Investigation of the electrogyration effect of ferroelectric Pb$_5$Ge$_3$O$_{11}$ by circular dichroism

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Abstract. The circular dichroism of the ferroelectric Pb$_5$Ge$_3$O$_{11}$ was precisely determined as a function of electric field and temperature in order to clarify the microscopic origin of the electrogyration effect. From the circular dichroic spectrum, which was observed near 410 nm and identified as being due to the intra-ionic $6s \rightarrow 6p$ transition in Pb^{2+}, the sign and magnitude of the rotatory strength could be determined. The rotatory strength exhibited a hysteresis loop under the electric field and its magnitude varied with the spontaneous polarization. The finding confirms our previous proposition that the electrogyration effect originates from the change in the rotatory strength. This conclusion is also examined on the basis of group theory. The optical rotatory power calculated through the Kramers–Kronig relation was compared with the experimental value. The origin of the enormous difference between the calculated and experimental magnitudes is discussed.

1. Introduction

The optical activity of ferroelectrics varies with the spontaneous polarization P_s or the square of P_s (Kizel' *et al* 1975). This phenomenon is known as the electrogyration (EG) effect. In order to clarify the microscopic mechanism of the EG effect, we have measured the circular dichroism (CD), the unequal absorption of left and right circularly polarized light, of some uniaxial ferroelectrics (Uesu *et al* 1987, 1988, 1989). In the course of the study, we found that the rotatory strength (RS) of the related optical transition changes in proportion to P_s^2 in the case of Ca$_2$Pb(C$_2$H$_5$CO$_2$)$_6$ (DLP), which manifests the second-order EG effect. On the basis of the result, we claimed that the EG effect could substantially be explained by the change in the RS and not by the change in the energy level of the corresponding transition. However, more straightforward evidence should be obtained from the CD measurement of ferroelectrics which show a first-order EG effect where the sign of the RS could be reversed by the electric field and its magnitude be proportional to P_s. For this purpose, we chose Pb$_5$Ge$_3$O$_{11}$ (5P3G) crystal in the present study and measured precisely the electric-field and temperature dependences of the CD spectrum observed near 410 nm to examine whether the above phenomena really occur in the crystal. We also discuss our experimental results on the basis of group theory and the result of the calculation of the optical rotatory power (ORP) through the Kramers–Kronig (KK) relation.

The CD Θ is expressed as (Condon 1937)

$$\Theta = \frac{16\pi^2 N}{3hc} \sum_b \frac{\nu^3 \Gamma_{ab} R_{ab}}{(\nu_{ab}^2 - \nu^2)^2 + \nu^2 \Gamma_{ab}^2}. \tag{1}$$

Here, h is Planck's constant, c the velocity of light, N the number of atoms in the unit volume, ν the frequency of light, ν_{ab} the absorption frequency and Γ_{ab} the damping factor. R_{ab} is the rotatory strength and is given by the product of electronic dipole moment $\langle a|\mu_e|b\rangle$ and magnetic dipole moment $\langle a|\mu_m|b\rangle$ as follows (Rosenfeld 1928):

$$R_{ab} = \mathrm{Im}\langle a|\mu_e|b\rangle \cdot \langle b|\mu_m|a\rangle. \tag{2}$$

Since the electric and magnetic dipole moments are produced by displacive and rotational motions, respectively, of electrons, the RS has an appreciable magnitude only when both kinds of motion exist. This corresponds to the spiral motion of electrons, for which we must differentiate the inter-ionic motion responsible for structural chirality from the intra-ionic motion responsible for electronic chirality. It is also a purpose of the present study to identify the observed CD spectrum according to this classification.

2. Experimental method

5P3G has a ferroelectric transition temperature at 177 °C (Iwasaki *et al* 1971). It belongs to an optically non-active space group $P\bar{6}$ in the paraelectric phase (Iwata 1977) and to an optically active $P3$ in the ferroelectric phase (Iwata *et al* 1973, Kay *et al* 1975). Both phases exhibit the first-order EG effect (Iwasaki and Sugii 1971). As the CD spectrum was measured along the optic c axis, the specimen had been cut perpendicular to the optic c axis from a crystal grown by the Czochralski technique. Transparent electrodes of In_2O_3 were sputtered onto the (001) plates. Misorientation of the incident (001) surfaces produces birefringence, which seriously affects the CD spectrum. For this purpose, we cut specimens observing a conoscopic figure under the polarizing microscope and examined the orientation by the x-ray diffraction method. A deviation of the orientation of the incidence surfaces from the optic axis could be suppressed within $\pm 0.1°$. In this case, the effect of the birefringence on the CD spectrum could be neglected (Uesu *et al* 1987). The influence of the In_2O_3 transparent electrode on the CD and the absorption spectra was also scrutinized before and after the sputtering. No significant change was observed in the wavelength region from 350 to 900 nm.

When linearly polarized light enters an optically active crystal along the optic axis, the transmitted light from the crystal is generally elliptically polarized with the azimuth ψ and the ellipticity K (Uesu *et al* 1987). The azimuth of unit length is the optical rotatory power ρ, while the ellipticity of unit length determines the CD Θ. In the present method, we used the modulation method to determine the ellipticity K of the transmitted light (see appendix).

3. Experimental results and discussion

3.1. Electric-field dependence of the CD spectrum

The CD and normal absorption spectra of 5P3G measured at room temperature are shown in figure 1. The CD spectrum observed near 410 nm (3 eV) corresponds to the
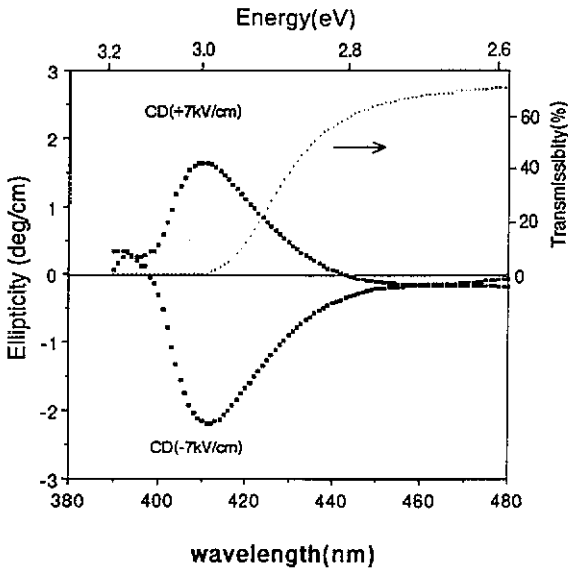
Figure 1. The CD spectra for an electric field of ± 7 kV cm^{-1} and the normal absorption spectrum of 5P3G observed at room temperature.
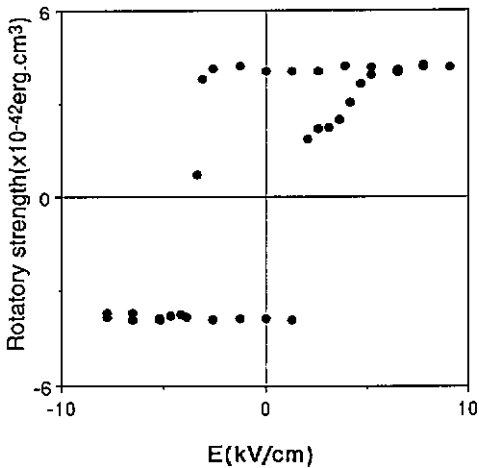
Figure 2. Electric-field dependence of the RS R of 5P3G at room temperature.

fundamental absorption edge of the crystal. Although the CD measurement was made in the wavelength region from 200 to 800 nm, no CD spectrum was observed above 480 nm, while a stable CD spectrum could not be obtained below 390 nm owing to large absorption of the crystal. According to the optical spectroscopy analysis of other inorganic substances containing a Pb^{2+} ion (Ito *et al* 1978, 1979), the electronic transition at 3 eV is estimated to be the 6s → 6p intra-ionic transition in the Pb^{2+} ion, where 6s constitutes the highest state in the valence band and 6p the lowest in the conduction band. In figure 1, the CD spectra for electric fields of ± 7 kV cm^{-1} with opposite senses were also shown. It clearly shows that the sign of the CD spectrum of 5P3G can be reversed
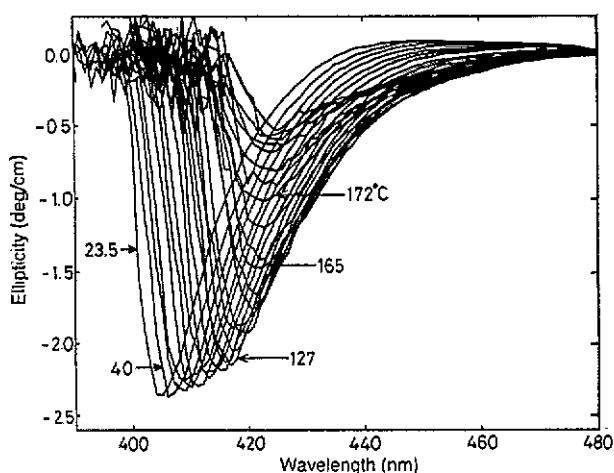
Figure 3. Temperature dependence of the CD spectrum of 5P3G for an electric field of $-7\,\text{kV}\,\text{cm}^{-1}$.

by the electric field in the ferroelectric phase. It is the first definite evidence for the electric-field-induced enantiomorphism that the CD measurement probed.

The RS can be calculated by performing the following integration over the CD spectrum:

$$R_{ab} = \frac{3hc}{8N\pi^3}\int_{band} \frac{\Theta(\lambda)}{\lambda}\,d\lambda. \tag{3}$$

By measuring the CD spectrum for various electric fields at room temperature, the dependence of the RS on the electric field was obtained. The result is shown in figure 2. The RS exhibits a typical hysteresis loop similar to the D–E loop of ferroelectrics. The observed RS hysteresis is not rectangular, probably owing to the pinning of ferroelectric domain motion by impurities.

3.2. Temperature dependence of the CD spectrum

The dependence of the CD spectrum on temperature was measured under the electric field of $-7\,\text{kV}\,\text{cm}^{-1}$. The result is shown in figure 3. With increasing temperature, the CD spectrum shifts to a higher-wavelength region and its magnitude falls towards zero and vanishes above the ferroelectric transition temperature $T_c = 177.5\,°\text{C}$. The RS, the peak wavelength λ_0 and the full width Γ at half-maximum determined from figure 3 are shown as functions of temperature in figures 4(a), 4(b) and 4(c), respectively. To examine the linearity between the RS and P_s these values are plotted on a log–log scale in figure 5. The power β was determined as 1.0 ± 0.1, where $R_{ab} \propto P_s^{\beta}$. These results clearly indicate that the RS changes in proportion to P_s for 5P3G.

In figure 4(b), λ_0 determined from the normal absorption measurement is also presented, since it was difficult to determine this quantity accurately from the CD spectrum, especially in the vicinity of T_c owing to the weak signal. Although a small
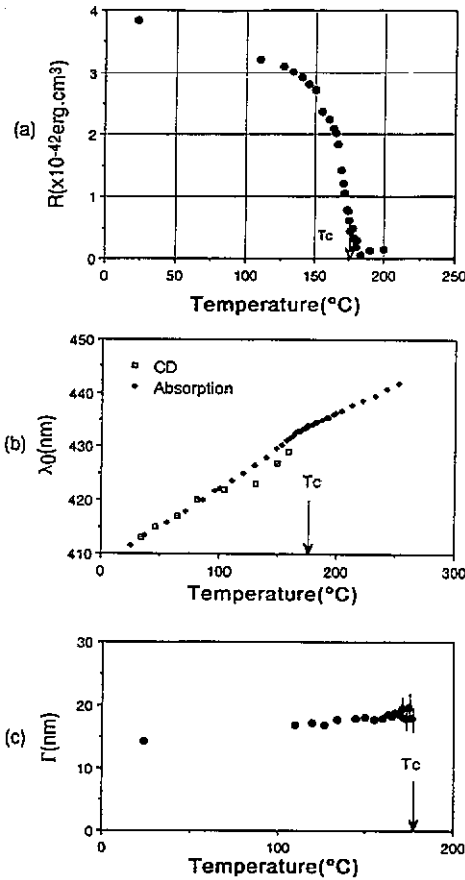
Figure 4. Temperature dependence of (a) the RS R, (b) the peak wavelength λ_0 and (c) the full width Γ at half-maximum of the CD spectrum of 5P3G.
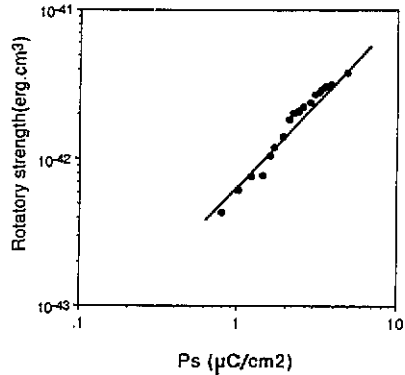
Figure 5. A log–log plot of the RS and the spontaneous polarization of 5P3G.

difference exists between the temperature coefficients of λ_0 in paraelectric and ferroelectric phases, it is the RS that contributes exclusively to the behaviour of the CD spectrum.

3.3. Group-theoretical consideration

The present results on the first-order EG effect, together with the previous results (Uesu *et al* 1988) on the second-order effect, lead to the conclusion that the EG effect can be explained by the change in the RS; R_{ab} varies in proportion to P_s for the first-order effect and to P_s^2 for the second-order effect. This conclusion is also supported by group theory as follows. Expressed as a product of μ_e and μ_m (see equation (2)), the RS is permitted only when a polar vector component x_i and an axial (rotational) vector component R_j belong to the same irreducible representation of the point group. This condition is a necessary condition for optical activity.

Table 1. Character table of the point group C_{3h} ($\bar{6}$). $\varepsilon = \exp(-2\pi i/3)$.

C_{3h}	E	C_3	C_3^2	σ_h	S_3	S_3^5	Basis
A'	1	1	1	1	1	1	R_z
E'	$\left\{\begin{array}{l}1\\1\end{array}\right.$	$\begin{array}{c}\varepsilon\\\varepsilon^*\end{array}$	$\begin{array}{c}\varepsilon^*\\\varepsilon\end{array}$	$\begin{array}{c}1\\1\end{array}$	$\begin{array}{c}\varepsilon\\\varepsilon^*\end{array}$	$\left.\begin{array}{c}\varepsilon^*\\\varepsilon\end{array}\right\}$	(x, y)
A''	1	1	1	-1	-1	-1	z
E''	$\left\{\begin{array}{l}1\\1\end{array}\right.$	$\begin{array}{c}\varepsilon\\\varepsilon^*\end{array}$	$\begin{array}{c}\varepsilon^*\\\varepsilon\end{array}$	$\begin{array}{c}-1\\-1\end{array}$	$\begin{array}{c}-\varepsilon\\-\varepsilon^*\end{array}$	$\left.\begin{array}{c}-\varepsilon^*\\-\varepsilon\end{array}\right\}$	(R_x, R_y)

Table 2. Character table of the point group D_4 (422).

D_4	E	$2C_4$	C_2	$2C_2$	$2C_2''$	Basis
A_1	1	1	1	1	1	
A_2	1	1	1	-1	-1	z, R_z
B_1	1	-1	1	1	-1	
B_2	1	-1	1	-1	1	
E	2	0	-2	0	0	$(x, y); (R_x, R_y)$

In tables 1 and 2, the character tables of the point groups of $\bar{6}$ (5P3G) and 422 (DLP) are given. In the case of $\bar{6}$, x_i and R_j belong to different irreducible representations whereas, in the case of 422, they belong to the same irreducible representation A_2 or E. Then, the above group theory considerations allow us to ascertain that the point group of $\bar{6}$ is optically non-active, while the point group of 422 is active. On the other hand, the first-order EG effect is permitted when the product $x_i^2(R_j)$ belongs to the identity representation. This is realized if R_j belongs to the identity representation; this is the case for 5P3G, where the RS should vary in proportion to P_s as found in the present experiment. In the case of DLP, the first-order EG effect is forbidden and only the second-order effect is observable, since R_j does not belong to the identity representation.

3.4. Calculation of the optical rotatory power by the Kramers–Kronig relation

The CD spectrum observed near 410 nm at room temperature was transformed into the ORP through the KK formula. The calculated and experimental ORPs (Iwasaki *et al* 1972) are compared in figure 6. It was found that the contribution of the CD spectrum near 410 nm to the ORP is quite small. This fact suggests the possible existence of another CD spectrum with much larger RS below the absorption edge, which could not be observed in the present experiment.

We discuss here the relation between the present experimental result and the Glazer–Stadnicka (GS) (1986) theory of optical activity. GS developed a quite general theory by which the sign and magnitude of the optical activity of the crystal of inorganic crystals can be well determined from the absolute configuration of atoms. In this theory, the helical arrangement of highly polarizable atoms and the direction of the anisotropic polarizabilities of the constituent atoms are the key quantities. They also found from the crystallographic data that some crystals contain plural helices with different pitches,
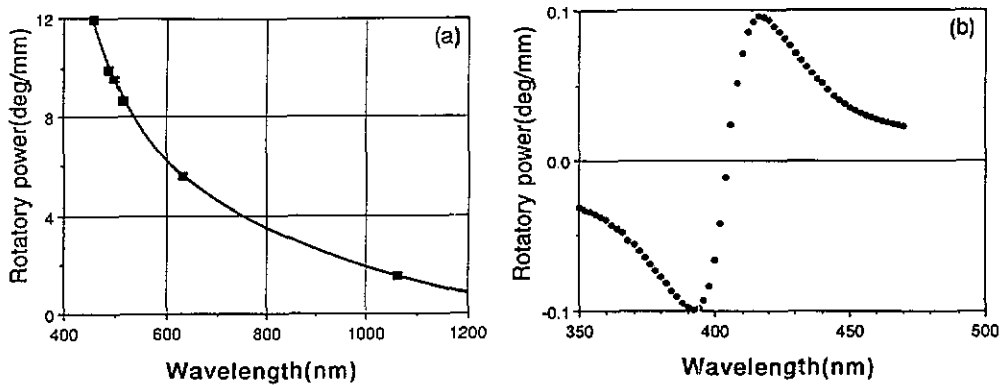
Figure 6. Dispersion of the ORP of 5P3G: (a) experimental values; (b) values calculated from the observed CD spectrum through the KK formula. The line in (a) is a guide to the eye.

radii and even senses of the rotation. These features should be reflected in the CD spectra in the sense that the helices with a different nature produce corresponding CD spectra. Thus the CD measurement is expected to provide a powerful tool for confirming the GS theory.

As mentioned above, the RS responsible for the CD spectrum originates from two kinds of optical transition: inter-ionic and intra-ionic. The helices responsible for the GS theory are structural and thus inter-ionic, whereas the CD spectrum observed for 5P3G is identified as being intra-ionic. It is then natural to conclude that there should be another CD spectrum below the absorption wavelength for 5P3G corresponding to the inter-ionic transition and to the structural helix. The CD spectrum originating from the intra-ionic transition has generally a weaker RS than the inter-ionic transition, being consistent with the present result of the ORP calculated from the CD spectrum through the KK formula. In order to verify the assumption experimentally, it is useful to construct the CD apparatus in the vacuum-ultraviolet wavelength region using the synchrotron radiation and to measure the CD spectrum below the absorption wavelength, as is now being planned.

Acknowledgment

Appendix. Principle of the measurement of circular dichroism by the modulation method

In order to measure the CD of an optically active crystal along the optic axis, we used the modulation method, in which the phase and the amplitude Φ_0 of the incident light are modulated with frequency ω as follows:

$$\Phi_0 = [1 + \sin^2(\omega t)]^{-(1/2)} \left\{ \begin{array}{c} 1 \\ i \sin(\omega t) \end{array} \right\}. \tag{A1}$$

Here, the intensity of the light is normalized to unity. This is realized when the quarter-wave voltage with frequency ω is applied to an electro-optic crystal. The optical principal axis of this crystal is inclined to the plane of the incident linearly polarized light by $45°$.

As the eigenstates of the light inside the crystal are right (Φ_r) and left (Φ_l) circularly polarized light, Φ_0 is decomposed into two states:

$$\Phi_0 = A_r\Phi_r + A_l\Phi_l \tag{A2}$$

with

$$\Phi_r = \left\{\begin{matrix}1\\i\end{matrix}\right\}, \Phi_l = \left\{\begin{matrix}1\\-i\end{matrix}\right\},$$

and

$$A_r = \tfrac{1}{2}[1 + \sin^2(\omega t)]^{-(1/2)}[1 + \sin(\omega t)]$$
$$A_l = \tfrac{1}{2}[1 + \sin^2(\omega t)]^{-(1/2)}[1 - \sin(\omega t)]. \tag{A3}$$

On passing through the crystal of thickness d, the state of the light is transformed into Φ:

$$\Phi = \exp[-\mu_r d + i(2\pi/\lambda)n_r d]$$
$$\times \left\{\begin{matrix}A_r + A_l \exp[-(\mu_l - \mu_r)d + i(2\pi/\lambda)(n_l - n_r)d]\\i\{A_r - A_l \exp[-(\mu_l - \mu_r)d + i(2\pi/\lambda)(n_l - n_r)d]\}\end{matrix}\right\} \tag{A4}$$

where n_i and μ_i denote the refractive index and the absorption coefficient of the right ($i = r$) and left ($i = l$) circularly polarized light, respectively.

From (A4), we obtain the expression for the intensity of the transmitted light as

$$I = \Phi\Phi^* = \tfrac{1}{2}[\exp(-2\mu_r d) + \exp(-2\mu_l d)]$$
$$+ [\exp(-2\mu_r d) - \exp(-2\mu_l d)]/[1 + \sin^2(\omega t)]. \tag{A5}$$

The first term of (A5) denotes the direct component I_d, while the second term is the alternate component I_a which is the difference between the intensity I_r related to the right-circular wave and the intensity I_l related to the left-circular wave:

$$I_d = \exp(-2\mu_r d)/[1 + \sin^2(\omega t)]$$
$$I_l = \exp(-2\mu_r d)/[1 + \sin^2(\omega t)]. \tag{A6}$$

From (A5) and (A6), the ellipticity $K = \tfrac{1}{4}(\mu_l - \mu_r)d$ of the transmitted light is expressed as

$$K = \tfrac{1}{8}\ln(I_r/I_l). \tag{A7}$$

With the amplitudes of I_r, I_l and I_a being defined as I_r^0, I_l^0 and I_a^0, the final expression for the ellipticity is obtained as

$$K = \tfrac{1}{8}(I_a^0/I_d) \tag{A8}$$

where $I_d = \tfrac{1}{2}(I_l^0 + I_r^0)$. Thus, the CD $\Theta = K/d$ can be determined directly from the alternate and direct components of the transmitted intensity.

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