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# Anisotropic thermal expansion of monoclinic potassium lutetium tungstate single crystals

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The anisotropic thermal expansion of a single crystal of $KLu(WO_4)_2$(KLuW), obtained by the top-seeded solution growth method, has been investigated over a wide temperature range (50–600 °C). The linear thermal-expansion tensor has been determined and its principal $X$, $Y$, and $Z$ axes are in the [705], [010], and [107] crystallographic directions, respectively. The principal thermal-expansion coefficients $\alpha_I$, $\alpha_{II}$, and $\alpha_{III}$ are $12.8 \times 10^{-6}$, $7.8 \times 10^{-6}$, and $22.2 \times 10^{-6}$ $K^{-1}$, respectively. The principal axis with maximum thermal expansion ($Z$ with $\alpha_{III}=22.2 \times 10^{-6}$) is located at 10.37° from the $c$ axis. In comparison with $KGd(WO_4)_2$ and $KYb(WO_4)_2$, the thermal-expansion anisotropy of KLuW is weaker and therefore optical-quality crystals are easier to obtain than with KGdW and KYbW from a thermal-expansion standpoint. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1991974]

Monoclinic KLuW is a promising laser material for application in diode-pumped solid-state lasers or Raman shifters.[1–4] Recently, rare-earth-doped and undoped crystals with large dimensions of up to $43 \times 35 \times 16$ mm$^3$ (78 g) have been grown in this laboratory using the top-seeded solution growth (TSSG) method.[5] We found that crystals grown along the $c$ direction possess good optical quality, but they exhibit a slow growth ratio and have worse quality along the $b$ and $a^*$ directions. In the crystal-growth process, the as-grown crystals often show a fracture or tend to form parasitic crystallites at the edges of the growing crystal. These phenomena greatly affect the integrity of the crystal, and in order to investigate their cause, thermal expansion is an important consideration. Thermal expansion is a fundamental property of a material and it arises from the anharmonic vibration of the crystal lattice. For a single crystal under no external stress, the coefficient of thermal expansion (CTE) is compliant with the crystal symmetry. For a monoclinic crystal such as KLuW, it normally has a high anisotropy. The CTE is an important parameter in the growth of crystals, not only from the thermophysical point of view, but also from the standpoint of obtaining good mechanical behavior in the material. As a laser host crystal, the determination and location of the thermal ellipsoid of KLuW is critical because a good part of the pumping power is converted into heat inside the laser material. As a result, the effects of thermal expansion on the crystal are a critical factor in the design of solid-state diode-pumped laser devices.

A large, optical-quality KLuW crystal with dimensions of $46 \times 23 \times 21$ mm$^3$ and a weight of 78 g has been grown by the top-seeded solution growth method. A seed crystal oriented normal to the $(\bar{1}11)$ face was used. Growth parameters

were as follows: the solvent was $K_2W_2O_7$, owing to its low melting temperature ($\sim$620 °C); the seed alternating rotation speed was 4.5 rpm; the rate of cooling was 1 °C/day during the first ten days, and subsequently the solution temperature was decreased at a rate of 2–4 °C/day. The crystal growth took a total of 32 days. Finally, the crystal was cooled to room temperature over 5 days.

The thermal expansion of the KLuW crystal was measured over the temperature range of 50–600 °C by using a thermal dilatometer (NETZSCH DIL 402C). The crystal bars used for thermal-expansion measurements were polished in order to allow the probe in the dilatometer apparatus to make close contact with their surfaces, thus enhancing the accuracy of the data. The bars were then annealed at 600 °C for 24 h in order to release any processing stress before measurement. During the thermal-expansion measurement, the samples were heated at a constant rate of 5 °C/min from 50 to 600 °C and the thermal-expansion ratio versus temperature curves along the $a$, $b$, $c$, and $a^*$ crystallographic directions were obtained.

The thermal-expansion coefficient of monoclinic KLuW is a second-rank tensor. The thermal-expansion tensor that is referred to as axes in the conventional orientation is[6]

$$[a_{ij}] = \begin{bmatrix} a_{11} & 0 & a_{31} \\ 0 & a_{22} & 0 \\ a_{31} & 0 & a_{33} \end{bmatrix}. \quad (1)$$

For a monoclinic crystal, one of the principal axes ($Y$) of the thermal-expansion ellipsoid coincides with the crystallographic $b$ axis. The other two principal axes are in the (010) plane, and they can be determined by measurements along three arbitrary directions in the (010) plane. Therefore measurements along four different directions including one along the $b$ axis are necessary to describe the thermal-expansion

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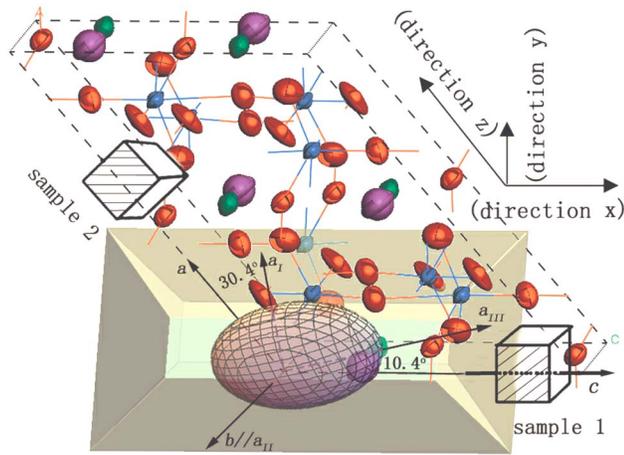
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FIG. 1. (Color online) Orientation sketch of two processed samples and the orientation relationship between the thermall-expansion ellipsoid and the real KLuW crystals.

ellipsoid. Two cuboid samples cut along four different orientations were made from a KLuW single crystal, as shown in Fig. 1. The measurement results are shown in Fig. 2. All the curves are nearly linear, but the slope increases slightly at higher temperatures. Table I lists the linear thermal-expansion coefficient over the specified temperature range along the four measured directions, We can see that the linear thermal-expansion coefficient is somewhat larger at high temperatures.

In the (010) plane, the three orientations $x$, $y$, and $z$ with corresponding angles $\xi_1 = 0\ ^\circ C$, $\xi_2 = 90\ ^\circ C$, and $\xi_3 = 130.7321\ ^\circ C$ with respect to the crystallographic $c$ axis were obtained, and the measured mean linear coefficients of thermal expansion are $\alpha_x = 21.9 \times 10^{-6}\ K^{-1}$, $\alpha_y = 13.1 \times 10^{-6}\ K^{-1}$, and $\alpha_z = 15.2 \times 10^{-6}\ K^{-1}$, respectively. In addi-
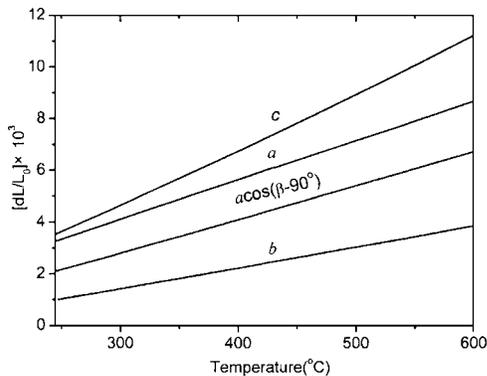


FIG. 2. Thermal expansion of KLuW along the $a$, $b$, $c$, and $a^*$ directions.

TABLE I. The linear thermal-expansion coefficient in the temperature range specified along the four measured directions.

| Temperature range (°C) | $\alpha_{22}$ ($10^{-6}$ K$^{-1}$) | $\alpha_x$ ($10^{-6}$ K$^{-1}$) | $\alpha_y$ ($10^{-6}$ K$^{-1}$) | $\alpha_z$ ($10^{-6}$ K$^{-1}$) |
|---|---|---|---|---|
| 50–100 | 7.1 | 19.9 | 11.8 | 14.6 |
| 100–300 | 7.8 | 21.8 | 13.3 | 15.3 |
| 300–600 | 8.5 | 24.0 | 14.2 | 15.7 |
| Mean | 7.8 | 21.9 | 13.1 | 15.2 |

tion, the expansion coefficient $\alpha_{22}$ in the direction of the $b$ axis was also determined to be $7.8 \times 10^{-6}\ K^{-1}$, which is the minimum thermal expansion in any direction of the crystal. The other thermal-expansion coefficients can be obtained by a method presented in the literature.[7] The operator $\xi$ formed by the angles $\xi_1$, $\xi_2$, and $\xi_3$ is determined as

$$[\xi] = \begin{bmatrix} \sin^2 \xi_1 & \sin 2\xi_1 & \cos^2 \xi_1 \\ \sin^2 \xi_2 & \sin 2\xi_2 & \cos^2 \xi_2 \\ \sin^2 \xi_3 & \sin 2\xi_3 & \cos^2 \xi_3 \end{bmatrix}. \tag{2}$$

Then the transformation matrix $[T]$ is

$$[T] = ([\xi]_T [\xi])^{-1} [\xi]_T = \begin{bmatrix} 0 & 1 & 0 \\ 0.43 & 0.58 & -1.01 \\ 1 & 0 & 0 \end{bmatrix}. \tag{3}$$

The three crystallographic expansion coefficients can be obtained by means of the equation

$$\begin{bmatrix} a_{11} \\ a_{31} \\ a_{33} \end{bmatrix} = [T] \begin{bmatrix} a_x \\ a_y \\ a_z \end{bmatrix} = \begin{bmatrix} 13.1 \\ 1.6655 \\ 21.9 \end{bmatrix} \times 10^{-6}/^\circ C, \tag{4}$$

and the linear thermal-expansion tensor at room temperature in the crystallophysical system is

$$[\alpha_{ij}] = \begin{bmatrix} a_{11} & 0 & a_{31} \\ 0 & a_{22} & 0 \\ a_{31} & 0 & a_{33} \end{bmatrix} = \begin{bmatrix} 13.1 & 0 & 1.66 \\ 0 & 7.8 & 0 \\ 1.66 & 0 & 21.9 \end{bmatrix} \times 10^{-6}/^\circ C.$$

The next step is to find the values of the principal expansion coefficients. For a monoclinic crystal, one of the principal axes, $Y$, coincides with the crystallographic $b$ axis. The other two values of the principal expansion coefficients along $X$ and $Z$ are in the (010) plane at an angle $\phi$ as measured counterclockwise from the $Z$ axis toward the $c$ axis. The angle can be determined by using the Mohr's circle construction[7] and is evaluated from the following equation:

$$\tan 2\phi = \frac{2|a_{31}|}{a_{33} - a_{11}} = 0.379, \tag{5}$$

i. e., $\phi = 10.37^\circ$.

The radius of the Mohr's circle is found to be

$$r_M^2 = \frac{1}{4}(a_{33} - a_{11})^2 + a_{31}^2 = 22.137. \tag{6}$$

So the two principal expansion coefficients $\alpha_I$ and $\alpha_{III}$ can be calculated,

$$a_I = \frac{1}{2}(a_{11} + a_{33}) - r_m = 12.8, \tag{7}$$

$$a_{III} = \frac{1}{2}(a_{11} + a_{33}) + r_m = 22.2. \tag{8}$$

Therefore the thermal-expansion tensor, when referred to its principal axes, takes the following form:

TABLE II. The principal-axis parameters $\alpha_I$, $\alpha_{II}$, and $\alpha_{III}$ and $\phi$ for KGd(WO$_4$)$_2$, KYb(WO$_4$)$_2$, and KLu(WO$_4$)$_2$.

| Crystals | $\alpha_I$ (10$^{-6}$ K$^{-1}$) | $\alpha_{II}$ (10$^{-6}$ K$^{-1}$) | $\alpha_{III}$ (10$^{-6}$ K$^{-1}$) | $\phi$ (°) | $\alpha_{III}/\alpha_{II}$ |
|---|---|---|---|---|---|
| KGdW | 10.64 | 2.83 | 23.44 | 12 | 8.3 |
| KYbW | 8.72 | 2.57 | 16.68 | 12 | 6.5 |
| KLuW | 12.8 | 7.8 | 22.2 | 10.4 | 2.8 |

$$\begin{bmatrix} 12.8 & 0 & 0 \\ 0 & 7.8 & 0 \\ 0 & 0 & 22.2 \end{bmatrix} \times 10^{-6} \text{ K}^{-1}.$$

For monoclinic KLuW the volume (bulk) expansion coefficient can be calculated from $\beta = \alpha_I + \alpha_{II} + \alpha_{III} = 42.80 \times 10^{-6}$ K$^{-1}$. From these results we have observed that KLuW exhibits strongly anisotropic thermal expansion along different crystallophysical axes and along the principal axes of the thermal-expansion ellipsoid.

The principal axis with maximum thermal expansion, $Z$, was found at 10.37° counterclockwise from the $c$ axis, while sighting along the negative $b$ axis. The principal axis with the medium thermal-expansion coefficient, $X$, was found at 30.37° rotating clockwise from the $a$ axis. The principal $X$, $Y$, and $Z$ axes are oriented along the [705], [010], and [107] directions in the crystallographic system, respectively. Figure 1 also shows the orientation relationship between the thermal-expansion ellipsoid and the KLuW crystal. We note that in the same directions the coefficient of thermal expansion is roughly proportional to the growth ratio. In our crystals, the dimension along the $c$ direction is about three times longer than that along the $b$ direction and 1.5 times longer than along $a^*$ direction, which corresponds well with the ratio of the measured coefficients of thermal expansion along the $b$, $a^*$, and $c$ directions: $7.8 \times 10^{-6}$, $13.1 \times 10^{-6}$, and $21.9 \times 10^{-6}$ K$^{-1}$, respectively ($b:a^*:c = 1:1.7:2.8$).

Thermal expansion in KLuW is anisotropic, likely due to a straightening of the flexible zigzag double WO$_6$ chains along the $c$ axis and the rigid joining of the WO$_6$ and LuO$_8$ polyhedra along the $b$ axis. Along the $b$ axis, by sharing edges, a unit of two distorted WO$_6$ octahedrons is formed and these units form a double chain along the $c$ direction. Along the $a^*$ direction we note that the double chains zigzag by sharing the vertex O atoms. At the same time we suggest that the thermal vibrations of the W atoms along the [105] direction may elongate the double chains. On the other hand, a stable network formed by WO$_6$ octahedrons and LuO$_8$ square antiprisms is formed by sharing edges or vertex O atoms along the $b$ axis. This tectostructure cannot deform much along the $b$ axis through the anharmonic vibration of the crystal lattice, although the [010] periodic bond chains (PBC's) with a period of 10.237 Å are very weak.

Table II lists the principal-axis parameters $\alpha_I$, $\alpha_{II}$, and $\alpha_{III}$ and $\phi$ for KGd(WO$_4$)$_2$,[8] KYb(WO$_4$)$_2$ (Ref. 9), and KLuW crystals. In comparison with the values of $\alpha_{III}/\alpha_{II}$ of KGdW and KYbW (8.3 and 6.5, respectively), the low value (2.8) for KLuW indicates that the thermal-expansion anisotropy is relatively weaker and thereby an optical-quality



FIG. 3. As-grown KLuW crystal containing fractures with seed orientation along the $c$ direction.

KLuW is relatively easier to obtain if the thermal-expansion anisotropy is considered.

During crystal growth, anisotropic thermal expansion will cause large thermal stress in the crystal, especially when the crystal grows larger or when the temperature varies. When the KLuW crystal is heated above the temperature range of 50–600 °C, the maximum and minimum thermal expansion will occur in the direction of the $c$ and the $b$ axes, respectively. The $c$-axis dimension will lengthen to approximately three times that along the $b$ axis. As a result, fractures often occur approximately perpendicularly to the $c$ axis. Figure 3 shows fracture due to thermal stress induced by overcooling. Therefore, we conclude that efforts should be made to avoid temperature fluctuations during crystal growth and the cooling rate should be sufficiently slow after the crystal is pulled out of the solution.

The thermal expansion of a single-crystal KLuW specimen was measured. The linear thermal-expansion tensor has been determined, and the principal $X$, $Y$, and $Z$ axes are oriented along the [705], [010], and [107] crystallographic directions, respectively. Thermal expansion in KLuW is sharply anisotropic most likely due to the straightening of the flexible zigzag double WO$_6$ chains along the $c$ axis and the rigid joining of the WO$_6$ and LuO$_8$ polyhedra along the $b$ axis.

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