Temperature dependent thermal conductivity of pure silica MEL and MFI zeolite thin films

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This paper reports the temperature dependent cross-plane thermal conductivity of pure silica zeolite (PSZ) MFI and MEL thin films measured using the 3ω method between 30 and 315 K. PSZ MFI thin films were b-oriented, fully crystalline, and had a 33% microporosity. PSZ MEL thin films consisted of MEL nanoparticles embedded in a nonuniform and porous silica matrix. They featured porosity, relative crystallinity, and particle size ranging from 40% to 59%, 23% to 47%, and 55 to 80 nm, respectively. Despite their crystallinity, MFI films had smaller thermal conductivity than that of amorphous silica due to strong phonon scattering by micropores. In addition, the effects of increased relative crystallinity and particle size on thermal conductivity of MEL thin films were compensated by the simultaneous increase in porosity. Finally, thermal conductivity of MFI zeolite was predicted and discussed using the Callaway model based on the Debye approximation. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.3692754]

I. INTRODUCTION

Zeolites are a group of nanoporous crystalline aluminosilicates with uniform micropores. They differ by their crystalline structure, microporosity, and their framework density defined as the number of tetrahedrally coordinated atoms per 1000 Å3. For example, the MFI structure has 0.55 nm wide sinusoidal channels along the a-axis and 0.53 nm wide straight channels along the b-axis.1 The MEL structure has 0.54 nm wide straight channels along both the a- and b-axis.1 The presence of these micropores contributes to the so-called microporosity. The framework density of PSZ MEL and MFI is 17.4 and 18.4, respectively.1 Pure silica zeolites (PSZs) have no aluminum in their framework.

Zeolites have been considered as adsorbents for sorption-based heat exchangers for heat recovery and cooling applications.2–5 They are also of interest for hydrogen storage as molecular sieves and as low-dielectric constant materials for very large scale integrated circuits.1,6 In addition, there is an emerging trend to use zeolite thin films in various micro-nanoscale applications, such as filters for air pollutants, microreactors, and miniature gas sensors.7–11 In all these applications, knowledge of thermal properties of zeolites over a wide range of temperature is of significant importance for their practical implementation in devices and systems.

Several studies have reported the thermal conductivity of powdered zeolites,12–15 Effects of temperature, filling gas, moisture, and pressure were investigated.12–15 In addition, Greenstein et al.16 and Hudiono et al.17 measured thermal conductivity of PSZ MFI zeolite films with thickness ranging from 10 to 20 μm and temperature varying from 150 to 450 K. The MFI films were synthesized by secondary growth through a seeded hydrothermal process on alumina substrates. The measured thermal conductivity of (h0l)-oriented PSZ MFI films varied from 1.0 to 1.4 W/m/K in the temperature range considered.17 That of calcined and uncalcined c-oriented PSZ MFI films deposited on silicon substrates was found to range from 0.75 to 1.1 and 1.0 to 1.6 W/m/K, respectively.16 More recently, Coquil et al.18 measured room temperature thermal conductivity of PSZ MFI and MEL zeolite thin films. The MFI thin films were b-oriented, fully crystalline, and had a porosity of 33%. The MEL thin films featured porosity, relative crystallinity, and particle size ranging from 40% to 59%, 23% to 47%, and 55 to 80 nm, respectively. The authors found the thermal conductivity to be around 1.02 ± 0.10 W/m/K for all films despite their different porosity, relative crystallinity, and nanoparticle size.

II. METHODS AND EXPERIMENTS

A. Sample film preparation

Synthesis of PSZ MFI and MEL thin films investigated in the present study were previously described in detail.1,6,18 MFI thin films were synthesized by in situ crystallization and were b-oriented. The MEL films were prepared by spin coating a zeolite nanoparticle suspension onto silicon substrates. The MEL suspension was synthesized by a two-stage process.1 The first stage consisted of a 2 days heating and stirring of a tetraethyl-orthosilicate (TEOS) based solution at 80 °C resulting in a MEL nanoparticle suspension. The second stage corresponded to the growth of the MEL nanoparticles from the same solution in a convection oven at 114 °C.
Finally, MEL thin films were obtained by spin-coating the solution onto silicon substrates. Both relative crystallinity and nanoparticle size of the PSZ MEL increased as the second stage synthesis time increased. Here, the relative crystallinity is defined as the ratio of the micropore volume to the micropore volume of a fully crystalline PSZ MEL microcrystal.1 Four different sets of MEL films corresponding to four different second stage synthesis times (15, 18, 21, and 24 h) were studied. Note that all the MEL and MFI thin films were made hydrophobic by vapor-phase silylation with trimethylchlorosilane as described in Ref. 1.

### B. Characterization

Detailed characteristics of the resulting PSZ MFI and MEL thin films have been reported in the literature.1,6,19,20 Table I summarizes the characteristics of five types of PSZ MFI and MEL thin films investigated. Figure 1(a) shows a SEM image of an *in situ* PSZ MFI film (type 1) consisting of well-intergrown MFI crystals along with an inset showing the MFI framework viewed down the *b*-axis.18 Figure 1(b) shows a SEM image of a spin-on PSZ MEL film (type 5) consisting of MEL nanoparticles embedded in a nonuniform, disordered, and porous silica matrix along with an inset showing the MEL framework viewed down the *a*-axis.18 In addition, unlike the MFI thin film, the MEL thin films featured also a mesoporosity corresponding to the volume fraction occupied by mesopores 2.3 to 2.6 nm in diameter.21 These mesopores were located between the disordered silica matrix and the MEL nanoparticles.22

### C. Thermal conductivity measurements

The cross-plane thermal conductivity of PSZ thin films was measured using the 3ω method.23,24 The principles, experimental apparatus, experimental procedure, and validation of the method have already been described elsewhere.25 The experimental uncertainty typically varied from 5% to 10% corresponding to 95% confidence interval. The thermal conductivity of two different samples for each type of film listed in Table I was measured between 30 and 315 K. The measurements agreed within 10% of each other. In addition, the film thickness had negligible effect on the measured data. This can be attributed to the fact that phonon scattering by nanopores and crystal grain boundary dominated over phonon scattering by film boundary in PSZ films.

### III. PHYSICAL MODELING

Finally, thermal conductivity of the PSZ MFI film was modeled using the following expression derived by Callaway,26

\[
k = \frac{k_B}{2\pi^2v_g} \left(\frac{k_B T}{h}\right)^3 \int_0^{\theta_D/\omega} \tau_{\text{eff}}(\omega) \frac{x^4 e^x}{(e^x - 1)^2} dx,\tag{1}\]

where \(k_B\) is the Boltzmann constant, \(h\) is the reduced Planck’s constant, \(\theta_D\) is the Debye temperature for MFI zeolite reported to be 377.6 K,27 \(\tau_{\text{eff}}(\omega)\) is the effective phonon relaxation time, and \(v_g\) is the average effective sound velocity in MFI reported

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**TABLE I. Physical characteristics of the synthesized PSZ MFI and MEL thin films.**

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Structure</th>
<th>Second stage duration (h)</th>
<th>MEL particle size (±1 nm)</th>
<th>Porosity (±2%)</th>
<th>Total pore vol. (cm³·g⁻¹)</th>
<th>Micropore vol. (cm³·g⁻¹)</th>
<th>BET surface area (m²·g⁻¹)</th>
<th>Micropore area (m²·g⁻¹)</th>
<th>Thickness (±10 nm)</th>
<th>Relative crystallinity (±2%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MFI</td>
<td>–</td>
<td>–</td>
<td>33%</td>
<td>0.19c</td>
<td>0.19c</td>
<td>457c</td>
<td>457c</td>
<td>320</td>
<td>100%</td>
</tr>
<tr>
<td>2</td>
<td>MEL</td>
<td>15</td>
<td>55</td>
<td>40%</td>
<td>0.60d</td>
<td>0.033d</td>
<td>691c</td>
<td>86c</td>
<td>350</td>
<td>23%c</td>
</tr>
<tr>
<td>3</td>
<td>MEL</td>
<td>18</td>
<td>60</td>
<td>45%</td>
<td>0.70d</td>
<td>0.048d</td>
<td>750c</td>
<td>119c</td>
<td>300</td>
<td>33%c</td>
</tr>
<tr>
<td>4</td>
<td>MEL</td>
<td>21</td>
<td>70</td>
<td>58%</td>
<td>0.80d</td>
<td>0.060d</td>
<td>852c</td>
<td>143c</td>
<td>280</td>
<td>44%c</td>
</tr>
<tr>
<td>5</td>
<td>MEL</td>
<td>24</td>
<td>80</td>
<td>59%</td>
<td>0.83d</td>
<td>0.068d</td>
<td>889c</td>
<td>149c</td>
<td>330</td>
<td>47%c</td>
</tr>
</tbody>
</table>

*a*From Flanigen et al.19

*b*From Tang et al.20

*c*Interpolated from Li et al.1

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**FIG. 1.** (Color online) SEM images of (a) *in situ* PSZ MFI and (b) spin-on MEL thin films. Insets show (a) the MFI framework viewed down the *b*-axis and (b) the MEL framework viewed down the *a*-axis.18
to be 3683 m/s.\textsuperscript{28} The variable $x$ is related to the phonon frequency $\omega$ and is equal to $h\omega/k_BT$. Note that Eq. (1) was obtained by using the Debye dispersion relation and density of states and ignoring the effect of phonon polarization as discussed in Ref. 29.

The effective phonon relaxation time $\tau_{\text{eff}}$ is related to the relaxation times for defect scattering $\tau_D$, Umklapp scattering $\tau_U$, and boundary scattering $\tau_B$ via the Matthiessen’s rule as:

$$
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_D} + \frac{1}{\tau_U} + \frac{1}{\tau_B}.
$$

Defect scattering refers to phonon scattering by point defects such as inclusion of impurity atoms or lattice vacancies.\textsuperscript{30} Boundary scattering refers to phonon scattering by the film boundaries as well as by micropores. Here, $\tau_D$, $\tau_U$, and $\tau_B$ were expressed as:\textsuperscript{17,30}

$$
\frac{1}{\tau_D} = A\nu^4, \quad \frac{1}{\tau_U} = B T \nu^2 \exp(-\theta_D/3T), \quad \text{and} \quad \frac{1}{\tau_B} = \nu_p/l_B,
$$

where $A$ and $B$ are empirical constants, and $l_B$ is the effective phonon mean free path (MFP) for boundary scattering.

IV. RESULTS AND DISCUSSION

A. Experimental results

Figure 2 shows the measured thermal conductivity of the PSZ MFI and MEL zeolite thin films as a function of temperature, along with data reported in the literature for calcined and uncalcined MFI zeolite\textsuperscript{16} and amorphous silica.\textsuperscript{31} The four MEL thin films differ from one another by their relative crystallinity. The inset shows a closer view of the measured data for temperatures $T > 150$ K in linear scale. The thermal conductivity of the in situ MFI film increased from 0.05 to 1.2 W/mK as temperature increased from 30 to 315 K. In addition, it was about 10% to 15% larger than that of calcined MFI zeolite measured by Greenstein \textit{et al.}\textsuperscript{16} between 150 and 315 K. However, the thermal conductivity of uncalcined MFI\textsuperscript{16} was about 20% to 40% larger than that measured in the present study.\textsuperscript{16} This was likely due to the fact that the uncalcined films measured by Greenstein \textit{et al.}\textsuperscript{16} were denser (2.1 g/cm$^3$) than the in situ MFI film (1.7 g/cm$^3$) investigated in the present study. Moreover, the measured thermal conductivity of our MFI films was comparable to or smaller than that of dense (nonporous) amorphous silica despite its crystalline nature. In fact, the MFI films had microporosity of about 33% due to the presence of subnanometer pores within the crystalline structures. Its thermal conductivity was thus greatly reduced by phonon scattering by micropores.

In addition, Fig. 2 indicates that all measured thermal conductivity $k$ was linearly proportional to $T^n$ with $n$ varying from 2 to 2.6 for temperature $T < 60$ K. At low temperatures, strongly disordered materials typically follows $k \propto T^2$ while for crystalline materials $k \propto T^{3.30}$ The present results can be attributed to the fact that the MFI and MEL films featured crystalline nanostructures which were highly disordered due to the large surface area of pores and nanocrystals.

Furthermore, the inset in Fig. 2 shows that the thermal conductivity of the PSZ MEL thin films was slightly smaller than that of the PSZ MFI thin film. This is due to the fact that the MEL thin films had larger porosity and were “partially” crystalline, consisting of crystalline nanoparticles embedded in an amorphous silica matrix. Moreover, the thermal conductivity of MEL thin films increased slightly when the MEL relative crystallinity and particle size increased from 23% to 44% and 55 to 70 nm, respectively. However, it remained nearly unchanged when the relative crystallinity and particle size further increased beyond 44% and 70 nm. Then, the effects of increased relative crystallinity and particle size were compensated by the simultaneous increase in porosity.

B. Modeling results

By analogy with other studies,\textsuperscript{14,16,17,30,32} the parameters $A = 1.38 \times 10^{-42}$ s$^3$, $B = 4.24 \times 10^{-24}$ s/K, and $l_B = 0.95$ nm in Eq. (3) were obtained by fitting the predictions of Eqs. (1) to (3) to the experimental data over the entire temperature range explored.

Figure 2 shows that the calculated thermal conductivity from Eqs. (1) to (3) agreed within 6% of the experimental data for the PSZ MFI film for all temperatures between 30 and 315 K. It establishes that using the Debye dispersion relation instead of the complete phonon dispersion was sufficient to predict the thermal conductivity of MFI zeolite films. In addition, phonon boundary scattering was found to dominate over phonon Umklapp scattering in MFI zeolite as discussed in the literature.\textsuperscript{14,16–19} In fact, the predicted thermal conductivity was insensitive to the Umklapp scattering relaxation time $\tau_U$ since $\tau_U \gg \tau_B$ and $\tau_U \gg \tau_D$ for all temperatures.
considered and all phonon frequencies up to the Debye cutoff frequency of \( \omega_D/2\pi = 8 \) THz. Similar conclusions were reached by Hudiono et al.\(^{17}\) and Greenstein et al.\(^{32}\) for MFI and LTA zeolite between 150 and 450 K.

Moreover, phonon defect scattering should be considered along with boundary scattering in order to accurately predict the thermal conductivity of the MFI films particularly at high temperatures. This was due to the fact that defect scattering strongly affects high frequency phonons particularly at high temperatures.\(^{30}\) At low temperatures, however, defect scattering was less important and boundary scattering dominated.

Finally, the fitted phonon boundary scattering MFP \( l_B = 0.95 \) nm was comparable with the distance between two adjacent micropores or the wall thickness. In fact, the lattice constant of MFI zeolite was reported to be about 2 nm along both \( a \)- and \( b \)-axis.\(^{33}\) Considering the pore width of 0.55 nm along the \( a \)-axis and 0.53 nm along the \( b \)-axis,\(^{1}\) the wall thickness was estimated to be about 1.5 nm. Note that Hudiono et al.\(^{17}\) reported a fitted value of \( l_B = 4.8 \) nm for MFI zeolite, also comparable with the wall thickness. The difference between \( l_B \) and MFI wall thickness may be attributed to the semiempirical relaxation time models as well as the differences between Debye and actual phonon dispersion and density of states in MFI zeolite.

V. CONCLUSION

This paper reports the temperature dependent cross-plane thermal conductivity of PSZ MEL and MFI thin films. Despite their crystallinity, MFI thin films were found to have thermal conductivity comparable to or smaller than that of nonporous amorphous silica due to strong phonon scattering by micropore boundaries. For PSZ MEL films, effects of increased relative crystallinity and size of MEL nanoparticle on the thermal conductivity were compensated by the simultaneous increase in porosity. Finally, the thermal conductivity for MFI films was successfully modeled using the Callaway model based on the Debye approximation. Umklapp scattering had negligible effect on the predicted thermal conductivity. Instead, phonon boundary scattering dominated for all temperatures while defect scattering was important at high temperatures.

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