^{79}Br Wideline NMR Study of $CsPbBr_3$ and Cs_4PbBr_6 Perovskite Crystals

Han, O.H. (Korea Basic Science Institute, Western Seoul Center); Hung, I., Gan, Z. (NHMFL); Cha, J.-H. and Jung, D.-Y. (Sungkyunkwan U., Chemistry)

Introduction

Perovskite quantum dots show potential for next generation displays, which are brighter and clearer than naked eye vision.[1] Cesium lead bromide ($CsPbBr_3$ and Cs_4PbBr_6) perovskite compounds promise outstanding optoelectrical properties and are significantly more stable than organic-inorganic hybrid perovskite, such as methylammonium lead halide ($MAPbX_3$). Recently, there are increasing numbers of reports concerning the synthesis and applications of $CsPbBr_3$ and Cs_4PbBr_6. However, there is a lacking in fundamental research about the intrinsic optical and electrical properties of these all-inorganic perovskite. To understand the intrinsic optoelectrical properties of these compounds, the investigation with high-quality perovskite samples in a single phase and macroscopic sizes is desired. We report here the investigation of Br sites by ^{79}Br wideline NMR at high magnetic fields.

Experimental

Static ^{79}Br wideline WURST/QCPMG [2] NMR spectra were acquired at a fixed carrier frequency of 375.84 MHz in a field stepping manner using the series-connected-hybrid (SCH) magnet at the NHMFL equipped with a Bruker NEO console and a 3.2 mm magic-angle spinning probe operated in static mode. Each spectral segment was acquired with 2 MHz WURST sweeps, a recycle delay of 0.1 s, and 4096 scans. The ^{79}Br wideline spectra were generated by skyline projection of the multiple spectral segments (4 for Cs_4PbBr_6 and 7 for $CsPbBr_3$) acquired at different magnetic field values (0.047 T intervals for Cs_4PbBr_6 and 0.093 T intervals for $CsPbBr_3$).

Results and Discussion

The ^{79}Br static NMR spectra of $CsPbBr_3$ and Cs_4PbBr_6 obtained at a center field of 35.1 T are shown in Figure 1. Even at this high field, the central transition spans over 5 MHz wide due to the large quadrupolar coupling. Spectral analyses show two distinguished bromine sites for $CsPbBr_3$ and a single site for Cs_4PbBr_6. The spectral lineshape allows for the extraction of ^{79}Br quadrupolar coupling parameters of these sites. Comparison of the electric-field-gradient (EFG) with DFT calculation would allow for structural refinement based on the quadrupolar coupling parameters measured on these bromine sites. Work along this direction is under way.

Conclusions

The high magnetic field of the NHMFL SCH magnet allows for the acquisition of ultra wideline ^{79}Br NMR spectra of $CsPbBr_3$ and Cs_4PbBr_6. The measured ^{79}Br quadrupolar coupling parameters provide pieces of puzzles in our effort for the fundamental understanding of $CsPbBr_3$ and Cs_4PbBr_6 perovskite quantum dots which have outstanding electric and optical properties.

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References

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^{79}Br WURST/QCPMG of CsPbBr samples centered at $\nu_0(^1H)$ = 1500 MHz

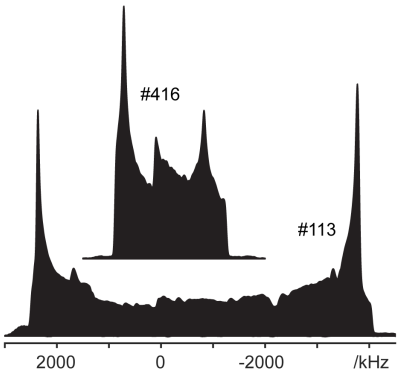

Fig.1 The ^{79}Br static NMR spectra of $CsPbBr_3$ (#113) and Cs_4PbBr_6 (#416) obtained at 35.2 T