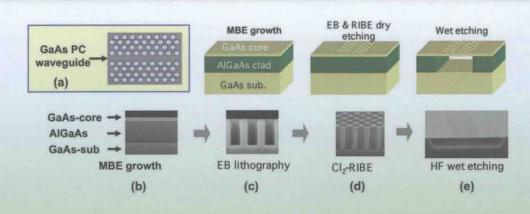


# Optical Materials and Applications

Edited by Moriaki Wakaki





# Optical Materials and Applications

常州大字山书彻藏书章

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# Optical Materials and Applications

# Edited by Moriaki Wakaki



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### **Preface**

Light propagates in free space with the velocity of  $2.997925 \text{ m/s}^{-1}$  as a wave spatially and a collection of photons with an energy of  $\varepsilon = h\nu$ . Various kinds of optical materials or media are developed to utilize the fundamental natural phenomena of light. Many types of refractive and reflective optical systems consisting of lenses and mirrors have been developed for the simple manipulation of the spatial distribution of light. To design the optical system with a specific character, the materials to conform the system must have desired optical spectra for transmission and reflection. Also to design a certain active element, desired absorption and emission spectra are required. A fundamental review of typical active materials such as LASER is given in Chapter 4, "Materials for Solid-State Laser," by T. Itatani. These optical properties are realized by utilizing and designing the dielectric dispersion of each material.

As the first step, we should understand the basic optical properties of typical materials. The definition of optical material has been expanded largely due to the rapid expansion of optoelectronic applications caused by the progress of information technology (IT). Various types of optical windows are the typical optical materials, and these are classified as a passive element. Many types of optical components for dispersion control such as prisms, gratings, and filters and for phase control such as wave plates are needed to form advanced optical systems. A review of the fundamental optical properties of solids is given in Chapter 1, "Basic Theory on Optical Properties of Solids," by M. Wakaki and K. Kudo. A review of fundamental optical materials is given in Chapter 2, "Optical Materials for Ultraviolet, Visible, and Infrared," by T. Arai and M. Wakaki in the linear regime and a review extended to the nonlinear regime is given in Chapter 3, "Materials for Nonlinear Optics," by T. Arai and M. Wakaki.

Bulk materials are the basic material and offer basic information on the materials for the design of various modifications. Optical thin films are the beginning of artificial components. Artificial structures with subwavelength dimensions have been recently formed with physical (vacuum evaporation) or chemical techniques to control the phase of the light wave. A fundamental review of optical thin films is presented in Chapter 6, "Materials for Optical Thin Films," by T. Shibuya. Starting from a one-dimensional (1D) structure typically applied as an interference filter, nanoprocess to two-dimensional (2D) and three-dimensional (3D) structures to control the dispersion of the material has been developed. A review of such typical systems is presented in Chapter 7, "Materials for Nanophotonics," by K. Asakawa. Finally, the progress of IT greatly depends on the progress of the optical waveguide, which gives the optical systems compact and high-efficiency characteristics. A review of such an optical waveguide is given in Chapter 5, "Materials for Optical Waveguides," by B. P. Pal.

The editor of this book, M. Wakaki, appreciates each author's contribution to the basic ideas for beginners in this field and advanced topics for active researchers in the field, and also expresses great thanks to T. Shibuya for assisting in the arrangement

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of the manuscripts. The editor also expresses great thanks to the promotional and management editors of CRC Press for encouraging authors to finish the manuscripts.

Finally, I feel indebted to my wife, T. Wakaki, and my sons for giving me the time to do this work.

M. Wakaki At old and stimulating city, Edinburgh

### The Editor

Moriaki Wakaki is a professor in the Department of Optical and Imaging Science and Technology, School of Engineering, Tokai University, Japan. He is a chief professor of electro photo optics, Graduate School of Engineering, Tokai University. He is the author or coauthor of over 100 scientific papers. He was the editor-inchief of the Journal of Advanced Science from 1996 to 2000, the newsletter of the Thermoelectric Conversion Research Society of Japan from 1997 to 2000, and Oyokougaku (Applied Optics in Japanese) from 2001 to 2003. Wakaki is a member of the Optical Society of America, the International Society for Optical Engineering, the Optical Society of Japan, the Laser Society of Japan, the Japan Spectroscopic Society, the Japan Society of Applied Physics, the Physical Society of Japan, the Surface Science of Japan, the Thermoelectric Society of Japan, the Carbon Society of Japan, the Japan Society of Plastic Surgery, and the Society of Advanced Science. He received MSc and DSc degrees in physics from Tokyo Educational University in 1972 and 1975, respectively. His current areas of research are solid state physics relating mainly to complex materials dispersed with nanoparticles, optoelectronics research, laser medicine and biophotonics, infrared astronomy relating mainly to the development of spectroscopic measuring systems and far-infrared detectors.

Wakaki has published the following works in English and Japanese: *Rediscover Optics* (Optronics Co. Press, Tokyo, 1997, in Japanese), *Introduction to Optical Engineering* (Jikkyou Syuppan Press, Tokyo, 1998, in Japanese), *Fundamentals of Quantum Optics* (Gendai Kougakusya Press, Tokyo, 1998, in Japanese), *Environment Conscious Material* (Nikka Giren Press, Tokyo, 2002, in Japanese), *Introduction to Wave Optics* (Jikkyou Syuppan Press, Tokyo, 2004, in Japanese), and *Physical Properties and Data of Optical Materials* (CRC Press, Boca Raton, Florida, 2007).

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# 1 Basic Theory on Optical Properties of Solids

Moriaki Wakaki and Keiei Kudo (deceased)

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The optical properties of solids are basically described using the dielectric functions of the materials. The function depends on the symmetry of the medium—that is, the crystal structure. The fundamental concept of the geometry of the crystal structure is given in Section 1.1. The propagation of light through the medium or the interaction between medium and light is described by the dispersion characteristics of the light in the medium. The summary of the dispersion of light in the medium is given in Section 1.2. The details of the dielectric properties are also described in Chapter 2 ("Optical Materials for Ultraviolet, Visible, and Infrared"). The detailed behavior of the reflection and transmission of the layers is treated in Chapter 2 and Chapter 6 ("Materials for Optical Thin Films"). The dielectric properties are contributed by many types of elementary excitations. Major excitations contributing to the optical excitations are caused by electrons and phonons. The optical absorptions by electrons and lattice vibrations in solids are reviewed in Sections 1.3 and 1.4, respectively. Light scattering effects like Raman and Brillouin scatterings, which offer the complementary information to the absorption spectra in solids are summarized in Section 1.5. The effects of external fields like magnetic and electric fields on optical properties are also reviewed in Chapter 2. The nonlinear optical properties are also reviewed in Chapter 3 ("Materials for Nonlinear Optics").

#### 1.1 GEOMETRY OF CRYSTAL<sup>1-3</sup>

Materials are classified according to their degrees of aggregation: These are gas, liquid, and solid in the order of increasing densities of molecules or atoms. Recent

advanced applications of devices require high-density integration of elements, and the device systems with a solid phase are dominant. Physical properties of solids are the main interest of this text. The solid phase is classified into random arrangements (glasses and amorphous) and regular arrangements (crystals) of molecules or atoms according to their topological forms. Recently, complex materials that are not classified simply to one of the above categories have been actively fabricated and studied for their interesting potentials.<sup>4–7</sup>

Crystalline solids offer the fundamental concepts of the material relating with basic physical properties, and it is still important to learn the basic concept to develop the advanced system of materials, like superlattices, ceramics, and composite materials including nanostructures.<sup>8–10</sup> Recent topics relating to nanophotonics materials are presented in Chapter 7 by K. Asakawa.

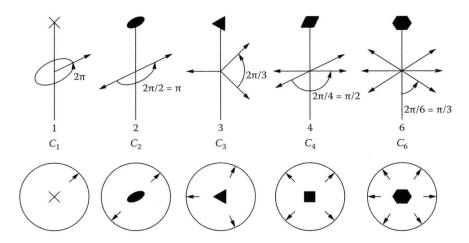
The physical properties of crystals are strongly correlated with the symmetry of the lattice that composes the material. In the crystal, the lattice arranges regularly in space and its minimum unit is called a primitive unit cell. The collection of primitive unit cells also arranges regularly to form a crystal. The type of crystal is first classified by the symmetry of the primitive unit cell.

#### 1.1.1 SYMMETRY OPERATIONS

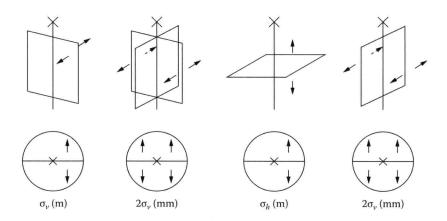
The symmetry is featured by using the symmetry operations not to change the original form by the operations. These operations are described as follows:

- 1. *Identity* (Einhelt): The rotation of 360 degrees around an axis does not change the form of the lattice. The operation is usually expressed by the symbol E.
- 2. Cyclic axis: The unit cell does not change its form by some rotation around the proper axis. If the cell returns its original form n times through the rotation of 360 degrees around the axis, the cell has the n-fold rotation axis. These symmetries are expressed as  $C_n$  (n = 1, 2, 3, 4, and 6) by Schönflies (S) expression and simply as n (1, 2, 3, 4, and 6) by Herman-Mauguin (H-M) expression as shown in Figure 1.1.11 If there are several cyclic axes, the axis with largest number n is called a *principal axis*.
- 3. Symmetry plane (mirror or reflection plane): If the unit cell is symmetrical with some plane within the cell, the plane is called the *symmetry plane* as shown in Figure 1.2. The symmetry plane is expressed by the symbol  $\sigma$  (S) or m (H-M).
- 4. Rotatory reflection axis: If the cell does not change form after  $2\pi/n$  rotation and the reflection is not perpendicular to the axis, the operation is called the rotatory reflection axis Sn (S) or n (H-M) as shown in Figure 1.3.<sup>11</sup>
- 5. *Inversion*: If the cell does not change form after the operation of the shift of the position of lattice point r to -r referring to the point within the unit cell, the operation is called *inversion* i (S) or 2 (H-M).

The unit cell has several symmetrical elements. For example, the square unit cell  $C_{4v}(4mm)$  has the symmetry elements,  $E 2C_4 C_4^2 2\sigma_v 2\sigma_d$  as shown in Figure 1.4(a),



**FIGURE 1.1** Rotation around the axis of symmetry. (See also K. Kudo: *Fundamentals of Optical Properties of Solids*, Ohmsha (1977) (in Japanese).) The upper scheme is a stereophonic description, and the lower is a projection description.

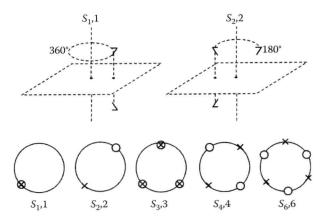


**FIGURE 1.2** Reflection through a plane that contains the principal axis  $\sigma_v$  and is perpendicular to the principal axis  $\sigma_h$ . The upper scheme is a stereophonic description, and the lower is a projection description.

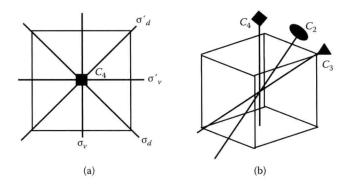
and order of 8, which is the total number of the symmetry elements. The cubic unit cell  $O_h$  (m3m) has the symmetry elements,  $E \ 8C_3 \ 3C'_2 \ 6C_2 \ 6C_4 \ I \ 8S_6 \ 3\sigma_h \ 6\sigma_d \ 6S_4$  and the order of 48.

#### 1.1.2 POINT GROUPS AND CRYSTALLINE GROUPS

If the symmetry elements of the unit cell are written as  $A_1$ ,  $A_2$ , ...,  $A_n$ , these elements constitute a group by satisfying the following four conditions:



**FIGURE 1.3** Rotation about an axis followed by reflection through a plane perpendicular to the axis of rotation. (See also K. Kudo: *Fundamentals of Optical Properties of Solids*, Ohmsha (1977) (in Japanese).) The upper scheme is a stereophonic description, and the lower is a projection description. Cross and circle symbols mean upper and lower position to the plane, respectively.



**FIGURE 1.4** Symmetry operations for square unit cell  $C_{4\nu}(4mm)$  (a), and for cubic unit cell  $O_h(m3m)$  (b).

- 1. The state obtained after two successive symmetry operations is expressed by a single operation within the set. That is, the following relation holds,  $A_i A_j = A_k$ .
- 2. The identity operation *E* gives the following relation for any element within the set. That is,

$$E A_j = A_j E = A_j$$

- 3. The following relation of combination holds—that is,  $A_i(A_i A_k) = (A_i A_i) A_k$ .
- 4. If the inverse operation of  $A_j$  is written as  $A_j^{-1}$ , the following relation holds,  $A_j^{-1}A_j = A_j A_j^{-1} = E$ , which means  $A_j^{-1}$  is also an element of this set (from condition 1).

	приса		ubic io		the Elements of C <sub>4v</sub> (mm)									
	Ε	$C_4$	$C_{4}^{2}$	$C_{4}^{3}$	$\sigma_{\text{v}}$	$\sigma_{\mathbf{v}'}$	$\sigma_{\text{d}}$	$\sigma_{\boldsymbol{d'}}$						
E	E	$C_4$	$C_4^{\ 2}$	$C_4^{\ 3}$	$\sigma_{\rm v}$	$\sigma_{v'}$	$\sigma_{\rm d}$	$\sigma_{d'}$						
$C_4$	$C_4$	$C_4{}^2$	$C_4^{\ 3}$	E	$\sigma_{d^{\prime}}$	$\sigma_{\mathrm{d}}$	$\sigma_{\rm v}$	$\sigma_{v'}$						
$C_4{}^2$	$C_4^{\ 2}$	$C_4{}^3$	E	$C_4$	$\sigma_{v'}$	$\sigma_{\rm v}$	$\sigma_{d'}$	$\sigma_{\rm d}$						
$C_4^{\ 3}$	$C_4^{\ 3}$	E	$C_4$	$C_4^{\ 2}$	$\sigma_{\rm d}$	$\sigma_{d^{'}}$	$\sigma_{\mathrm{v}'}$	$\sigma_{v}$						
$\sigma_{\rm v}$	$\sigma_{v}$	$\sigma_{d}$	$\sigma_{v'}$	$\sigma_{d^{\prime}}$	E	$C_{4}^{2}$	$C_4$	$C_4^{\ 3}$						
$\sigma_{\mathbf{v}^{'}}$	$\sigma_{v'}$	$\sigma_{d^{\prime}}$	$\sigma_{\rm v}$	$\sigma_{\rm d}$	$C_4{}^2$	E	$C_4{}^3$	$C_4$						
$\sigma_{\rm d}$	$\sigma_{\rm d}$	$\sigma_{v'}$	$\sigma_{d'}$	$\sigma_{\rm v}$	$C_4^{\ 3}$	$C_4$	E	$C_{4}^{2}$						
$\sigma_{d^{\prime}}$	$\sigma_{d'}$	$\sigma_{\rm v}$	$\boldsymbol{\sigma}_{d}$	$\sigma_{v^{\prime}}$	$C_4$	$C_4^{3}$	$C_4^{\ 2}$	E						

TABLE 1.1 Multiplication Table for the Elements of  $C_{4v}$  (4mm)

For example, the operation  $A_i A_j$  for the square unit cell  $C_{4v}$  (4mm) gives the result shown in Table 1.1.

The result satisfies the condition indicated above. These groups of symmetry elements express the lattice points of the crystal and are called the *point group*. Each unit cell is kept invariant for respective symmetry operation in the point group. But each unit cell must also cover the whole crystal by the translational movement. To meet the requirement, the rotation angles in  $C_n$  and  $S_n$  are limited to the integral multiple of  $60^\circ$  or  $90^\circ$ , which is derived from the properties of the point group. Only 32 point groups are allowed from these results. The 32 point groups give the possible arrangement of the crystal lattice and are often called the *crystal class*.

Two types of symbols are usually used to express these point groups (crystal class): Schönflies and Hermann–Maugin expressions. As shown in the example of a square unit cell, both expressions are shown as  $C_{4\nu}(4mm)$ .

#### 1.1.3 SPACE GROUPS

The point groups described in Section 1.1.2 are the set of operations not to change the unit cell. The unit cell after the operation cannot be distinguished with the original form. In the case of a simple lattice, the entire crystal lattice can be constructed only by the primitive translations. As the unit cell becomes complex to have ions or ion clusters around or between lattice points, the same arrangement as the original is obtained after a nonprimitive translation (translation by several parts of the lattice constant) and rotation or reflection.

#### 1.1.3.1 Screw Axis

If the cell does not change after a rotation  $2\pi/n$  (n = 1, 2, 3, 4, 6) around the certain axis and a translation by a distance T along the axis, the lattice has a screw axis.

#### 1.1.3.2 Glide Plane

If the cell does not change after some translation along a plane and a reflection against the plane, the lattice has a glide plane.

The number of the nonprimitive space group is 157, and that of the primitive one is 73. As a result, the total number of the space group is 230 as shown in Table 1.2.<sup>11</sup>

3,, 230)11	50. $D_{2h}^4(Pban)$	51. $D_{2h}^{5}(Pmma)$	52. $D_{2h}^{6}(Pnna)$	53. $D_{2h}^{7}(Pmna)$	54. $D_{2n}^{8}(Pcca)$	55. $D_{2h}^{o}(Pbma)$	56. $D_{2h}^{10}(Pccn)$	57. $D_{2h}^{11}(Pbcm)$	58. $D_{2h}^{12}(Pnnm)$	59. $D_{2h}^{13}(Pmmm)$	60. $D_{2h}^{14}(Pbcn)$	61. $D_{2h}^{15}(Pbca)$	62. $D_{2h}^{16}(Pnma)$	63. $D_{2h}^{17}(Cmcm)$	64. $D_{2h}^{18}(Cmca)$	65. $D_{2h}^{19}(Cnnnm)$	66. $D_{2h}^{20}(Cccm)$	67. $D_{2h}^{21}(Cmma)$	68. $D_{2h}^{22}(Ccca)$	69. $D_{2h}^{23}(Fnunm)$
Crystalline System (I, II, III,, VII), Crystal Class ((1), (2), (3),,(32)) and Space Group (1, 2, 3,, 230) <sup>11</sup>	31. C <sub>2</sub> <sup>7</sup> (Pmn2 <sub>1</sub> )	32. $C_{2v}^{8}$ (Pba2)	33. $C_{2v}^{9}$ (Pna2 <sub>1</sub> )	34. C <sub>2v</sub> (Pnn2)	35. C <sub>2v</sub> (Cmm2)	36. C <sub>2v</sub> (Cmc2 <sub>1</sub> )	37. $C_{2\nu}^{13}$ (Ccc2)	38. $C_{2v}^{14}$ (Amm2)	39. $C_{2v}^{15}$ (Abm2)	40. C <sub>2v</sub> (Ama2)	41. $C_{2v}^{17}$ (Aba2)	42. C <sub>2v</sub> (Fmm2)	43. C <sub>2v</sub> (Fdd2)	44. C <sub>2v</sub> (Imm2)	45. $C_{2\nu}^{21}$ (Iba2)	46. $C_{2v}^{22}$ (Ima2)	(8) $D_{2h}(mmm) = V_h$ , $[EC_2C_2'C_2'' i\sigma_h\sigma_v'\sigma_v'']$	47. $D_{2h}^1(Pmmm)$	48. $D_{2h}^2(Pnnn)$	49. $D_{2h}^3(Pccm)$
I, III,, VII), Crystal Class ((1), (2	14. $C_{2h}^{5}$ (P2 <sub>1</sub> /b)	15. $C_{2h}^6$ (B2/b)	III. Orthorhombic	(6) $D_2(222)$ , $[EC_2C'_2C''_2]$	16. $D_2^1$ (P222)	17. $D_2^2$ (P222 <sub>1</sub> )	18. $D_2^3$ (P2 <sub>1</sub> 2 <sub>1</sub> 2)	19. $D_2^4$ (P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> )	20. D <sub>2</sub> (C222 <sub>1</sub> )	21. $D_2^{\circ}$ (C222)	22. $D_2^{\prime}$ (F222)	23. $D_2^8$ (1222)	24. $D_2^9 (12_1 2_1 2_1)$	(7) $C_{2\nu}$ (mm2), $[EC_2\sigma_\nu\sigma^*_\nu]$	25. $C_{2v}^{l}$ (Pmm2)	26. $C_{2v}^2$ (Pmc2 <sub>1</sub> )	27. $C_{2v}^3$ (Pcc2)	28. C <sub>2v</sub> (Pma2)	29. $C_{2v}^5$ (Pca2 <sub>1</sub> )	30. $C_{2v}^6$ (Pnc2)
Crystalline System (I, II	I. Triclinic	(1) C <sub>1</sub> (1), [E]	1. C <sub>1</sub> (P1)	$(2) C_i(\bar{1}), [Ei]$	2. C' (PĪ)	II. Monoclinic	(3) C <sub>2</sub> (2), [EC <sub>2</sub> ]	3. C <sub>2</sub> (P2)	4. $C_2^2$ (P2 <sub>1</sub> )	5. $C_2^3$ (B2)	(4) $C_5(m)$ , $[E \sigma_h]$	6. C <sub>3</sub> (Pm)	7. $C_5^2$ (Pb)	8. C <sub>5</sub> (Bm)	9. C <sub>3</sub> (Bb)	(5) $C_{2h}(2/m)$ , $[EC_2i \sigma_h]$	10. $C_{2h}^{i}$ (P2/m)	11. $C_{2h}^2$ (P2 <sub>1</sub> /m)	12. $C_{2h}^3$ (B2/m)	13. C <sub>2h</sub> (P2/b)