

Unusual thermal conductivity of the negative thermal expansion material, ZrW_2O_8

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Received 3 December 2004; accepted 18 January 2005 by R. Merlin

Abstract

In order to investigate the relationship between negative thermal expansion and other thermal properties, the thermal conductivity of the α -phase of ZrW_2O_8 has been determined from 1.9 to 390 K. In addition, the heat capacity was measured from 1.9 to 300 K. The thermal conductivity of ZrW_2O_8 is low, glass-like and close to its theoretical minimum value. The phonon–phonon coupling of the highly anharmonic low-frequency modes which are responsible for negative thermal expansion in ZrW_2O_8 appears to be highly efficient, leading to short phonon mean free paths and exceptionally low thermal conductivity. © 2005 Elsevier Ltd. All rights reserved.

PACS: 44.10.+i; 65.90.+i; 65.40.+g; 63.20.–e; 63.20.Ry

Keywords: D. Heat conduction; D. Heat capacity; D. Phonons

1. Introduction

The framework solid ZrW_2O_8 exhibits negative thermal expansion (NTE) over a wide temperature range, 0.5–1050 K, [1–3]. The magnitude is also significant, $-8.7 \times 10^{-6} \text{ K}^{-1}$ over the temperature range from 0.3 to 693 K [2]. Although negative thermal expansion has been observed in many oxides with structures similar to ZrW_2O_8 [4], and indeed many other materials such as zeolites [5], silica [6], ice [7], and quartz [8], their NTE is over much smaller temperature ranges.

Several researchers have analysed the phonon density of states of ZrW_2O_8 to determine the nature of negative thermal expansion in ZrW_2O_8 [9–13]. Earlier work has focused on explaining the NTE in ZrW_2O_8 in terms of the Rigid Unit Mode (RUM) model [14]. This model attributes NTE in this material to the thermally excited motions of the

$[\text{ZrO}_6]^{8-}$ octahedra and $[\text{WO}_4]^{2-}$ tetrahedra in the unusual structure. The polyhedra in ZrW_2O_8 are connected at almost all vertices, the exception being one terminal oxygen atom in each $[\text{WO}_4]^{2-}$ tetrahedron. The $[\text{ZrO}_6]^{8-}$ and $[\text{WO}_4]^{2-}$ polyhedra are very rigid due to the high strength of the Zr–O and W–O bonds. When the material is heated, the rigid polyhedra rock with essentially no distortion, and thus give rise to transverse vibrations perpendicular to the Zr–O–W linkage axis [3]. These vibrations are low-frequency librational and translational modes of the undistorted polyhedra; the solid is pulled tighter on excitation, leading to negative thermal expansion. However, recently Tao and Sleight [15] show that the presence of RUMs is not a reliable indicator of NTE, although some correlation exists.

A more recent view of ZrW_2O_8 proposes that the low-energy modes responsible for NTE correspond to the correlated vibrations of the $[\text{WO}_4]^{2-}$ tetrahedra and their three nearest $[\text{ZrO}_6]^{8-}$ octahedral [16,17]. XAFS results show that the $[\text{WO}_4]^{2-}$ polyhedra are rigid, however, the $[\text{ZrO}_6]^{8-}$ are stiff but not rigid as temperature increases [17]. The motion involves translation as well as libration,

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and the low-energy optic modes play a central role in the NTE mechanism [13].

A perfect harmonic solid has no thermal expansion and normal (positive) thermal expansion in solids arises from anharmonicity in lattice dynamics. Peierls determined that thermal resistance in insulators arises from phonon–phonon interactions which cause the phonons to turn back onto themselves, in Umklapp processes [18]. Phonon–phonon coupling requires anharmonic interactions. Interestingly, the negative thermal expansion of ZrW_2O_8 has been attributed to the presence of highly anharmonic low-frequency vibrational modes [9,19–21]. Thus, both NTE and thermal resistance have their origins in anharmonic terms in the lattice dynamics.

Recent results have shown unusually low thermal conductivity for ZrW_2O_8 at and above room temperature [22]. Our goal was to carry out low-temperature measurements of the thermal conductivity of ZrW_2O_8 to delineate the origins of its unusually low thermal conductivity.

2. Experimental

2.1. Material preparation and characterization

ZrW_2O_8 was obtained as a crystalline powder from Alfa Aesar (99.7% on metal basis excluding Hf with Hf < 0.3%). Instrumental neutron activation analysis indicated Hf at 50 ppm by mass ($\text{Zr}_{1-x}\text{Hf}_x\text{W}_2\text{O}_8$ with $x=0.00016$).

The α -phase of zirconium tungstate, cubic space group $P2_13$ and $Z=4$, is stable at atmospheric pressure, below 431 ± 1 K [23]. Above 431 K, the β -phase, cubic $\text{Pa}\bar{3}$, is stable. Upon applying pressure, α - ZrW_2O_8 transforms to orthorhombic γ - ZrW_2O_8 , space group $P2_12_12_1$, at about 0.2 GPa [24–26].

X-ray powder diffraction confirmed that the as-received sample was α - ZrW_2O_8 with a small amount (<5%) of γ - ZrW_2O_8 . Differential scanning calorimetry (DSC) experiments, performed with a Perkin–Elmer Pyris 1 DSC calibrated with 99.9999% indium at a scan rate of 10 K min^{-1} , indicated a feature with an onset temperature of 403 K, $\Delta H=0.97 \text{ J g}^{-1}$, likely due to water [27,28]. This was removed by subsequent heating (vide infra). The α – β phase transition at 431 K was not apparent from our DSC experiments; others also have found that this is not observable by DSC [2] due to the higher-order nature of the transition.

The samples were pressed into disk-shaped pellets with a diameter of 4.74 mm using a load of 2000 lbs (0.5 GPa). The pressing step was required to create sample morphologies suitable for thermal conductivity and relaxation heat capacity measurements, and also to decrease grain boundaries effects between the crystallites. Table 1 gives the dimensions and densities of the ZrW_2O_8 pellets used in this study.

X-ray powder diffraction showed that during the pressing

Table 1

Size and density of ZrW_2O_8 pellets used to measure thermal conductivity with PPMS

Sample	Thickness (mm)	Density (g cm^{-3})	% Theoretical density
1	1.24	3.78	74.4
2	1.05	3.96	78.0
3	1.00	3.79	74.6
4	1.18	3.79	74.6
5	1.22	3.82	75.2

step a fraction ($\sim 5\%$) of α - ZrW_2O_8 was transformed to the γ -phase. DSC measurements of the as-pressed pellets showed a peak at 403 K, $\Delta H=1.32 \text{ J g}^{-1}$ (attributed to water) along with a second smaller peak with an onset temperature at ~ 410 K, $\Delta_{\text{tr}}H=0.36 \text{ J g}^{-1}$ (attributed to the γ – α transition [27,28]).

The pressed samples were heated for 24 h in atmosphere at 408 K. Subsequently, they were characterized by X-ray powder diffraction and DSC. The diffraction results indicated that the pressed-and-heated samples were α - ZrW_2O_8 (<1% γ -phase). DSC experiments showed no discernable transitions, indicating that pressed-and-heated pellets were converted fully back to α - ZrW_2O_8 .

2.2. Thermal conductivity of ZrW_2O_8

Temperature-dependent thermal conductivities of α - ZrW_2O_8 were determined using the thermal transport option of a Quantum Design Physical Properties Measurement System (PPMS). A two-probe configuration (heater and hot thermometer shared one lead while the coldfoot and cold thermometer shared the other) was used and the pellets were epoxied (0.2 mm of silver-loaded epoxy, Tra-Bond 816H01 from Tra-Con, Inc.) to two disc-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 [29].

The geometry of the thermal conductivity sample was constrained in several ways. A die was designed to make pellets with a diameter of 4.74 mm so that the entire surface area would be covered by the QD copper lead (diameter of 6.30 mm). The thickness of the sample, ℓ , is limited by the thermal diffusion time constant for the sample defined as $\tau \sim C\ell^2/\kappa$ where C is heat capacity per unit volume and κ is 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 Ω heater in the PPMS is 50 mW where $P = \kappa\Delta T(A/\ell)$ and A is the sample area. For sample 1, measurements were taken both in the continuous scanning mode (measurements taken continuously as the software adjusts parameters, such as the heater power and period, to optimize the measurements) and the step-wise mode (more direct than the

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