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Specific Heat and Thermal Diffusivity and Conductivity of $PbWO_4$ Single Crystal Related to Its Crystal Orientation at (300 to 673) K

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Supporting Information

ABSTRACT: Lead tungstate ($PbWO_4$, PWO) single crystal has been chosen as a new generation scintillation material. The specific heat and thermal diffusivity of PWO single crystal grown by the vertical Bridgman technique is investigated for the first time by differential scanning calorimetry (DSC) and a laser flash technique at (300 to 673) K, respectively. The thermal conductivity is calculated, and it exhibits anisotropy with the values along the [100] axis ($K_{x,y}$) higher than that along the [001] axis (K_z), which is 2.40 $W \cdot m^{-1} \cdot K^{-1}$ and 2.00 $W \cdot m^{-1} \cdot K^{-1}$ at room temperature, respectively. Because of the heavier elements of the Pb atom, the PWO crystal has a higher degree of anharmonicity of lattice vibrations and thus has a smaller thermal conductivity than another scintillation material bismuth germanate (BGO).

INTRODUCTION

In recent years, lead tungstate ($PbWO_4$, PWO) crystal has been chosen as a scintillation detector material for building the largest collider in CERN[1,2] (the European Organization for Nuclear Research) and has been used extensively in high energy physics and nuclear medicine imaging due to their outstanding properties such as high density, high radiation hardness, fast decay time, and rather low cost.[3] The PWO crystal has a tetragonal structure and is anticipated to have evident anisotropy of physical properties. The mechanical properties, thermal expansion, and refractive index had been investigated and proved to be clearly different in different orientations.[3,4] Scintillation detectors may operate at temperatures higher than normal room temperature. Therefore, it is important to know their thermophysical properties. So far, the thermal diffusivity and thermal conductivity of PWO crystals are not found in literature. The aim of this work is to investigate possible specific features of the temperature dependence of thermophysical properties of PWO single crystal. In this paper, the specific heat C_P and thermal diffusivity α along [100] ($\alpha_{x,y}$) and [001] (α_z) at (300 to 673) K of the PWO crystal grown by the vertical Bridgman technique are investigated by differential scanning calorimetry (DSC) and a laser flash technique for the first time. The thermal conductivity K is calculated, and the anisotropy of thermal conductivity of PWO crystal along different major crystallographic axes is discussed.

EXPERIMENTAL METHODS

The PWO single crystal with dimensions of 2.3 × 2.6 × 2.6 cm^3 was grown[2] by the vertical Bridgman method at Shanghai Institute of Ceramics, Chinese Academy of Sciences. Glow-discharge mass spectrometry (GDMS) of the crystal was performed to obtain the impurities, and the results were shown in Table 1. Two round sample plates with the diameter of 10 mm and the thickness of 1.5 mm were cut from the large PWO crystal along the [100] and [001] directions normal to the planes of the plates to perform the thermal diffusivity measurement by a laser flash technique. Samples with mass of about 80 mg were used for the specific heat measurement.

The laser flash experimental setup has been described elsewhere.[5,6] The thermal diffusivity α is obtained by:

$$\alpha = \frac{\omega \cdot 1.37 \cdot L^2}{\pi^2 \cdot t_{1/2}} \quad (1)$$

where L is thickness of sample, $t_{1/2}$ is the time needed for the rear face temperature to reach one-half of the maximum rise, and ω is the Cowan[7] correction factor for heat loss.

The sample temperatures were controlled to 0.5 K by automatic adjustment of the current in a graphite heater. When the sample reaches the test temperature, thermal equilibrium of the sample is held for half an hour before a laser pulse is shot. The sample holder assembly is enclosed in a chamber evacuated to 10^{-2} Pa. The front surface of the sample is coated with 1 μm thick Ag film and 5 μm graphite coatings to absorb laser pulse with 1.06 μm wavelength and 1 ms pulse width from neodymium glass laser source. To achieve one-dimensional heat flow along the normal of the sample plate, a laser pulse with diameter of 12 mm is used. Its diameter is large enough to cover the specimen. The specimen is located at the center of the laser pulse to ensure the specimen is radiated evenly. A point contact between the sample holder and the sample is established to minimize axial heat loss. The pulse energy is adjusted to give a temperature rise of about 3 K. Thermal radiation emitted from the rear surface is focused by lens and led to PV type HgCdTe detector (Infrared Associates, Inc.) in (300 to 500) K and to PC type PbS detector

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Table 1. GDMS Analytic Results of PWO Single Crystal

element	concentration (ppm wt)	element	concentration (ppm wt)	element	concentration (ppm wt)
Li	< 0.01	Sc	< 0.05	Se	< 0.01
Be	< 0.005	Ti	< 0.01	Br	< 0.01
B	< 0.005	V	< 0.005	Ru	< 0.01
F	< 0.02	Cr	0.02	Sr	0.005
Na	0.1	Mn	< 0.01	Bi	< 0.5
Mg	< 0.01	Fe	0.02	Mo	0.35
Al	0.01	Co	< 0.005	Ag	0.15
Si	< 0.01	Ni	<0.02	Ba	0.03
P	0.02	Cu	0.2	Gd	< 0.005
S	0.03	Zn	< 0.01	Eu	< 0.05
Cl	< 0.01	Ga	< 0.05	Yb	< 0.005
K	0.13	Ge	0.1	Ce	0.03
Ca	0.03	As	0.46	Ta	< 1

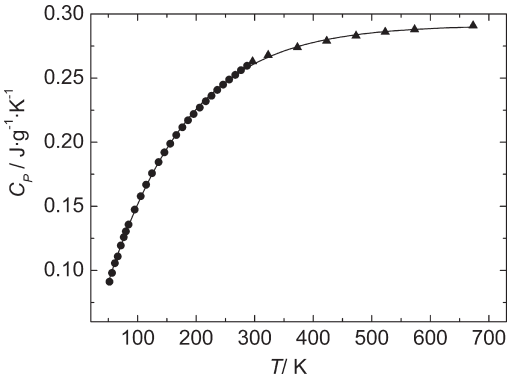

Figure 1. Temperature dependence of specific heat of PWO crystal (●, values from ref 9; ▲, this work).

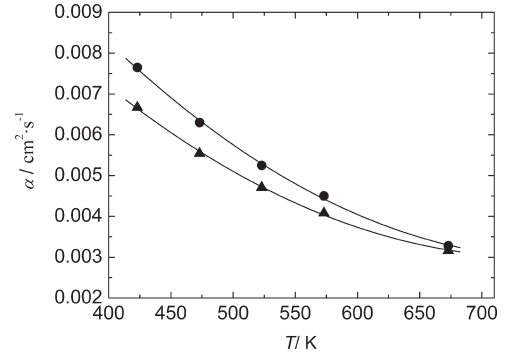

Figure 2. Temperature dependence of thermal diffusivity of PWO crystal (●, values along [100] axis; ▲,values along [001] axis).

above 500 K. The relative uncertainty of thermal diffusivity measurement is estimated to be 3 %, which arises largely from the sample's coatings and noise in the infrared detector. This uncertainty has been verified by comparing our measurement on a standard reference material, Armco iron.[8]

The density of PWO crystal ρ is 8.28 g·cm^{-3}, which is measured by Archimedes' principle. Its uncertainty is less than 0.5 %. The specific heat C_P of the sample was measured at a Perkin-Elmer DSC-2C differential scanning calorimetry (DSC) at a heating rate 10 K·min^{-1}. The relative uncertainty of 1.5 %

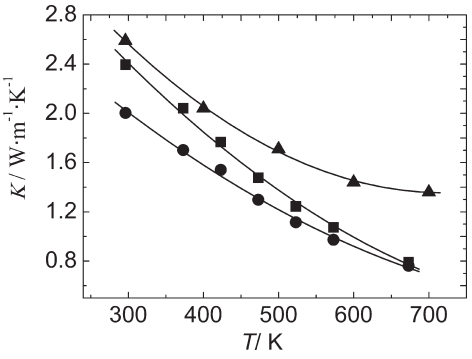

Figure 3. Temperature dependence of thermal conductivity of PWO and BGO crystal (■, values along [100] axis; ●, values along [001] axis; ▲, ref 10 of BGO crystal).

has been verified by measurements on standard reference material sapphire. The thermal conductivity K is calculated through the relation

$$K = \rho \cdot C_P \cdot \alpha \qquad (2)$$

Thus, the relative uncertainty of the thermal conductivity measurement is about 5 %.

RESULTS AND DISCUSSION

The measured specific heat is plotted in Figure 1 and combined with data from literature[9] to give wide temperature range values. As is seen from Figure 1, specific heat increases significantly with increasing temperature at low temperature but approaches saturation above 400 K.

The thermal conductivity K is calculated from the measured thermal diffusivity α (Figure 2), the specific heat data (Figure 1), and density. Measured values are listed in Table 2. The K along different orientations is plotted as functions of temperatures in Figure 3. The results show that K decreases substantially with increasing temperature. The value of K of another scintillation crystal bismuth germanate ($Bi_4Ge_3O_{12}$, BGO) measured by us[10] is plotted in Figure 3 for comparison. PWO crystal has a tetragonal structure, which is no more or less complex than a cubic structure that BGO crystal has. The presence in a crystal composition of a heavy element such as Pb and Bi suggests a high degree of anharmonicity of lattice thermal vibrations, which

Table 2. Thermal Properties of PWO Single Crystal at Selected Temperatures

T	C_P	α [001]	α [100]	K [001]	K [100]
K	$J \cdot g^{-1} \cdot K^{-1}$	$cm^2 \cdot s^{-1}$	$cm^2 \cdot s^{-1}$	$W \cdot m^{-1} \cdot K^{-1}$	$W \cdot m^{-1} \cdot K^{-1}$
300	0.263	0.0110	0.00920	2.40	2.00
373	0.274	0.00900	0.00750	2.04	1.70
423	0.279	0.00765	0.00667	1.77	1.54
473	0.283	0.00630	0.00554	1.48	1.30
523	0.286	0.00525	0.00471	1.24	1.12
573	0.288	0.00450	0.00408	1.07	0.973
673	0.291	0.00328	0.00316	0.790	0.761

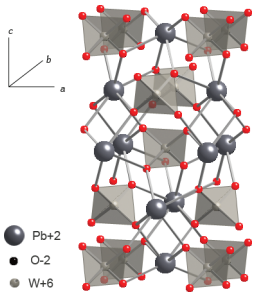

Figure 4. Crystal structure and D_{2d} symmetry of Pb−O octahedron.

correlates with the low melting temperature of PWO[3] and BGO. The vibration anharmonicity is due to high efficiency of phonon−phonon scattering. The element Pb is heavier than element Bi, and PWO has a smaller thermal conductivity than BGO crystal.

As shown in Figure 3, the K of PWO crystal exhibits anisotropy with the values along [100] axis ($K_{x,y}$) higher than that along [001] axis (K_z). This phenomenon is associated with the layer structure of PWO along [001] (z) axis. The crystals grown in melt have been claimed as scheelite crystals, which are characterized by symmetry group $I4_1/a$ with lattice parameters $a = b = 5.456$ Å, $c = 12.02$ Å.[2] The whole crystal structure could be imaged as a three-dimensional structure[2] of isolated WO_4^{2-} tetrahedron connected by Pb^{2+} ions, as shown in Figure 4. Actually, WO_4^{2-} in the crystal turned into a flattened tetrahedron along the z axis with D_{2d} symmetry. Eight oxygen ions nearby Pb^{2+} have two different bond lengths with Pb^{2+}. Four O^{2-} with longer bond lengths form a flattened tetrahedron along the z-axis, while the other four O^{2-} with shorter bond lengths form a stretched one along the z-axis. Therefore, the velocity of sound propagating along the [001] axis is slower than that along the [100] axis and yields a smaller K in the [001] (z) direction than that in the [100] (x) direction.

CONCLUSION

The specific heat, thermal diffusivity, and thermal conductivity of PWO crystal at (300 to 673) K are reported for the first time. Because of heavier elements of the Pb atom, the PWO crystal has higher degree of anharmonicity of lattice vibrations and thus has a smaller thermal conductivity than another scintillation material BGO. The thermal conductivity of PWO crystal exhibits an anisotropy with the values along [100] axis ($K_{x,y}$) higher than that along [001] axis (K_z). This phenomenon is associated with the layer structure of PWO along [001] (z) axis.

ASSOCIATED CONTENT

Supporting Information. Calculations of specific heat and thermal diffusivity in Table 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) Burachas, S.; Bondar, V.; Borodenko, Y.; Katrunov, K.; Martinov, V.; Nagornaya, L.; Ryzhikov, V.; Tamulaitis, G.; Gutbrod, H.; Manko, V. Lead tungstate $PbWO_4$ crystals for high energy physics. *J. Cryst. Growth* **1999**, *198*, 881–884.

(2) Wang, H.; Zhang, Z. J.; Zhao, J. T.; Xu, J. Y.; Hu, G. Q.; Li, P. J. Mechanical Properties and Anisotropy in $PbWO_4$ Single Crystal. *Chin. Phys. Lett.* **2010**, *27*, 4–7.

(3) Annenkov, A. A.; Korzhik, M. V.; Lecoq, P. Lead tungstate scintillation material. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2002**, *490*, 30–50.

(4) Ishii, M.; Harada, K.; Kobayashi, M.; Usuki, Y.; Yazawa, T. Mechanical properties of PbWO4 scintillating crystal. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1996**, *376*, 203–207.

(5) Choy, C. L.; Leung, W. P.; Ng, Y. K. Thermal-Conductivity of Metallic Glasses. *J. Appl. Phys.* **1989**, *66*, 5335–5339.

(6) Taylor, R. E. Thermal conductivity determinations of thermal barrier coatings. *Mater. Sci. Eng., A* **1998**, *245*, 160–167.

(7) Cowan, R. D. Pulse Method of Measuring Thermal Diffusivity at High Temperatures. *J. Appl. Phys.* **1963**, *34*, 926–927.

(8) Touloukian, Y. S.; Powell, R. W.; Ho, C. Y.; Nicolaou, M. C. *Thermophysical Properties of Matter Vol. 10, Thermal Diffusivity*; Plenum Press: New York, 1973.

(9) Touloukian, Y. S.; Buyco, E. H. *Thermophysical Properties of Matter Vol. 5, Thermal Diffusivity*; Plenum Press: New York, 1970.

(10) Xi, T. G.; Fei, Y.; Leung, W. P.; Choy, C. L. Thermal-Properties of Bismuth-Germanate $Bi_4Ge_3O_{12}$. *J. Mater. Sci. Lett.* **1989**, *8*, 1317–1319.