Effects of Non-Framework Metal Cations and Phonon Scattering Mechanisms on the Thermal Transport Properties of Zeolite LTA Thin Films

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We present a systematic study to investigate the effects of non-framework cations and the role of phonon scattering mechanisms on thermal transport properties of zeolite LTA, via experiment and semi-empirical lattice dynamics calculations. Our study is motivated by the increasing need for accurate thermal transport property measurements and mechanistic understanding of thermal properties of zeolite materials. The presence of a nanostructured pore network, extra-framework cations, and tunable framework structure and composition confer interesting thermophysical properties to these materials, making them a good model system to investigate thermal transport in complex materials.

Continuous films of zeolite LTA with different non-framework cations (Na^+, K^+, and Ca^{+2}), were synthesized via secondary hydrothermal method followed by ion-exchange. These films were characterized by several techniques. The thermal conductivity was measured using 3w methods over a wide range of temperature (150-450 K). This method provided accurate thermal conductivity of zeolite materials because the bulk thermal conductivity was measured directly in comparison to conventional methods involving the use of compacted zeolite powders. Our data showed significant dependence of the thermal conductivity on the extra-framework cations as well the temperature.

A similar modeling approach as described earlier by us for MFI zeolite [1] was employed for LTA zeolite. The initial atomic positions of each type of LTA zeolite crystal were acquired from X-ray crystal structure data found in the literature. The full phonon spectra for each type of LTA zeolite were calculated from the energy-minimized LTA zeolite structural models. The phonon spectra were then used in conjunction with semi-empirical relaxation time expressions to calculate the thermal conductivity, with a minimal number of fitted parameters. The results both validated, and suggested the limitations of, this modeling approach. Optic phonons dominated the thermal conductivity and boundary-like scattering associated with the pore network was apparently the strongest phonon scattering mechanism, as also observed in MFI zeolite. Our approach was previously able to explain how small amounts of aluminum impurities influence the thermal conductivity of zeolite MFI. However, it was unable to fully explain how each cation influences the thermal conductivity of zeolite LTA. Despite the shortcomings of the present model, our approach still provided insight into heat transport in porous materials and is shown to be transferable to multiple materials. Analysis of our experiments, our calculations, and molecular dynamics simulations from the literature, revealed that the relationship between phonon lifetime and relaxation time is complex and may hold further insight into the weak temperature dependence of the phonon mean free paths observed in the present material.

1. Hudiono, Y., et al., *Effects of composition and phonon scattering mechanisms on thermal transport in MFI zeolite films.* Journal of Applied Physics, 2007. **102**(5), p. 053523