

Absolute optical rotation of $\text{CsLiB}_6\text{O}_{10}$

Javier Herreros-Cedr s, Cecilio Hern ndez-Rodr guez and Werner Kaminsky

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Absolute optical rotation of CsLiB₆O₁₀Javier Herreros-Cedr s,^{a*} Cecilio Hern ndez-Rodr guez^a and Werner Kaminsky^b^aDepartamento de F sica B sica, Universidad de La Laguna, Avda. Francisco S nchez, s/n , 38206 La Laguna, S/C de Tenerife, Spain, and ^bDepartment of Chemistry, University of Washington, Seattle, Washington 98195, USA. Correspondence e-mail: jherrero@ull.es

The optical rotation (OR) of CsLiB₆O₁₀ (CLBO, space group $I\bar{4}2d$) along the **a** axis has been determined by the HAUP method [Kobayashi & Uesu (1983). *J. Appl. Cryst.* **16**, 204–211] at a wavelength of 632.8 nm and by the TILTER method [Kaminsky & Glazer (1996). *Ferroelectrics*, **183**, 133–141] at 532 nm and 650 nm. The respective rotatory powers were found to be 17 (1), 24 (2) and 19 (2)  mm^{−1}. The absolute chirality has been established by comparing Bijvoet differences, {*hkl*} and {*h l*}, on the same crystal on which OR was measured. Atomic positions and electron density Fourier peak heights were exploited as input for semi-empirical calculations of refractive indices and OR, using WinOPTACT [Glazer (2002). *J. Appl. Cryst.* **35**, 652] with only one free parameter fitted to match the average refractive index.

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1. Introduction

Cesium lithium borate, CsLiB₆O₁₀ (CLBO), is attractive because not only does it have excellent nonlinear optical properties, it is easily grown from melt or from solution (Mori *et al.*, 1995). Among other borate crystals, it has been tested for solid-state UV laser applications (Mori *et al.*, 1995). CLBO is monophasic between room temperature and 1073 K, and transparent between 180 and 2750 nm. The material is remarkable for its efficient fourth (266 nm) and fifth (213 nm) harmonics generation with Nd:YAG laser irradiation and its optical stability (Takei *et al.*, 1997). On the other hand, CLBO single crystals tend to crack under ambient conditions (Pang *et al.*, 2002; Sasaki *et al.*, 2000).

Despite the potential technical importance of CLBO, we wanted to understand the chiro-optical properties of CLBO by calculating refractive indices and optical rotation using the atomic structure and empirical polarizability volumes as parameters. These calculations employ the OPTACT model of Devarajan and Glazer (Devarajan & Glazer, 1986; Glazer, 2002; Mucha *et al.*, 1996) (see Appendix A). The optical rotation is determined experimentally in this report. Since it is important to estimate the reliability of experimental data, two different techniques to obtain OR in birefringent samples are tested on the same crystal.

CLBO crystallizes in the tetragonal system, space group $I\bar{4}2d$ with *a* = 10.49 and *c* = 8.94   (Sasaki *et al.*, 1995). CLBO is optically uniaxial negative and the dispersion of the refractive indices were obtained by Mori *et al.* (1995):

$$n_o^2 = 2.208964 + \frac{1.0493 \times 10^{-2}}{\lambda^2 - 1.2865 \times 10^{-2}} - 1.1306 \times 10^{-2} \lambda^2 \quad (1)$$

and

$$n_e^2 = 2.058791 + \frac{8.711 \times 10^{-3}}{\lambda^2 - 1.1393 \times 10^{-2}} - 6.069 \times 10^{-3} \lambda^2 \quad (2)$$

(wavelength expressed in  m).

Optical rotation is described by a symmetric axial tensor. For CLBO in the point group $\bar{4}2m$, it has two non-zero components, $\rho_{11} = -\rho_{22}$. The extreme values of OR are along the **a** and **b** axes. These axes cannot be distinguished by the crystal morphology. In addition, the space group is non-enantiomorphic. We used anomalous X-ray scattering to distinguish the **a** and **b** axes from each other on the basis of a set of atomic coordinates (see below). All tensors in the following are given with reference to the assignment of the physical reference system **e_i**, which, by convention, is related to the crystallographic **a**, **b** and **c** axes (see for example Hauss hl, 1983), as **e₂**||**b***, **e₃**||**c**, **e₁**||**e₂** × **e₃**. In the case of CLBO crystal, **e₁**||**a**, **e₂**||**b** and **e₃**||**c**.

To measure OR along the **a** or **b** axis in CLBO, one has to deconvolve the influence of linear birefringence ($\Delta n = n'' - n'$). A practical solution to this difficult task was published by Kobayashi & Uesu (1983) who called their method HAUP (high-accuracy universal polarimetry). This method, however, fails for specific values of birefringence and additional techniques were introduced to improve HAUP. Kaminsky & Glazer (1996) proposed the TILTER method, which circumvented the limitations of HAUP by modulating the birefringence, as is done similarly in the Maker fringes technique (Herman & Hayden, 1995). The TILTER setup is less expensive and faster than the established HAUP apparatus in several laboratories worldwide. We set out to determine whether the simpler device would reach the precision of the standard HAUP setup.

We have determined the optical activity of a CLBO sample using the HAUP setup designed in the laboratory of the

University of La Laguna (ULL) (Gomez & Hernández, 1998; Hernández-Rodríguez *et al.*, 2000; Herreros-Cedr s *et al.*, 2002, 2003) and the TILTER setup designed by W. Kaminsky in the Chemistry Department of the University of Washington (UW) (Kaminsky, 1996, 1997a,b; Mucha *et al.*, 1997; Kim *et al.*, 2001; Kaminsky *et al.*, 2002) for comparison.

Herein, a detailed comparison of the two methods is presented.

2. Description of the HAUP and TILTER methods

In a typical polarimetric system, the intensity of light after passing through a polarizer, chiral anisotropic sample, and analyzer contains all the information that is needed for extracting OR. Common to HAUP and TILTER experiments is a sample placed between two orthogonal polarizers at extinction angle θ_0 towards the polarizer. This situation can be studied using the Jones matrix formalism (Appendix B). The intensity of the light passing through polarizer, sample and analyzer, is written approximately as a biquadratic polynomial that is normalized to the amplitude of Y^2 :

$$I/I_0 = a_0 + a_1 Y + a_2 \theta + a_3 \theta Y + a_4 \theta^2 + Y^2, \quad (3)$$

where Y is the rotation angle of the analyzer, which is considered to be small (less than 1°). Depending on method, θ and the coefficients a_i are expressed as shown below.

In the HAUP setup at ULL, the sample and analyzer are rotated by small angles θ and Y , while the polarizer is fixed. In this case the coefficients a_i are:

$$a_{H1} = -2 \left(\frac{\rho L}{\Delta} - p \right) \sin \Delta + 2\delta Y + 2\theta_0(1 - \cos \Delta), \quad (4)$$

$$a_{H2} = 2(p + q) \sin \Delta + 4\delta Y \sin^2 \Delta/2 + 4\theta_0(1 - \cos \Delta), \quad (5)$$

$$a_{H3} = a_{H4} = 4 \sin^2 \Delta/2, \quad (6)$$

where p and q are the residual ellipticities of the polarizer and analyzer, respectively, δY is the error in the determination of the position of the crossed polarizers, Δ is the phase difference due to linear birefringence Δn (and OR), ρ is the specific rotatory power and L is the thickness of the sample.

In the TILTER system at UW, the polarizer and analyzer are rotated by angles θ and Y with respect to the sample. In this case, the coefficients of equation (3) can be written as:

$$a_{T1} = 2 \left(-\frac{\rho L}{\Delta} + p \right) \sin \Delta + 2\delta Y - 2\theta_0(1 - \cos \Delta), \quad (7)$$

$$a_{T2} = -2 \left(\frac{\rho L}{\Delta} + q \right) \sin \Delta + 2\delta Y \cos \Delta + 2\theta_0(1 - \cos \Delta), \quad (8)$$

$$a_{T3} = 2 \cos \Delta, \quad (9)$$

and $a_{T4} = 1$.

The optical parameters are obtained from a_{H3} (a_{T3}) in the HAUP (TILTER) method and from the coefficient

$$y = a_{H1} - \frac{a_{H2}}{2} = \frac{a_{T1} + a_{T2}}{2} = \left(p - q - 2 \frac{\rho L}{\Delta} \right) \sin \Delta + 2\delta Y \cos^2(\Delta/2). \quad (10)$$

In the case of the HAUP method, phase factor Δ and OR are modulated with the temperature, while in the TILTER technique the modulation of Δ and OR (due to its anisotropy) is established by tilting the sample by angle α around the $\mathbf{t}$ axis (Fig. 1b) parallel to the polarizer direction.

The effects of parasitic ellipticities (p , q) are eliminated following the method proposed by Moxon & Renshaw (1990), from the average of two successive experiments with the crystal rotated by 90° around the beam direction. The phase Δ and also the value of the misalignment of polarizer and analyzer, (δY) differ in sign between the successive measurements when the crystal is rotated by 90° . The average of the coefficients y and y_{90° for the two extinction angles (0 and 90°) of the crystal is

$$\bar{y} = \frac{y + y_{90^\circ}}{2} \simeq -2 \frac{\rho L}{\Delta} \sin \Delta + (\delta Y - \delta Y_{90^\circ}) \cos^2(\Delta/2), \quad (11)$$

where it has been taken into account that the p and q parameters practically cancel out (Hern ndez *et al.* 2000):

$$|(p - q) - (p - q)_{90^\circ}| \ll 4 \left| \frac{\rho L}{\Delta} \right|. \quad (12)$$

HAUP systems require a very careful adjustment to minimize δY , while in the TILTER experiment δY is calculated from a Fourier analysis with respect to the phase modulation

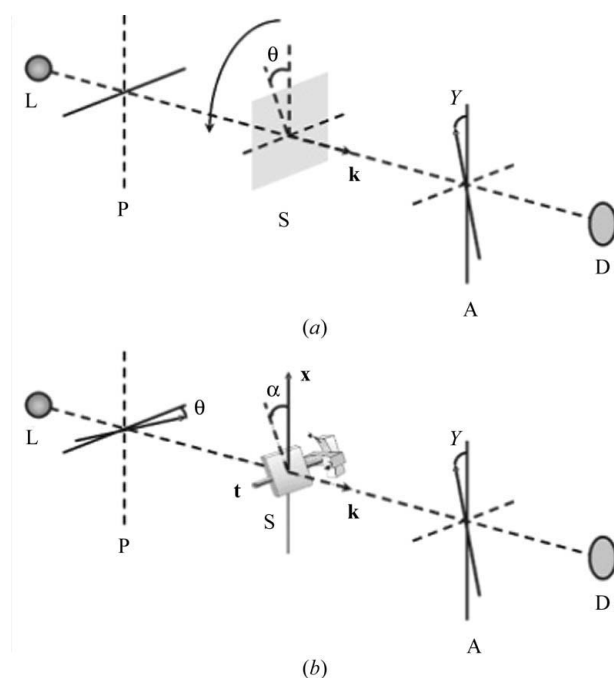


Figure 1 Schematic representation of the HAUP (a) and TILTER (b) setups. L: laser; P: polarizer; S: sample; A: analyzer; D: detector; $\mathbf{k}$: wavevector; Y : rotation angle of analyzer; θ : rotation angle of sample around an axis along $\mathbf{k}$ in (a), rotation angle of polarizer in (b); $\mathbf{x}$, $\mathbf{t}$: TILTER axes; α : tilt angle around an axis along $\mathbf{t}$.

Table 1

Refractive indices and birefringence of CLBO crystal at the wavelengths used in this work (Mori *et al.*, 1995).

λ (nm)	n_o	n_e	Δn
532	1.4982	1.4454	0.0528
632.8	1.4938	1.4418	0.0520
650	1.4934	1.4414	0.0520

to remove δY from the final OR. These equations only have meaning for measurements far from the optic axes.

3. Experimental

CLBO crystals, supplied by Molecular Technology GmbH (Berlin, Germany), were of very good optical quality (transparency and homogeneity, with well-polished faces). The measurements were carried out on a (100) cut (see below) of CLBO with 0.620 ± 0.005 mm thickness. The HAUP system at ULL (Fig. 1a) measured OR in the temperature range between 293 and 423 K (in steps of 5 K) at a wavelength of 632.8 nm over a cross section of 2 mm, while the TILTER at UW (see Fig. 1b) was set to room temperature and operated at wavelengths of 532 and 650 nm; effective cross section 0.05 mm; tilt angle α varied between $\pm 15^\circ$, in steps of 1° . Table 1 lists the refractive indices calculated from equations (1) and (2) along with the birefringence for these wavelengths.

3.1. Modulation of phase with the temperature and with the tilt angle

Fig. 2 shows the temperature dependence of the experimental values of the a_{H3} HAUP coefficient derived from equation (3) at a wavelength of 632.8 nm, taking into account the average of parameter a_{H3} of two consecutive extinction directions (0 and 90°) of the sample. The solid line represents a linear regression to the temperature variation of the phase Δ in first approximation to equation (13) (Fig. 3):

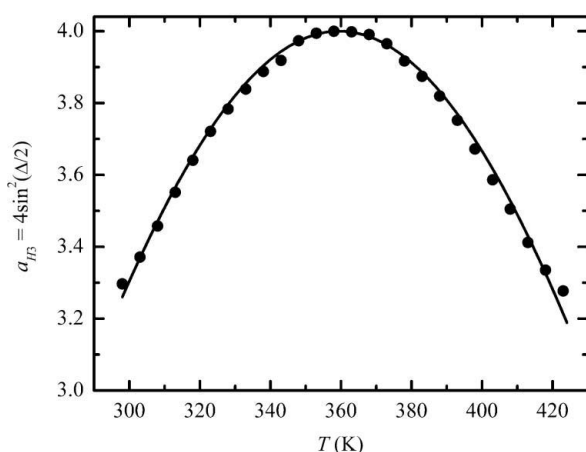


Figure 2
Temperature dependence of the mean HAUP parameter a_{H3} for the (100)-cut sample of CLBO.

$$\Delta n = \frac{\lambda}{2\pi L} \left[\Delta_{T_0} + \frac{\partial \Delta}{\partial T} (T - T_0) \right] = \Delta n [1 + k(T - T_0)], \quad (13)$$

where λ is the wavelength of the light. The linear temperature coefficient $k = 2.4 (3) \times 10^{-6} \text{ K}^{-1}$. This result is consistent with the thermo-optic coefficients reported previously for CLBO (Unemura, 1997; Unemura *et al.*, 1997; Ryu *et al.*, 1998).

The variation of the a_{T3} TILTER coefficient is drawn in Fig. 4 at a wavelength of 650 nm. Open (i) and filled circles (ii) represent the values of a_{T3} for two consecutive extinction directions of the crystal (the sample is rotated by 90° between the two experiments). Appendix C discusses the analytic expressions relating Δ to tilt angle α :

$$(i) \quad \Delta = \frac{2\pi}{\lambda} L \left[(n_o^2 - \sin^2 \alpha)^{1/2} - \left(n_e^2 - \frac{n_e^2}{n_o^2} \sin^2 \alpha \right)^{1/2} \right], \quad (14)$$

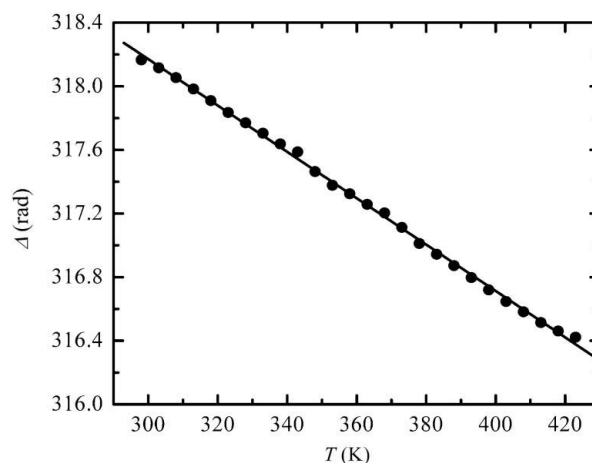


Figure 3
Variation with the temperature of the experimental values of the phase for the (100) plane of CLBO. The solid line represents the linear fit of the phase to the temperature, equation (13).

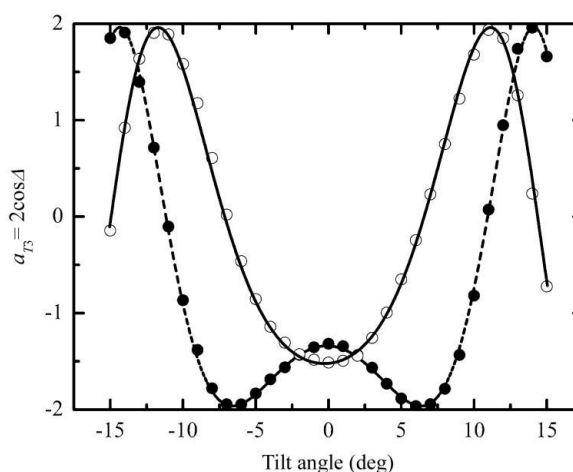


Figure 4
Dependence on the tilt angle of the TILTER parameter a_{T3} , where open and filled circles are the experimental values for the $n_o || t$ and $n_e || t$ cases, respectively. Lines represent the best fit to equation (9).

$$(ii) \quad \Delta = \frac{2\pi}{\lambda} L [(n_o^2 - \sin^2 \alpha)^{1/2} - (n_e^2 - \sin^2 \alpha)^{1/2}]. \quad (15)$$

The solid lines in Fig. 4 represent the best fit to equation (9) with Δ given by expression (14) or (15). The variation of Δ with the tilt angle is also represented in Fig. 5 for two consecutive extinction directions of the crystal, where open (i) and filled (ii) circles are the measured Δ and the solid (i) and dashed (ii) lines represent the least-squares regressions of expressions (14) or (15), respectively.

3.2. Determination of rotatory power for the (100) plane of CLBO crystal

The rotatory power varies with the direction of the wave vector:

$$\rho = \rho_{11} \sin^2 \varphi \cos^2 \theta + \rho_{22} \sin^2 \varphi \sin^2 \theta = \rho_{11} \sin^2 \varphi \cos 2\theta, \quad (16)$$

where φ is the angle between the wavevector and the **c** axis, and θ the angle in the (**ab**) plane.

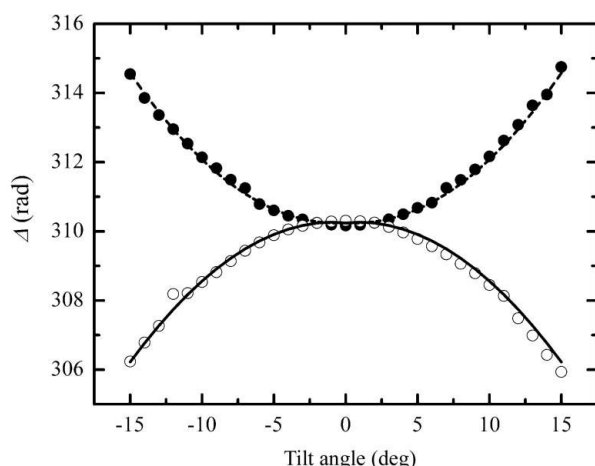


Figure 5
Variation with the tilt angle of the phase, where open and filled circles are the experimental values for the $n_o || t$ and $n_e || t$ cases, respectively. Solid and dashed lines represent the best fit to equations (14) and (15).

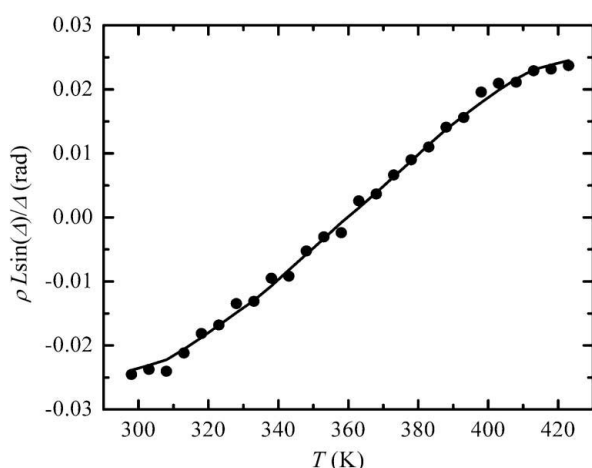


Figure 6
Dependence on temperature of the so-called 'ellipticity' signal in the HAUP method, with the solid line the best fit to equation (17).

In the HAUP experiment, assuming that the light beam is normally incident to the (100) plane of the sample, the rotatory power can be obtained from equation (11) with $\rho = \rho_{11}$. Fig. 6 shows the behaviour of the 'ellipticity' signal ρ' :

$$\rho' = \frac{\rho L}{\Delta} \sin \Delta, \quad (17)$$

where the solid line corresponds to the linear regression to equation (17). The value of optical rotation along [100] was $17 (1)^\circ \text{ mm}^{-1}$ at 633 nm (positive value: clockwise rotation of the plane of polarization facing the light source).

In TILTER measurements, the situation is more complex. Experiments for 0 and 90° extinction settings of the sample relate to disparate expressions of Δ and OR:

(i) The optical activity varies from ρ_{11} for $\alpha = 0^\circ$ towards ρ_{22} according to

$$\rho = \rho_{11} \cos^2 \beta - \rho_{11} \sin^2 \beta, \quad (18)$$

where $\cos^2 \beta = (\cos^2 \beta_e \cos^2 \beta_o)^{1/2}$; β is the tilt angle inside the sample. This geometric averaging is permissible in this case as their values do not differ substantially. For the angle of incidence $\alpha = 15^\circ$ ($\beta_e = 10.33^\circ$ and $\beta_o = 9.98^\circ$) differ by only 5×10^{-3} . The $\sin^2$ term in equation (18) does not exceed 3% at maximum tilt and is neglected here.

(ii) In this case, the expression for the optical activity as a function of β leads to

$$\rho = \rho_{11} \cos^2 \beta. \quad (19)$$

In addition to equations (18) and (19), one has to take account of an increase in optical path through tilting the sample.

In the TILTER experiment, the specific rotatory power is obtained from equation (17) with ρ given by (18) for the ordinary index parallel to the tilter axis **t**, or (19) for the extraordinary index parallel to **t**. In Fig. 7, the experimental values $\bar{y}$, filtered to show the 'ellipticity' signal, are represented for two consecutive extinction positions of the sample at a

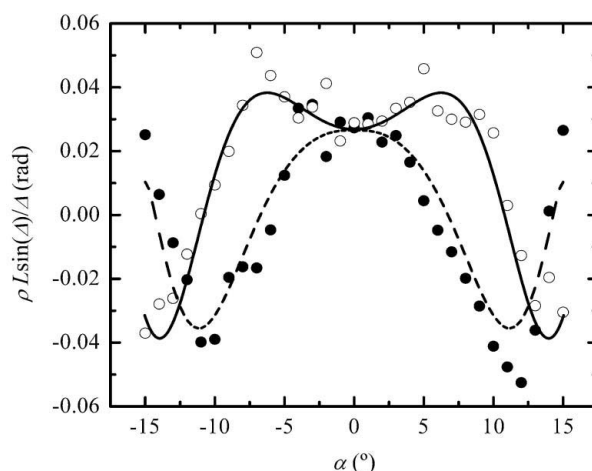
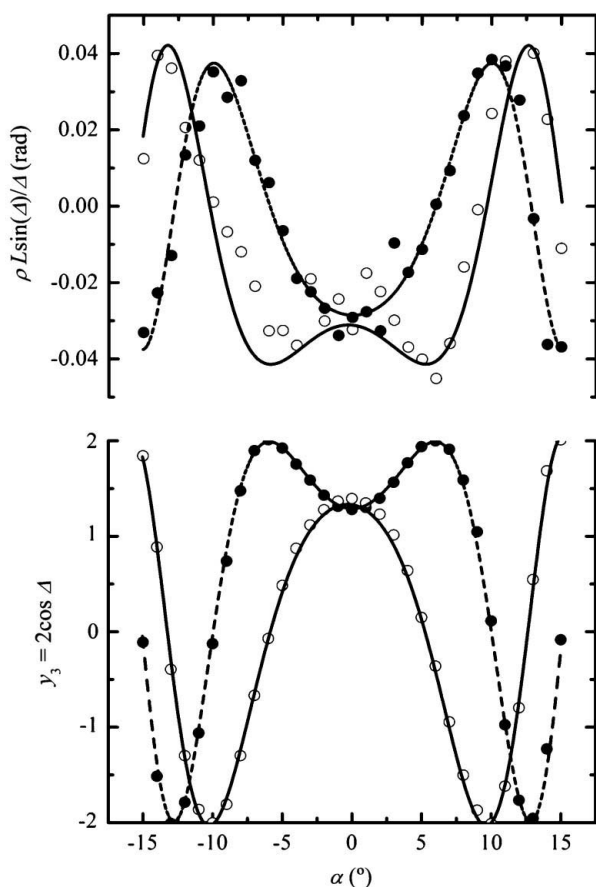


Figure 7
Dependence on tilt angle of the 'ellipticity' signal in the TILTER method. Open and filled circles are the experimental values and solid and dashed line represent the best fit to equations (17)–(19) for the $n_o || t$ and $n_e || t$ cases, respectively.

**Figure 8**

Tilt scan and fit of the ellipticity and the coefficient a_{T3} for the (100) plane of CLBO at a wavelength of 532 nm. Experimental results for the wavevector tilted towards n_o are marked by open circles and for the wavevector tilted towards n_o by filled circles. Solid and dashed lines are calculated.

wavelength of 650 nm, where the solid lines represent the best fits to equation (17) with ρ given by (18) (open circles) or by (19) (filled circles). The average optical rotation was found to be $19(2)^\circ \text{ mm}^{-1}$. Similarly, Fig. 8 shows the dependence of phase and ‘ellipticity’ with the tilt angle for the (100) plane of CLBO at a wavelength 532 nm, with an optical rotation of $24(2)^\circ \text{ mm}^{-1}$.

The representation surface (longitudinal effect) for OR at a wavelength of 632.8 nm has been drawn in Fig. 9 (Wintensor; see Kaminsky, 1997b, 2000a,b).

3.3. Absolute indexing

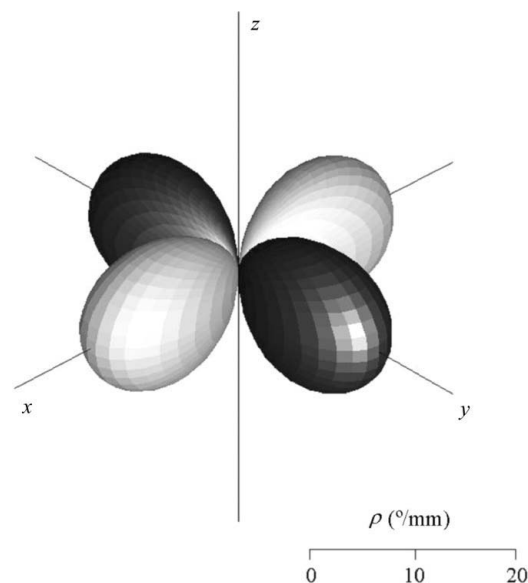
The absolute optical configuration for a given crystal structure in this case has to specify if the positive optical rotation relates to the **a** or **b** axis (Glazer & Stadnicka, 1986, 1989).

When assigning the indices to the faces of a crystal, it is convenient to calculate first the intensity difference of scattered X-rays between pairs (hkl) and $(\bar{h}\bar{k}l)$ from the known structural model

Table 2

Atom coordinates for absolute indexing of the $\text{CsLiB}_6\text{O}_{10}$ sample and experimental Fourier peak maxima.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Peak (a.u.)
Cs1	0	0	0	4503
Li1	0	0	0.5	123
B1	0.2326 (7)	0.1484 (7)	0.5601 (9)	218
B2	0.25	−0.0244 (8)	0.375	189
O1	0.1022 (5)	0.1444 (5)	0.5703 (7)	424
O2	0.2994 (7)	0.25	0.625	399
O3	0.3020 (5)	0.0575 (5)	0.4948 (7)	485

**Figure 9**

The gyration surface of CLBO crystal at room temperature and for a wavelength of 632.8 nm. The values correspond to the optical rotatory power ($^\circ \text{ mm}^{-1}$). White and black areas represent the positive and negative gyrations.

$$\frac{\Delta I}{I} = \frac{I(hkl) - I(\bar{h}\bar{k}l)}{\frac{1}{2}[I(hkl) + I(\bar{h}\bar{k}l)]} \quad (20)$$

in order to find those reflections sensitive to anomalous dispersion. The crystal structure coordinates in Table 2 were taken as a reference. The calculated differences, using the program *Crystallographica* (Oxford Cryosystems, Oxford, UK), are listed in Table 5 (Appendix D). If the experiment shows the same differences by and large, the assignment of indices in the X-ray data can be taken as absolute. If the differences consistently exhibit the opposite sign, the indices have to be transformed to match the reference structure. Our observation is: seven disagreements and three agreements for Friedel pairs with expected difference larger than 5%. The Flack enantiopole parameter was 0.72 (24). The polished face through which the optical rotation was determined was assigned (010) by the software. Taking account of the sensitive Friedel pairs and the Flack enantiopole parameter, which imply a rotation by 90° around the **c** axis, the polished face refers to the structure in Table 2 as a (100) face. Details of the

Table 3

Input polarizability volumes ($\text{\AA}^3$) for calculations of optical rotation ρ_{11} ($^\circ \text{ mm}^{-1}$) for different models (i)–(iv), along with diagonal elements of the thermal parameters and the maximum Fourier peaks from the X-ray structure experiment of this report (Table 2), at wavelength 632.8 nm.

	(i) $\langle\alpha\rangle$	(ii) $\langle\alpha\rangle$	(iii) α_{11}	α_{22}	α_{33}	(iv) $\langle\alpha\rangle$	Fourier peak	Z_i
Cs ⁺	3.0	6.59	6.13	6.13	6.4	7.987	4503	54
Li ⁺	0.03	0.18	0.22	0.22	0.09	0.2	123	2
B1 ³⁺	0.01	0.31	0.32	0.34	0.30	0.441	218	2
B2 ³⁺	0.01	0.27	0.33	0.33	0.10	0.441	189	2
O1 ²⁻	1.5	0.62	0.72	0.62	0.47	0.441	424	10
O2 ²⁻	1.5	0.58	0.34	0.56	0.79	0.441	399	10
O3 ²⁻	1.5	0.71	0.72	0.65	0.73	0.441	485	10
	Calculated values						Experimental values	
n_o	1.6317	1.4988	1.4940			1.4980	1.4938	
n_e	1.5500	1.4417	1.4054			1.4292	1.4418	
ρ_{11} ($^\circ \text{ mm}^{-1}$)	−30.39	+4.87	−11.65			+9.82	+19 (1)	

X-ray structure refinement are given in Appendix D. Thus we have observed a positive (clockwise) OR along the **a** axis.

4. Discussion

4.1. Measurement of optical rotation

The HAUP and the TILTER method agree well within the standard deviations of the individual experiments, bearing in mind that the rotatory power is proportional to λ^{-2} : 24 (2) $^\circ \text{ mm}^{-1}$ and 19 (2) $^\circ \text{ mm}^{-1}$ at 532 and 650 nm (TILTER), and 17 (1) $^\circ \text{ mm}^{-1}$ at 632.8 nm (HAUP) along the [100] direction. Only once in the past has the TILTER method been compared with a HAUP system (temperature and wavelength modulated) on the same sample, also showing good agreement (Kaminsky, 1996). Are there situations where one method is better than the other?

It is obvious that in cases of small thermo-optic coefficients it is better to use a TILTER setup. However, the theoretical description for the phase in the TILTER method is more complicated. In fact, the TILTER requires a detailed knowledge of the indicatrix of the sample and the sample orientation. Nevertheless, the TILTER's analytical description is advantageous compared with HAUP's empirical temperature variation of refractive indices, which can be complicated in the vicinity of a phase transition. The output of the TILTER method includes refined values of the refractive indices relative to that along the tilt axis and anisotropy of optical rotation in a single experiment, while the HAUP method refines only the phase and OR normal to the wavevector and the variation of both depends only on the temperature or wavelength. Sufficient modulation with the TILTER method may be difficult to achieve for light incident along n_β in biaxial samples, or in case of very thin samples.

The TILTER device measures OR much faster than standard HAUP systems and with small sample cross sections, enabling sample scanning for OR imaging (Kaminsky, 2000b).

4.2. Calculation of optical rotation

We set out to calculate the optical rotation of CLBO using a dipole–dipole interaction model. This requires atomic elec-

tronic polarizabilities as input. The structure of CLBO consists of ionic and covalent bonds. It was observed earlier that the bond character is correlated with the ellipsoidal representations of the thermal motion and inversely related to that of the polarizability volumes of the single atoms (Glazer & Stadnicka, 1986). In addition, the polarizability volumes are related to the electron density of the atoms as derived from an X-ray structure determination. The calculation of OR and the refractive indices used in *WinOPTACT* (Devarajan & Glazer, 1986; Glazer, 2002; Mucha *et al.*, 1996) uses the anisotropic polarizability volumes as input (see Appendix A). We tried the following models.

(i) Use of polarizability volumes as published by Tessmann *et al.* (1953).

(ii) Use of isotropic polarizability volumes scaled to the Fourier peaks (Newkirk, 1972; Claborn *et al.*, 2002) F_x of the x th atom with only one free scaling parameter S to reproduce the average experimental refractive index: $\alpha_x = SF_x$. This approach reflects that the polarizability is, in classic electronic polarizability theory, proportional to the number Z_i of electrons of atom i : $\langle\alpha\rangle = Z_i e^2 / m \omega_0^2$, where e is the electron charge, m its mass and ω_0 is the frequency of vibration of the electronic shell, which differs between atoms.

(iii) Use of only one free scaling parameter S , where in first approximation the diagonal coefficients of the polarizability volumes are obtained from the diagonal thermal coefficients u_{ii} according to

$$(\alpha_{ii})_x = S F_x \frac{(u_{ii})^{-1}}{\frac{1}{3} \sum_{i=1}^3 (u_{ii})^{-1}}. \quad (21)$$

(iv) Treatment of the system B–O equally as a result of the covalent character of the bond that leads to an electron distribution that is no longer sufficiently well approximated by point dipoles. When the polarizability volume of Li⁺ is fixed (its value was found to be affecting the system only marginally), the polarizability volumes for the B–O system and Cs⁺ can be found objectively from a least-squares fit to the experimental refractive indices.

The results are summarized in Table 3. The best fit of data comes from model (iv), which agrees excellently in its calcu-

Table 4

Calculated non-linear optical properties of CLBO [experimental results from Sifi *et al.* (2003)].

Effect	i,j,k	Value	i,j,k	Value
Electro-optics: r_{ijk}/ϵ_r polar	123 = 213	−1.13 pm V ^{−1}	132 = 231 = 312 = 321	−1.02 pm V ^{−1}
Experiment		n.a.		n.a.
SHG: d_{ijk} polar	123 = 132 = 213 = 231	0.88 pm V ^{−1}	312 = 321	0.80 pm V ^{−1}
Experiment		0.92 pm V ^{−1}		0.93 pm V ^{−1}
Electrogyration: g_{ijk}/ϵ_r axial	132 = 312 = −231 = −321	−3.4 µdeg V ^{−1}	n.a.	n.a.
Experiment		n.a.		n.a.

lated refractive indices. All models predict the correct optical character. Models (i) and (iii) do not produce the correct sign of optical rotation and the rotatory powers from models (ii) and (iv) fall short of the experimental value. The failure of model (iii) was expected: when inserting isotropic polarizability volumes, the *OPTACT* formalism already takes care of the directional dependence of the polarizability and produces as output anisotropic polarizability volumes. Reinserting these into the program results in divergent polarizabilities that after a few iterations of this kind lead to a collapse of the calculations. Thus, inserting anisotropic polarizability volumes is not advisable. In general, if the electron densities are known, their use will effectively remove the uncertainty in polarizability volume selection.

Models (ii) and (iv), however, cannot be generalized. For the simple system of quartz, SiO₂, for example, the Fourier peak heights [a structure refinement yielded the Fourier heights (a.u.) O^{2−} 1251, Si⁴⁺ 3589] are opposite to the best fit of polarizabilities to represent birefringence and optical rotation [polarizability volumes (a.u.) O^{2−} 1.2, Si⁴⁺ 0.2]. Here we have to assume that ω_0 has shifted the polarizability values considerably.

With the set of parameters for model (iv), we are able to estimate higher optical properties based on the DES model (see Appendix E). The results are summarized in Table 4.

The electro-optic coefficients are in the range of that of other non-linear optical materials. Electrogyration is practically non-measurable in birefringent crystals and the values found from calculation agree in size with previously discussed results for other materials (Kaminsky, 2000b).

Of special interest here is the result for the d coefficients. The value from numerous experimental determinations of the d coefficients is 0.93 pm V^{−1} for d_{312} and 0.92 pm V^{−1} for d_{123} (Sifi *et al.*, 2003), which agree well with our estimates in Table 4. Taking into account that the birefringence has been calculated fairly well from model (iv), the knowledge of the average refractive index and the crystal structures are sufficient to predict the extraordinary optical properties of CLBO.

APPENDIX A

Dipole–dipole interaction

Optical rotation may be calculated using the dipole–dipole interaction theory and has been applied with success to ionic crystals. This theory, based on electronic polarizabilities, is

described elsewhere (Beurskens-Kerssen *et al.*, 1963; Bijvoet *et al.*, 1951; Born & Goepfert-Mayer, 1933; Bruhat & Grivet, 1935; Van Laar *et al.*, 1968; Reijnhart, 1970). Here, we outline the basic ideas behind the calculations.

Polarizability volumes were selected so that the dipole–dipole model calculations were close to the refractive indices derived experimentally. The cumulative effect of the dipole–dipole interactions between all atoms in the crystal lattice acting on an atom s in unit cell l at a position $\mathbf{r}_s^l$ is described by an electrical potential, V :

$$\begin{aligned} \mathbf{V} &= \mathbf{Z}_{s'}^l(\mathbf{r}_s^l) \\ &= \exp(-i\omega t) \sum_{s'} \mathbf{p}_{s'} \exp(i\mathbf{k}\mathbf{r}_s^l) \\ &\times \left\{ \sum_{l'} \frac{\exp[ik_0|\mathbf{r}_s^l - \mathbf{r}_{s'}^{l'}| - i\mathbf{k}(\mathbf{r}_s^l - \mathbf{r}_{s'}^{l'})]}{4\pi\epsilon_0|\mathbf{r}_s^l - \mathbf{r}_{s'}^{l'}|} \right\}, \end{aligned} \quad (22)$$

where $\mathbf{Z}$ is the Hertz vector potential. The term in braces has the periodicity of the lattice. The overall Hertz potential is built from terms describing the frequency-dependent incident wave, the interaction between all atoms in the unit cell and the interaction between all unit cells in the lattice, respectively.

The electric field $\mathbf{E}(\mathbf{r}_s^l)$ at atom $\mathbf{r}_s^l$ originating from the dipole waves emanating from all other atoms (point dipoles) in the structure is described by

$$\mathbf{E}(\mathbf{r}_s^l) = \text{grad div } \mathbf{V} - \frac{\partial^2 \mathbf{V}}{c^2 \partial t^2} = \sum_{s'} A_{ss'} \mathbf{p}_{s'}^l = \alpha_s^{-1} \mathbf{p}_s^l \quad (23)$$

where $\mathbf{p}_s^l$ is the electronic polarization at position $\mathbf{r}_s^l$ and α_s is the electronic polarizability volume of atom s . $A_{ss'}$ is a matrix of complex numbers. The imaginary part contained therein describes the phase shifts that result in radiative interference and optical rotation. When the sum of the contributions to the electric field is then taken, the series converges only conditionally. As a remedy, the function is decomposed into a Fourier series that can be separated into two absolutely convergent parts, one in real space and the other in reciprocal space according to the Ewald theorem (Ewald, 1921).

A new matrix $C_{ss'}$ is defined from variables describing the electric field $\mathbf{E}(\mathbf{r}_s^l)$:

$$C_{ss'} = (\alpha_s^{-1} \delta_{ss'} - A_{ss'} + \text{const})^{-1} = (\alpha_s^{-1} \delta_{ss'} - Q_{ss'})^{-1}, \quad (24)$$

the imaginary part of which is related to optical rotation.

$$Q_{ss'} = Q_{ss'}^0 + i \sum_{\gamma} Q_{ss'}^1 k_{\gamma},$$

$$\mathcal{Q}_{ss'}^0 = -\frac{1}{\varepsilon_0 \nu R^2} \sum_{\mathbf{h}} h_{\alpha} h_{\beta} G \exp[i\mathbf{h}(\mathbf{r}_s - \mathbf{r}_{s'})] \\ + \frac{R^3}{4\pi\varepsilon_0} \sum_{l'} H_{\alpha\beta}(R\mathbf{r}_{ss'}^{l'}) + \delta_{\alpha\beta} \delta_{ss'} \frac{R^3}{3\varepsilon_0\pi(\pi^{1/2})},$$

$$\mathcal{Q}_{ss'}^1 = -\frac{1}{\varepsilon_0 \nu R^2} \sum_{\mathbf{h}} \left[(h_{\alpha} \delta_{\beta\gamma} + h_{\beta} \delta_{\alpha\gamma}) \right. \\ \left. + \frac{2}{R^2} h_{\alpha} h_{\beta} h_{\gamma} G' \exp[i\mathbf{h}(\mathbf{r}_s - \mathbf{r}_{s'})] \right] \\ - \frac{R^3}{2\pi\varepsilon_0} \sum_{l'} H_{\alpha\beta}(R\mathbf{r}_{ss'}^{l'}) \mathbf{r}_{ss'}^{l'},$$

$$G = \frac{\exp(-h^2/R^2)}{h^2/R^2}, \quad G' = \partial G / \partial k_{\gamma},$$

$$H_{\alpha\beta}(\mathbf{x}) = \frac{x_{\alpha} x_{\beta}}{x^2} \psi(|\mathbf{x}|) - \delta_{\alpha\beta} \Phi(|\mathbf{x}|),$$

$$\psi(|\mathbf{x}|) = 3\Phi(|\mathbf{x}|) + \frac{4 \exp(-|\mathbf{x}|^2)}{\pi^{1/2}},$$

$$\Phi(|\mathbf{x}|) = \frac{1}{|\mathbf{x}|^3} \operatorname{erfc}(|\mathbf{x}|) + \frac{2 \exp(-|\mathbf{x}|^2)}{\pi^{1/2}},$$

$$\mathbf{r}_{ss'}^{l'} = \mathbf{r}^{l'} + \mathbf{r}_{s'} - \mathbf{r}_s. \quad (25)$$

Indices α , β and γ refer to a Cartesian reference system and R is a parameter chosen so as to ensure convergence. The term corresponding to unit-cell index $l' = 0$ with $S = S'$ is ignored in the summation over l' . In the summation over the face-normal vector $\mathbf{h}$, the term $\mathbf{h} = (000)$ should be omitted.

The optical rotation $\rho(\mathbf{k})$ and optical dielectric constants ε_{ij} are derived as follows:

$$\rho(\mathbf{k}) = \frac{-e_{rij} k_r}{2n\nu} \operatorname{Im} \sum_{ss'} (C_{ss'})_{ij}, \quad \varepsilon_{ij} = \delta_{ij} + \frac{1}{\nu} \sum_{ss'} (C_{ss'})_{ij} \quad (26)$$

(e_{rij} = Levi-Civita symbol, $\mathbf{k}$ = wavevector, n = average refractive indices, ν = unit volume and δ_{ij} = Kronecker delta). The Levi-Civita operation e_{rij} accomplishes the cross product between the spatial coordinates of $C_{ss'}$ and the wavevector. The dipole-dipole interaction distorts the polarizabilities of the atoms resulting in an anisotropy described by the effective polarizabilities α_s^{eff} :

$$\alpha_s^{\text{eff}} = \operatorname{Re} \sum_{s'} C_{ss'}. \quad (27)$$

This theoretical model reliably calculates optical rotation on the basis of the interacting forces in inorganic structures. It was further applied successfully to molecular crystals where the interacting fields within a molecule are more significant than those between the molecules (Kaminsky & Glazer, 1997, 1998). While progress has been made in the application of quantum mechanics to the calculation of optical rotation in molecules (Kondru *et al.*, 1998), in crystals we have to choose a

theory that embodies long-range interactions and accommodates the periodicity.

APPENDIX B

Jones formalism of HAUP-TILTER equations

In TILTER- and HAUP-related experiments, the sample at extinction angle θ_0 is placed between two orthogonal polarizers. The optical train explicitly written out for the TILTER setup is represented by a string of matrices where A is the light amplitude with rotation matrices for the polarizer (R_{θ}), analyzer (R_Y), and sample (R_{θ_0}), and parasitic ellipticities of polarizer and analyzer ($\bar{R}_p$), ($\bar{R}_q$):

$$A = \bar{R}_q R_Y \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} R_Y \bar{R}_q R_{\theta_0}^t J R_{\theta_0} R_{\theta} \bar{R}_p \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad (28)$$

or alternatively for the HAUP setup

$$A = \bar{R}_q R_Y \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix} R_Y \bar{R}_q R_{\theta_0}^t J R_{\theta_0} \bar{R}_p \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad (29)$$

with

$$R_{\theta} = \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix}, \quad R_Y = \begin{bmatrix} \cos \Upsilon & -\sin \Upsilon \\ \sin \Upsilon & \cos \Upsilon \end{bmatrix}, \\ R_{\theta_0} = \begin{bmatrix} \cos \theta_0 & -\sin \theta_0 \\ \sin \theta_0 & \cos \theta_0 \end{bmatrix}, \quad (30) \\ \bar{R}_q = \begin{bmatrix} 1 & -iq \\ iq & 1 \end{bmatrix}, \quad \bar{R}_p = \begin{bmatrix} 1 & -ip \\ ip & 1 \end{bmatrix},$$

and

$$J = \begin{bmatrix} \exp(i\delta/2) & (2\varphi/\delta) \sin(\delta/2) \\ -(2\varphi/\delta) \sin(\delta/2) & \exp(-i\delta/2) \end{bmatrix}, \quad (31)$$

representing OR (φ) and linear birefringence (δ).

Further details of the treatment including parasitic ellipticities and the δY error (misalignment of polarizer and analyzer) are given elsewhere (Moxon & Renshaw, 1990; Hernández-Rodríguez *et al.*, 2000; Kaminsky, 1996, 1997a,b). The result of these operations approximates to a bi-quadratic polynomial that is normalized to the amplitudes of Y^2 :

$$I/I_0 = A A^* = a_0 + a_1 Y + a_2 \theta + a_3 \theta Y + a_4 \theta^2 + a_5 Y^2. \quad (32)$$

When allowing for a misalignment of the kind $Y = Y' + \delta Y$, the polynomial transforms according to:

$$I/I_0 = b_0 + b_1 Y + b_2 \theta + b_3 Y \theta + b_4 \theta^2 + b_5 Y^2, \quad (33)$$

where the b_i coefficients are given by:

$$b_1 = a_1 + 2(\delta Y) a_4, \quad b_2 = a_2 + (\delta Y) a_3, \\ b_3 = a_3, \quad b_4 = a_4, \quad b_5 = a_5. \quad (34)$$

The first term (b_0) is the overall offset in the intensity measurement. Parameters φ and δ are found from combinations of the parameters b_i .

Table 5

Observed and calculated Friedel differences for the CsLiB₆O₁₀ sample used in the optical rotation and X-ray anomalous scattering experiment.

The calculated differences (>5%) are based on the structural coordinates in Table 2.

<i>h k l</i>	<i>I(hkl)</i>	<i>I(khl)</i>	$\Delta I/I^{\text{observed}} (\%)$	$I/I^{\text{calculated}} (\%)$
1 1 2	Not observed			
3 2 3	14592 (282)	15901 (333)	−8.6 (26)	+15.06
4 3 1	6796 (120)	7163 (127)	−5.3 (24)	+15.64
4 1 3	20657 (321)	20962 (365)	−1.5 (23)	+5.54
2 2 4	39667 (1508)	34494 (991)	+14.0 (45)	−14.18
5 2 1	28248 (504)	27815 (600)	+1.6 (28)	−10.62
4 3 3	29829 (620)	32796 (694)	−9.6 (29)	−7.87
6 1 1	12544 (258)	13386 (287)	−6.5 (30)	−10.13
5 4 1	16781 (335)	17795 (369)	−6.0 (29)	9.64
4 1 5	16494 (275)	16934 (443)	−2.7 (25)	−10.79
6 3 3	3067 (69)	3291 (63)	−7.2 (28)	11.04

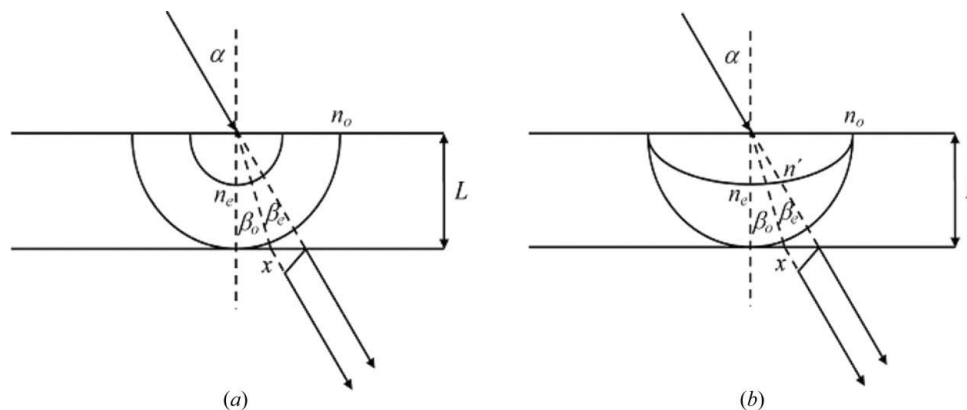


Figure 10

Wavevectors for double refraction in an optically uniaxial, negative crystal as a function of the tilt angle α , with the optic axis (a) parallel to the boundary and parallel to the plane of incidence, (b) parallel to the boundary and perpendicular to the plane of incidence. Subscripts o and e stand for ordinary and extraordinary waves, respectively, and n' is the refractive index of the extraordinary wave.

APPENDIX C

Double refraction and the TILTER method

The dependence of the phase with the tilt angle has to distinguish two possible cases for the (100) plane of the CLBO uniaxial crystal expressed analytically from the birefringence.

(i) Ordinary index (n_o) parallel to the tilter axis $\mathbf{t}$ (see Fig. 10a). Consider a linearly polarized beam along the tilter axis $\mathbf{t}$, incident at an external angle α . The light beam splits into two components (extraordinary and ordinary waves) propagating with different velocities (Hartshorne & Stuart, 1964; Nye, 1985). The optical path for the extraordinary wave is given by

$$nL/\cos\beta_e, \quad (35)$$

and for the ordinary wave (see Fig. 10a)

$$n_oL/\cos\beta_o + nx = n_oL/\cos\beta_o + n\sin\alpha L(\tan\beta_e - \tan\beta_o), \quad (36)$$

where n' is the extraordinary wave refractive index, n is the air refractive index, and β_e and β_o are the corresponding tilt angle 'inside the sample', defined according to

$$n\sin\alpha = n\sin\beta_e \quad (37)$$

and

$$n\sin\alpha = n_o\cos\beta_o. \quad (38)$$

The phase difference for the plate is given by

$$\Delta = \frac{2\pi}{\lambda} L \left[\frac{n_o}{\cos\beta_o} - \frac{n}{\cos\beta_e} + n\sin\alpha(\tan\beta_e - \tan\beta_o) \right]. \quad (39)$$

Introducing (37) and (38), the delay as a function of the angle of incidence α is expressed as

$$\begin{aligned} \Delta &= \frac{2\pi}{\lambda} L(n_o\cos\beta_o - n\cos\beta_e) \\ &= \frac{2\pi}{\lambda} L[(n_o^2 - \sin^2\alpha)^{1/2} - (n^2 - \sin^2\alpha)^{1/2}]. \end{aligned} \quad (40)$$

The refractive index n' can be obtained from the dielectric permeability normal to the direction of the wave normal,

$$\frac{1}{n^2} = \frac{\cos^2\beta_e}{n_e^2} + \frac{\sin^2\beta_e}{n_o^2}, \quad (41)$$

which can be written using equation (37) as

$$n^2 = n_e^2 + \left(1 - \frac{n_e^2}{n_o^2}\right) \sin^2\alpha. \quad (42)$$

Finally, equation (40) takes the form

$$\Delta = \frac{2\pi}{\lambda} L \left[(n_o^2 - \sin^2 \alpha)^{1/2} - \left(n_e^2 - \frac{n_e^2}{n_o^2} \sin^2 \alpha \right)^{1/2} \right]. \quad (43)$$

(ii) Extraordinary index (n_e) parallel to the tilt axis **t** (see Fig. 10*b*). In this case, the situation is quite different because the birefringence keeps constant through all the tilting scan. By substituting n' by n_e in equation (40), one obtains

$$\Delta = \frac{2\pi}{\lambda} L \left[(n_o^2 - \sin^2 \alpha)^{1/2} - (n_e^2 - \sin^2 \alpha)^{1/2} \right]. \quad (44)$$

APPENDIX D Absolute indexing

The colorless crystal was mounted in random orientation on a glass fiber on a Nonius Kappa CCD diffractometer, Mo $K\alpha$ ($\lambda = 0.71073$ Å). Cell constants and an orientation matrix for data collections were obtained by least-squares refinements of the diffraction data from more than 100 reflections. The structure was solved by direct methods. Scattering factors are from Waasmaier & Kirfel (1995). The structures were solved with *MaXus* (Mackay *et al.*, 1997); structure refinement was carried out with *SHELXL97* (Sheldrick, 1997). Table 5 represents the observed and calculated Friedel differences based on the structural coordinates in Table 2.

The obtained structure agrees well with that of Tu *et al.* (1995); however, our set of coordinates relate to Tu's coordinates by inversion of the y coordinates, *i.e.* with the set of atomic coordinates of the cited paper as reference, one would find clockwise optical rotation when looking towards the light source along the **b** axis.

APPENDIX E The DES model

Induced effects like the electro-optic effect, electrogyration or second harmonic generation can be estimated roughly with the dipole–dipole interaction model (Kaminsky & Glazer, 1997, 1998; Kaminsky *et al.*, 1998; Claborn *et al.*, 2002). The basic idea is to calculate the shift between the electron cloud and an atom nucleus in a crystal due to a simulated external field, where the experimental values of the relative dielectric constants ε are used to find the local electric field (E^{loc} = local field; E^{external} = applied electric field; P = polarization, ε_0 = vacuum permeability):

$$E^{\text{loc}} = E^{\text{external}} + \frac{P}{3\varepsilon_0} = \frac{(\varepsilon + 2)}{3} E^{\text{external}}. \quad (45)$$

The shift x of the nuclei relative to the cloud for the k th atom is derived from

$$x_i(k) = \frac{4\pi\varepsilon_0}{e} \alpha_{ij}(k) E_j^{\text{loc}} \quad (46)$$

The tensor components of the non-linear effects follow from the differences of the relative dielectric constants ε_{ij} , polar-

ization tensor a_{ij} and rotatory power ρ_{ij} , calculated for appropriate values of the external electric field E_k^{external} :

$$\varepsilon_{ij}(E_k^{\text{external}}) - \varepsilon_{ij}(0) = 0.5d_{ijk} E_k^{\text{external}} \quad (\text{SHG}),$$

$$a_{ij}(E_k^{\text{external}}) - a_{ij}(0) = r_{ijk}^e E_k^{\text{external}} \quad (\text{electro-optic effect at constant strain}), \quad (47)$$

$$\rho_{ij}(E_k^{\text{external}}) - \rho_{ij}(0) = 180g_{ijk}^e E_k^{\text{external}} / n\lambda \quad (\text{electrogyration at constant strain}).$$

Ionic polarizabilities of the atoms for static external electric fields are not known and are approximated by the electronic polarizabilities at optical frequencies.

Calculation of d coefficients with the DES model requires inverting cause and action. The virtual crystal interacts with incident light at the ground frequency and a polarization is created through the virtually applied field. The polarizability volumes for the long wavelength radiation are found from a least-squares fit of calculated to experimental refractive indices. The dielectric constant at optical frequencies is derived from the squared refractive indices. The internal tensor symmetry $d_{ijk} = d_{ikj}$ (Kleinmann, 1962) is applied to the calculated d coefficients.

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