1. Introduction

Various single crystals have been utilized as optical materials such as optical lenses, widows of optical systems, laser rods, etc. In such uses of single crystals, birefringence is an important phenomenon that affects optical performance of single crystals. Birefringence is defined as double refraction of light in a transparent and molecularly ordered material, which is manifested by the existence of orientation-dependent differences in refractive index.

Crystals are classified as being either isotropic or anisotropic depending on their optical behavior and whether or not their crystallographic axes are equivalent. Even though crystals are isotropic, they show birefringence when they are subjected to stresses. Such a phenomenon is called stress birefringence. The experimental method called photoelasticity used for stress measurement is based on this physical phenomenon (Niitsu et al., 1997; Gomi and Niitsu, 1984).
1998). Such a method has been applied to measuring residual stresses in crystals, which are induced by defects in crystals (Ledaerhandler, 1959; Yamada, 1985; Solcher et al., 1990; Yamada, 1993; Chu et al., 2002; Pinto and Jones, 2009; Ouisse et al., 2010; Xu et al., 2012; Hoa et al., 2013; Sakakura et al., 2015). Recently special attention has been paid to birefringence of single crystals used for solid-state lasers, because birefringence has strong influence on the beam quality and output power of a laser amplifier (Schmid et al., 2000; Mousavi et al., 2013; Graupeter and Pflaum, 2014; Graupeter et al., 2014; Hartmann et al., 2014; Rehak and Di Nicola, 2015; Asoubar and Wyrowski, 2015; Pflaum and Rahimi, 2015, Brickus and Dement’ev, 2016).

When crystals with residual stress are used as optical elements such as lenses, windows, etc., they show deterioration of optical performance. Let us consider a photolithography system, which is utilized to depict fine and complex integrated circuits on a silicon wafer. Such a system is consisted of many optical elements, as shown in Fig. 1. Large bulk crystals are required for manufacturing optical elements. Such large bulk crystals are grown by the Czochralski method or the Bridgman method. In the Czochralski method, residual stress is induced in a bulk crystal by thermal stress, whereas, in the Bridgman method, residual stress is not only by thermal stress but also by mechanical stress due to the contact of a crystal ingot and a crucible. In general, as-grown single crystals with larger diameter have larger residual stress, which results in larger stress birefringence in as-grown crystals. Therefore, annealing after crystal growth is the indispensable process, when single crystals are used as optical elements. Such annealing reduces the residual stress and suppresses the stress birefringence to a low level, but very long annealing period is required to reduce the stress birefringence to a target value. Numerical simulations of residual stress and the birefringence play an important role for searching effective annealing conditions.

In the present review article, we deal with calcium fluoride and magnesium fluoride (hereafter abbreviated as CaF\textsubscript{2} and MgF\textsubscript{2}, respectively) single crystals. These single crystals have excellent transmission transparency and high durability in vacuum ultraviolet region, compared with quartz, and they are expected to being optical elements in high power lithography systems. CaF\textsubscript{2} single crystal is expected as the alternative of quartz for a lens material and a chamber-window material of an ArF excimer laser light source in a high power lithography system (Yanagi et al., 2004; Hatanaka et al., 2005; Sumiya et al., 2004). MgF\textsubscript{2} single crystal is also expected as an alternative of quartz for a polarizing material (Nawata et al., 2008; Hashimoto et al., 2011). Large-sized CaF\textsubscript{2} bulk single crystals with 10 inch in diameter are produced both by the Czochralski method (Hatanaka et al., 2005) and by the vertical Bridgman method (Sumiya et al., 2004). As for MgF\textsubscript{2} single crystal, bulk crystals with 10 inch in diameter are also grown by the Czochralski method (Hashimoto et al., 2011).

Based on the paper published by the present authors (Ogino et al., 2008; Kitamura et al., 2009; Miyazaki et al., 2009; Kitamura et al., 2010a, 2010b, 2010c, 2012), we present the followings in this review article:

- Theory of stress birefringence
- Simulation methods for stress birefringence
- Stress birefringence simulations after annealing of CaF\textsubscript{2} single crystal
- Stress birefringence simulations after annealing of MgF\textsubscript{2} single crystal
- Birefringence simulations of CaF\textsubscript{2} single crystal chamber window of ArF excimer laser light source

![Fig. 1 Photolithography system.](image-url)
2. Theory of stress birefringence

2.1 Photoelastic effect

Based on the reference (Nye, 1985), we summarize the theory of stress birefringence. The change of refractive index caused by stress is called the photoelastic effect. It is given by

\[ \Delta B_{ij} = \pi_{ijkl} \sigma_{kl} \]  

(1)

where \( \sigma_{ij} \) is the stress tensor, \( \Delta B_{ij} \) is the change of the inverse dielectric tensor and \( \pi_{ijkl} \) is the piezo-optic tensor. In the above tensors, the subscripts \( ij \) and \( kl \) are abbreviated as \( 11 \rightarrow 1, 22 \rightarrow 2, 33 \rightarrow 3, 23 \rightarrow 4, 31 \rightarrow 5, \) and \( 12 \) and \( 21 \rightarrow 6 \). Hereafter we use the piezo-optic matrix \( [\pi_{ij}] \), the stress vector \( \{\sigma_i\} \) and the change of the inverse dielectric vector \( \{\Delta B_i\} \). Then the Eq.(1) can be written in the following matrix-vector form:

\[
\begin{bmatrix}
& \Delta B_1 \\
& \Delta B_2 \\
& \Delta B_3 \\
& \Delta B_4 \\
& \Delta B_5 \\
& \Delta B_6 \\
\end{bmatrix}
= \begin{bmatrix}
\pi_{11} & \pi_{12} & \pi_{13} & \pi_{14} & \pi_{15} & \pi_{16} \\
\pi_{21} & \pi_{22} & \pi_{23} & \pi_{24} & \pi_{25} & \pi_{26} \\
\pi_{31} & \pi_{32} & \pi_{33} & \pi_{34} & \pi_{35} & \pi_{36} \\
\pi_{41} & \pi_{42} & \pi_{43} & \pi_{44} & \pi_{45} & \pi_{46} \\
\pi_{51} & \pi_{52} & \pi_{53} & \pi_{54} & \pi_{55} & \pi_{56} \\
\pi_{61} & \pi_{62} & \pi_{63} & \pi_{64} & \pi_{65} & \pi_{66} \\
\end{bmatrix}
\begin{bmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3 \\
\sigma_4 \\
\sigma_5 \\
\sigma_6 \\
\end{bmatrix}
\]  

(2)

Different from the elastic constant matrix, the piezo-optic matrix \( [\pi_{ij}] \) is generally asymmetric. The relation between the component of the piezo-optic tensor and that of the piezo-optic matrix can be derived. Eqs.(1) and (2) are written by

\[ \Delta B_{ij} = \pi_{ijkl} \sigma_{kl} + \pi_{ijkl} \sigma_{kl} + 2\left( \pi_{ijkl} \sigma_{kl} + \pi_{ijkl} \sigma_{kl} \right) \]  

(3)

\[ \Delta B_{mn} = \pi_{ijkl} \sigma_{kl} + 2\pi_{ijkl} \sigma_{kl} \]  

(4)

\[ \pi_{mn} = \pi_{ijkl} \ (k = l), \ 2\pi_{ijkl} \ (k \neq l) \]  

(5)

For cubic single crystal with class \( m3m \) such as CaF\(_2\), the piezo-optic matrix has only three independent piezo-optic coefficients, \( \pi_{11}, \pi_{12}, \) and \( \pi_{44}, \) and can be simplified as follows, when the analysis coordinate system, \( x_1', x_2', x_3' \), is coincident with the crystal coordinate system, \( x_1-x_2-x_3 \) (Nye, 1985):

\[
[\pi_{ij}] = \begin{bmatrix}
\pi_{11} & \pi_{12} & \pi_{13} & 0 & 0 & 0 \\
\pi_{11} & \pi_{12} & 0 & 0 & 0 & 0 \\
\pi_{11} & 0 & 0 & 0 & 0 & 0 \\
\pi_{44} & 0 & 0 & \pi_{44} & 0 & 0 \\
\text{Sym.} & \pi_{44} & 0 & 0 & 0 & \pi_{44} \\
\pi_{44} & 0 & 0 & \pi_{44} & 0 & 0 \\
\end{bmatrix}
\]  

(6)

On the other hand, tetragonal single crystal with class \( 4/mmm \) such as MgF\(_2\) has seven independent piezo-optic coefficients, \( \pi_{11}, \pi_{12}, \pi_{13}, \pi_{31}, \pi_{33}, \pi_{44} \) and \( \pi_{66}, \) and given as follows by Nye (1985):

\[
[\pi_{ij}] = \begin{bmatrix}
\pi_{11} & \pi_{12} & \pi_{13} & 0 & 0 & 0 \\
\pi_{12} & \pi_{11} & \pi_{13} & 0 & 0 & 0 \\
\pi_{31} & \pi_{31} & \pi_{33} & 0 & 0 & 0 \\
0 & 0 & 0 & \pi_{44} & 0 & 0 \\
0 & 0 & 0 & 0 & \pi_{44} & 0 \\
0 & 0 & 0 & 0 & 0 & \pi_{66} \\
\end{bmatrix}
\]  

(7)
Here the piezo-optic matrices \([\pi_{ij}]\) are given only for the cubic single crystal with class \(m\bar{3}m\) and for tetragonal single crystal with class \(4/mmm\) in the case where the analysis coordinate system is coincident with the crystal coordinate system, but those for other crystal systems are provided by Nye (1985).

In the case where the analysis coordinate system is not coincident with the crystal coordinate system, the components of piezo-optic matrix are obtained using tensor transformation. The relationship between the tensor components of piezo-optic coefficient in the crystal coordinate system \(\pi_{ijkl}\) and those in the analysis coordinate system \(\pi'_{ijkl}\) is given as follows:

\[
\pi'_{ijkl} = a_{ia} a_{jb} a_{kc} a_{ld} \pi_{abcd} \tag{8}
\]

where \(a_{ij}\) is given by

\[
a_{ij} = e_{i} \cdot e_{j} \tag{9}
\]

In the above equation, \(e_{x}'\) and \(e_{y}\) are the base vectors of the analysis coordinate \(x'_{i}\) and the crystal coordinate \(x_{j}\) respectively.

In the cubic single crystal such as \(\text{CaF}_2\), the components of the inverse dielectric constant \(B_i\) are expressed in the crystal coordinate system by the refractive index \(n\) as follows, when no stress is applied to the crystal (Nye, 1985):

\[
\begin{bmatrix}
B_1 \\
B_2 \\
B_3 \\
B_4 \\
B_5 \\
B_6
\end{bmatrix} = \begin{bmatrix} \frac{1}{n^2} \\ \frac{1}{n^2} \\ \frac{1}{n^2} \\ 0 \\ 0 \\ 0 \end{bmatrix}
\tag{10}
\]

In this case, the crystal without stress is optically isotropic, and has no intrinsic birefringence.

On the other hand, the tetragonal single crystal such as \(\text{MgF}_2\) shows intrinsic birefringence even without stress because of its optical anisotropy, and the components of the inverse dielectric constant \(B_i\) are expressed in the crystal coordinate system by the refractive index for an ordinary-ray \(n_0\) and that for an extraordinary-ray \(n_e\) as follows (Nye, 1985):

\[
\begin{bmatrix}
B_1 \\
B_2 \\
B_3 \\
B_4 \\
B_5 \\
B_6
\end{bmatrix} = \begin{bmatrix} \frac{1}{n_0^2} \\ \frac{1}{n_0^2} \\ \frac{1}{n_e^2} \\ 0 \\ 0 \\ 0 \end{bmatrix}
\tag{11}
\]

For the trigonal and hexagonal single crystals, \(\{B_i\}\) vectors are expressed by the same equation.

According to Nye's textbook (Nye, 1985), \(\{B_i\}\) vector for the orthorhombic, monoclinic and triclinic crystals without stress are given in the crystal coordinate system by

\[
\begin{bmatrix}
B_1 \\
B_2 \\
B_3 \\
B_4 \\
B_5 \\
B_6
\end{bmatrix} = \begin{bmatrix} \frac{1}{n_0^2} \\ \frac{1}{n_0^2} \\ \frac{1}{n_0^2} \\ 0 \\ 0 \\ 0 \end{bmatrix}
\tag{12}
\]

2.2 Indicatrix

We consider the following indicatrix in the analysis coordinate system, \(x_1-x_2-x_3\), to obtain the refractive indices:
\[ B_1 x_1^2 + B_2 x_2^2 + B_3 x_3^2 + 2B_4 x_2 x_3 + 2B_5 x_3 x_1 + 2B_6 x_1 x_2 = 1 \]  
\[ \text{(13)} \]

When stress is applied to a single crystal, the indicatrix is expressed by adding the increment of \( \Delta B_i \) calculated from Eq.(2).

\[ \begin{align*} 
(B_1 + \Delta B_1) x_1^2 + (B_2 + \Delta B_2) x_2^2 + (B_3 + \Delta B_3) x_3^2 \\
+ 2(B_4 + \Delta B_4) x_2 x_3 + 2(B_5 + \Delta B_5) x_3 x_1 + 2(B_6 + \Delta B_6) x_1 x_2 &= 1 
\end{align*} \]
\[ \text{(14)} \]

The refractive indices are determined as follows. As shown in Fig. 2, let us consider an ellipsoidal section, which is perpendicular to wave normal and passes through the origin. Such a section is an ellipse. Light can be decomposed into oscillation components along the two principal axes, the long axis and the short axis, of the ellipse. The long axis and the short axis are called the slow axis and the fast axis, respectively. The lengths of the principal axes of the ellipse correspond to the refractive index along the slow axis \( n_s \) and that along the fast axis \( n_f \).

When the wave normal coincides with the \( x_3 \)-axis of the analysis coordinate system, the following equation is obtained by taking \( x_3 = 0 \) in Eq.(14).

\[ \begin{align*} 
(B_1 + \Delta B_1) x_1^2 + (B_2 + \Delta B_2) x_2^2 + 2(B_6 + \Delta B_6) x_1 x_2 &= 1 
\end{align*} \]
\[ \text{(15)} \]

From this ellipse, we can calculate the birefringence \( \Delta n = n_s - n_f \) defined by the difference between the two refractive indices and the azimuth \( \rho \) defined by the angle between the fast axis and the \( x_1 \)-axis as follows:

\[ \Delta n = \frac{1}{2} \left( \frac{B_1 + \Delta B_1 + B_2 + \Delta B_2}{2} \right)^{3/2} \sqrt{(B_1 + \Delta B_1 - B_2 - \Delta B_2)^2 + 4(B_6 + \Delta B_6)^2} \]
\[ \text{(16)} \]

\[ \tan 2\rho = \frac{2(B_6 + \Delta B_6)}{B_1 + \Delta B_1 - B_2 - \Delta B_2} \]
\[ \text{(17)} \]

Fig. 2 An indicatrix, and determination of refractive indices; \( X_1 \)-\( X_2 \)-\( X_3 \) is the crystal coordinate system (Kitamura et al., 2009).

### 3. Calculation methods for stress birefringence

The stress birefringence is experimentally measured by optical path difference. Let us consider a single crystal ingot, the thickness of which is along the wave normal. Stress changes continuously along the wave normal, so that birefringence also changes continuously along this direction. An exact method for calculating optical path difference is the Jones calculus (Kliger et al., 1990). A simple method was proposed by Abbott et al. (2003). In their method, the stress components averaged along the wave normal are utilized to calculate optical path difference. Hereafter this method is called the average stress method. We will show the relationship between the Jones calculus and the average stress method after briefly describing both methods. In the following discussion, the \( x_3 \)-axis is assumed to coincide with the wave normal shown in Fig. 2.

#### 3.1 Jones calculus

In the Jones calculus, polarized light propagating along the \( x_3 \)-direction is expressed using the Jones vector \( \mathbf{J} \) as follows:
into \( \Delta q \). Let us consider a medium with the refractive index along the slow axis.

The Jones matrix consists of the Jones vectors for an input beam and an output beam, respectively, and \( \mathbf{M}(\rho) \) is a 2 \( \times \) 2 matrix to describe a polarizing optical element with the azimuth \( \rho \), which indicates the transformation matrix that converts \( \mathbf{J} \) into \( \mathbf{J}' \). Let us consider a medium with the refractive index along the slow axis \( n_s \), that along the fast axis \( n_f \), and the thickness \( d \). When the fast axis coincides with \( x_1 \)-axis, the Jones matrix of this medium is written for the wavelength of \( \lambda \) as

\[
\mathbf{M}(0) = e^{-i\phi} \begin{bmatrix} e^{i\phi/2} & 0 \\ 0 & e^{-i\phi/2} \end{bmatrix}
\]

where \( \delta \) and \( q \) are given by

\[
\delta = \frac{2\pi d}{\lambda} \Delta n, \quad \Delta n = n_f - n_s, \quad q = \frac{2\pi d}{\lambda} \frac{(n_i + n_f)}{2}
\]

\( \delta \) is called retardation. In Eq.(20), the term \( e^{-i\phi} \) represents the intensity of light, and we redefine \( \mathbf{M}(0) \) as follows by omitting this term because our concern is the phase of light:

\[
\mathbf{M}(0) = \begin{bmatrix} e^{i\phi/2} & 0 \\ 0 & e^{-i\phi/2} \end{bmatrix}
\]

The Jones matrix \( \mathbf{M}(\rho) \) of a medium with the azimuth \( \rho \) and the retardation \( \delta \) can be obtained by applying the rotation matrix \( \mathbf{T}(\rho) \) to \( \mathbf{M}(0) \).

\[
\mathbf{M}(\rho) = \mathbf{T}(\rho)\mathbf{M}(0)\mathbf{T}(-\rho)
\]

\[
= \begin{bmatrix} \cos^2(\rho)e^{i\phi/2} + \sin^2(\rho)e^{-i\phi/2} & 2i\sin(\rho)\cos(\rho)\sin(\delta/2) \\ 2i\sin(\rho)\cos(\rho)\sin(\delta/2) & \cos^2(\rho)e^{-i\phi/2} + \sin^2(\rho)e^{i\phi/2} \end{bmatrix}
\]

where \( \mathbf{T}(\rho) \) is given by

\[
\mathbf{T}(\rho) = \begin{bmatrix} \cos \rho & -\sin \rho \\ \sin \rho & \cos \rho \end{bmatrix}
\]

Let us consider the light passing through a crystal ingot along the \( x_3 \)-direction, as shown in Fig. 3. The ingot is divided into \( m \) layers along the \( x_3 \)-axis, within which the stress and birefringence are assumed to be uniform. Now we consider the Jones matrix \( \mathbf{M}_k \) of the \( k \)-th layer in the ingot. \( \Delta \mathbf{B}_k \) in the \( k \)-th layer can be obtained by substituting the stress components in the \( k \)-th layer into Eq.(2), and the difference between the two refractive indices \( \Delta n_k \) and the azimuth \( \rho_k \) in the \( k \)-th layer are obtained from Eqs.(16) and (17). Then \( \mathbf{M}_k \) is derived from Eq.(23) using \( \Delta n_k \) and \( \rho_k \).

The total Jones matrix \( \mathbf{M}_{\text{total}} \) of the ingot along the \( x_3 \)-direction is expressed as

\[
\mathbf{M}_{\text{total}} = \prod_{k=1}^{m} \mathbf{M}_k
\]

\[
= \prod_{k=1}^{m} \begin{bmatrix} \cos^2(\rho_k)e^{i\phi_k/2} + \sin^2(\rho_k)e^{-i\phi_k/2} & 2i\sin(\rho_k)\cos(\rho_k)\sin(\delta_k/2) \\ 2i\sin(\rho_k)\cos(\rho_k)\sin(\delta_k/2) & \cos^2(\rho_k)e^{-i\phi_k/2} + \sin^2(\rho_k)e^{i\phi_k/2} \end{bmatrix}
\]

The retardation \( \delta_k \) is given by
The ingot itself has one azimuth $\rho_{\text{total}}$ and one retardation $\delta_{\text{total}}$. Referring to eq.(23), $M'_{\text{total}}$, a diagonal form of $M_{\text{total}}$, can be obtained as follows:

$$M'_{\text{total}} = T(-\rho_{\text{total}})M_{\text{total}}T(\rho_{\text{total}})$$

(27)

It is found that the retardation of the ingot $\delta_{\text{total}}$ is equal to the difference in the argument of diagonal terms of $M'_{\text{total}}$. In other words, $\delta_{\text{total}}$ is equal to the difference in argument of two eigenvalue of $M_{\text{total}}$. Finally the optical path difference of the ingot $\Gamma_{\text{total}}$ is given by

$$\Gamma_{\text{total}} = \frac{\delta_{\text{total}}}{2\pi \lambda}$$

(28)

Almost all numerical simulations of stress birefringence are based on the Jones calculus. Moreover several software packages (Doyle et al., 2002a, 2002b; Pflaum and Rahimi, 2015; Rehak and Di Nicola, 2015) have been developed to obtain stress birefringence based on the Jones calculus. They use the stress components calculated from the finite element method.

### 3.2 Average stress method

Although almost all numerical simulations are based on the Jones calculus, an exact method for calculating the optical path difference, Abott et al. (2003) proposed an approximate method called average stress method. In the average stress method, the stress components averaged along the wave normal are utilized to calculate the optical path difference without dividing an ingot into a multi-layer system.

When the wave normal coincides with the $x_3$-axis of the analysis coordinate system, the average stress components along the wave normal $\bar{\sigma}_i$ are calculated as follows by using the stress components $\sigma_i$:

$$\bar{\sigma}_i = \frac{1}{d} \int_0^d \sigma_i \, dx_3$$

(29)

where $d$ is the propagation length in the crystal ingot.

The change of the inverse dielectric constant is given by

$$
\begin{align*}
\Delta \bar{B}_1 &= \begin{bmatrix} \pi_{11} & \pi_{12} & \pi_{13} & \pi_{14} & \pi_{15} & \pi_{16} \end{bmatrix} \bar{\sigma}_1 \\
\Delta \bar{B}_2 &= \begin{bmatrix} \pi_{21} & \pi_{22} & \pi_{23} & \pi_{24} & \pi_{25} & \pi_{26} \end{bmatrix} \bar{\sigma}_2 \\
\Delta \bar{B}_3 &= \begin{bmatrix} \pi_{31} & \pi_{32} & \pi_{33} & \pi_{34} & \pi_{35} & \pi_{36} \end{bmatrix} \bar{\sigma}_3 \\
\Delta \bar{B}_4 &= \begin{bmatrix} \pi_{41} & \pi_{42} & \pi_{43} & \pi_{44} & \pi_{45} & \pi_{46} \end{bmatrix} \bar{\sigma}_4 \\
\Delta \bar{B}_5 &= \begin{bmatrix} \pi_{51} & \pi_{52} & \pi_{53} & \pi_{54} & \pi_{55} & \pi_{56} \end{bmatrix} \bar{\sigma}_5 \\
\Delta \bar{B}_6 &= \begin{bmatrix} \pi_{61} & \pi_{62} & \pi_{63} & \pi_{64} & \pi_{65} & \pi_{66} \end{bmatrix} \bar{\sigma}_6 
\end{align*}
$$

(30)

The birefringence $\Delta \bar{n}$ and azimuth $\bar{\rho}$ of the average stress method is obtained by replacing $\Delta B_i$ in Eqs.(16) and (17) with $\Delta \bar{B}_i$. 

---

Fig. 3  Layed-division along $x_3$-direction (Ogino et al., 2008)
\[
\Delta \pi = \frac{1}{2} \left( \frac{B_1 + \Delta B_1 + B_2 + \Delta B_2}{2} \right)^{3/2} \sqrt{(B_1 + \Delta B_1 - B_2 - \Delta B_2)^2 + 4\left(B_6 + \Delta B_6\right)^2}
\]  
(31)
\[
\tan 2\theta = \frac{2(B_6 + \Delta B_6)}{B_1 + \Delta B_1 - B_2 - \Delta B_2}
\]  
(32)

Then the optical path difference \( \Gamma \) is expressed as follows:

\[
\Gamma = d\Delta \pi
\]  
\[
= \frac{d}{2} \left( \frac{B_1 + \Delta B_1 + B_2 + \Delta B_2}{2} \right)^{3/2} \sqrt{(B_1 + \Delta B_1 - B_2 - \Delta B_2)^2 + 4\left(B_6 + \Delta B_6\right)^2}
\]  
(33)

### 3.3 Equivalence of the Jones calculus and the average stress method

Equivalence of the Jones calculus and the average stress method is shown here. Let us assume the condition, \( B_i >> \Delta B_i \) \((i = 1, 2)\). In the cubic single crystal, the indicatrix without stress is a sphere because of Eqs. (10) and (13), so that the relation \( B_6 = 0 \) holds for any analysis coordinate system. For other crystal systems such as the tetragonal single crystal without stress, \( B_6 \) is not always equal to zero, when the analysis coordinate system does not coincide with the crystal coordinate system, but \( B_6 \) becomes zero, when the long and short axes of the indicatrix are, respectively, coincident with the axes of the analysis coordinate system. So we can assume \( B_6 = 0 \).

In the Jones calculus, the birefringence in the \( k \)-th layer, \( \Delta n_k \), is written as follows from Eq. (16) by considering \( B_6 = 0 \) and \( B_i >> \Delta B_i \) \((i = 1, 2)\):

\[
\Delta n_k = \frac{1}{2} \left( \frac{B_1 + B_2}{2} \right)^{3/2} \sqrt{(B_1 + \Delta B_1 - B_2 - \Delta B_2)^2 + 4\Delta B_6^2}
\]  
(34)

Thus the retardation in the \( k \)-th layer is expressed as

\[
\delta_k = \frac{2\pi\Delta x}{\lambda} \Delta n_k
\]  
\[
\frac{\pi\Delta x}{\lambda} \left( \frac{B_1 + B_2}{2} \right)^{3/2} \sqrt{(B_1 + \Delta B_1 - B_2 - \Delta B_2)^2 + 4\Delta B_6^2}
\]  
(35)

The azimuth of the fast axis in the \( k \)-th layer is obtained from eq. (17) by considering \( B_6 = 0 \).

\[
\tan 2\rho_k = \frac{2\Delta B_6}{B_1 + \Delta B_1 - B_2 - \Delta B_2}
\]  
(36)

If the retardation is very small, i.e., \( \delta_k << 1 \), the Jones matrix of the \( k \)-th layer, \( M_k(\rho_k) \), given in eq. (23) becomes

\[
M_k(\rho_k) = \begin{bmatrix}
1 + \frac{i\delta_k}{2} \cos(2\rho_k) & \frac{i\delta_k}{2} \sin(2\rho_k) \\
\frac{i\delta_k}{2} \sin(2\rho_k) & 1 - \frac{i\delta_k}{2} \cos(2\rho_k)
\end{bmatrix}
\]  
(37)

The assumption \( \delta_k << 1 \) would hold if the birefringence caused by residual stress is small, and the number of layers \( m \) shown in Fig. 4 is chosen to be large enough. The following equation is obtained by substituting Eqs. (35) and (36) into Eq. (37):

\[
M_k(\rho_k) = I + H_k
\]  
(38)

where \( I \) is the unit matrix with \( 2 \times 2 \), and \( H_k \) is denoted by
\[
\mathbf{H}_i = \frac{i\pi}{2\lambda} \left( \frac{B_i + B_2}{2} \right)^{-3/2} \begin{bmatrix}
(B_i + \Delta B_1 - B_2 - \Delta B_2) \Delta x_3 & 2\Delta B_6 \Delta x_3 \\
2\Delta B_6 \Delta x_3 & -(B_i + \Delta B_1 - B_2 - \Delta B_2) \Delta x_3
\end{bmatrix}
\]

(39)

Then the total Jones matrix is given by

\[
\mathbf{M}_{\text{total}} = \prod_{i=1}^{m} \prod_{i=1}^{m} (\mathbf{I} + \mathbf{H}_i)
\]

(40)

Eq. (40) leads to the following by neglecting higher-order terms because of infinitesimal small value:

\[
\mathbf{M}_{\text{total}} = \mathbf{I} + \sum_{i=1}^{m} \mathbf{H}_i = \mathbf{I} + \frac{i\pi}{2\lambda} \left( \frac{B_i + B_2}{2} \right)^{-3/2}
\]

\[
\sum_{i=1}^{m} (B_i + \Delta B_1 - B_2 - \Delta B_2) \Delta x_3 \quad \sum_{i=1}^{m} 2\Delta B_6 \Delta x_3
\]

\[
\sum_{i=1}^{m} 2\Delta B_6 \Delta x_3 \quad -\sum_{i=1}^{m} (B_i + \Delta B_1 - B_2 - \Delta B_2) \Delta x_3
\]

(41)

At the limit of \( \Delta x_3 \rightarrow 0 \) and \( m \rightarrow \infty \), Eq. (41) becomes

\[
\mathbf{M}_{\text{total}} = \mathbf{I} + \frac{i\pi}{2\lambda} \left( \frac{B_i + B_2}{2} \right)^{-3/2}
\]

\[
\int_0^d (B_i + \Delta B_1 - B_2 - \Delta B_2) \, dx_3
\]

\[
\int_0^d 2\Delta B_6 \, dx_3
\]

\[
\int_0^d (B_i + \Delta B_1 - B_2 - \Delta B_2) \, dx_3
\]

(42)

According to Eq. (2), the components of \( \Delta B_i \) are represented by the stress components \( \sigma_i \), so that the matrix components in Eq. (42) are expressed by the stress components \( \sigma_i \). For example,

\[
\int_0^d (B_i + \Delta B_1 - B_2 - \Delta B_2) \, dx_3
\]

\[
= (B_i - B_2) \, dx_3 + \int_0^d (\sigma_{i1} - \sigma_{21}) \, dx_3 + \int_0^d (\sigma_{i2} - \sigma_{22}) \, dx_3 + \left( \int_0^d \sigma_{13} \, dx_3 + \int_0^d \sigma_{23} \, dx_3 \right) \int_0^d \sigma_{35} \, dx_3
\]

(43)

The above equation can be written by the average stress components \( \overline{\sigma}_j \), which is defined by Eq. (29), as follows:

\[
\int_0^d (B_i + \Delta B_1 - B_2 - \Delta B_2) \, dx_3
\]

\[
= (B_i - B_2) \, dx_3 + \left( \int_0^d \overline{\sigma}_j \, dx_3 \right) \int_0^d \sigma_{i2} \, dx_3 + \left( \int_0^d \overline{\sigma}_j \, dx_3 \right) \int_0^d \sigma_{13} \, dx_3
\]

(44)

Considering Eq. (30), Eq. (44) becomes

\[
\int_0^d (B_i + \Delta B_1 - B_2 - \Delta B_2) \, dx_3 = (B_i + \Delta B_1 - B_2 - \Delta B_2) \, dx_3
\]

(45)

Other matrix components of \( \mathbf{M}_{\text{total}} \) given by Eq. (42) are also represented by \( \Delta \overline{B}_j \), and the matrix \( \mathbf{M}_{\text{total}} \) is expressed as

\[
\mathbf{M}_{\text{total}} = \mathbf{I} + \frac{i\pi}{2\lambda} \left( \frac{B_i + B_2}{2} \right)^{-3/2}
\]

\[
\begin{bmatrix}
(B_i + \Delta \overline{B}_1 - B_2 - \Delta \overline{B}_2) \, dx_3 & 2\Delta \overline{B}_d \, dx_3 \\
2\Delta \overline{B}_d \, dx_3 & -(B_i + \Delta \overline{B}_1 - B_2 - \Delta \overline{B}_2) \, dx_3
\end{bmatrix}
\]

(46)

The eigenvalues \( t \) and eigenvectors \( p \) of \( \mathbf{M}_{\text{total}} \) are given as follows:

\[
t = 1 \pm \frac{i\pi}{2\lambda} \left( \frac{B_i + B_2}{2} \right)^{-3/2} \sqrt{\left( B_i + \Delta \overline{B}_1 - B_2 - \Delta \overline{B}_2 \right)^2 + 4\Delta \overline{B}_d^2}
\]

(47)
Eqs. (47) and (48) are double sign correspondence. As mentioned in 3.1, $\delta_{\text{total}}$ is equal to the difference in argument of two eigenvalues of $M_{\text{total}}$. Then $\delta_{\text{total}}$ is obtained from eq. (47) as follows, considering $\delta_{\text{total}} \ll 1$:

$$\delta_{\text{total}} = \frac{\pi d}{\lambda} \left( \frac{B_1 + B_2}{2} \right)^{3/2} \sqrt{(B_1 + \Delta B_1 - B_2 - \Delta B_2)^2 + 4\Delta B_6^2}$$

The azimuth is defined by the angle between the fast axis and the $x_1$-axis, so that it is expressed as follows using the eigenvectors $p$:

$$\tan 2\rho_{\text{total}} = \frac{2 \tan \rho_{\text{total}}}{1 - \tan^2 \rho_{\text{total}}} = \frac{2 \Delta B_6}{B_1 + \Delta B_1 - B_2 - \Delta B_2}$$

where $\tan \rho_{\text{total}}$ in eq. (50) can be obtained from the eigenvector $p$ given by eq. (48) as follows:

$$\tan \rho_{\text{total}} = \frac{2 \Delta B_6}{B_1 + \Delta B_1 - B_2 - \Delta B_2}$$

As shown here, the retardation $\bar{\delta}$ and the azimuth $\bar{\rho}$ obtained from the average stress method are the same as those ($\delta_{\text{total}}$ and $\rho_{\text{total}}$) derived from the Jones calculus. In conclusion, the Jones calculus, the exact method for a birefringence analysis, and the average stress method, an approximate method for a birefringence analysis, provide the same results in case of $B_i \gg \Delta B_i$ ($i = 1, 2$).

For various single crystals, the order of the piezo-optic coefficients $\pi_{ij}$ is $10^{-12}\text{Pa}^{-1}$ (Nye, 1985), and that of the inverse dielectric constants $B_i$ is estimated to be $10^{-1}$ from Eqs. (10), (11) or (12). Considering Eq. (4), the condition $B_i \gg \Delta B_i$ ($i = 1, 2$) holds, if stress level is less than $10^9\text{Pa}$. In such a case, the error of the average stress method, which is derived from eq. (40) by neglecting higher-order terms of $\Delta B_i$, is less than 1% in comparison with the exact Jones calculus. In the examples shown in this article, the stress level is less than $10^9\text{Pa}$, so that the average stress method provides accurate results for stress birefringence.

4. Stress birefringence simulations after annealing of CaF$_2$ single crystal

Based on the papers published by the present authors (Ogino et al., 2008; Miyazaki et al., 2009; Kitamura et al., 2010a, 2010b), the results of birefringence simulations of CaF$_2$ single crystal after annealing process are presented here. Such simulations comprise the heat transfer analysis that provides the temperature distribution in the single crystal during annealing process, the stress analysis to calculate the residual stress after annealing, and the analysis of birefringence in an annealed ingot induced by the residual stress.

4.1 Heat transfer analysis

The surface temperature of a crystal ingot are calculated by taking account of the heat radiation from a furnace for ingot annealing using a computer code such as CrystU (Kurcz et al., 1999; Molchanov et al., 2002). Then the temperature distribution in the crystal ingot is obtained by a transient heat conduction analysis using the finite element code MSC Marc (MSC Software, 2003).
4.2 Residual stress analysis

Residual stress can be calculated from the temperature distribution in an ingot obtained by the heat conduction analysis. In the residual stress calculation, we can select either the elastic thermal stress analysis using the assumption of a stress-free temperature or more exact stress analysis considering the time-dependent nonlinear behavior of a material called creep.

As Abbott et al. (2003) proposed, the residual stress can be estimated by assuming a stress-free temperature. The conceptual figure of this method is shown in Fig. 4. At elevated temperatures, the decrease of critical resolved shear stress induces a lot of dislocations in an ingot, which lead to stress relaxation. A stress-free temperature is an ideal temperature of an ingot defined as follows. When the average temperature of an ingot exceeds a stress-free temperature, the ingot is assumed to be completely stress-free due to the effect of stress relaxation, and stress begins to be generated when the average temperature of the ingot becomes below a stress-free temperature. By assuming such a stress-free temperature, we can obtain the residual stress in the ingot as an elastic thermal stress induced by the variation from the stress-free temperature to the room temperature without using nonlinear analysis. This method, however, has its ambiguity in choosing a stress-free temperature.

CaF$_2$ single crystal ingots undergo creep deformation under elevated temperatures. Exactly speaking, we should perform the residual stress calculation considering creep deformation. For this purpose, we need a creep constitutive equation for CaF$_2$ single crystal, which can be obtained from compressive tests of CaF$_2$ single crystal ingots under elevated temperatures by varying the strain rate. The details of the compressive tests will be given later.

The cubic single crystal CaF$_2$ has crystal anisotropy in the elastic constants, so that anisotropic residual stress analysis should be performed using a finite element code such as MSC Marc.

4.3 Analysis for optical path difference

The average stress method was applied to calculating optical path difference $\Gamma$ given by Eq.(33). We dealt with a circular slab ingot, as shown in Fig. 5, in which the $x_3$-axis coincides with the normal direction of the wave surface of light. The stress changes continuously along the $x_3$-axis, so that the birefringence also changes continuously along the $x_3$-axis. In the average stress method, the average stress components along the wave normal $\bar{\sigma}_i$ defined by Eq.(29) are utilized to calculate the optical path difference. The results of the optical path difference are shown by the optical path difference per unit thickness $\Gamma_{\text{unit}}$, that is,

$$\Gamma_{\text{unit}} = \frac{\Gamma}{d}$$

Fig. 5 Geometry and finite element mesh of a CaF$_2$ single crystal ingot (Ogino et al., 2008).
4.4 Material properties of CaF₂ single crystal

The material properties of CaF₂ single crystal for the heat conduction analysis are given in Table 1. The temperature dependence of thermal conductivity is made based on the data of Isp Optics Corp., Varlamov et al’s paper (1989) and Lindan and Gillan’s paper (1991), and that of the heat capacity by Lyusternik’s paper (1999). The density is quoted from a catalog of Schott Lithotec.

For the residual stress analysis of a CaF₂ single crystal ingot using a stress-free temperature, we need the elastic constants and thermal expansion coefficient. The data given by Vidal (1974) and Sirdeshmukh and Deshpande (1964) are used to obtain the temperature dependence of the elastic constants, \( C_{11} \), \( C_{12} \) and \( C_{44} \), and that of the thermal expansion coefficient, respectively. They are summarized in Table 2.

Table 1  Material properties of CaF₂ single crystal for the heat conduction analysis (Unit of \( T \): K).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity [W/m·K]</td>
<td>(-6.00 \times 10^{-9} T^3 + 2.49 \times 10^{-5} T^2 - 0.0347 T + 17.3)</td>
</tr>
<tr>
<td>Heat capacity [J/kg·K]</td>
<td>(0.4326T + 743.52)</td>
</tr>
<tr>
<td>Density [kg/m³]</td>
<td>3180</td>
</tr>
</tbody>
</table>

In addition to these material properties, we need the creep constitutive equation of CaF₂ single crystal for the residual stress analysis of CaF₂ single crystal ingot taking account of creep deformation. Phillips (1961) and Munoz et al. (1994) pointed out that the critical resolved shear stresses of various slip systems become almost the same at the elevated temperatures over 600 °C, so that CaF₂ single crystal shows isotropic creep behavior in the temperature range where creep deformation is dominant. The CaF₂ single crystal test specimens with 20mm in diameter and 40mm in height were used in the compressive test to obtain creep constitutive equation of the CaF₂ single crystal. The test specimens were cut from an ingot in such a way that the compressive direction is the <111> direction, and surfaces of the test specimens were mirror-polished. As shown in Fig. 6, compressive tests were performed at the temperatures of 1150 °C, 1250 °C and 1350 °C in Ar atmosphere. The crosshead speed was changed at 0.5mm/min, 0.05mm/min and 0.01mm/min. Stress-strain curves at the respective temperatures are shown in Fig. 7. We can see a region with nearly constant stress for respective values of crosshead speed. The relation between the constant stress and the constant crosshead speed gives the steady state creep strain rate under the constant stress (Karato et al., 1994). The relations between the creep strain rate and the stress in the steady state creep region are summarized in Fig. 8. From these experimental data, we can obtain the Norton type creep constitutive equation for CaF₂ single crystal, as follows:

\[
\dot{\varepsilon}^c = 1.203 \times 10^{-10} \sigma^{3.704} \exp \left( \frac{8.652 \times 10^{-19}}{kT} \right) \tag{55}
\]

where \( \dot{\varepsilon}^c \) denotes creep strain rate, \( k \) the Boltzmann constant, and the units of \( \sigma \) and \( T \) are respectively Pa and K. The creep constitutive equation under multiaxial stress state is given as

\[
\dot{\varepsilon}^c_{\sigma} = \frac{3\dot{\varepsilon}^c}{2\tilde{\sigma}} \sigma'_{\sigma} \tag{56}
\]

where \( \tilde{\sigma} \) and \( \sigma'_{\sigma} \) are the Mises equivalent stress and the deviatoric stress, respectively, and \( \dot{\varepsilon}^c \) is the equivalent creep strain rate and equivalent to uniaxial creep strain rate given by Eq.(55). Finally the following multiaxial creep strain rate is obtained for CaF₂ single crystal:
Fig. 6  Configuration for compressive test of CaF$_2$ single crystal.

Fig. 7  True stress–true strain curves of CaF$_2$ single crystal test specimens obtained from compressive tests (Fig. 7(b) is cited from Miyazaki et al., 2009).
In the finite element creep analysis to obtain the residual stress of a CaF$_2$ single crystal ingot, we employed the tangent modulus method or the implicit method for a creep analysis (Peirce et al., 1984) together with the above creep constitutive equation.

In the calculation of the optical path difference for CaF$_2$ single crystal, we need the piezo-optic coefficients, which are quoted from Nye’s textbook (1985). A reflective index $n$ is also required to calculate $B_1 = B_2 = 1/n^2$, and we use a value given in a catalog of Schott Lithotec as $n$. They are summarized in Table 3.

Table 3 Material properties of CaF$_2$ single crystal for the optical path difference analysis for the light with 633 nm wavelength.

<table>
<thead>
<tr>
<th>Piezo-optic coefficients [Pa$^{-1}$]</th>
<th>$\pi_{11} = -0.29 \times 10^{-12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pi_{12} = 1.16 \times 10^{-12}$</td>
<td></td>
</tr>
<tr>
<td>$\pi_{44} = 0.698 \times 10^{-12}$</td>
<td></td>
</tr>
<tr>
<td>Reflective index</td>
<td>$n = 1.43380$</td>
</tr>
</tbody>
</table>

4.5 Results and Discussion

4.5.1 Evaluation of stress birefringence using residual stress calculated from a stress-free temperature

Seven cases of annealing period were dealt with to calculate the optical path difference caused by residual stress. They are Long-term annealing 1, 2 and 3 as long term annealing patterns, Mid-term annealing 1 and 2 as mid term annealing patterns, and Short-term annealing 1 and 2 as short term annealing patterns. The temperature histories of an annealing furnace for the respective annealing cases were used as input data for CrysVUn to obtain the surface temperature of a crystal ingot. The geometries of circular slab specimens used in the respective annealing patterns are shown as follows:

(i) Long-term annealing 1 and Mid-term annealing 1 --- 160mm in diameter and 45mm in thickness.
(ii) Long-term annealing 2, Long-term annealing 3, Mid-term annealing 2, Short-term annealing 1 and Short-term annealing 2 --- 200mm in diameter and 40mm in thickness.

The axis of an ingot, that is, the $x_3$-axis shown in Fig. 5, is coincident with the $<100>$ direction. The finite element method was applied to both the heat conduction analysis and the residual stress analysis. We used the twenty-noded isoparametric element. The finite element model used in the analyses assuming a stress-free temperature has 2568 elements and 12289 nodes.
The results of the optical path difference were obtained based on the residual stress calculated from the stress analysis using a stress-free temperature. The optical path difference was obtained for four cases of a stress-free temperature, that is, 1443K, 1263K, 973K and 873K. Figure 9 shows the comparison of the optical path difference distribution between a typical experimental result and the analysis result for the stress-free temperature \( T_f \) of 1443K in case of Long-term annealing 1. Experimental measurements were made by Exicor 450AT, HINDS Instruments. The method for measurement used in Exicor 450AT is provided by Oakberg (1997). If a stress-free temperature for residual stress calculation is selected adequately, the optical path difference obtained from the analysis agrees reasonably well with the experimental result both qualitatively and quantitatively, as shown in Fig. 9, where both the distribution and value of the optical path difference are in good agreement between the experiment and the analysis. If we can select such a unique stress-free temperature irrespective of the annealing conditions, the method based on the assumption of a stress-free temperature is useful for calculating the optical path difference. Table 4 shows the stress-free temperature whose result for the distribution of the optical path difference agrees qualitatively well with experimental result. It is found from the table that the stress-free temperature, which provides the distribution of the optical path difference similar to the experimental result, depends on the annealing conditions. It is therefore concluded that there exists no unique stress-free temperature. In addition to the distribution of the optical path difference, we cannot find a unique stress-free temperature whose result agrees quantitatively well with the value of optical path difference obtained from the experiment.

![Image](image1)

(a) Experimental result  
(b) Analysis result

**Fig. 9** Typical optical path difference distributions of a CaF\(_2\) single crystal ingot for Long-term annealing 1. Analysis result is obtained from the residual stress analysis assuming the stress-free temperature \( T_f \) of 1443K (Miyazaki et al., 2009).

**Table 4** The stress-free temperature whose result for the distribution of the optical path difference agrees qualitatively well with the experimental result.

<table>
<thead>
<tr>
<th>Annealing condition</th>
<th>Stress-free temperature ( T_f ) whose result for the distribution of the optical path difference qualitatively agrees well with the experimental result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long-term annealing 1</td>
<td>( T_f &gt; 1263K )</td>
</tr>
<tr>
<td>Long-term annealing 2</td>
<td>( T_f &gt; 973K )</td>
</tr>
<tr>
<td>Long-term annealing 3</td>
<td>(*)</td>
</tr>
<tr>
<td>Mid-term annealing 1</td>
<td>( T_f = 873K )</td>
</tr>
<tr>
<td>Mid-term annealing 2</td>
<td>( T_f &gt; 1263K )</td>
</tr>
<tr>
<td>Short-term annealing 1</td>
<td>( T_f = 873K )</td>
</tr>
<tr>
<td>Short-term annealing 2</td>
<td>( T_f = 873K )</td>
</tr>
</tbody>
</table>

(*) \( T_f \) cannot be determined because agreement between the experimental result and the analysis result is not so good for the distribution of the optical path difference.
4.5.2 Evaluation of stress birefringence using residual stress calculated from the finite element stress analysis considering the creep deformation

Next we will show the results of the optical path difference obtained based on the residual stress calculated from the finite element stress analysis considering the creep deformation given in Eq.(57) without the assumption of a stress-free temperature. The analyses were performed for a circular slab of CaF$_2$ single crystal with 200mm in diameter and 40mm in thickness, as shown in Fig. 5. We dealt with the <100>-growth single crystal and the <111>-growth single crystal, respectively. Analysis was performed for Mid-term annealing 2, the temperature history of which is given in Fig. 10. The finite element model used in this case has 3456 elements and 15885 nodes.

First of all, we will show the results of the residual stress analysis considering the creep deformation given by Eq.(57). Figures 11(a) and (b) respectively show the residual Mises stress distribution of the <100>-growth single crystal and that of the <111>-growth single crystal after annealing. Symmetric patterns are observed in the residual Mises stress distribution. We can find four-fold symmetry in the <100>-growth single crystal and three-fold symmetry in the <111>-growth single crystal on their surfaces. Such symmetric patterns are caused by the anisotropy in the elastic constants. Although the symmetric patterns of the stress distribution are different between these two crystals, the overall distribution and the magnitude of stress are almost the same between them.

Next we will show the results of the optical path difference obtained from the results of the residual stress analysis. As shown in Figs. 11(a) and (b), the order of the residual stress is 10$^8$ Pa, so that the average stress method for the calculation of the optical path difference is accurate enough. Figures 12(a) and (b) show the optical path difference distributions. Both in the <100>-growth single crystal and in the <111>-growth single crystal, we can see the symmetric patterns of the optical path difference distribution caused by the stress anisotropy in the elastic constants and the piezo-optic coefficients. The <100>-growth single crystal has four-fold symmetry, which is the same as that of the residual stress distribution shown in Fig. 11(a). On the other hand, the <111>-growth single crystal has six-fold symmetry shown in Fig. 12(b). In the latter single crystal, the residual stress distributions are three-fold symmetry both in the upper part and in the lower part of the crystal, and the residual stress distribution of both parts are point-symmetric with a point of symmetry at the center of the crystal. The optical path difference reflects the stress distribution along the thickness direction. That is why the six-fold symmetry of optical path difference appears in the <111>-growth single crystal.

Figures 13(a) and (b) show the distributions of the typical optical path difference obtained from the experiment. It is found from Figs. 12(a) and 13(a) that we can obtain reasonable analysis results for both the distribution and magnitude of the optical path difference in the <100>-growth single crystal, compared with the experimental results. It is also found from Figs. 12(b) and 13(b) that the magnitude of the optical path difference in the <111>-growth single crystal is in good agreement between the analysis and the experiment, but the distribution of optical path difference is not clear in the experimental result. This is because the magnitude of the optical path difference in the <111>-growth single crystal is too small to measure it as precisely as we can recognize the distribution of optical path difference in experimental result. The six-fold symmetry obtained from the analysis in the <111>-growth single crystal is presumed to be valid by considering the cubic crystal symmetry.

As shown in Figs. 12 and 13, it is found that the magnitude of the optical path difference in the <111>-growth single crystal is much smaller than that in the <100>-growth single crystal. On the other hand, as shown in Fig. 11, the magnitude of stress is almost the same both in the <100>-growth single crystal and in the <111>-growth single crystal. From these results, we can guess that the large difference of the optical path difference in the <100>- and <111>-growth single crystals is due to the effect of the coordinate transformation of the piezo-optic coefficients.

Another stress birefringence analysis was performed for different conditions described above to confirm the effectiveness of the present simulation method for stress birefringence, in which the residual stress was calculated from the finite element stress analysis considering the creep deformation. In this analysis, the analysis was performed for a circular slab of the <100>-growth CaF$_2$ single crystal with 160mm in diameter and 45mm in thickness. The annealing condition is Long-term annealing 1. The analysis and experimental results of the optical path difference are respectively shown in Figs. 14(a) and (b). The analysis result agrees well with experimental one both qualitatively and quantitatively.

In conclusion, the evaluation method using residual stress calculated from the finite element stress analysis considering the creep deformation provides better result of stress birefringence compared with the evaluation method using residual stress calculated from the stress-free temperature.
Fig. 10  Temperature history of annealing condition (Mid-term annealing 2) (Kitamura et al., 2010b).

(a)<100>-growth single crystal          (b) <111>-growth single crystal

Fig. 11  Residual Mises stress distributions of CaF$_2$ single crystal ingots obtained from the residual stress analysis taking account of creep deformation (Mid-term annealing 2) (Kitamura et al., 2010b).

(a) <100>-growth single crystal          (b) <111>-growth single crystal

Fig. 12  Optical path difference distributions of CaF$_2$ single crystal ingots obtained from the residual stress analysis taking account of creep deformation (Mid-term annealing 2) (Kitamura et al., 2010b).
5. Stress birefringence simulations after annealing of MgF$_2$ single crystal

Based on the papers published by the present authors (Kitamura et al., 2009), the results of birefringence simulations of MgF$_2$ single crystal after annealing process are presented here. The analysis was performed for a circular cylindrical ingot with 100mm in diameter and 100mm in thickness, as shown in Fig. 15. The size of the analysis model was the same as that of an ingot used for the experimental measurement of optical path difference. We dealt with a $<$001$>$-growth crystal, a $<$100$>$-growth crystal and a $<$111$>$-growth crystal, in which the $x_3$-axis corresponds to the $<$001$>$-direction, the $<$100$>$-direction and $<$111$>$-direction, respectively.

Figure 16 shows the surface temperature history of the ingot for the annealing period of about 17 days. A heat conduction analysis was performed to obtain the temperature distribution in a crystal ingot by assuming that the surface temperature of an ingot is uniform during annealing process. Finite element method was used both in the transient heat conduction analysis and the residual stress analysis. The material properties of MgF$_2$ single crystal used in the heat conduction analysis are shown in Table 5. The thermal conductivity at the room temperature was measured by the present authors (Kitamura et al., 2009), but there exists no data on the temperature dependence. So we used the temperature dependence of CaF$_2$ single crystal based on Varlamov et al’s paper (1989) and Lindan and M. J. Gillan’s paper (1991). The specific heat and density of MgF$_2$ single crystal are cited from present authors’ paper (Kitamura et
al., 2009) and a catalog of Isp Optics Corp., respectively. The results show that there is no large difference in the temperature distribution among three kinds of MgF₂ single crystal ingots regardless of anisotropy in the thermal conductivity.

The transient heat conduction analysis was followed by the elastic thermal stress analysis to estimate the residual stress of the ingot. The residual thermal stress analysis was performed using the same finite element model as that of the heat conduction analysis. The material properties of MgF₂ single crystal for the elastic thermal stress analysis are shown in Table 6. The elastic constants are obtained by the present authors (Kitamura et al., 2009) and the thermal expansion coefficients are given in a catalog of Isp Optics Corp. The stress-free temperature was assumed to be 800 K, which is less than the melting temperature of MgF₂ (1528 K). Figure 17 shows the residual Mises stress distributions at the room temperature after annealing. There exist symmetric patterns in the residual Mises stress distributions caused by the anisotropy in the elastic constants. We can find four-fold symmetry in the <001>-growth crystal, and two-fold symmetry in the <100>-growth crystal. In the <111>-growth crystal, two-fold symmetry is found both at the upper and lower surfaces of a cylindrical ingot and the stress distribution is point-symmetric with a point of symmetry at the center of the ingot. Although the distributions of stress are quite different among respective crystals, the magnitudes of stress are almost the same among them.

Table 5  Material properties of MgF₂ single crystal for the heat conduction analysis (Unit of T : K).

<table>
<thead>
<tr>
<th>Property</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity [W/m·K]</td>
<td>$\lambda_{11}=\lambda_{22}=0.2788\exp(1379/T), \lambda_{33}=0.1897\exp(1379/T)$</td>
</tr>
<tr>
<td>Heat capacity [J/kg·K]</td>
<td>243.4$\log_{10}T + 370.7$</td>
</tr>
<tr>
<td>Density [kg/m³]</td>
<td>3180</td>
</tr>
</tbody>
</table>

Table 6  Elastic constants and thermal expansion coefficient of MgF₂ single crystal for the residual stress analysis (Unit of T : K).

<table>
<thead>
<tr>
<th>Elastic Constants [Pa]</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$</td>
<td>$-1.863 \times 10^7T + 1.509 \times 10^{11}$</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>$-1.334 \times 10^7T + 9.777 \times 10^{10}$</td>
</tr>
<tr>
<td>$C_{13}$</td>
<td>$-4.328 \times 10^6T + 6.720 \times 10^{10}$</td>
</tr>
<tr>
<td>$C_{33}$</td>
<td>$-3.614 \times 10^7T + 2.173 \times 10^{11}$</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>$-9.514 \times 10^6T + 6.032 \times 10^{10}$</td>
</tr>
<tr>
<td>$C_{66}$</td>
<td>$-2.498 \times 10^7T + 1.037 \times 10^{11}$</td>
</tr>
<tr>
<td>Thermal expansion coefficient [1/K]</td>
<td>$\alpha_{11}=\alpha_{22}=5.682 \times 10^{-6}\log_{10}T - 2.380 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>$\alpha_{33}=7.083 \times 10^{-6}\log_{10}T - 2.663 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Table 7  Material properties of MgF₂ single crystal for the optical path difference analysis.

<table>
<thead>
<tr>
<th>Piezo-optic coefficients [ Pa⁻¹ ]</th>
<th>( \pi_{11} = 3.107 \times 10^{-12} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \pi_{12} = 9.871 \times 10^{-13} )</td>
</tr>
<tr>
<td></td>
<td>( \pi_{13} = -4.508 \times 10^{-12} )</td>
</tr>
<tr>
<td></td>
<td>( \pi_{31} = 1.869 \times 10^{-12} )</td>
</tr>
<tr>
<td></td>
<td>( \pi_{33} = -4.117 \times 10^{-12} )</td>
</tr>
<tr>
<td></td>
<td>( \pi_{44} = 1.361 \times 10^{-12} )</td>
</tr>
<tr>
<td></td>
<td>( \pi_{66} = 4.717 \times 10^{-13} )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reflective indices</th>
<th>( n_o = 1.37698 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n_e = 1.38876 )</td>
</tr>
</tbody>
</table>

Fig. 17  Residual Mises stress distributions of MgF₂ single crystal ingots after annealing. Analysis results were obtained from the residual stress analysis by assuming the stress-free temperature \( T_f \) of 800 K. (a) \(<001>-growth single crystal ingot, (b) \(<100>-growth single crystal ingot, (c) \(<111>-growth single crystal ingot (Kitamura et al., 2009).

Fig. 18  Optical path difference distributions of MgF₂ single crystal ingots. These results were obtained by assuming the stress-free temperature \( T_f \) of 800K (kitamura et al., 2009)
The optical path difference was then calculated from the residual stress. The material properties of MgF$_2$ single crystal for the optical path difference calculation are shown in Table 7. The piezo-optic coefficients are given by

$$\pi_{ij} = p_{ik}S_{kj}$$  \hspace{1cm} (58)

where $p_{ik}$ and $S_{kj}$ are the elasto-optic constant and the elastic compliance, respectively, and given in a catalog in ISP Optics Corp. and by Kumari et al. (1983) for MgF$_2$ single crystal. The refractive index for an ordinary-ray $n_o$ and that for an extraordinary-ray $n_e$ are given in a catalog of Corning. The average stress method was applied in the calculation of optical path difference.

Figures 18(a), (b) and (c) show the distributions of optical path difference at the room temperature after annealing for the respective crystals. These distributions are observed when light passes perpendicularly through the ingot in thickness direction. For all crystal ingots, we can see the symmetric patterns of the optical path difference distribution corresponding to the residual stress distribution. Although the magnitudes of residual stress are almost the same, those of the optical path difference are quite different. This is because there exists the intrinsic birefringence caused by the crystal asymmetry in the <100>-growth and <111>-growth MgF$_2$ single crystals. Without stress, the optical path difference for the <100>-growth single crystal should be 117800 nm/cm, which is calculated from the refractive index for an ordinary-ray $n_o$ and that for an extraordinary-ray $n_e$ are given in a catalog of Corning. The average stress method was applied in the calculation of optical path difference.

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Figure 19 shows a typical distribution of optical path difference obtained from the experiment for the <001>-growth crystal. The annealing schedule of an ingot specimen is the same as that shown in Fig.16. The birefringence was measured using the light of 633nm wavelength with Exicor 450AT of HINDS Instruments. In comparison between Fig. 18(a) and Fig. 19, it is found that the analysis can predict the distribution of optical path difference adequately. Such qualitative agreement between the calculation and the experiment in addition to the fact that the present calculation provides the exact intrinsic birefringence values indicates the reliability and effectiveness of the present analysis method for birefringence induced by residual stress. Figure 20 shows the distribution of optical path difference at the room temperature after ingot annealing for the <001>-grown crystal obtained from the analysis in the case of the stress free temperature of 1100K. As shown in Figs. 19 and 20, the present analysis method provides good agreement of the maximum value of optical path difference as well as the distribution of optical path difference with the experiment, if the stress-free temperature is assumed to be 1100K. It may be difficult to choose a unique stress-free temperature for MgF$_2$ single crystal irrespective of different kinds of annealing condition, as in the case of CaF$_2$ single crystal. In the
case of MgF$_2$ single crystal, we should perform inelastic analysis taking account of creep deformation to obtain residual stress after annealing.

6. Birefringence simulations of CaF$_2$ single crystal chamber window of ArF excimer laser light source

Based on the papers published by the present authors (Kitamura et al., 2010c; 2012), we will show here the method for evaluating the birefringence of CaF$_2$ single crystal used as a crystal chamber window of an ArF excimer laser light source of 193 nm wavelength. CaF$_2$ single crystal has high durability and excellent transmission characteristics in the vacuum ultraviolet region (Gerasimova, 2006). Because of this reason, CaF$_2$ single crystal is used as a chamber window material for gas laser light sources, instead of conventional synthetic quartz. A chamber window particularly requires higher durability than other optical elements used in semiconductor lithography. Extremely high material performances are required for a window material to achieve high efficiency and quality for the gas laser light sources. However, when using CaF$_2$ single crystal under these conditions, birefringence phenomenon becomes an issue. Birefringence is classified into two categories according to its cause. One is the stress birefringence caused by the photoelastic effect owing to the stress in the crystal, and the other is the intrinsic birefringence caused by crystal anisotropy. It has been thought that CaF$_2$ single crystal, which belongs to the cubical system, does not show intrinsic birefringence because of its high crystal symmetry. Recently, the wavelength of the light used for semiconductor lithography has become shorter for fine process of electronic devices, and it is found that CaF$_2$ single crystal shows intrinsic birefringence in the vacuum ultraviolet region (Burnett et al., 2001). The influence of intrinsic birefringence is increasing with continuing trend toward greater fine processing.

When CaF$_2$ single crystal is used as a chamber window of a gas laser light source, mechanical stresses are induced in the chamber window by mechanical loads, as shown in Fig. 21. The window is fixed with a window holder tightened by bolts, and O-rings are set both on the upper and lower surfaces of the single crystal window such that laser gas and purge gas do not leak. The window is subjected to loads through these O-rings. In addition, both window faces are subjected to laser gas pressure and purge gas pressure. Such loads and gas pressures also induce stress on the window, which causes stress birefringence. When the light wavelength is in the vacuum ultraviolet region, intrinsic birefringence appears in addition to stress birefringence. Such birefringence phenomena lead to performance degradation of the laser.

6.1 Intrinsic birefringence

A method for stress birefringence has been already described in Chapters 2 and 3 of this article. So we derive the intrinsic birefringence formulation based on Burnett et al’s paper (Burnett et al., 2002).

The inverse dielectric constant $B_{ij}$ is assumed to be constant in the stress birefringence formulation shown in Chapter 2. In fact, it depends on the wavelength and propagation direction of light, and it is expressed as follows:

$$B_{ij} = B_{ij}(\lambda, \mathbf{q})$$

(59)

where $\lambda$ is the wavelength and $\mathbf{q}$ is the wave number vector, the direction of which is coincident to the wave normal and its magnitude is defined by $2\pi/\lambda$. When $\lambda$ is large enough compared with unit cell, $B_{ij}$ is independent of $\mathbf{q}$, and given by

Fig. 21 Mechanical loads acting on CaF$_2$ single crystal chamber window of gas laser light source (Kitamura et al., 2012).
The effect of \( q \) on \( B_{ij} \) becomes large with decreasing \( \lambda \). Such an effect induces intrinsic birefringence even in the cubic single crystal such as CaF\(_2\) under incidence of vacuum ultraviolet light. The expression of the inverse dielectric constant \( B(\lambda, q) \) is derived here in the short wavelength region.

According to crystal symmetry, \( B(\lambda, q) \) of CaF\(_2\) single crystal can be written as follows:

\[
B_{ij}(\lambda, q) = B_{ij}(\lambda, 0) \delta_{ij} + \sum_k \alpha_{ijk}(\lambda) q_k + \sum_{ijkl} \beta_{ijkl}(\lambda) q_i q_j q_k q_l + \cdots
\]  

where \( \delta_{ij} \) is the Kronecker delta, \( q_i \) is the \( i \)-th component of the vector \( q \), and \( \alpha_{ijk}, \beta_{ijkl} \) and \( \gamma_{ijklm} \) are tensors of rank three, four and five, respectively. In the above equation, the coefficients of the odd power of \( q_i \) such as \( \alpha_{ijk} \) and \( \gamma_{ijklm} \) are equal to be zero, because CaF\(_2\) single crystal has a center of symmetry. Moreover higher order terms are neglected, and then Eq.(62) can be expressed as

\[
B_{ij}(\lambda, q) = B_{ij}(\lambda, 0) \delta_{ij} + \Delta B_{ij}(\lambda, q)
\]  

where \( \Delta B_{ij}(\lambda, q) \) is given by

\[
\Delta B_{ij} = \sum_{kl} \beta_{ijkl}(\lambda) q_k q_l
\]  

Because of the symmetry of \( B(\lambda, q) \) and \( q_i q_j, \beta_{ijkl}(\lambda) \) can be abbreviated as a matrix form \( \beta_{ab}(\lambda) \). From the crystal symmetry of cubic single crystal CaF\(_2\), there are three independent components in \( \beta_{ab}(\lambda) \) and Eq.(64) is rewritten as follows:

\[
\begin{bmatrix}
\Delta B_{11}^1 \\
\Delta B_{22}^1 \\
\Delta B_{33}^1 \\
\Delta B_{23}^1 \\
\Delta B_{32}^1 \\
\Delta B_{12}^1
\end{bmatrix} =
\begin{bmatrix}
\beta_{11} & \beta_{12} & 0 & 0 & 0 & q_1^2 \\
\beta_{12} & \beta_{12} & 0 & 0 & 0 & q_2^2 \\
0 & 0 & \beta_{11} & 0 & 0 & q_3^2 \\
\beta_{44} & 0 & 0 & 2q_1 q_2 & 2q_1 q_3 & 2q_2 q_3
\end{bmatrix}
\]  

Now, we divide \( \Delta B_{ij}^1 \) into three terms as follows:

\[
\begin{align*}
\Delta B_{11}^1 &= A_1(\lambda) \begin{bmatrix} q_1^2 + q_2^2 + q_3^2 & 0 & 0 \\ 0 & q_1^2 + q_2^2 + q_3^2 & 0 \\ 0 & 0 & q_1^2 + q_2^2 + q_3^2 \end{bmatrix} + A_2(\lambda) \begin{bmatrix} q_1 q_2 & q_1 q_3 & q_2 q_3 \\ q_2 q_1 & q_2 q_3 & q_3 q_2 \\ q_3 q_1 & q_3 q_2 & q_1 q_2 \end{bmatrix} + A_3(\lambda) \begin{bmatrix} q_1^2 & 0 & 0 \\ 0 & q_2^2 & 0 \\ 0 & 0 & q_3^2 \end{bmatrix}
\end{align*}
\]  

where \( A_1(\lambda), A_2(\lambda) \) and \( A_3(\lambda) \) are defined as
\[
\begin{align*}
A_1 &= \beta_{12} \\
A_2 &= 2\beta_{44} \\
A_3 &= \beta_{11} - \beta_{12} - 2\beta_{44}
\end{align*}
\] (67)

If we use a unit vector \( l \) defined by \( l = q/\|q\| \), Eq. (66), the matrix form of \( \Delta B^l_{ij} \), becomes
\[
\Delta B^l_{ij} (\lambda, q) = A_1 (\lambda) \|q\|^2 \delta_{ij} + A_2 (\lambda) \|q\|^2 l_l l_j + A_3 (\lambda) \|q\|^2 \delta_{ij} l_i^2
\]
(68)

In the above equation, the summation convention does not apply to \( \delta_{ij} l_i^2 \). Burnett et al. (2002) obtained the optical path difference caused by intrinsic birefringence by solving an eigenvalue problem. On the other hand, we discuss the influence of \( \Delta B^l_{ij}(\lambda, q) \) by using indicatrix in order to consider the intrinsic birefringence with the stress birefringence.

\[A_1 (\lambda) \|q\|^2 \delta_{ij}\]

the first term on the right side of Eq. (68), does not include \( l \) and is not changed by the propagation direction of light. Considering this term, the indicatrix is written as
\[
(B \lambda, 0) + A_1 (\lambda) \|q\|^2 \left(x_1^2 + x_2^2 + x_3^2\right) = 1
\]
(69)

Eq. (69) expresses that the spherical indicatrix changes its form in an isotropic manner as shown in Fig. 22. This suggests that \( A_1 (\lambda) \|q\|^2 \delta_{ij} \) has an effect on the refractive index but not on the anisotropy of the optical characteristics, which result in birefringence.

Next, we consider \( A_2 (\lambda) \|q\|^2 l_l \), the second term on the right side of Eq. (68). This term includes \( l \) and is affected by the propagation direction of light and changes the shape of the indicatrix. Let us consider the \( x'_1 - x'_2 - x'_3 \) coordinate system, where the \( x'_1 \) axis is parallel to vector \( q \). Transforming \( A_2 (\lambda) \|q\|^2 l_l \) from the \( x_1 - x_2 - x_3 \) crystal coordinate system to the \( x'_1 - x'_2 - x'_3 \) coordinate system yields
\[
\left( A_2 (\lambda) \|q\|^2 l_l \right)' = A_2 (\lambda) \|q\|^2 \left(x'_1 \cdot x'_1\right)^2
\]
(70)

The right side of Eq. (70) is zero except for \( i = j = 3 \). Therefore, considering \( A_2 (\lambda) \|q\|^2 l_l \), the indicatrix in the \( x'_1 - x'_2 - x'_3 \) coordinate system is expressed as follows:
\[
B_{11} (\lambda, 0) x'^2_1 + B_{11} (\lambda, 0) x'^2_2 + B_{11} (\lambda, 0) + A_2 (\lambda) \|q\|^2 \left(x'_3 \cdot x'_3\right) = 1
\]
(71)

As shown in Fig. 23, Eq. (71) means that the indicatrix changes its shape in the \( x'_1 \) axis direction, i.e., the light propagation direction. The ellipse cut from the indicatrix by a wave surface is not affected by \( A_2 (\lambda) \|q\|^2 l_l \) at all. We can say that \( A_2 (\lambda) \|q\|^2 l_l \) has no influence on the birefringence phenomenon.

From these facts, it is possible to say that the term related to the intrinsic birefringence is \( A_2 (\lambda) \|q\|^2 \delta_{ij} l_i^2 \), the third term in the right side of Eq. (68). If we remove \( A_2 (\lambda) \|q\|^2 l_l \) from Eq. (68), which does not have any influence on birefringence, and we obtain
\[
\Delta B^l_{ij} (\lambda, q) = A_1 (\lambda) \|q\|^2 \delta_{ij} + A_3 (\lambda) \|q\|^2 \delta_{ij} l_i^2
\]
(72)

By substituting Eq. (72) into Eq. (63), we obtain

Fig. 22 An indicatrix with consideration of \( A_1 (\lambda) \|q\|^2 \delta_{ij} \) (Kitamura et al., 2012).

Fig. 23 An indicatrix with consideration of \( A_2 (\lambda) \|q\|^2 l_l \) (Kitamura et al., 2012).
When we redefine $A_i(\lambda) \parallel \mathbf{q} \parallel d_l = \frac{1}{n(\lambda)}$, the birefringence $\Delta n$, taking into account the intrinsic birefringence in addition to the stress birefringence, is expressed as follows:

$$\Delta n = \frac{1}{2} \left( B_i + \frac{1}{2} \left( \Delta B_{11}^i + \Delta B_{12}^i + \Delta B_{22}^i + \Delta B_{22}^i \right) \right)^{3/2} \sqrt{\left( \Delta B_{11}^i + \Delta B_{12}^i - \Delta B_{22}^i \right)^2 + 4 \left( \Delta B_{12}^i + \Delta B_{12}^i \right)^2}$$

(76)

where $\Delta B_{ij}^i$ denotes the change in inverse dielectric constant second-order tensor caused by the action of stress $\sigma_{ij}$, which is given by

$$\Delta B_{ij}^i = \pi_{ijkl}^i \sigma_{kl}$$

(77)

### 6.2 Method of analysis

In the birefringence simulation of CaF$_2$ single crystal used for the chamber window of a gas laser light source shown in Fig. 21, a stress analysis was first performed to yield the stress caused by the mechanical loads. Then, the optical path difference was calculated based on the birefringence theory stated above.

#### 6.2.1 Stress analysis

A stress analysis of an anisotropic CaF$_2$ single crystal ingot was performed using the finite element code MSC Marc. The stress distribution caused by the mechanical loads from a window holder and gas pressures was obtained in this analysis.

#### 6.2.2 Birefringence analysis

In the birefringence analysis, the average stress method proposed by Abbott et al. (2003) was applied to calculate the birefringence. When we define the $l$-axis as the wave normal, the average stress $\bar{\sigma}_{ij}$ along the wave normal is calculated from $\sigma_{ij}$ as follows:

$$\bar{\sigma}_{ij} = \frac{1}{d} \int_0^d \sigma_{ij} dl$$

(78)

where $d$ is the propagation length in the crystal ingot. Then, the change of the inverse dielectric constant is given by

$$\Delta B_{ij}^i = \pi_{ijkl}^i \bar{\sigma}_{kl}$$

(79)

The birefringence $\Delta n$ is obtained by substituting $\Delta B_{ij}^i$ into $\Delta B_{ij}^i$ in Eq. (76).

$$\Delta n = \frac{1}{2} \left( B_i + \frac{1}{2} \left( \Delta B_{11}^i + \Delta B_{12}^i + \Delta B_{22}^i + \Delta B_{22}^i \right) \right)^{3/2} \sqrt{\left( \Delta B_{11}^i + \Delta B_{12}^i - \Delta B_{22}^i \right)^2 + 4 \left( \Delta B_{12}^i + \Delta B_{12}^i \right)^2}$$

(80)

The optical path difference $\Gamma$ is expressed as follows:

$$\Gamma = d \Delta n$$

$$\frac{d}{2} \left( B_i + \frac{1}{2} \left( \Delta B_{11}^i + \Delta B_{12}^i + \Delta B_{22}^i + \Delta B_{22}^i \right) \right)^{3/2} \sqrt{\left( \Delta B_{11}^i + \Delta B_{12}^i - \Delta B_{22}^i \right)^2 + 4 \left( \Delta B_{12}^i + \Delta B_{12}^i \right)^2}$$

(81)
The result for the optical path difference is expressed as the optical path difference per unit length $\Gamma_{\text{unit}}$ defined by Eq.(54).

The value of an unknown coefficient $A_3(\lambda)$ is required to determine the birefringence $\Delta n$. The value of $A_3(\lambda)$ is determined as follows. Burnett et al. (2001) provide the intrinsic birefringence values of CaF$_2$ single crystal for several lights with wavelength ranging from 156nm to 365nm propagating along the <110>-crystal orientation. These values were obtained both from the experimental measurements and from the first-principles calculations. The results show that the intrinsic birefringence becomes significant for a light with the wavelength shorter than 200 nm, although it is negligible small for a light with the wavelength longer than 250nm. According to Burnett et al.’s results, the intrinsic birefringence values of CaF$_2$ single crystal for an ArF excimer laser of 193nm wavelength is $-3.4$nm/cm for the experimental measurement, and $-1.4$nm/cm for the first-principles calculation. The value of $A_3$ was determined in such a way that the birefringence of a light propagating along the <110>-crystal orientation corresponds with the measured value, $-3.4$nm/cm or the calculated value, $-1.4$nm/cm. $A_3$ is equal to $3.788 \times 10^{-22}$ m$^{-2}$ in the former case and $1.560 \times 10^{-22}$ m$^{-2}$ in the latter case. Birefringence measurements of CaF$_2$ single crystal, which was annealed enough to reduce residual stress as low as possible, were made for the light with 193nm wavelength, that is, the ArF excimer laser, in order to examine which value is better, $A_3=3.788 \times 10^{-22}$ m$^{-2}$ or $1.560 \times 10^{-22}$ m$^{-2}$. The EXICOR DUV system, HINDS Instruments, was used to measure birefringence. A <111>-growth single crystal ingot with 50mm in diameter and 7mm in thickness was used in these measurements, as shown in Fig. 24. In the <111>-growth single crystal, the <111> direction of the crystal corresponds to the $x_3$-axis of the analysis coordinate system, which is the thickness direction as shown in Fig. 25. The angle of incidence $\Phi$ is the Brewster’s angle 55.7° as shown in Fig. 26. The rotation angle $\theta$ is defined by the angle between the light wave normal direction and the <001> direction of the crystal in the $x_1$–$x_2$ plane. Birefringence measurements were made by changing the rotation angle $\theta$ from 0° to 60°.

![Fig. 24](image1.png)  Geometry of circular slab ingot and its finite element mesh for stress analysis (Kitamura et al., 2012).

![Fig. 25](image2.png)  Crystal orientation, light axis and analysis coordinate system for a <111>-growth CaF$_2$ single crystal window (Kitamura et al., 2012).

![Fig. 26](image3.png)  Angle of incidence, rotation angle and definition of $u_1$–$u_2$–$u_3$ light axis coordinate system (Kitamura et al., 2012).
The distributions of the optical path difference of CaF$_2$ single crystal ingot are shown in Figs. 27(a) - (g) for respective rotation angles. The figures show the homogeneity of the optical path difference for the respective rotation angles, which indicates that the residual stress is low enough in the CaF$_2$ single crystal ingot. Figure 28 shows the variations of the optical path difference $\Gamma$ averaged in the measuring area with the rotation angle $\theta$. The optical path difference measured by the experiment is caused by the intrinsic birefringence, because the CaF$_2$ single crystal ingot is expected to be stress-free. In Fig. 28, the experimental result is compared with the analytical result using $A_3 = 3.788 \times 10^{-22} \text{m}^{-2}$ and $A_3 = 1.560 \times 10^{-22} \text{m}^{-2}$. The experimental result agrees with the analytical result using $A_3 = 3.788 \times 10^{-22} \text{m}^{-2}$ rather than the analytical result using $A_3 = 1.560 \times 10^{-22} \text{m}^{-2}$. Hereafter $A_3 = 3.788 \times 10^{-22} \text{m}^{-2}$ is used for birefringence calculations.

6.3 Analysis conditions
6.3.1 Finite element mesh and crystal orientation
As shown in Fig. 24, a circular slab ingot with 50mm in diameter and 7mm in thickness is considered in the analysis. The finite element mesh used in the analysis is also shown in this figure. The analysis considered three types...
of crystal orientation, that is, <111>-growth single crystal, <110>-growth single crystal and <100>-growth single crystal. In the <111>-growth single crystal, the <111> direction of the crystal corresponds to the $x_3$-axis of the analysis coordinate system, which is the thickness direction as shown in Fig. 25. The <110> and <100>-growth single crystals have their analysis coordinate systems in the same way as the <111>-growth single crystal, as shown in Figs. 29(a) and (b).

![Diagram of crystal orientation, light axis and analysis coordinate system for <110>- and <100>-growth CaF$_2$ single crystal windows.](image)

(a) <110>-growth single crystal ingot

(b) <100>-growth single crystal ingot

6.3.2 Incident direction of light

Two types of light are considered in the analysis. One is the light with a wavelength of 633 nm, which is used in the birefringence measurement system EXICOR 150AT manufactured by HINDS instruments, Inc. The other is the light with a wavelength of 193 nm, that is, the ArF excimer laser. The angle of incidence $\Phi$ is the Brewster’s angle 55.7° as shown in Fig. 26. The birefringence analyses were performed for the rotation angle $\theta$ from 0° to 60° in the <111>-growth single crystal, from 0° to 90° in the <110>-growth single crystal, and from 0° to 45° in the <100>-growth single crystal. A coordinate system of the light axis, $u_1$–$u_2$–$u_3$, is shown in Fig. 26. The $u_3$-axis corresponds to the wave normal direction of the incident light, and the $u_1$-axis is in the plane of incidence. As shown in 6.4, the results of the birefringence analysis are represented by this coordinate system. The laser beam size is a rectangle with 3mm × 13mm.

6.3.3 Mechanical loads

We showed the mechanical loads applied to the CaF$_2$ single crystal used as the chamber window of the gas laser light source in Fig. 21. We considered the holding load through the O-rings and the pressure loads from laser gas and purge gas. One O-ring and the laser gas touch the upper surface of the circular slab ingot. The other O-ring and the purge gas touch the lower surface. The holding load measured by a torque wrench is 265 N, the laser gas pressure is 400 kPa and the purge gas pressure is 100 kPa.
6.3.4 Material properties

For the stress analysis of a single crystal ingot, we need the elastic constants of CaF₂ single crystal. The temperature dependence of the elastic constants, \( C_{11}, C_{12}, \) and \( C_{44} \), is already given in Table 2.

In the calculation of the optical path difference for CaF₂ single crystal, we need the piezo-optic coefficients \( \pi_{11}, \pi_{12}, \) and \( \pi_{44} \) and the refractive index \( n \) for the lights with 633nm and 193nm wavelengths. The material properties for the light with 633nm wavelength are already given in Table 3. The piezo-optic coefficients \( \pi_{ij} \) for the light with 193nm wavelength can be calculated from the photoelastic coefficients \( K_{ij} \) given by Levine et al. (2003) and the elastic compliance constants \( S_{ij} \) given by Corning. The detailed derivation of \( \pi_{ij} \) related to \( K_{ij} \) and \( S_{ij} \) is shown in Appendix. The refractive index \( n \) for the light with 193nm wavelength is given in Schott Lithotec: Calcium Fluoride Catalog. The material properties for the light with 193nm wavelength are summarized in Table 8. In addition to these material properties, we need the coefficient for intrinsic birefringence \( A_3 \) for the light with 193nm wavelength. This value is already given in 6.2, that is, \( A_3 = 3.788 \times 10^{-22} \text{ m}^2 \).

<table>
<thead>
<tr>
<th>Material properties of CaF₂ single crystal for the optical path difference analysis for the light with 193nm wavelength.</th>
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<tbody>
<tr>
<td><strong>Piezo-optic coefficients [Pa⁻¹]</strong></td>
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<td></td>
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<tr>
<td><strong>Reflective index</strong></td>
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6.4 Results and discussion

The birefringence analyses for a CaF₂ single crystal chamber window for an ArF excimer laser light source were performed by using the analysis conditions described above. The temperature is 273 K.

First, the optical path difference was calculated for the light with 633nm wavelength, which does not generate the intrinsic birefringence, and then the analysis results were compared with the experimental ones obtained from a birefringence measurement system EXICOR 150AT manufactured by HINDS instruments. Figure 30 shows the analysis results of optical path difference distributions of a <111>-growth single crystal window for the rotation angles \( \theta = 0°, 30°, \) and \( 60° \). These figures show the optical path differences of the light, which enters in the area of radius 12.5 mm around the center of the ingot and passes through the ingot. Figure 31 shows the experimental results of these conditions. It is found by comparing Figs. 30 and 31 that the analytical and experimental results agree well, both qualitatively and quantitatively. It is confirmed from these figures that the stress of a CaF₂ single crystal ingot used as a chamber window of an ArF excimer laser light source is accurately calculated, and that the optical path difference caused by the stress birefringence is appropriately evaluated. The analysis results of optical path difference in the case of \( \theta = 0° \) are shown in Fig. 32 for the respective single crystal windows, that is, the <111>- and <110>-growth single crystal windows. The <100>-growth single crystal window has much smaller optical path difference than the <111>- and <110>-growth single crystal windows.

Then, the birefringence analysis was performed for the 193nm wavelength ArF excimer laser. The typical analysis results of the <111>, <110>, and <100>-growth single crystal windows are shown here. The distributions of the optical path difference are shown in Figs. 33–35 for the respective single crystal windows. In these figures, the results are shown for respective rotation angles \( \theta \). It is observed from these figures that the uniformity of the optical path difference is best in the <100>-growth single crystal window, and worst in the <111>-growth single crystal window. Moreover, the optical path difference is smallest in the <100>-growth single crystal window. These results are similar to those of the light with 633 nm wavelength shown in Fig.32. In comparison between Fig.32 and Figs. 33-35, we can find that the optical path difference is smaller in the light with 633nm wavelength than in the light with 193nm wavelength. Such an effect of wavelength on the optical path difference results from intrinsic birefringence, which does not show in the light with 633nm wavelength but shows in the light with 193nm wavelength, and wavelength dependence of the optical properties, as shown in Tables 3 and 8.

Next, the optical performance was evaluated by using the degree of P-polarization, which is defined as a ratio of P-polarization component of light after passing through an ingot to that of light incident on an ingot. The higher the
The degree of P-polarization is, the better the optical performance of the chamber window is. The formulation of the degree of P-polarization is as follows. The incident light is polarized in the direction parallel to the plane of incidence, which is the $u_1$-$u_3$ plane, because it has only the P-polarization component and does not reflect at the Brewster’s angle of incidence. This polarizing direction corresponds to the $u_1$-axis in the $u_1$-$u_2$ plane. After passing through an ingot, the polarized light is described as follows, because it is split into two components, i.e., the component in the $u_1$-axis direction and that in the $u_2$-axis direction:

![Diagram](image1)

Fig. 30 Analysis results of optical path difference distribution for a $<111>$-growth CaF$_2$ single crystal window under incidence of 633nm wavelength light.

![Diagram](image2)

Fig. 31 Experimental measurements of optical path difference distribution for a $<111>$-growth CaF$_2$ single crystal window under incidence of 633nm wavelength light (Fig. 31(a) are quoted from Kitamura et al., 2012).

![Diagram](image3)

Fig. 32 Analysis results of optical path difference distribution for respective growth CaF$_2$ single crystal windows under incidence of 633nm wavelength light ($\theta = 0^\circ$) (Fig. 32(a) is quoted from Kitamura et al., 2012).
Fig. 33 Analysis results of optical path difference for a <111>-growth CaF$_2$ single crystal window under incidence of 193nm wavelength light.

(a) $\theta = 0^\circ$  (b) $\theta = 30^\circ$  (c) $\theta = 60^\circ$

Fig. 34 Analysis results of optical path difference for a <110>-growth CaF$_2$ single crystal window under incidence of 193nm wavelength light.

(a) $\theta = 0^\circ$  (b) $\theta = 45^\circ$  (c) $\theta = 90^\circ$

Fig. 35 Analysis results of optical path difference for a <100>-growth CaF$_2$ single crystal window under incidence of 193nm wavelength light.

(a) $\theta = 0^\circ$  (b) $\theta = 22.5^\circ$  (c) $\theta = 45^\circ$
From these components, we can obtain the degree of P-polarization by

\[ E_{n1} = A_{n1}(t) \cos \phi_{n1} \]  
\[ E_{n2} = A_{n2}(t) \cos \phi_{n2} = A_{n2}(t) \cos(\phi_{n1} + \Delta) \]  

From these equations, we can obtain the degree of P-polarization by

\[ P_P = \frac{\left< E_{n1} \right|^2 - \left< E_{n2} \right|^2}{\left< E_{n1} \right|^2 + \left< E_{n2} \right|^2} = \frac{\left< A_{n1}^2 \right> - \left< A_{n2}^2 \right>}{\left< A_{n1}^2 \right> + \left< A_{n2}^2 \right>} \]  

where \( \left< \right> \) denotes a time-averaged value.

We calculated the degree of P-polarization of the 193 nm wavelength light, which entered in the area of radius 2.0 mm around the center of the ingot and passed through the ingot. Figure 36 shows the degrees of P-polarization obtained from the analyses in this study with and without consideration of the intrinsic birefringence. In Fig.36, the <100>-growth single crystal shows totally higher degree of P-polarization. It is also found that the effect of intrinsic birefringence is highest in the <111>-growth single crystal and lowest in the <110>-growth single crystal. Relatively high degrees of P-polarization are found at the starting and ending points of each rotation angle, owing to the absence of intrinsic birefringence. This is because such rotation angles have high symmetry between light and crystal. In addition, the highest degree of P-polarization is at \( \theta = 0^\circ \) for the <100>-growth single crystal.

As shown in Chapter 4, the <111>-growth CaF\(_2\) single crystal ingot provides smaller optical path difference than the <100>-growth CaF\(_2\) single crystal ingot after ingot annealing under no mechanical loading condition, when incident light is normal to the ingot surface and passes along the thickness direction of the ingot. Due to the above reason, the <111>-growth single crystal ingot has been conventionally used at the rotation angle \( \theta = 0^\circ \) for the chamber window of a gas laser light source. The condition of minimizing the optical path difference for optical elements subjected to mechanical loads under real use condition are not always the same as that for no mechanical loading condition.

7. Concluding remarks

In the present review article, we dealt with the birefringence of single crystals, which is one of the important technical issues, when single crystals are utilized as optical elements, and reviewed this issue mainly based on previous works performed by the present authors.
The Jones calculus and the average stress method can be applied to the simulations of stress birefringence. The former is an exact method and the latter is an approximate one. The average stress method is easier to calculate optical path difference than the Jones calculus. Moreover it provides accurate results for stress birefringence equivalent to those of the Jones calculus for the stress level less than $10^9$ Pa. It is therefore concluded that the average stress method is the alternative to the Jones calculus and enable faster stress birefringence calculation than the Jones method in a practical stress level.

Birefringence phenomenon of single crystals is classified into stress birefringence caused by the photoelastic effect when single crystals are subjected to stress, and intrinsic birefringence resulted from crystal anisotropy. In the present article, the results of birefringence analyses for CaF$_2$ single crystal belonging to the cubic crystal system were shown as an example of stress birefringence. This single crystal does not show intrinsic birefringence for visible light because of its weak crystal anisotropy. On the other hand, MgF$_2$ single crystal belonging to the tetragonal crystal system shows intrinsic birefringence even for visible light because of its strong crystal anisotropy. The results of birefringence analyses are shown for MgF$_2$ single crystal as an example of combining stress birefringence with intrinsic birefringence under a visible light condition. The Jones calculus, an exact method, and the average stress method, an approximate method, were shown for stress birefringence calculations. It was shown that the relative error of the optical path difference obtained from the average stress method is within 1% compared with that of the Jones calculus, if the stress level in a single crystal is less than $10^9$ Pa. So an accurate stress birefringence analysis can be done by the average stress method for most stress birefringence problems.

It is known that the effect of intrinsic birefringence cannot be ignored in CaF$_2$ single crystal under the incidence of ArF excimer laser with 193nm wavelength. The methodology for the calculation of optical path difference taking account of intrinsic birefringence in addition to stress birefringence was shown in this article. This methodology was applied to the birefringence analysis of CaF$_2$ single crystal chamber window of ArF excimer laser light source, and the effect of intrinsic birefringence was quantitatively evaluated.

References


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Schott Lithotec, Calcium Fluoride Catalog.


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Appendix : Detailed derivation of piezo-optic coefficients $\pi_{ij}$ for 193 nm wavelength light

Levine (2003) obtained the photoelastic coefficients $K_{ij}$ for the light with short wavelength including 193nm wavelength both experimentally and analytically. The photoelastic tensor $K_{ijkl}$ is defined by

$$\Delta e_{ij} = K_{ijkl} \epsilon_{kl}$$

(A.1)

where $\Delta e_{ij}$ and $\epsilon_{ij}$ are the change of dielectric tensor and the strain tensor, respectively. The change of inverse dielectric tensor $\Delta B_{ij}$ is related to the stress tensor $\sigma_{ij}$ using the piezo-optic tensor $\pi_{ijkl}$ as follows:

$$\Delta B_{ij} = \pi_{ijkl} \sigma_{kl}$$

(A.2)

The values of piezo-optic coefficients $\pi_{ij}$ for the 193nm wavelength light were obtained by deriving a relation between $K_{ijkl}$ and $\pi_{ijkl}$. For this purpose, let us derive the relation between $\Delta e_{ij}$ and $\Delta B_{ij}$ respectively given by Eqs.(A.1) and (A.2). The inverse dielectric $B_{ij}$ is the inverse of dielectric $e_{ij}$.

$$e_{ik} B_{kj} = B_{ik} e_{kj} = I_{ij}$$

(A.3)

where $I_{ij}$ is the unit matrix with $3 \times 3$. The values of $e_{ij}$ and $B_{ij}$ can be expressed by the summation of their values without stress, $e_{ij}^0$ and $B_{ij}^0$, and their changes due to photoelastic effect, $\Delta e_{ij}$ and $\Delta B_{ij}$.

$$e_{ij} = e_{ij}^0 + \Delta e_{ij}$$

(A.4)

$$B_{ij} = B_{ij}^0 + \Delta B_{ij}$$

(A.5)

where the following relation holds for $e_{ij}^0$ and $B_{ij}^0$:

$$e_{ik} B_{kj}^0 = I_{ij}$$

(A.6)

Substituting Eqs.(A.4) and (A.5) into Eq.(A.3) and considering Eq.(A.6) lead to

$$e_{ik}^0 \Delta B_{kj} + \Delta e_{ik} B_{kj}^0 + \Delta e_{ik} \Delta B_{kj} = 0$$

(A.7)

We shall consider the dielectric tensor $e_{ij}^0$ and the inverse dielectric tensor $B_{ij}^0$ of CaF\(_2\) single crystal at the stress-free condition. As described in 6.2.2, intrinsic birefringence of CaF\(_2\) single crystal can be neglected for the light with the wavelength longer than 200nm. In such a case, $e_{ij}^0$ and $B_{ij}^0$ do not depend on the direction of light propagation, and they are expressed by the reflective index $n$ as follows:

$$e_{ij}^0 = n^2 \delta_{ij}$$

(A.8)

$$B_{ij}^0 = n^{-2} \delta_{ij}$$

(A.9)

For the light with the wavelength shorter than 200nm, CaF\(_2\) single crystal has intrinsic birefringence, which induces the change of dielectric tensor $\Delta e_{ij}^l$ and inverse dielectric tensor $\Delta B_{ij}^l$, and $e_{ij}^0$ and $B_{ij}^0$ are expressed by

$$e_{ij}^0 = n^2 \delta_{ij} + \Delta e_{ij}^l$$

(A.10)
\[ B_{ij}^0 = n^2 \delta_{ij} + \Delta B_{ij} \]  

(A.11)

In Eqs.(A.10) and (A.11), \( n^2 \) is the order of \( 10^{-1} \), and \( \Delta B_{ij} \) is the order of \( 10^{-7} \) for the light with 193nm wavelength based on the order-estimation of \( A_j(\lambda) |\mathbf{q}|^{1/2} \delta J_\lambda \). Thus the relation \( n^2 \gg \Delta B_{ij} \) holds. \( \Delta e_{ij} \) should be nearly equal to zero under the condition of Eq.(A.6). For these reasons, Eqs.(A.8) and (A.9) hold irrespective of wavelength. By substituting these equations into Eq.(A.7), we obtain

\[ \Delta e_{ij} = -n^2 \Delta B_{ij} \left( n^2 I_{ij} + \Delta B_{ij} \right)^{-1} \]  

(A.12)

The piezo-optic tensor \( \pi_{ijkl} \) of materials are generally the order of \( 10^{-11}\text{Pa}^{-1} \) to \( 10^{-12}\text{Pa}^{-1} \). We can assume the same order in the case of CaF\(_2\) single crystal for the light with 193 nm wavelength. Moreover the relation \( n^2 \gg \Delta B_{ij} \) holds when the order of stress \( \sigma \) is smaller than \( 10^3 \text{Pa} \) in Eq.(A.2). According to our researches presented in this article (Ogino et al., 2008; Kitamura et al., 2009, 2010a, 2010b, 2010c, 2012; Miyazaki et al., 2009), the order of \( \sigma \) does not exceed \( 10^3 \text{Pa} \). Therefore we assume that the order of residual stress in single crystal ingots is smaller than \( 10^8 \text{Pa} \) in the experiments performed by Levine et al. (2003). In consideration of the relation \( n^2 \gg \Delta B_{ij} \), Eq.(A.12) becomes

\[ \Delta e_{ij} = -n^2 \Delta B_{ij} \left( n^2 I_{ij} \right)^{-1} = -n^4 \Delta B_{ij} \]  

(A.13)

The piezo-optic tensor \( \pi_{ijkl} \) is represented by the strain-optic tensor \( p_{ijkl} \) and the elastic compliance tensor \( S_{ijkl} \) as follows:

\[ \pi_{ijkl} = p_{ijkl} S_{pqkl} \]  

(A.14)

Then Eq.(A.2) can be rewritten as

\[ \Delta B_{ij} = p_{ijkl} E_{kl} \]  

(A.15)

From Eqs.(A.1), (A.13) and (A.15), we obtain

\[ K_{ijkl} = -n^4 p_{ijkl} \]  

(A.16)

In consideration of Eq.(A.14), the photo-elastic tensor \( K_{ijkl} \) can be express by piezo-optic tensor \( \pi_{ijkl} \) as

\[ \pi_{ijkl} = -n^4 K_{ijkl} S_{pqkl} \]  

(A.17)

We can calculate piezo-optic tensor \( \pi_{ijkl} \) from the photo-elastic tensor \( K_{ijkl} \) and the elastic compliance tensor \( S_{ijkl} \) using this equation.

Now let us calculate for the light with 193nm wavelength. The results of wavelength-dependence of \( K_{ij} \), abbreviated representation of tensor \( K_{ijkl} \), are shown in Figs. A.1(a), (b) and (c) which show \((K_{11}+2K_{12})/3, (K_{11}-K_{12}) \) and \( K_{44} \), respectively. The abscissa in these figures represents photon energy \( E \) and the vertical line corresponding to the energy of 1.96eV and that of 6.42eV represent the photon energy of 633 nm wavelength light and that of 193 nm wavelength light, respectively. In these figures, the results of the first-principles calculation are denoted by the various symbols, and the experimental measurements are denoted by the various symbols. \( \zeta \) in Fig. A.1(c) represents the internal strain parameter used in the analysis and \( 0 \leq \zeta \leq 1 \).

In Fig. A.1(a), the analysis results agree reasonably well with the experimental measurements. It is also found from Fig. A.1(c) that the analysis results agree well with the experimental measurements in the range below 6.42eV in photon energy, or over 193nm in wavelength by adjusting the internal strain parameter \( \zeta \). On the other hand, we can see the large difference between the analysis results and experimental measurements in Fig. A.1(b). The experimental results denoted by different symbols were measured by different researchers. They agree well with each other. According to Levine’s paper (2003), similar experimental measurements are obtained for BaF\(_2\) and SrF\(_2\) single crystals in addition to CaF\(_2\) single crystal. Thus the experimental measurements in Fig. A.1(b) are supposed to be reliable. We calculated the piezo-optic coefficients \( \pi_{ij} \) for the light with 1.96 eV in photon energy or 633nm in wavelength from the photo-elastic coefficients \( K_{ij} \) obtained from Figs. A.1(a) to (c) in order to examine which one is reliable for \( K_{ij} \), the analysis result or the experimental measurement. In conclusion, the analysis result \( 8 \times 8 \times 8 \) in Fig. A.1(a) and the experimental measurements \( + \) and \( \Delta \) in Figs. A.1(b) and (c) provide the piezo-optic coefficients \( \pi_{ij} \) close to their values at the 633nm wavelength shown in Table 3, and we used the analysis result in Fig. A.1(a) and the experimental measurements in Figs. A.1(b) and (c) as the photo-elastic coefficients \( K_{ij} \) at the 193nm wavelength. Table A.1
summarizes the values of $K_{ij}$ obtained by the above-mentioned method and the elastic compliance constants $S_{ijkl}$ given in Corning catalog. The piezo-optic coefficients $\pi_{ij}$ at the 193 nm wavelength given in Table 8 were calculated based on Eq.(A.17) from $K_{ij}$ and $S_{ij}$ in Table A.1 and refractive index $n$ in Table 8.

(a) $\left( K_{11} + 2K_{12} \right)/3$

(b) $K_{11} - K_{12}$

(c) $K_{44}$

Fig. A.1  Wavelength dependence of photoelastic constants for CaF$_2$ single crystal (Levine et al., 2003).

Table A.1  Material properties of CaF$_2$ single crystal for the calculation of piezo-optic coefficients for 193 nm wavelength light.

<table>
<thead>
<tr>
<th></th>
<th>Photo-elastic coefficients</th>
<th>Strain-optic coefficients</th>
<th>Elastic compliance constants [Pa$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{11}$</td>
<td>0.352</td>
<td>$p_{11}$ = -0.0691</td>
<td>$S_{11}$ = 6.867 × 10$^{-12}$</td>
</tr>
<tr>
<td>$K_{12}$</td>
<td>-0.738</td>
<td>$p_{12}$ = 0.145</td>
<td>$S_{12}$ = -1.451 × 10$^{12}$</td>
</tr>
<tr>
<td>$K_{44}$</td>
<td>-0.113</td>
<td>$p_{44}$ = 0.0222</td>
<td>$S_{44}$ = 29.764 × 10$^{12}$</td>
</tr>
</tbody>
</table>