Mixed Ionic Conduction in Nano- and Microcrystalline $BaLiF_3$

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$BaLiF_3$ is one of the rare compounds which crystallize in the cation inverted perovskite structure, i. e. in which Li^+ instead of the higher charged Ba^{2+} is octahedrally coordinated by the anions. $BaLiF_3$ 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 BaF_2 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, $BaLiF_3$ 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 $BaLiF_3$ 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 ^{19}F 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 $BaLiF_3$ 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 ^{19}F NMR spectrum recorded while decoupling ^7Li from ^{19}F. Since the rigid lattice linewidth of the ^{19}F 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 $BaLiF_3$ revealed a dc conductivity being increased by about 1.5 orders of magnitude compared to that of microcrystalline $BaLiF_3$[1] whereas temperature variable ^7Li as well as ^{19}F NMR spectra of nanocrystalline $BaLiF_3$ 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 $BaLiF_3$ than in the microcrystalline material.

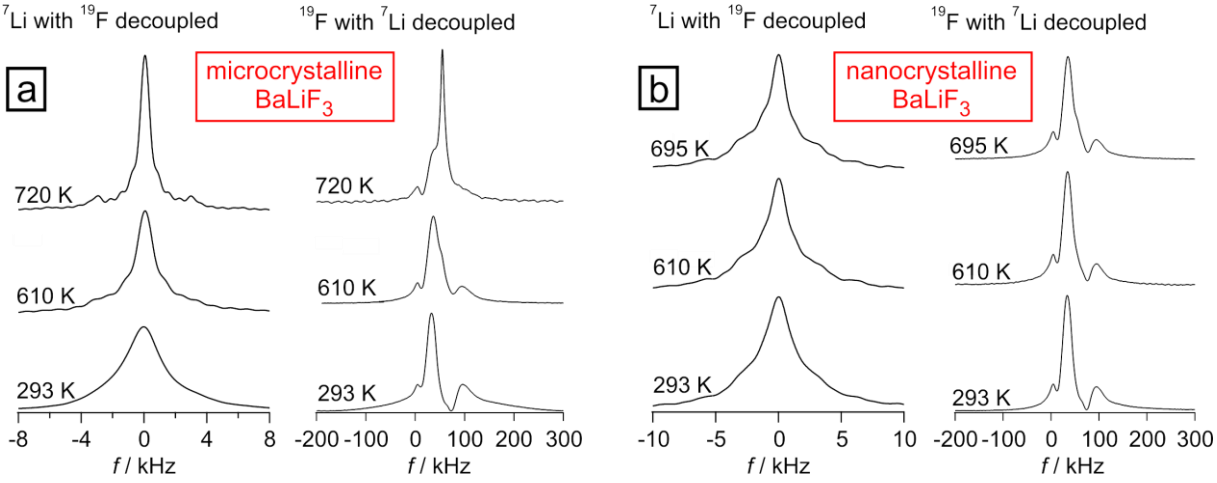

Figure 1: Temperature variable ^7Li and ^{19}F MAS NMR spectra recorded while decoupling the respective other nuclei for microcrystalline (a) and nanocrystalline $BaLiF_3$ (b) with $\nu_0(^7Li)$ = 233 MHz, $\nu_0(^{19}F)$ = 565 MHz and ν_r = 3 kHz.

References

[1] A. Düvel, M. Wilkening, S. Wegner, A. Feldhoff, V. Sepelak, P. Heitjans, Solid State Ionics 184 (2011) 65.
[2] R.A. Jackson, M.E.G. Valerio, J.F. de Lima, J. Phys.: Condens. Matter 8 (1996) 10931.