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2020

Feng, F., Karimata, I., Hong, H.-W., Tachikawa, T., Tominaga, K., Hayashi, M., & Sasaki, T.
(2020).Determination of the fine structure of a halide perovskite using THz spectroscopy.
Proc. Of the 7th Asian Spectroscopy Conference (ASC 2020).
doi:10.32655/ASC_8-10_Dec2020.66

<https://hdl.handle.net/10356/144349>

https://doi.org/10.32655/ASC_8-10_Dec2020.66

Determination of the Fine Structure of a Halide Perovskite using THz Spectroscopy

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Abstract

In a crystalline solid, many types of disorders exist. Revealing the localized structures induced by disorder is one of the central issues of crystallography. Retrieving information about disorder from the scattering patterns of X-ray and/or neutron diffractions is still facing vital challenges. New experimental observations, whenever available, are greeted to shed additional light on this problem. We have in one previous work demonstrated a ubiquitous capability of terahertz (THz) spectroscopy to detect the fingerprint vibrational peaks of correlated molecular arrangements at the nano-scale level in an occupation disorder system.[1] We will, in this work, employ THz spectroscopy to study the fine structure of the halide perovskite systems where the short-range order of the disordered methylammonium (MA) molecules remains an open question.

The upper panel of Figure 1 shows the THz spectrum of polycrystalline MAPbBr₃ recorded at 10 K using a high-resolution THz spectrometer. Since each unit cell contains four MA molecules, and each MA has two ways of orientations, there are 16 correlation possibilities of the MAs in one unit cell. We have thoroughly considered the 16 correlations patterns and show the calculated normal modes in the lower panel of Figure 1. One may readily agree that the primary absorption feature of the THz spectrum has been reproduced in theory.[2] Based on this result, we suggest that the 16 forms of short-range order of the MA cations exist in this halide perovskite. These short-range ordered arrangements of MA produce both nonpolarized and polarized domains, which may have an impact on the electron-hole separation and charge carrier transport.

Fig. 1: Comparison between experimentation and theory. The above panel shows the THz spectrum recorded with 100 MHz resolution and at 10 K. The bottom panel shows the calculated THz modes. Lorentzian line shapes with arbitrary full-width-at half-maximum are convolved into all modes to provide a visual guide.

Keywords: THz spectroscopy, perovskite, short-range order, solid-state density functional theory

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