Ion Transport Properties of the Inverse Perovskite BaLiF$_3$ Prepared by High-Energy Ball Milling

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For many applications such as advanced energy storage systems, chemical sensors or electrochromic devices fast ionic conduction plays an important role. In many cases, see *e.g.*, Refs. [1-3], nanocrystalline ceramics with crystallite diameters smaller than 50 nm show an enhanced ion conductivity compared to their coarse-grained counterparts, *i.e.*, single crystals or materials with µm-sized particles. This observation can be explained by their large fraction of structurally disordered interfacial regions providing fast migration pathways for the ions [2,3]. Mechanical treatment of µm-sized particles in a high-energy ball mill represents a simple technique to obtain large quantities of a nanocrystalline material. In addition to that it is also possible to synthesize ceramics directly by ball milling [3]. In many cases this leads to metastable, non-equilibrium compounds which cannot be prepared following conventional synthesis methods [4,5].

In the present paper, BaLiF$_3$, the only known inverted perovskite of the AMF$_3$ compounds [6], was prepared by high-energy ball milling using a Fritsch P7 planetary mill (premium line). An equimolar mixture of LiF and BaF$_2$ with an overall mass of 2 g was treated in a 45 mL zirconia vial with 140 balls of the same material for 3 h at a rotational speed of 600 rpm. As verified by X-ray diffraction highly pure BaLiF$_3$ is obtained which shows an average crystallite size d of about 30 nm. d was estimated with the equation introduced by Scherrer [7]. This is in contrast to a sample which was synthesized via conventional solid state synthesis showing µm-sized crystallites. The latter was prepared by heating an equimolar mixture of LiF and BaF$_2$ for two hours at 620 K. After that the sample was fired at 1020 K for 5 hours under nitrogen atmosphere. Ionic conductivities were measured by impedance spectroscopy using an HP 4192A analyzer (5 Hz to 1 MHz) in combination with a home-built cell. The dc-conductivities were obtained from the frequency independent plateau of the corresponding impedance spectra (not shown for the sake of brevity). In Fig. 1 $\sigma_{dc}T$ vs the inverse temperature $1/T$ of the two samples is shown in semi-logarithmic representation. As can be clearly seen, at $T = 550$ K, for example, σ_{dc} of the mechanosynthesized product is by approximately three orders of magnitude
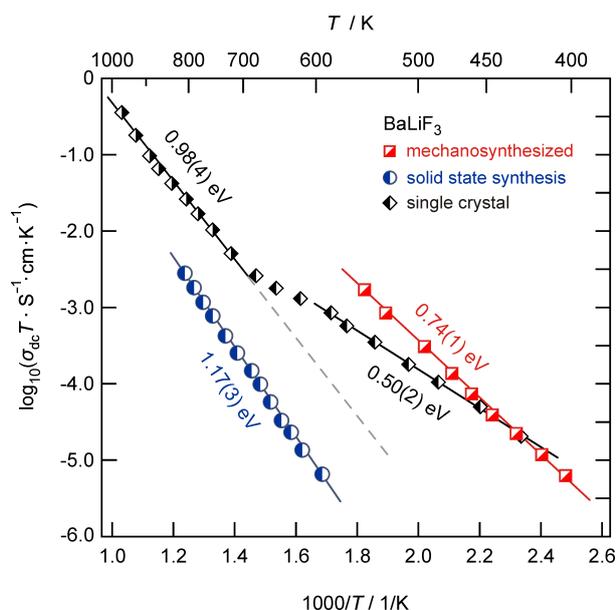
Fig. 1 Temperature dependence of $\sigma_{dc}T$ of mechanosynthesized and conventionally prepared BaLiF$_3$. Whereas the first shows a crystallite size in the nm-range, the latter consists of μm-sized particles. For comparison, the ionic conductivity of a single crystal is also shown. Solid lines represent fits according to equation (1).

larger than that of the conventionally prepared material. As a function of temperature $\sigma_{dc}T$ follows Arrhenius behavior according to

$$\sigma_{dc}T = \sigma_0 \exp\left(-E_a / (k_B T)\right) \qquad (1)$$

where σ_0 is the pre-exponential factor, k_B Boltzmann's constant and E_a the activation energy characterizing long-range ion transport. E_a of the ball milled sample (0.74(1) eV) is by about 40 % lower than that of the coarse-grained product (1.17(4) eV). For comparison, Fig. 1 includes also $\sigma_{dc}T$ values of a BaLiF$_3$ single crystal whose electrical response is characterized by ideal Debye behavior as can be clearly seen when the impedance spectra and complex plane plots are regarded [8]. Whereas at temperatures higher than 700 K (intrinsic region of ionic conduction) an activation energy (0.98(4) eV) similar to that of the sample prepared by solid state synthesis is found, in the low temperature range ($T < 650$ K, extrinsic region) the activation energy is only 0.5 eV. Interestingly, in that temperature region single crystalline BaLiF$_3$ shows a rather high ionic conductivity, see also Ref. [9], which is comparable to that of the mechanosynthesized, nanocrystalline fluoride. This is in contrast to a similar study using LiNbO$_3$ as model substance; the ionic conductivity of single-crystalline LiNbO$_3$ is by many orders of magnitude smaller than those of ball milled as well as amorphous LiNbO$_3$ [2].

Obviously, the microstructure of the coarse-grained sample prepared at 1020 K has a blocking effect on long-range ion transport in BaLiF$_3$ which is not the case for the single crystal as well as the structurally disordered, nanocrystalline material. A detailed characterization of the samples by high-resolution transmission electron microscopy as well as by temperature-dependent ^{7}Li and ^{19}F NMR spectroscopy is currently under way in our lab. This will help (i) to determine diffusion parameters on a shorter length-scale, (ii) to clarify the dominant charge carriers in the structurally different samples as well as (iii) to characterize their different microstructures from an atomic-scale point of view.

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