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Ionic Transport in Mechanosynthesized Nanocrystalline $LiBaF_3$

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1. Introduction

$LiBaF_3$ single crystals are considered to act as promising window material in the vacuum-ultraviolet wavelength region [1]. $LiBaF_3$ is the only known ternary fluoride which crystallizes in the cubic inverse perovskite-type structure with the space group $Pm\bar{3}m$ (a = 0.3996 nm) [2, 3]. In this paper we report on a very simple and efficient method to synthesize nanocrystalline $LiBaF_3$ by high-energy ball milling of LiF and BaF_2. Ionic transport properties of the mechanically prepared sample were investigated by complex impedance spectroscopy. The results are compared with those obtained for microcrystalline $LiBaF_3$ which was prepared by conventional solid state synthesis.

2. Experiment

Mechanosynthesis of $LiBaF_3$ using reagent grade BaF_2 (99,99 %, Sigma Aldrich) and LiF_2 (99,99 %, Alfa Aesar) was carried out at room temperature with a Fritsch planetary mill (Pulverisette 7, premium line). The mixture was milled at 600 rpm for 3 h in a 45 mL grinding beaker made of ZrO_2 together with 140 milling balls (5 mm in diameter) made of the same material. For comparison, $LiBaF_3$ was also prepared by ceramic synthesis at 1023 K under nitrogen atmosphere. Details can be found in Ref. [4].
All products were characterized by X-ray powder diffraction with a Philips X'Pert MPD using Cu-K_α radiation. Impedance spectra were recorded by means of an HP 4192A analyzer working at frequencies ν ranging from 5 Hz to 13 MHz.

3. Results and Discussion

In Fig. 1(left) the X-ray diffraction patterns of $LiBaF_3$ are shown which was prepared by solid state synthesis (a) and high-energy ball milling (b) of an equimolar mixture of BaF_2 and LiF. Evidently LiF and BaF_2 transform completely into $LiBaF_3$ since there are no peaks visible pointing to residual LiF and BaF_2. The third X-ray pattern of Fig. 1 shows that of a ball milled mixture with excess BaF_2 (c). Besides cubic nanocrystalline BaF_2 the formation of a small amount of the orthorhombic phase being a high-pressure modification of BaF_2 is detected. The average crystallite diameter $\langle d \rangle$ of mechanosynthesized $LiBaF_3$, which was estimated using Scherrer's equation, is about 30 nm irrespective of the volume fraction of BaF_2 present. Expectedly, $\langle d \rangle$ of $LiBaF_3$ prepared via solid state synthesis at high T lies in the µm-range.

The dc conductivities σ_{dc} of the three samples differ greatly. σ_{dc} values were determined from the frequency independent plateau of the corresponding impedance spectra. In Fig. 1 (right) $\sigma_{dc}T$ is plotted *vs* reciprocal temperature. The sample prepared by solid state synthesis shows the lowest conductivity and the highest activation energy E_A of 1.2 eV. Compared to that result, σ_{dc} of the mechanosynthesized sample is increased by

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about 2.5 orders of magnitude while E_A decreases to ca. 0.8 eV. This increase of σ_{dc} might be attributed to highly mobile ions in the structurally disordered interfacial regions of nanocrystalline $LiBaF_3$. Quite recently, a similar trend of σ_{dc} was also observed for mechanically treated pure BaF_2 and CaF_2 [5].

The presence of excessive BaF_2 leads to a further increase of σ_{dc} by about two orders of magnitude. However, σ_{dc} of this composite does not exceed that of nanocrystalline BaF_2 which was prepared from coarse grained BaF_2 under the same milling conditions, see Refs. [5,6].

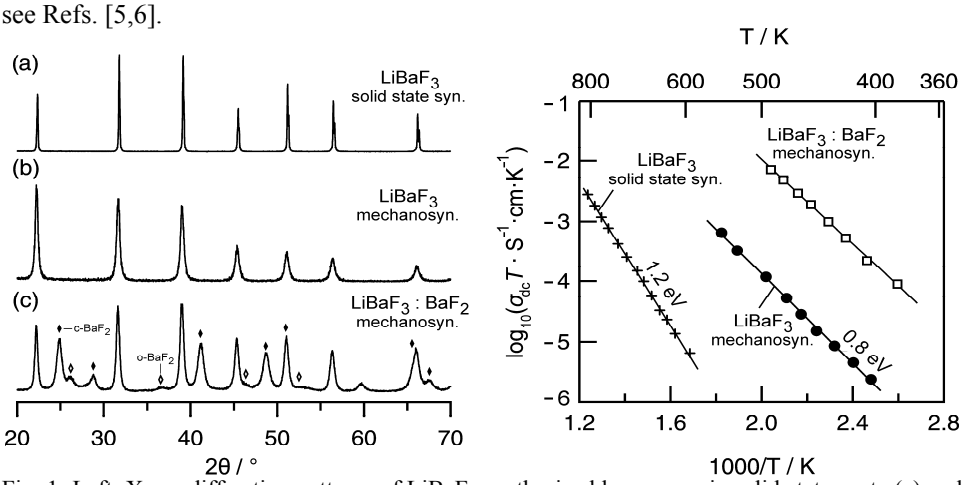

Fig. 1: Left: X-ray diffraction patterns of $LiBaF_3$ synthesized by a ceramic solid state route (a) and mechanically by high-energy ball milling (b) and (c). Right: Arrhenius plot of the ionic conductivities of the samples indicated on the left, plotted as $\sigma_{dc}T$ *vs* $1/T$, with activation energies as given.

4. Conclusion

$LiBaF_3$ can easily and with high purity be prepared by high-energy ball milling. The obtained material shows improved transport properties compared to conventionally prepared $LiBaF_3$. This opens a wide field for materials engineers to use high-energy ball milling for the synthesis of fast ionic conductors.

References

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