

Thermal Expansion Coefficients of Optical Crystal CsLiB₆O₁₀

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Thermal expansions of bulk CsLiB₆O₁₀ (CLBO) crystal were measured by a dilatometer for the first time. Thermal expansion measurements were carried out in the temperature range between room temperature and 500 °C. The obtained expansion coefficients for tetragonal *c*- and *a*-axes were $-1.69 \pm 0.01 \times 10^{-5}/\text{K}$ and $2.12 \pm 0.01 \times 10^{-5}/\text{K}$, respectively. The thermal expansion coefficient along the *c*-axis was smaller than that reported previously.

KEYWORDS : optical nonlinear crystal, CsLiB₆O₁₀ (CLBO), thermal expansion, dilatation

One of the recent advances in optical nonlinear crystals which enable us to obtain higher order harmonic generations, such as 266 nm (4th) and 213 nm (5th) from a Nd:YAG laser (1064 nm), is the development of a new borate crystal, CsLiB₆O₁₀ (CLBO). This crystal has superior optical nonlinearities in the ultra-violet wavelength regions; for example, the shortest optical absorption edge lying at around 180 nm. On the other hand, the crystal has less mechanical properties which can be associated with a large anisotropy of the thermal expansion coefficients between the crystallographic *c*- and *a*-axes.

Takei et al.¹⁾ reported the thermal expansion of CLBO for the first time by measuring lattice constants using a high-temperature X-ray powder diffractometer, and found that the thermal expansion coefficient along the *c*-axis is negative, while that along the *a*-axis is positive. However, as they reported in the literature, the X-ray diffraction lines became considerably broad at elevated temperatures, which may lead to fluctuation of the lattice constants. In addition, the lattice constants changed abruptly to about 100 °C, showing irregular jumps from room temperature to 100 °C. CLBO belongs to a tetragonal symmetry from the growth temperature to room temperature (RT); therefore, the jumps of the lattice constants must be caused by measurement processes.

This letter reports the linear thermal expansion coefficients of CLBO single crystal along the crystallographic *c*- and *a*-axis using bulk samples by means of dilatometry. As a result, thermal expansions along both directions were evaluated more accurately, and in particular the ambiguity up to 100 °C from RT was refined clearly.

A CLBO single crystal used in this study was grown by the top-seeded solution growth (TSSG) method. Typical growth conditions are described elsewhere.²⁾ From a grown boule, approximately $3 \times 3 \times 7 - 15 \text{ mm}^3$ samples along the *c*- and *a*-axes were prepared with a X-ray back Laue technique. Orientation accuracy was $\pm 0.3^\circ$. In this experiment, these as-cut rods were used as samples without any further treatment.

Thermal expansions were directly measured for RT up to 500 °C under N₂ gas flow. An Al₂O₃ ceramic rod of a length close to that of each CLBO sample was used as a reference, and the measurement accuracy was calibrated by its thermal expansion coefficient. The heating followed by cooling measurements were carried out 2 or 3 times to clarify their reproducibility.

Figures 1(a) and 1(b) show the as-recorded thermal

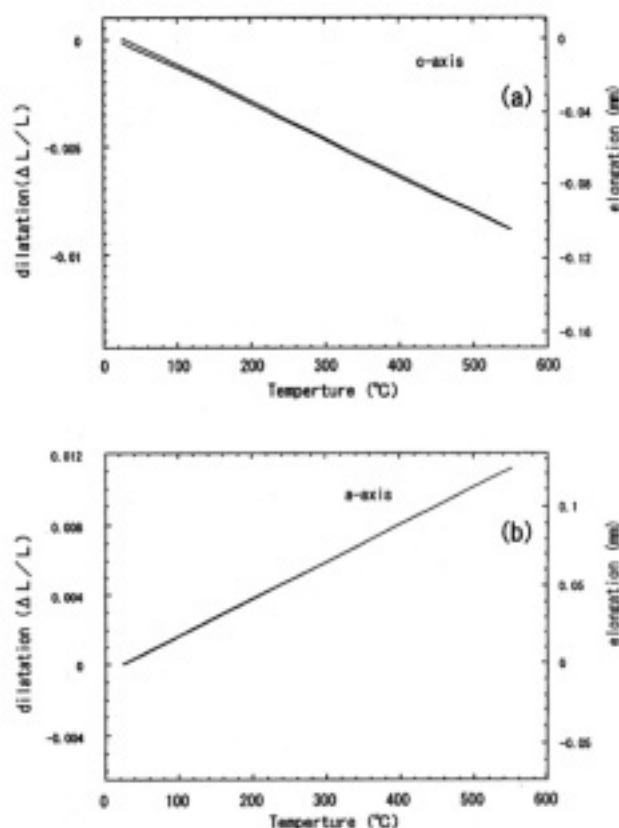


Fig. 1. (a) and (b) are the thermal expansion of CLBO along the *c*- and *a*-axes samples, respectively. Dilatation defined as $\Delta L/L$, ΔL is elongation or shrinkage of the sample and L is length at RT.

expansion dilatation ($\Delta L/L$) of the *c*- and *a*-axes samples, respectively. The crystal undergoes almost linear shrinkage along the *c*-axis and elongation along the *a*-axis upon heating. Because of its sensitivity, a fractional change of sample length is often found before and after the measurement, as in Fig. 1(a). Takei et al.¹⁾ reported remarkable jumps from RT to about 100 °C for both the crystallographic directions. It is noted that no remarkable irregularities from RT to around 100 °C were observed. This discrepancy must be caused by the difference in samples used in experiments; Takei *et al.* used powder samples, while bulk samples were investigated in the present work. It was clearly demonstrated³⁾ that CLBO was very sensitive to moisture even for a short period, and therefore a powder sample must be hydrated to some degree during sample preparation in air.

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Table 1. Thermal expansion coefficient is defined as $\Delta L/L\Delta T$, where L is the sample length, ΔL and ΔT are the elongation and the temperature difference, respectively. Cubical expansion coefficient is defined as $\Delta V/V_0\Delta T$.

	Length at RT (mm)	Thermal expansion coefficient ($\times 10^{-5} \text{ K}^{-1}$)	
		Present work	Reported by Takei <i>et al.</i>
Along <i>c</i> -axis	11.77	-1.68	-2.2
	13.99	-1.68	
	15.78	-1.70	
Along <i>a</i> -axis	11.13	+2.13	+2.0
	12.75	+2.11	
		Cubical expansion coefficient ($\times 10^{-5} \text{ K}^{-1}$)	
		+2.51	+1.9

From our direct measurements of the thermal expansion, we deduced linear thermal expansion coefficients along the *c*- and *a*-axes, as summarized in Table I. In the table, we compare the values for different sample lengths, but each thermal expansion coefficient is almost the same within the error of measurements. The evaluated thermal expansion coefficient along the *a*-axis was $2.12 \pm 0.01 \times 10^{-5} / \text{K}$, which is roughly even with the reported value, $2.0 \times 10^{-5} / \text{K}$, while that along the *c*-axis was $-1.69 \pm 0.01 \times 10^{-5} / \text{K}$, which does not coincide fairly with the reported one, $-2.2 \times 10^{-5} / \text{K}$, even in the case for which we calculated the dilatation from 100 to 500 . As is shown in Fig. 1, any irregularities or discontinuities from RT up to 500 were recognized by the recorded thermal expansion.

Figure 2 shows the temperature dependence of lattice constants calculated from the measured dilations with temperature using the lattice constants of CLBO at room temperature, i.e., $c = 8.956$ and $a = 10.476$, where the lattice constants reported by Takei *et al.* were replotted for comparisons. The temperature variations of the *a*-axis lattice constant are close to each other, while those of the *c*-axis differ to some degree. Here again, we note the difference in thermal expansion from RT up to about 100 . Our results are based on the direct measurement of the length of bulk samples under varying temperatures.

The cubical expansion coefficient defined as $\Delta V/V_0\Delta T$ was $2.51 \times 10^{-5} / \text{K}$, as listed in Table I, which also doesn't coincide fairly with the reported one, $1.9 \times 10^{-5} / \text{K}$. This discrepancy must result from the difference in thermal expansion of the *c*-axis.

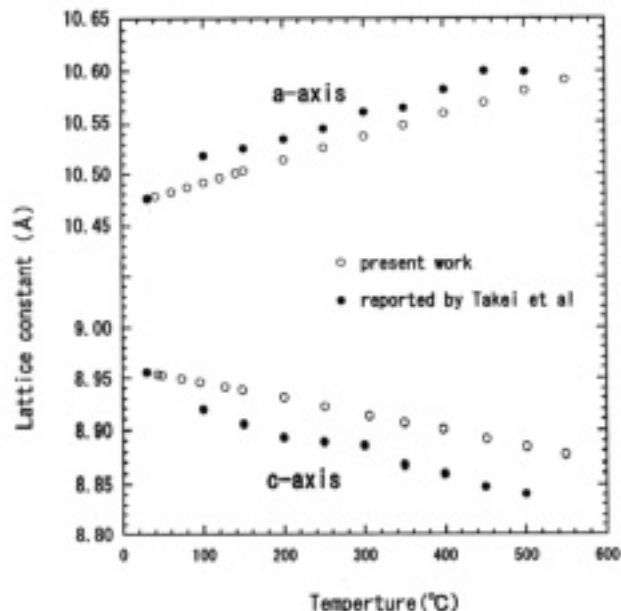


Fig. 2. Changes in the lattice constant calculated from the measured dilations.

In conclusion, the thermal expansion coefficients of TSSG-grown CLBO were directly measured from RT up to 500 using a dilatometer using bulk samples. Thermal expansion coefficients along the *c*- and *a*-axes were $-1.69 \pm 0.01 \times 10^{-5} / \text{K}$ and $2.12 \pm 0.01 \times 10^{-5} / \text{K}$, respectively. The present values are useful in designing the CLBO optical unit in a solid-state laser system.

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