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Low thermal conductivity of the negative thermal expansion material, HfMo$_2$O$_8$

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The thermal conductivity of the cubic polymorph of hafnium molybdate, HfMo$_2$O$_8$, was determined over the temperature range of 2–400 K. The values of thermal conductivity were low (0.64±0.15 W m$^{-1}$ K$^{-1}$ at $T=300$ K for a fully dense sample), with a positive temperature coefficient throughout the temperature range examined. Calculations of the theoretical minimum thermal conductivity and the effective phonon mean free path show that the heat-carrying phonons are nearly fully coupled in HfMo$_2$O$_8$, consistent with the rather large magnitude of its Grüneisen parameter. The low-frequency optic modes which lead to negative thermal expansion in HfMo$_2$O$_8$ are likely responsible for the low thermal conductivity. © 2007 American Institute of Physics. [DOI: 10.1063/1.2721860]

Although most materials expand when heated, a surprising number exhibit the opposite behavior, sometimes over wide temperature ranges and over more than one crystallographic direction. Of particular interest is the family of materials of the general formula $AB_2O_8$. With $A=Zr$ and $B=W$, thermal expansion is large and negative (approximately $-9\times10^{-6}$ K$^{-1}$) over the temperature range of 0.5–K to 1050 K. Other members of this group with negative thermal expansion include ZrMo$_2$O$_8$, HfW$_2$O$_8$, and HfMo$_2$O$_8$.

On the basis that the low-frequency modes that give rise to negative thermal expansion could also influence other thermal properties, we determined the thermal conductivity of ZrW$_2$O$_8$ and found it to be very low, close to the theoretical minimum thermal conductivity. Here, we report the thermal conductivity of the cubic polymorph of hafnium molybdate, HfMo$_2$O$_8$, which is also known to exhibit negative thermal expansion. $\alpha_1=\alpha_{\text{Thermal}}$ (4.0 $\times$ 10$^{-6}$ K$^{-1}$ or $T=77–573$ K). $HfMoO_2(\text{OH})_2\cdot2\text{H}_2\text{O}$ was produced by the reaction of aqueous solutions of $HfCl_2\cdot8\text{H}_2\text{O}$ (Alfa Aesar, Ward Hill, MA) and $(\text{NH}_2)_2\text{MoO}_2\cdot4\text{H}_2\text{O}$ (Strem Chemicals, Newburyport, MA) in acid medium during 3 days of refluxing. Then HfMo$_2$O$_7$–(OH)$_2\cdot2\text{H}_2\text{O}$ was dehydrated by a series of low-temperature heat treatment steps (350 °C for 12 h, 375 °C for 20 min, 400 °C for 20 min, 425 °C for 30 min, 450 °C for 30 min, 475 °C for 30 min, and, finally, an additional 30 min at 475 °C), separated by cooling to room temperature for x-ray analysis.

Thermogravimetric analysis gave a Hf:Mo mole ratio of 1:2.03. From x-ray diffraction, the thermal conductivity of cubic trigonal HfMo$_2$O$_8$ was estimated to be $-0.1\%$. Scanning calorimetry from $T=300$ to 460 K indicated no thermal anomalies and put an upper limit on water content of 0.5 mass %. To check the sample’s amorphous content, laboratory powder x-ray diffraction data were collected on 70:30, 60:40, and 50:50 mass % mixtures of HfMo$_2$O$_8$ with an internal standard, Y$_2$O$_3$. The data were analyzed using the Rietveld method to obtain mass fractions for the two major crystalline phases. The sample was estimated to be $\sim92\%$ crystalline cubic HfMo$_2$O$_8$ from these mass fraction determinations.

The sample was kept under vacuum except when making pellets for thermal conductivity measurements, which required brief exposure to air. The HfMo$_2$O$_8$ powder was pressed into disk-shaped pellets with a diameter of 4.74 mm using a load of 0.5 GPa. High-pressure x-ray diffraction studies have shown that cubic HfMo$_2$O$_8$ starts to amorphize above 0.3 GPa and undergoes a phase transition between 0.7 and 2.0 GPa, but x-ray diffraction results before and after pressing of the pellets were identical.

Temperature-dependent thermal conductivities were determined using the thermal transport option of a Quantum Design Physical Properties Measurement System (PPMS, QD). A two-probe configuration (heater and hot thermometer shared one lead, while the cold foot and cold thermometer shared the other) was used and the pellets were epoxied (0.2 mm of epoxy, Tra-Bond 816H01 from Tra-Con, Inc., loaded with silver powder) to two disk-shaped copper leads. The thermal conductivities were measured under vacuum of $10^{-4}$ Torr. The principles of operation for this technique are based on a pulse method.* The geometry of the thermal conductivity sample was constrained in several ways. A pellet diameter of 4.74 mm was chosen so that the entire surface area would be covered by the QD copper lead (diameter of 6.30 mm). The thickness of the sample, $\ell$, is limited by the thermal diffusion time constant for the sample defined by $\tau=C_p\times\ell^2/\kappa$, where $C_p$ is the heat capacity per unit volume and $\kappa$ is the thermal conductivity. Too thick a sample would...
result in excessively long measurement times; the minimum
thickness is governed by the optimal temperature drop across
the sample ($\Delta T \sim 0.03T$). The maximum heater power $P$
for the 2 k$\Omega$ heater in the PPMS is 50 mW, where
$P = \kappa \Delta T (A/\ell)$ and $A$ is the pellet’s cross-sectional area.
The optimal thickness for the pellets was approximately 0.8 mm.
Thermal conductivities were measured using continuous
methods, where measurements are taken continuously as the
software adjusts parameters, such as the heater power and
period, to optimize the measurements. The HfMo$_2$O$_8$ pellets
were very fragile and many are fractured while the $\kappa$
measurements were underway, as noted by a sudden drop in the
apparent thermal conductivity. Often, the samples would
break at the sample-epoxy interface, but in other instances,
the pellet itself would fracture. In total, 27 samples were
made to collect the data for HfMo$_2$O$_8$; details of the five
pellets that gave useful data are given in Table I.

Table I. Size and density (at $T=300$ K) of HfMo$_2$O$_8$ pellets used for
thermal conductivity measurements.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (mm)</th>
<th>Density (g cm$^{-3}$)</th>
<th>% theoretical density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.74</td>
<td>2.74</td>
<td>62.4</td>
</tr>
<tr>
<td>2</td>
<td>0.74</td>
<td>2.75</td>
<td>62.6</td>
</tr>
<tr>
<td>3</td>
<td>0.80</td>
<td>2.68</td>
<td>61.0</td>
</tr>
<tr>
<td>4</td>
<td>0.84</td>
<td>2.49</td>
<td>56.7</td>
</tr>
<tr>
<td>5</td>
<td>0.78</td>
<td>2.65</td>
<td>60.4</td>
</tr>
</tbody>
</table>

Figure 1 shows the temperature dependence of the ther-
mal conductivity of HfMo$_2$O$_8$ for the samples measured. The
uncertainties in $\kappa$ were estimated from the accuracies in ther-
mal conductance reported by the PPMS along with the un-
certainties in the pellet dimensions $[\kappa=(K\ell)/A$, where $K$
is the thermal conductance]. The overall uncertainty in the
HfMo$_2$O$_8$ measurements is 20% for temperatures above
30 K but larger below 30 K.

The sample porosity $\phi$, defined as $\phi = [100 \times (\rho_{\text{bulk}} - \rho_{\text{at}})/\rho_{\text{bulk}}] = 100 - $ (% theoretical density), can affect $\kappa$, and
methods have been developed to estimate the correction for
the porosity if the bulk $\kappa$ is known, but it is not known for
HfMo$_2$O$_8$. Another method developed by Klemens allows
the calculation of the ratio of $\kappa_{\text{porous}}$ to $\kappa_{\text{dense}}$
directly from the porosity of the material,

$$\frac{\kappa_{\text{porous}}}{\kappa_{\text{dense}}} = 1 - \frac{4}{3} \phi,$$

for randomly oriented and randomly distributed voids. This
approximation has been used recently by Schlichting et al. to
determine the effect of porosity in yttria-stabilized zirconia.

The values of $\kappa_{\text{dense}}$ (for the average value of $\kappa$) of HfMo$_2$O$_8$
are shown as a function of temperature in Fig. 1. We find
$\kappa_{\text{dense}} = 0.64 \pm 0.15$ W m$^{-1}$ K$^{-1}$ at $T=300$ K for HfMo$_2$O$_8$.

As also found for ZrW$_2$O$_8$, the present results indicate
that HfMo$_2$O$_8$ does not exhibit the thermal conductivity tem-
perature dependence of a “normal” (simple) crystalline solid.
The thermal conductivities of both HfMo$_2$O$_8$ and ZrW$_2$O$_8$
are low, with positive temperature coefficients, $d\kappa/dT$, similar
to the thermal conductivities of glasses, despite being
crystalline materials.

In order to understand the low thermal conductivity, the
theoretical minimum thermal conductivity $\kappa_{\text{min}}$ of HfMo$_2$O$_8$
was calculated in Eq. (2) based on fully coupled oscillators
for each of the transverse and longitudinal polarizations,

$$\kappa_{\text{min}} = \frac{1}{2.48} \kappa_{\text{th}}^{2/3} \nu_0 \left( \frac{\kappa}{\Theta_D^e} \right)^2 \int_0^{\Theta_D^e} \frac{x^2 \sin x}{(e^x - 1)^2} dx,$$

where $n$ is the number density of atoms per unit volume and
the Debye characteristic temperature $\Theta_D^e$ is defined as

$$\Theta_D^e = \frac{h}{2 \pi k_B} n (6\pi n)^{1/3},$$

i.e., treating all the lattice modes (in this case 3 acoustic and
129 optical) as Debye-like. From the heat capacity of HfMo$_2$O$_8$,
we find $\Theta_D^e = 290$ K and a mean velocity of sound, $v_s$,
for 2900 m s$^{-1}$. The unit cell dimensions used for the
calculation of molar volume were from the unit cell pa-
tameters at $T=300$ K and the temperature-dependent thermal
expansion coefficient. The experimental thermal conductivity
of HfMo$_2$O$_8$ is very low (Fig. 1) and close to the
theoretical minimum, as was also observed for ZrW$_2$O$_8$.

Using the experimental thermal conductivity data, the
effective phonon mean free path $\lambda$ was calculated in the
Debye equation [Eq. (4)] for thermal conductivity,

$$\kappa = \frac{C\nu_0 \lambda}{3},$$

where $C$ is the heat capacity per unit volume. (We refer to
this as an effective mean free path because it generally un-
derestimates the mean free path by comparison with a more
accurate model that includes dispersion.) The results are
shown in Fig. 2. The effective mean free path at $T>40$ K is
approximately 10 Å or less, on the same order as for non-
crystalline materials such as amorphous SiO$_2$ despite the fact
that HfMo$_2$O$_8$ is crystalline. A similar result was found for ZrW$_2$O$_8$. The effective mean free path is close to its theoretical minimum, especially for $T > 50$ K (Fig. 2), indicating highly coupled phonons and high thermal resistance.

Anharmonic terms in the phonon-phonon interactions are responsible for thermal resistance in insulating materials, and the degree of anharmonicity can be quantified through the average Grüneisen parameter $\gamma$, defined in terms of bulk properties of a cubic solid,

$$\gamma = \frac{3BV\alpha_t}{C_V},$$

where $B$ is the bulk modulus ($\approx 43$ GPa for HfMo$_2$O$_8$) (Refs. 7 and 8), $V$ is the molar volume, $\alpha_t$ is the linear thermal expansion coefficient, and $C_V$ is the specific heat. The magnitudes of the average Grüneisen parameters for HfMo$_2$O$_8$ (Fig. 3) are rather large in comparison with other ceramics, and the magnitude increases for $T < 150$ K, as for ZrW$_2$O$_8$. Analyses of the contributions of various modes to the heat capacity of ZrW$_2$O$_8$ (Ref. 6) and HfMo$_2$O$_8$ (Ref. 15) indicate that for $T > 60$ K the modes below 10 meV, which are most relevant for negative thermal expansion, are essentially fully excited. From the calculation of $\gamma$, these modes are highly anharmonic, as $\gamma$ deviates significantly from zero, as shown in Fig. 3. However, the values of $\gamma$ for HfMo$_2$O$_8$ are of smaller magnitude than for ZrW$_2$O$_8$, coinciding with the less negative thermal expansion coefficient. (HfW$_2$O$_8$ is intermediate in both $\gamma$ (Ref. 20) and thermal expansion.) The low-frequency optical modes are essentially fully coupled with the heat-carrying acoustic modes for both HfMo$_2$O$_8$ and ZrW$_2$O$_8$, leading to high resistance to heat flow, and low thermal conductivity. It is likely that low thermal conductivity is a general feature of this family of materials, intrinsically related to their negative thermal expansion.

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