

How Lattice Dynamics Moderate the Electronic Properties of Metal-Halide Perovskites : A Study

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ABSTRACT

Metal-halide perovskites have emerged as highly promising semiconductors with excellent optoelectronic properties. This Perspective outlines how the dynamic response of the ionic lattice affects key electronic properties such as exciton binding energies and charge-carrier mobilities in hybrid perovskites. Such links are shown to derive from the frequency-dependence of the dielectric function, which is governed by contributions from electronic interband transitions, polar vibrations of the metal-halide sublattice, organic cation collective reorientations, and ionic movement. The influence of each of these contributions to charge-carrier screening and carrier–lattice interactions is discussed, which allows for general trends with material composition to be revealed. Overall, this Perspective highlights the challenges and questions arising from the peculiar combination of a soft polar metal-halide sublattice interspersed with rotationally mobile dipolar molecules that is encountered in hybrid metal-halide perovskites.

INTRODUCTION

Metal-halide perovskites have proven to be a fascinating class of semiconductors, offering excellent optoelectronic properties(1,2) that have underpinned the superior performance of photovoltaic devices based on these materials.(3) An understanding of how the stoichiometry and structure of such perovskites affects their basic electronic properties will be essential for future advances in performance. Currently, the precise mechanisms determining fundamental electronic properties, such as exciton binding energies, charge-carrier mobilities, and recombination are still under scrutiny. These properties are strongly influenced by the lattice, which interacts directly with charge carriers but also moderates the interaction between electrons and holes through dielectric screening. Therefore, an examination of the dynamic response of the lattice and its effect on the dielectric environment is a necessary step toward a fuller understanding of the electronic properties of any semiconductor.

For hybrid metal-halide perovskites of ABX₃ stoichiometry, such investigations are particularly intriguing, because these materials exhibit a complex vibrational space that stretches over a vast frequency range. While organic A-cations may leave a vibrational footprint in the infrared part of the spectrum that arises from internal molecular vibrations,(4–9) the polar (optical) modes of the metal-halide sublattice are found at much lower THz frequencies.(5,8–12) In the 100 GHz range, collective reorientations of the A-cation may onset,(13–17) while at very low frequencies (<104 Hz), slow motion of ions through the lattice commence.(15,18,19)

As a second consideration, the temperature-dependence of the exciton binding energy could help identification of the mechanisms contributing to screening, given that the relevant dielectric contributions should mirror such changes. An analysis of the onset of the absorption spectrum through Elliott's theory(52) is particularly convenient here, as it can yield a value of E_b at any given temperature by unravelling bound excitons from continuum electron-hole contributions. Such measurements have been repeatedly carried out(45–48) for MAPbI₃ and typically show a decline in E_b with increasing temperature from 20–30 meV near 10 K to 12 meV near room temperature, with a step-like change occurring over a narrow temperature range near the tetragonal-to-orthorhombic phase transition at 160 K.(45–48) Figure 2b,c displays an example of such trends, as reproduced from Ref (45). A broader survey across multiple literature studies(45–48) similarly reveals that E_b typically declines with increasing temperature by approximately 35% upon entry into the tetragonal phase, which corresponds to an increase by roughly 20% of the equivalent dielectric constant ϵ_{eff} relevant to excitonic screening (according to eq 1). Because the MA cation reorientation is frozen out in the low-temperature orthorhombic phase,(16,17,24,39) these changes have been viewed as evidence for a contribution of molecular dipole reorientation to excitonic screening upon entry into the tetragonal phase.(34,35) However, at the tetragonal-to-orthorhombic phase transition, variations in the electronic transitions (such as a change in band gap energy by 100 meV)(45,53) and the optical phonon modes (a splitting of peaks)(5,11,54) are also evident, which could potentially serve as markers for a modification of the polarizability associated with these resonances. Temperature-dependent measurements of optical absorption and refraction at near-IR ($\epsilon_{\text{optical}}$) and low-THz (ϵ_{THz}) frequencies(11,26,45) for MAPbI₃ show small changes in magnitude with temperature but clear modifications nearer the optical phonon resonances. More detailed measurements and analysis would be needed to understand whether the alterations observed in the optical phonon resonances at the phase transition could sufficiently affect exciton binding energies.

Secondary effects on charge-carrier mobilities, such as lattice anharmonicity and temperature-dependent ionic screening, are still currently under scrutiny. Here, the power-law temperature-dependence of the charge-carrier mobility in metal-halide perovskites has intensely been discussed and contrasted with theoretical model solutions. However, analogous investigations conducted on

classic inorganic semiconductors decades ago suggest that one has to be cautious about drawing definite conclusions from modeling such trends with a single contributing mechanism. The wide variety of exponents reported for various metal-halide perovskites (and sometimes even for the same stoichiometry) indicates that multiple effects, some of which are linked to extrinsic parameters such as doping, may still be operational in some cases. In addition, room-temperature values of the charge-carrier mobilities recorded for most metal-halide perovskites are still somewhat below values expected from Fröhlich theory,⁽¹⁾ indicating lingering additional effects. Any comparison with theoretical models or simulations will therefore need to take account of the many minor and major overlapping contributions that can influence the charge-carrier mobility over various temperature ranges.

In summary, this Perspective highlights some of the fascinating challenges raised by the intriguing dielectric response of perovskites that comprise a soft, polar metal-halide sublattice of potentially heavy atomic ingredients, interspersed with organic dipolar molecules that exhibit temperature-dependent rotational freedoms. Discussions about the nature of the electronic properties of such peculiar systems will no doubt continue for some time to come.

References

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