example.com/fig9.png)  \[\log_{10}(\sigma') \text{ vs. } 1000/T(1/K)\]

**Fig. 9** (a) Impedance spectra of mechanosynthesized BaLiF$_3$ after the sample was exposed to about 500 K. Spectra recorded at 416, 474 and 548 K are those already shown in Fig. 4(b). (b) dc-conductivity of the spectra displayed on the left. For comparison, the data of Fig. 4(c) are shown, too. (c) ac-conductivity $(\sigma'_{ac(1 \text{ MHz})})$ read out at 1 MHz, of mechanosynthesized BaLiF$_3$ (1st and 2nd run). (d) Comparison of the ac-conductivity of Fig. 9(c) with that of a mechanosynthesized BaLiF$_3$ sample which was annealed for 50 h at 870 K. For further comparison, $\sigma'_{ac(1 \text{ MHz})}$ (1) and $\sigma'_{dc}$ (2) of BaLiF$_3$ prepared by solid-state synthesis are also shown. See text for further details.

\[2.2 \times 10^{13} \text{ s}^{-1}\]

\[0.75(2) \text{ eV}\]

\[k_B T\]

\[E_{a,M} \approx 0.75(2) \text{ eV}\]

\[\tau_M^{0} = 2.2 \times 10^{13} \text{ s}^{-1}\]

\[1 - n_\sigma\]

\[\tau_M^{-1} \exp(-E_{a,M}/(k_BT))\]

\[\sigma'_{dc(1 \text{ MHz})} T\]

\[\sigma'_{ac(1 \text{ MHz})}\]

\[\sigma'_{dc}\]

\[\sigma'_{ac(1 \text{ MHz})}\]

\[\sigma'_{dc}\]
activation energy of approximately 0.6 eV. It is worth noting in this context that grain growth is not observed when nanocrystalline BaLiF₃ is exposed to 550 K for several hours. Most likely, internal strain is released and/or the structure of the material is locally relaxed at elevated temperatures. Interestingly, the effect observed here is less pronounced when \( t_{\text{mill}} \) is increased from 3 to 20 h. Internal strain seems to be generated in the early stages of milling and is still preserved even after 3 h of mechanical treatment. Obviously, at larger milling times structural relaxation can be induced also mechanically. Recently, such a process was reported for mechanically treated LiAlSi₂O₆ glass samples. ⁶¹

Nevertheless, the modulus peaks of structurally disordered, nanocrystalline BaLiF₃ prepared by ball milling remain asymmetric in shape. The non-Debye behaviour observed is a clear indication of non-random correlated motions of interacting charge carriers. As shown in the next subsection, this is in contrast to a perfectly ordered single crystal of BaLiF₃ where the ions move randomly from site to site.

2. BaLiF₃ single crystal—comparison with mechanosynthesized (nanocrystalline) and microcrystalline BaLiF₃

\textit{a Comparison of} \( \sigma' \) and \( M'' \). Provided the ions do not interact with each other or with their surrounding matrix, \( \sigma(\omega) \) will be constant. Indeed, exactly this electrical behaviour is observed for the BaLiF₃ single crystal. In Fig. 10 and 11 the data from impedance spectroscopy are shown which were recorded at temperatures ranging from ca. 450 K to 720 K. The shape of the complex modulus \( M''(\omega) \) (Fig. 11) is independent of temperature and the peak width turned out to be about 1.15 which is in agreement with the expected value for Debye behaviour. Fitting eqn (9) to the \( M''(\omega) \) data yields \( n_{\text{e}} = 0 \) reflecting fully symmetric modulus peaks which clearly indicates that ion hopping in the BaLiF₃ crystal is governed by an exponential correlation function which is characteristic of random hopping processes via point defects. The same features show up in the corresponding Cole–Cole plots (Fig. 10(a)) and impedance spectra (see Fig. 10(b)). The complex plane representation reveals (perfect) semicircles whose centers lie on the \( Z' \)-axis, i.e. they can be represented with a single \( RC \) unit. Expectedly, any dispersive regimes are absent in the impedance spectra at least in the frequency range covered here.

\textit{b dc-conductivity of single crystalline BaLiF₃.} In Fig. 10(c) \( \sigma_{\text{dc}} \) of the single crystal is plotted vs. the inverse temperature. The data were recorded starting from the lowest temperature. Interestingly, below 625 K single crystalline BaLiF₃ shows a rather high ionic conductivity following an Arrhenius law with an activation energy of only 0.5 eV (Fig. 10(c)). A similar value (see also Fig. 10(c)) is found when the modulus peaks of Fig. 11 are analyzed. For comparison, in Fig. 10(c) the corresponding conductivity relaxation rates \( 1/t_M \) are also included.

Below 660 K \( \sigma_{\text{dc}} \) of single crystalline BaLiF₃ can be attributed to extrinsic ion conduction. Above 660 K the \( \sigma_{\text{dc}} \) values sharply increase. Obviously, the ionic dc-conductivity at higher \( T \) is of intrinsic nature with an activation energy of 0.98 eV. Although this behaviour was not observed by the impedance measurements on single crystalline BaLiF₃ carried out earlier by Rush et al., ⁶² it is expected for an undoped, i.e.,

![Fig. 10](https://example.com/fig10.png)

**Fig. 10** (a) Cole–Cole plots of single crystalline BaLiF₃. The centers of the semicircles lie on the real axis reflecting ideal Debye behavior. From the intercepts at low frequencies (see the arrows in Fig. 4(a)) the resistances can be read out which show the same temperature dependence as the dc-conductivity (see Fig. 10(c)). (b) Corresponding impedance spectra which are, up to a frequency of 1 MHz, composed of dc plateaus, only. (c) \( \sigma_{\text{dc}} \) vs. \( 1000/T \). Solid lines represent fits according to \( \sigma_{\text{dc}} = \sigma_0 \exp(-E_a/(k_B T)) \) with the activation energies indicated. For comparison, the electrical relaxation rate \( 1/t_M \) deduced from the \( M'' \) maxima are shown, too.

![Fig. 11](https://example.com/fig11.png)

**Fig. 11** Frequency dependence of the imaginary part of the electric modulus of single crystalline BaLiF₃. The complex modulus curves were recorded at the temperatures indicated. The corresponding relaxation rates \( 1/t_M \) are shown in Fig. 10(c). The dashed line shows a fit according to eqn (9). The peaks are fully symmetric leading to an exponent \( n_{\text{e}} = 0 \).
nominally pure ionic crystal. Halide crystals, in particular, may contain heterovalent cations and other impurities leading in the case of BaLiF$_3$ to a variety of impurity-related defects. The two activation energies probed represent the migration (0.50 eV) and the total activation energy (0.98 eV) of the charge carriers, respectively. The latter comprises both the formation activation energy as well as the migration activation energy of the ions due to the permanent lattice defects. Rush et al. have shown that doping of BaLiF$_3$ with oxygen anions causes an increase of the ionic conductivity suggesting that the mobile defects are F$^-$ vacancies. They reported an activation energy of 0.50 eV for F$^-$ vacancy migration and 0.55 eV for F$^-$ interstitial migration. The latter was deduced from BaLiF$_3$ crystals doped with Ce$^{3+}$ which most likely produces F$^-$ interstitials at large Ce$^{3+}$ concentrations. Li vacancies are reported to be formed at low Ce$^{3+}$ concentrations. One might suppose that ion conductivity in the extrinsic region is due to F$^-$ vacancy migration. However, it is worth noting that preliminary $^7$Li NMR line shape measurements give evidence that the Li cations are mobile, too. Certainly, it cannot be excluded that F$^-$ vacancies are particularly formed during the crystal-growth process described above. Hence, the observation of an extrinsic dc-conductivity region is not surprising at all. We have observed a slight shift of the extrinsic dc-conductivities towards larger values when the single crystal, which was kept under inert gas atmosphere inside the impedance cell, was exposed to very high temperatures of about 1000 K. Presumably, point defects formed at high T are responsible for the enhanced conductivity in the extrinsic region pointing out that the thermal history of the sample is relevant for its transport behaviour.

c Influence of grain boundaries on ion transport. When the single crystal was ground by hand using an agate mortar and the resulting powder was pressed into a pellet for impedance measurements afterwards, the dc-conductivity clearly decreased as is shown in Fig. 12. Obviously, grain boundaries introduced have a pronounced blocking effect on long-range ionic transport and mask the observation of the fast transport processes in the bulk. The activation energies of both the intrinsic and extrinsic conduction processes increase by about 0.4 eV. From the corresponding complex plane plots as well as the impedance spectra the electrical response resulting from grain boundaries can be clearly differentiated from that which is attributed to ion transport taking place in the bulk material. As an example, in Fig. 13 the Cole–Cole plot of the powdered BaLiF$_3$ crystal is compared with that of the intact single crystal recorded at the same temperature and corrected for the different sample thickness and diameter. In accordance with this plot, the corresponding impedance spectra show another plateau at frequencies larger than 10$^3$ Hz. The corresponding conductivities $\sigma'$ of the second plateau are in good agreement with those of the single crystal (see Fig. 10(b)). Consistently, below 650 K the modulus peaks of the powdered sample exhibit a shallow shoulder located on the low frequency side of $\eta''(\omega)$. This might be attributed to ions located near the grain boundary regions showing electrical relaxation frequencies in the kHz range. In contrast, the electrical response of the microcrystalline sample which was conventionally prepared by solid-state synthesis (see above, cf. Fig. 1(d)) seems to be fully determined by grain boundary effects which drastically limit long-range transport in BaLiF$_3$.
at least below 750 K. The corresponding activation energy $E_a$ energy turns out to be about 1.2 eV.

**d Ionic dc-conductivity of structurally different forms of BaLiF$_3$.** For comparison, the temperature dependencies of $\sigma_{dc}$ of single crystalline BaLiF$_3$, the conventionally prepared counterpart as well as of the mechanosynthesized material are shown in Fig. 14. Although the mechanosynthesized, nanocrystalline material can be characterized by a large volume fraction of grain boundaries, its dc-conductivity is comparable to that of the extrinsic one of the single crystal (450 $K < T < 500$ K). Obviously, the increased defect concentration in nanocrystalline BaLiF$_3$ introduced by ball milling compensates for the effect of blocking grain boundaries so that long-range transport can occur resulting in an overall high ionic dc-conductivity. Above 500 K the dc-conductivity of the nanocrystalline material even starts to exceed that of the single crystalline material. Compared to the activation energy characterizing intrinsic ion conduction in the single crystal, $E_a$ of the mechanosynthesized sample is by a factor of about 3/4 lower. However, it is worth noting that in many cases the microstructure of the grain boundaries of mechanically treated materials is expected to differ from that of coarse-grained and even structurally well-ordered nanocrystalline materials. Recently, this was shown using LiNbO$_3$ which can be prepared in structurally different forms, too. The dc-conductivity of ball-milled LiNbO$_3$ ($\langle d \rangle = 20$ nm) is by many orders of magnitude higher than that of the single crystalline LiNbO$_3$ counterpart. Moreover, it is comparable to that of fully X-ray amorphous LiNbO$_3$. High-resolution (HR) TEM and EXAFS measurements gave direct evidence for an amorphous grain boundary structure of the nanocrystalline material which was prepared using a high-energy shaker mill. This is in contrast to a nanocrystalline sample obtained by partial calcination of amorphous LiNbO$_3$. No indications could be found for a large volume fraction of amorphous LiNbO$_3$ in such a sample. In contrast to that result, preliminary HR-TEM images of mechanosynthesized BaLiF$_3$ show that the nm-sized crystallites are covered by a thin amorphous layer of about 2 nm in thickness. Thus, one might assume that once again structurally disordered interfacial regions have to be considered when discussing the observed trends of $\sigma_{dc}$ presented in Fig. 14.

For the sake of completeness, the dc-conductivity values of mechanosynthesized BaLiF$_3$ which was annealed for some tens of hours at elevated temperature are included in Fig. 14, too. The samples annealed at 870 K for 24 h and 50 h, respectively, have average crystallite diameters with values in the nm range (see the corresponding XRD-pattern of the sample annealed for 24 h in Fig. 1). The activation energies $E_a$ found are very similar and amount to be about 1.0 eV, thus, almost identical with that one of intrinsic conduction in single crystalline BaLiF$_3$. Preliminary TEM micrographs reveal that the annealed samples consist of nm-sized particles which are sintered together forming relatively large interconnected cluster assembled agglomerates.

Annealing a mechanosynthesized sample at 1020 K for 5 h resulted in an additional decrease of $\sigma_{dc}$ finally reaching the ionic conductivity of the microcrystalline material as expected. It is worth mentioning that an increase of the uniaxial pressure applied to prepare dense impedance pellets by about a factor of four does not lead to any changes of the conductivity results of the annealed samples. Thus, the lower conductivity found for the annealed samples cannot be interpreted in terms of the samples’ package densities.

Interestingly, ac-conductivities read out at 1 MHz, see Fig. 9, reveal that short range ion motions in the nanocrystalline as prepared sample are very similar to those of the annealed one which was heated at, e.g., for 50 h at 870 K. This indicates a comparable and relatively high bulk conductivity of the two samples which is characterized by an activation energy of about 0.6 eV (see above).

Note that both ball milling and annealing of the materials were carried out in air atmosphere. As mentioned above, one might expect that if oxygen incorporation occurs this would lead to an increase of the dc-conductivity presumably due to the formation of vacant fluorine positions. To explore this, we have mechanosynthesized BaLiF$_3$ under inert gas atmosphere, too. Remarkably, a slight enhancement of $\sigma_{dc}$ by a factor of approximately two is found (see Fig. 14) rather than a decrease. Accordingly, the activation energy is reduced to 0.68 eV. Careful inspection of the $\sigma_{dc}$ values of the sample prepared under inert gas atmosphere reveals a slight deviation from Arrhenius behaviour below 410 K (see dotted line in Fig. 14). It has still to be checked if this is caused by extrinsic ion conduction. For comparison with the data of the single crystal, the activation energy corresponding to the dashed line in Fig. 14 turns out to be 0.45(5) eV. In order to confirm or rule out such a contribution, an impedance analyzer being able to detect dc-conductivities smaller than $10^{-17}$ S will be employed.

Finally, preliminary impedance measurements show that by appropriate doping of mechanosynthesized BaLiF$_3$ with Sr$^{2+}$, which can be easily carried out by milling a mixture consisting of BaF$_2$, SrF$_2$, and LiF, the electric conductivity can be further

![Fig. 14 Temperature dependence of $\sigma_{dc}$ of single-crystalline, conventionally prepared microcrystalline and mechanosynthesized BaLiF$_3$. For comparison, the $\sigma_{dc}$ values of mechanically synthesized BaLiF$_3$ which was annealed for 24 and 50 h, respectively, are also shown. Solid lines show fits according to an Arrhenius law (cf. eqn (6)).](image-url)
increased by one order of magnitude. Details about BaLiF₃ samples modified in such a way will be reported in a subsequent paper.

IV. Summary and conclusion

BaLiF₃ served as an interesting model system to study the effects of nanostructuring and structural disorder on long-range as well as short-range ion motions in solids. It belongs to one of the rare fluorides which crystallize with the anti-perovskite structure. Nanocrystalline samples can be prepared with high purity by high-energy ball milling of a stoichiometric mixture of LiF and BaF₂. Mechanical treatment of the binary source materials for 3 h in a planetary mill at 600 rpm yields BaLiF₃ nano-crystallites with a mean diameter of approximately 30 nm. Interestingly, the activation energy of the nanocrystalline sample is much smaller than that of the coarse-grained counterparts including also samples which were obtained by appropriate heat-treatment of the as prepared mechano-synthesized material. It was shown that both ball-milling and subsequent annealing allow the adjustment of desired transport parameters over a dynamic range of some decades. Such a knowledge-based controlling of transport properties is essential for the design of new functional materials.

The influence of grain boundary regions on ion transport was studied by comparing a single crystal, which shows a relatively high extrinsic ionic conductivity from the outset. Single crystalline BaLiF₃ shows two conductivity regions which can be ascribed to intrinsic and extrinsic ionic transport. As expected, the respective activation energies differ by about a factor of two reflecting the migration activation energy and the total activation energy. The latter comprises both the migration as well as the formation activation energy of the charge carriers. In the powdered sample the extrinsic conductivity region starts to be masked by grain boundary effects obviously limiting ion transport in the inverse perovskite structure of BaLiF₃. These seem to have a non-blocking character in the case of mechanically prepared, nanocrystalline BaLiF₃ with a large amount of interfacial regions and grain boundaries. The blocking character reappears when the nanocrystalline sample is annealed at higher temperatures. It became obvious that the microstructure of a material with a given chemical composition can have a drastic effect on its ionic transport parameters, see also ref. 21, 64–67.

It will be a challenge to study the structural details of the different samples from a microscopic point of view. For this purpose NMR measurements, see, e.g., ref. 21, 68–72, are underway which are suitable to study Li and F diffusion parameters separately from each other.

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