Nanoscale Origins of Thermal Transport Phenomena in Hybrid Layered Perovskites

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An exciting and fundamentally powerful modern methodology for materials development is the process by which artificial solids are rationally built piece-by-piece from nanoscale "building blocks". Among the library of nanomaterials currently at the forefront of this pursuit, two-dimensional layered lead halide perovskites (2D LHPs), are of particular interest. These materials, solid crystals composed of alternating layers of atomically thin organic and inorganic subphases, possess novel optical and electronic properties that make them particularly suited for use in devices including solar cells, LEDs, flexible electronics, and even lasers. While significant early strides have been made in investigating charge carrier transport through dynamic models and sophisticated experiments, comparatively little attention has been given to understanding the manner in which the design of these nanostructured solids impacts their macroscopic thermal properties via thermal carrier (phonon) transport. This knowledge, however, is critical to addressing the thermal management constraints necessary to the design of reliable and stable devices.

To this end, we seek to elucidate the fundamental pathways for heat transport within 2D LHP artificial solids. We establish that the thermal energy storage and phase behavior for these solids suggest that 2D LHPs retain their bulk phonons and vibrational density of states even at the nanoscale. Using a frequency domain thermoreflectance technique to effectively monitor cross-plane thermal transport in macroscopic 2D LHP crystals, the first measurements of the thermal conductivity for 2D LHPs are presented. This experimental study reveals that lead bromide 2D LHPs exhibit structure-property relationships characteristic of ballistic phonon transport within the isolated subphases and diffuse scattering at the organic-inorganic interfaces between layers. Specifically, since the individual layers within the nanostructure are so thin, the typical phonon scattering pathways that constrain the thermal conductivity of bulk perovskites do not occur and instead interface-scattering between the organic and inorganic phases drives thermal transport. Utilizing the ballistic phonon transport through the organic junctions separating the inorganic layers, we find that thermal transport can be significantly enhanced through the chemistry of the organic subphase. Finally, we specifically probe the phonon spectrum for 2D LHPs via low frequency Raman spectroscopy. This investigation identifies the retention of bulk-like phonons even in the atomically thin 2D LHPs, in addition to revealing coherent acoustic phonons in softer lead iodide 2D LHPs potentially capable of carrying thermal energy across the organic-inorganic interfaces without scattering.

Each of these observations suggest that a thermophysical representation of 2D LHPs as composite materials serves as a useful framework for understanding their thermal transport properties. That so many material properties can be effectively predicted/controlled simply from the bulk properties of the component phases is surprising given both the long-range order of the artificial solids and the sub-nanometer length scale of the individual component layers. Furthermore, these results reveal the ability to selectively retain/remove the channels for thermal transport in 2D LHPs as the engineer so chooses, without affecting the prodigious optical and electronic properties.

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