

# Accurate determinations of vibrational and radiative thermal transport in perovskite, rocksalt, and related structures

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That thermal diffusivity is connected with cooling front speed has gone unrecognized until recently [Hofmeister, 2010]. Consequently, ballistic radiative transport affecting virtually all measurements intended to probe the vibrational mechanisms, even cryogenic, has been overlooked [Hofmeister, 2010]. In addition, failure to correct for refraction, not simply reflection, effects has provided large systematic errors in estimating radiative thermal conductivity from spectra obtained in the diamond anvil cell for lower mantle phases. [Hofmeister, 2010; (in review)]. Recent discovery that thermal diffusivity ( $D$ ) is linked to thermal expansivity ( $\alpha$ ) [Hofmeister, (in review); Hofmeister, Whittington (in review)] coupled with overestimation of transport values for simple solids by acoustic models indicate that a much different theoretical approach wants consideration. To address these issues, to provide uncompromised values of thermal transport properties, and a means to extrapolate such data to lower mantle conditions, various spectroscopic-based measurements on analogues have been conducted and a new model is under construction.

We have recently measured the phonon component of thermal diffusivity ( $D$ ) for lower mantle structures from ambient temperature ( $T$ ) up to  $\sim 2000$  K using contact-free, laser-flash analysis, from which effects of ballistic radiative transfer were removed. We focused on 13 compounds (e. g., synthetic  $\text{YAIO}_3\text{:Tm}$ , natural  $\text{Ca}_{1.01}\text{Mn}_{0.001}\text{Fe}_{0.007}\text{Ti}_{0.99}\text{O}_3$ ) with perovskite and perovskite-like structures, a dozen

alkali halides, and a few magnesiowüstites, and also studied a wide variety of glasses and upper mantle materials. Perovskites [Hofmeister, (in review)] in the absence of phase transitions) are best described as  $D^{-1}$  following a low order polynomial in  $T$ . Ordered, cubic perovskites occupy a single trend, defining the contribution of the ideal lattice. Distortion, disorder, polymorphism, and temperature affect  $D^{-1}$  in a

manner that is consistent with the damped harmonic oscillator-phonon gas model which relates phonon lifetimes to infrared peak widths. Combining our data with cryogenic measurements of  $\text{YAIO}_3$  and  $\text{LaAlO}_3$  [Agarwal et al., 2005] and similarly for fused silica [Agarwal et al., 2005] shows that the best description for  $D^{-1}(T)$  is a proportionality to  $\alpha T$  from  $\sim 0$  K to the limit of measurements. At low  $T$ ,  $D^{-1} \sim T^3$ , so acoustic modes dominate and  $k_{\text{lat}} = k_0 + k_1 T$ . Defects being present preclude scattering at sample walls,

adding a small constant  $D_0^{-1} \sim 0,0001 \text{ mm}^{-2} \text{ s}$  as  $T \rightarrow 0$ , and an additional contribution of  $k_{\text{defct}} T^3$ . Forms previously inferred for thermal insulators include systematic errors stemming from ballistic radiative transfer and/or interface resistance, and misunderstand mechanisms. Our results show that optical phonons largely govern heat transport of complex insulators, including glasses. Alkali halides behave differently wherein interactions of optic and acoustic modes govern heat transfer up to melting [Yu, Hofmeister, (in prep.)].

Visible-UV spectra of  $\text{Fe}^{2+}$  and Fe charge transfer in single-crystal perovskite-types have overall moderate absorption coefficients and flat baselines, consistent with reflectivity data, confirming that DAC spectra are plagued by insufficient baseline corrections. We find that diffusive radiative thermal conductivity values are similar to results obtained for olivines, permitting recasting of results to focus on iron concentrations for a given site speciation (e.g., [Hofmeister, 2007]).

Combining spectroscopic with direct heat transport measurements reveals microscopic mechanisms permitting extrapolation to the mantle. A detailed model with application to diverse materials will be presented in this talk.

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