Ion conduction and dynamics in mechanosynthesized nanocrystalline BaLiF₃

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Abstract

Highly pure nanocrystalline BaLiF₃ (space group Pn̅3m, inverse perovskite structure) with a mean crystallite size of the order of 30 nm was mechanosynthesized from the binary fluorides LiF and BaF₂. The source materials with μm-sized crystallites were treated in a planetary mill for several hours at ambient temperature. The product is characterized by X-ray diffraction and transmission electron microscopy. Its ionic conductivity was probed by solid state impedance spectroscopy. For comparison, a coarse-grained sample of BaLiF₃ with a mean crystallite diameter in the μm range was synthesized by conventional high-temperature ceramic synthesis. The ionic conductivity (dc) of the mechanosynthesized nanocrystalline sample, which is characterized by a large fraction of interfacial regions, is by about three orders of magnitude (T = 570 K) larger than that of the conventionally prepared one. Preliminary temperature-variable ⁷Li NMR spectra provide first insights into the Li dynamics of the samples studied.

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1. Introduction

Nanocrystalline ceramics [1,2], which show fast ionic conduction, increasingly play an important role in the development of sustainable energy storage systems, chemical sensors or advanced electrochromic devices [3–7]. The investigation of ion transport in materials with the same chemical composition but different crystallite sizes and microstructures might inter alia help to understand the influence of interfacial effects on dynamic properties [8–11]. Such a knowledge is crucial for the development of new functional materials.

Recently, it has been shown that the Li ion conductivity in lithium tantalate (LiTaO₃), which was used as a model substance to study the influence of structural disorder on ionic transport, can be increased by several orders of magnitude when the coarse-grained source material is treated for several hours in a high-energy ball mill [8]. Similar results are obtained for other materials such as lithium niobate (LiNbO₃) [9,10] or the binary fluorides BaF₂ and CaF₂ which form a highly defective nanocrystalline mixed phase (Ba, Ca)F₂ when milled together [12,13].

The ternary fluoride BaLiF₃ crystallizing with the space group Pm̅3m (inverse perovskite structure) [14] is another interesting model system to study ionic transport in a ceramic which can be prepared in a nano- and microcrystalline as well as single crystalline form [15]. In the present study nanocrystalline BaLiF₃ was mechanosynthesized from LiF and BaF₂ using a high-energy planetary mill at ambient temperature. Its ionic conductivity (dc), which was measured by impedance spectroscopy, exceeds that of the microcrystalline counterpart by nearly three orders of magnitude. This might be ascribed to the large fraction of interfacial regions providing fast diffusion pathways of the ions as well as the large amount of defects introduced by ball milling. Remarkably, the material is relatively stable against grain growth up to approximately 550 K so that the high ionic conductivity is preserved even at elevated temperatures.

2. Experimental

2.1. Preparation of BaLiF₃

Nanocrystalline BaLiF₃ was prepared by high-energy ball milling of an equimolar mixture of LiF (99.99%, Alfa Aesar) and BaF₂ (99.99%, Sigma Aldrich) in a Fritsch Pulverisette 7 (premium line). A grinding beaker made of stabilized ZrO₂ (45 mL) and 140 balls (5 mm in diameter) of the same material were used. The mixture was milled for tₘₐₓ = 180 min with 600 rpm under ambient atmosphere. A part of the so obtained material was pressed to pellets with a diameter of 8 mm by applying a uniaxial pressure of 1 GPa. After that these pellets were annealed at 870 K in air for 24 h.

For comparison, a sample of BaLiF₃ was prepared by conventional solid state synthesis [16]. To this end an equimolar mixture of BaF₂ and LiF was initially milled for 10 min at 600 rpm under air. After heating the mixture for 3 h at 620 K for drying purpose it was fired at 1020 K for 5 h. The complete synthesis was strictly done under N₂.

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atmosphere. It has to be mentioned that the conventional synthesis is disadvantageous compared to the one-step mechanochemical routine. Since Li starts to evaporate at high temperatures it needed several attempts to find a tolerable mixing ratio close to LiF:BaF₂. Nevertheless this synthesis route leads to a less pure and less stoichiometric product.

2.2. XRD, TEM, impedance and NMR measurements

The characterization of the samples was carried out at room temperature using X-ray diffraction (XRD) with a Philips PW 1800 operating with Cu-Kα radiation at 40 kV. An HP 4192 A analyzer connected to a home-built cell was employed to record the impedance data. Frequencies investigated ranged from 5 Hz to 13 MHz. Conductivity jigs with a four terminal configuration were used. The samples were pressed to cylindrical pellets (8 mm in diameter, about 1 mm in thickness) with a uniaxial pressure of about 1 GPa. Electrodes were applied by subsequent pressing the uncoated pellet between Pt powder. During the measurements the pellet was kept under inert gas atmosphere by using a constant flow of dry nitrogen (99.999%).

\(^{19}\)F magic angle spinning (MAS) NMR spectra were acquired with a Bruker Avance III 500 wideband spectrometer operating at a radio frequency of 471 MHz. The spectra were recorded using a single excitation pulse (pulse length π/2 = 2 μs) at an ultra-fast spinning speed of 60 kHz. Static \(^{7}\)Li NMR spectra were recorded with a Bruker MSL 400 spectrometer connected to a shimmed Oxford cryomagnet with a fixed field of 9.4 T corresponding to a \(^{7}\)Li resonance frequency of 155 MHz. The π/2 pulse length was about 3 μs.

For transmission electron microscope (TEM) investigations, a powder specimen was dispersed in ethanol, and a drop of 10 μL of suspension was dried on a copper-supported holey carbon film. (Scanning) transmission electron microscopy (STEM) was made at 200 kV on a field-emission instrument of the type JEOL JEM-2100F-UHR in bright-field, dark-field, and phase contrasts.

3. Results and discussion

In Fig. 1 the XRD patterns of the samples investigated are shown. BaLiF₃ is the only phase which is formed by high-energy ball milling a stoichiometric mixture of LiF and BaF₂. Compared to the sample prepared by solid state synthesis, which shows a small amount of residual BaF₂ [17], the mechanosynthesized product is remarkably pure. As expected, the XRD peaks of the nanocrystalline material are broadened due to size effects and strain. Disregarding the latter, a mean crystallite size of approximately 30 nm can be roughly estimated using the equation introduced by Scherrer [18]. Details for such an estimation in a similar system can be found elsewhere [12]. Annealing the nanocrystalline material at 870 K for 24 h causes a decrease of the diffraction peak widths leading to crystallites with diameters in the μm range. Interestingly, the XRD peak widths of this annealed sample are even smaller than those of the material which was prepared by solid state synthesis, i.e., fired for 5 h at about 1020 K.

The particle sizes determined from TEM micrographs (see Fig. 2) are in fair agreement with the values deduced from XRD peak broadening. The nanocrystalline sample consists of cluster-assembled particles whose diameters range from 50 to 100 nm. A significant amount of amorphous material is not observed. However, the particles seem to be covered with an amorphous-like layer with a thickness of only 1 nm, see the high-resolution (HR) TEM micrograph in Fig. 3. In contrast to that, the TEM image of the annealed sample reveals a homogenous material consisting of μm-sized particles being interconnected to each other, while those of the sample prepared by solid state synthesis are characterized by a large distribution of different sizes ranging from some tens of nanometer to some μm. However, the volume fraction of μm-sized particles clearly dominates as compared to that of the nano-particles. The presence of very small crystallites next to larger ones points to an unfinished Ostwald ripening process, i.e., larger particles grow on expense of the smaller ones in order to minimize the energy of the system [19]. Let us mention that it is known for some materials that annealing of a metal or ceramic powder consisting of particles with diameters in the range of some nanometers leads to microcrystalline materials with improved properties such as hardness and ductility [20–22]. Here, annealing of mechanosynthesized nanocrystalline BaLiF₃ seems to represent an interesting synthesis route to obtain μm-sized and uniformly shaped crystallites.

Further characterization of the samples was carried out by \(^{19}\)F MAS NMR. Corresponding spectra are shown in Fig. 4. Expectedly, BaLiF₃ shows only a single NMR line whose isotropic chemical shift δ is 66 ppm when referenced to C⁶F₆. This is in perfect agreement with the value reported in the literature [23].

![Fig. 1. X-ray powder diffraction patterns of a) mechanosynthesized nanocrystalline BaLiF₃, b) the mechanosynthesized sample after annealing for 24 h at 870 K and c) the sample prepared by solid state synthesis at higher temperature. Vertical lines indicate the positions and intensities of the XRD peaks of the source materials BaF₂ and LiF, respectively.](image-url)
was annealed for 24 h, the $^{19}$F MAS NMR line width of the nanocrystalline material is broadened indicating a large distribution of slightly different chemical environments of the F ions. This unequivocally points to a material with a large number density of structural defects.

In Fig. 5 the temperature dependence of the dc conductivity $\sigma_{dc}$ of mechanosynthesized BaLiF$_3$, its annealed counterpart as well as that prepared by conventional solid state synthesis are shown in an Arrhenius plot. $\sigma_{dc}$ values were determined from the frequency independent plateau of the corresponding impedance spectra. The mechanosynthesized sample shows the highest dc conductivity with an activation energy $E_a$ of 0.74(1) eV. After annealing, $\sigma_{dc}$ decreases by about 1.5 orders of magnitude and $E_a$ increases to 1.04(3) eV. The sample prepared by solid state synthesis exhibits a dc conductivity which is about three orders of magnitude ($T = 560$ K) lower than that of the sample prepared by ball milling. Accordingly, it shows the highest activation energy ($E_a = 1.18(1)$ eV). Regarding the TEM micrographs presented above, it seems reasonable that the lower dc conductivity of the conventionally prepared material is caused by grain boundaries blocking long-range ionic transport (see also Ref. [17]). Let us note that annealing the mechanosynthesized sample for 5 h at 1020 K leads to a microcrystalline material whose $\sigma_{dc}$ values are very similar to those obtained for the material prepared conventionally.
Although the mechanosynthesized sample is characterized by a large volume fraction of grain boundaries and interfacial regions its dc conductivity is higher than those found for the other two samples. Therefore, it seems reasonable that the interfacial regions, in contrast to those of the samples with µm-sized crystallites, provide pathways for fast ion transport. Most likely, these regions are characterized by a large number fraction of defects introduced by mechanical treatment.

In Fig. 6 temperature-variable $^7$Li NMR spectra recorded at a resonance frequency of 155 MHz are shown. The spectra were obtained by Fourier transformation of the free induction decay which is obtained after excitation of the sample with a single radio frequency pulse. Due to the cubic symmetry of BaLiF$_3$ quadrupole intensities are absent although $^7$Li is a spin-3/2 nucleus. In the case of the mechanosynthesized sample NMR echo techniques may be helpful to detect Li ions residing in distorted polyeder with lower symmetry. Presumably, such quadrupole intensities are expected for those Li ions residing near or in the interfacial regions of the nanocrystalline sample. Here, we will restrict ourselves to discuss the central transition only. At low temperatures the NMR lines of all three samples are dipolarly broadened due to $^7$Li–$^7$Li as well as $^7$Li–$^{19}$F interactions. In the so-called rigid-lattice regime the line width $\Delta$ (full width at half maximum) is of the order of 8 kHz. It is worth mentioning that the NMR line shape of a powder sample of BaLiF$_3$ significantly deviates from a pure Gaussian. This can be explained regarding the investigation of Goto et al. who recorded NMR line widths of a BaLiF$_3$ single crystal as a function of its orientation in the static magnetic field [24]. The observed line shape here for a powder sample is the superposition of the NMR lines shown by Goto et al [24].

In general, with increasing temperature Li diffusivity increases and the mean jump rate reaches the order of the rigid-lattice value of $\Delta$. Consequently, $\Delta$ decreases due to averaging of dipole–dipole interactions [25]. Therefore, the NMR line shows the typical motional narrowing due to Li jumps with rates of the order of $10^{-4} \text{ s}^{-1}$ [26]. Finally, at sufficiently high temperatures the line width is solely determined by the inhomogeneity of the static magnetic field used (extreme narrowing regime). Motional line narrowing is clearly seen for the sample prepared conventionally (Fig. 6c) as well as for that which was mechanosynthesized but annealed at higher temperatures (Fig. 6b). More precisely, the conventionally prepared sample exhibits a so-called heterogeneous motional narrowing. For comparison, it shows a heterogeneous distribution of crystallite sizes. For example, at $T = 510$ K the $^7$Li NMR line is composed of a broad and narrow contribution (Fig. 6c). The latter increases with increasing $T$ reaching an area fraction of about 45% at 630 K. In contrast, the NMR line of the annealed sample is composed of only a single Lorentzian shaped NMR line at this temperature. Motional narrowing of this sample seems to

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**Fig. 5.** Arrhenius diagram of the dc conductivity plotted as $\sigma_\text{dc}T$ vs. the inverse temperature of mechanosynthesized BaLiF$_3$ as well as its annealed counterpart. For comparison, data of the sample synthesized via a ceramic route is also shown.

**Fig. 6.** a) Temperature-variable $^7$Li NMR spectra of mechanosynthesized BaLiF$_3$ which were recorded at a resonance frequency of 155 MHz. b) $^7$Li NMR spectra obtained after the nanocrystalline sample (see (a)) was exposed to 870 K for 24 h. c) Corresponding NMR spectra of BaLiF$_3$ prepared using a ceramic synthesis route.
be more homogenous which might be related to the microstructure observed by TEM, see above.

Surprisingly, up to $T = 630 \, \text{K}$ no such significant motional narrowing of the $^7\text{Li}$ NMR line is observed for the mechanosynthesized sample (Fig. 6a), which, in contrast to the $\mu\text{m}$-sized samples, shows the highest dc conductivity (Fig. 5). So far, preliminary $^{19}\text{F}$ NMR spectra at temperatures up to 473 K do not indicate a large amount of highly mobile F anions overcompensating the apparently low Li diffusivity observed (Fig. 6a). It is worth noting that dc conductivity measurements are sensitive to long-range Li transport rather than to short range motions which also affects NMR line shapes. Thus, the observed motional narrowing of the coarse-grained samples might be caused by fast Li motions within a crystallite but grain boundaries might block long-range motions of the Li ions. Interestingly, these fast Li ions cannot be clearly resolved in the case of the mechanosynthesized sample. The enhanced dc conductivity of the nanocrystalline material might be explained by a small number fraction of highly mobile Li (and/or F anions) located in the interfacial regions which are different in microstructure when compared to those of the annealed counterpart. Possibly, these regions form a network of fast diffusion pathways for the ions. A rather small number fraction of mobile ions might be hardly detectable by recording NMR line shapes.

Certainly, further $^7\text{Li}$ NMR and $^{19}\text{F}$ NMR measurements including spin-lattice relaxation techniques\cite{2,25} are necessary to figure out the different diffusivities of the two charge carriers in BaLiF$_3$. However, already now the NMR results indicate that ionic conduction in nanocrystalline BaLiF$_3$ seems to be quite different from that observed for the microcrystalline counterpart.

4. Conclusion

Nanocrystalline BaLiF$_3$ can be easily prepared and in high purity by high-energy ball milling from BaF$_2$ and LiF at ambient temperature. The dc conductivity (at $T = 560 \, \text{K}$) is about three orders of magnitude higher than that of a sample obtained by conventional solid state synthesis carried out at high temperature. Probably, in the coarse-grained material blocking grain boundaries affect charge carrier transport over long distances. A similar situation is found for a sample which was obtained by annealing the as-prepared nanocrystalline material. However, $^7\text{Li}$ NMR line shape measurements indicate fast Li motion in the microcrystalline materials. Although a higher dc conductivity and lower activation energy is found for the mechanosynthesized sample, a significant motional narrowing of the $^7\text{Li}$ NMR line is not observed. However, the enhanced transport properties might be explained by a fast interfacial diffusion process.

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References

\cite{2} P. Heitjans, M. Wilkening, MRS Bull. 34 (2009) 915.
\cite{6} S. Davis, A.V. Chadwick, J.D. Wright, J. Mater. Chem. 8 (1998) 2065.
\cite{14} A. Boumrirche, J.Y. Gesland, A. Bulou, M. Rousseau, J.L. Fourquet, B. Hennion, Solid State Commun. 91 (1994) 125.
\cite{18} P. Scherrer, Göttinger Nachrichten 2 (1918) 89.