Mixed Ionic Conduction in Nano- and Microcrystalline BaLiF₃

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BaLiF₃ is one of the rare compounds which crystallize in the cation inverted perovskite structure, i. e. in which Li⁺ instead of the higher charged Ba²⁺ is octahedrally coordinated by the anions. BaLiF₃ is a potential material for vacuum ultraviolet (VUV) lasers and lenses. It can be prepared easily and phase pure by high-energy ball milling a stoichiometric mixture of BaF₂ and LiF in a planetary ball mill. Furthermore it consists solely of NMR active nuclei of which two might be mobile in the material. Therefore, BaLiF₃ is an interesting model system for the investigation of ion transport phenomena. Nevertheless, the question whether F⁻, Li⁺ or both ions are mobile still remained open. First temperature variable ⁷Li NMR measurements revealed a motional narrowing of the NMR line of BaLiF₃ at elevated temperatures [1]. However, it was unclear whether this motional narrowing is due to the fast motion of Li ions or the fast motion of neighboring fluoride ions coupling with the Li ions.

To reveal which ion species is moving, the ¹⁹F nuclei were decoupled from the ⁷Li nuclei in an NMR experiment. Therefore, the motional narrowing of the ⁷Li NMR line observed at temperatures beyond ~610 K for microcrystalline BaLiF₃ shown in Fig. 1a is clearly caused by the fast motion of the Li ions. At the very same temperature a narrow NMR line occurs also in the ¹⁹F NMR spectrum recorded while decoupling ⁷Li from ¹⁹F. Since the rigid lattice linewidth of the ¹⁹F NMR line is clearly larger than the one of the ⁷Li NMR line, see Fig. 1a, it seems plausible to assume a higher jump rate for the fluoride ions than for the Li ions at 610 K, which is in qualitative agreement with theoretical predictions reported in the literature [2]. Interestingly, mechanosynthesized, nanocrystalline BaLiF₃ revealed a dc conductivity being increased by about 1.5 orders of magnitude compared to that of microcrystalline BaLiF₃ showed almost no fast moving ions at all, see Fig. 1b. Since polarization measurements exhibited no noteworthy electronic conduction in the mechanosynthesized material, it seems that the number of ions contributing to the conductivity is larger in nanocrystalline BaLiF₃ than in the microcrystalline material.

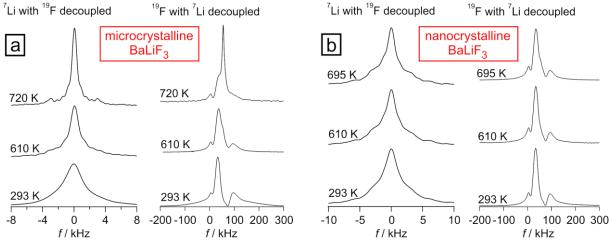


Figure 1: Temperature variable ⁷Li and ¹⁹F MAS NMR spectra recorded while decoupling the respective other nuclei for microcrystalline (a) and nanocrystalline BaLiF₃ (b) with $v_0(^7Li) = 233$ MHz, $v_0(^{19}F) = 565$ MHz and $v_r = 3$ kHz.



References

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