CRC Handbook of Laser Science and Technology

Volume III
Optical Materials
Part 1: Nonlinear Optical Properties/Radiation Damage

Editor

Marvin J. Weber, Ph.D.

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CRC Press, Inc.
Boca Raton, Florida

Library of Congress Cataloging-in-Publication Data
Main entry under title:

Optical materials.

(CRC handbook of laser science and technology ; v. 3)
Bibliography: p.
Contents: pt. 1. Nonlinear optical properties
radiation damage.
1. Optical materials. 2. Optical materials--
Effect of radiation on. 3. Nonlinear optics.
I. Weber, Marvin J., 1932- . II. Series.
QC374.068 1986 621.36 86-983
ISBN 0-8493-3503-5

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Direct all inquiries to CRC Press, Inc., 2000 Corporate Blvd., N.W., Boca Raton, Florida, 33431.

International Standard Book Number 0-8493-3503-5

Library of Congress Card Number 86-983
Printed in the United States

PREFACE

Laser action has been observed in all forms of matter and spans a spectrum ranging from radiowaves to X-rays. The object of the *CRC HANDBOOK OF LASER SCIENCE AND TECHNOLOGY* is to provide a concise, readily accessible source of critically evaluated data for workers in all areas of laser research and development. The emphasis is on the presentation of tabular and graphical data compiled by recognized authorities. Definitions of properties and references to the original data sources and to supplementary reviews and surveys are also provided, as appropriate. The previous two volumes in this series dealt with laser action in all media and contained extensive tables of laser transitions and references. Volumes III, IV, and V are devoted to the physical and chemical properties of optical materials used in laser systems and applications.

The earlier *CRC Handbook of Lasers with Selected Data on Optical Technology* contained several sections on optical materials. These sections have been updated and expanded and many new sections added to form Volumes III to V. The materials covered are almost exclusively condensed matter. Because many properties are dependent in varying degrees on preparation methods, materials imperfections and measurement techniques, several sections included discussions and descriptions of these specific characteristics and of materials compositions.

Optical materials for laser systems encompass an extremely wide range of special property requirements and operating wavelengths and environments. Of necessity, the topics covered in these volumes are selective. In some sections it was possible to be exhaustive; in others, a more general survey is provided because extensive data tabulations already exist elsewhere. The applications of optical materials are continually expanding. Therefore an attempt has been made throughout to include not only currently useful materials but also representative examples of broader classes of materials of possible future interest. One can frequently use observed trends in materials properties with composition to select and tailor new materials having specific operating characteristics.

Data on optical materials can be presented from different points of view — by material, by properties, or by application. For laser materials no single approach seemed fully appropriate, therefore several formats have been utilized. A number of properties may be relevant to a given application. As an example, for transmitting materials one may be interested in optical, thermal, and mechanical properties, thus these properties are grouped together within a single section. However, not all properties are covered within a particular section. Because of their special character, properties such as optical nonlinearities, radiation damage, and fabrication are discussed separately. Characteristics of specific classes of materials such as glasses may also be covered in several sections depending upon its use as a transmitting material, a filter material, an optical waveguide material, or a laser host material. Indices at the end of each volume list individual materials and where data on specific properties are located.

With the advent of lasers, nonlinear optical phenomena have become important and have been the subject of intense study and application. The properties of materials for harmonic generation and two-photon absorption, nonlinear refractive index, and stimulated Raman scattering properties of various opticals materials are included in Volume III. Data on radiation damage of optical crystals and glasses are also surveyed in this volume. Volume IV covers materials for fundamental uses: transmission (laser windows and lenses), filtering, reflection, and polarization. Materials for more specialized uses involving linear electrooptic, magnetooptic, elastooptic, and photorefractive effects and liquid crystals are also covered in this volume. Volume V presents data on properties of materials for optical waveguides, optical storage and recording, phase conjugation, lasers, and quantum counter applications. Other sections cover optical coatings and thin films. The final section describes fabrication techniques and procedures for all types of optical materials.

Laser-induced damage to optical components is an extremely important consideration for many laser applications. Although it was originally planned to include a section on laser damage, this topic will be covered separately elsewhere. In this regard, I welcome comments about the contents and presentation in the present volumes and suggestions for materials and properties to be included in future editions.

A handbook can never be completely current with the journal literature. Because of the very nature of the preparation and publication process, one must accept the fact that a handbook becomes out-of-date at the time of the final type setting. Although all sections for Volumes III to V were solicited concurrently, there were delays in the receipt of some manuscripts. Some sections were updated, but variations in timeliness, as evident from the reference dates, remain.

These volumes are the result of the efforts and talents of many people to whom I am indebted. I thank especially the contributors for the time devoted to preparing these compilations and texts and the Advisory Board and contributors for their numerous helpful comments and suggestions regarding the content and format. The staff of CRC Press, and Senior Editor Marsha Baker in particular, have my thanks and appreciation for the preparation of these volumes. Finally, I am grateful to my wife Pauline for her generous support of this project.

Marvin J. Weber
Danville, California
February 1984

THE EDITOR

Marvin J. Weber received his education at the University of California, Berkeley, and was awarded the A.B., M.A., and Ph.D. degrees in physics in 1954, 1956, and 1959. After graduation Dr. Weber joined the Research Division of the Raytheon Company where he was a Principal Scientist. As Manager of Solid State Lasers, his group developed many new rare earth laser materials. While at Raytheon, he also discovered luminescence in bismuth germanate, a scintillator crystal widely used for the detection of high energy particles and radiation.

During 1966-67 Dr. Weber was a Visiting Research Associate in the Department of Physics, Stanford University.

In 1973 Dr. Weber joined the Laser Fusion Program at the Lawrence Livermore National Laboratory. As Head of Basic Materials Research, he had the responsibility for the physics and characterization of optical materials for high-power laser systems. His work on laser glass resulted in an Industrial Research IR-100 Award in 1979 for research and development of fluorophosphate laser glasses. In 1983 Dr. Weber was the recipient of the George W. Morey Award of the American Ceramics Society for his basic studies of fluorescence and stimulated emission in glasses and for the insight that research has provided into glass structure.

Dr. Weber has published numerous scientific papers and review articles in the areas of lasers, luminescence, optical spectroscopy, and magnetic resonance in solids and has been granted several patents on solid-state laser materials. He is a Fellow of the American Physical Society, a Fellow of the Optical Society of America, and a member of the American Ceramics Society, the Materials Research Society, and the American Association for Crystal Growth.

Among other activities, Dr. Weber has been a consultant for the National Science Foundation's Division of Materials Research, a member of the National Academy of Science - National Research Council Evaluation Panel for the National Bureau of Standard's Inorganic Materials Division, and a participant in various advisory panels. He is currently an Associate Editor of the *Journal of Luminescence* and a member of the Editorial Advisory Board of the *Journal of Non-Crystalline Solids*.

In 1984 Dr. Weber began a temporary transfer assignment with the Division of Materials Sciences, Office of Basics Energy Sciences, of the U.S. Department of Energy in Washington, D.C., where he has been involved with planning for advanced synchrotron radiation facilities and applications of computers for materials simulations.

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HANDBOOK OF LASER SCIENCE AND TECHNOLOGY

VOLUME I: LASERS AND MASERS

VOLUME II: GAS LASERS

HANDBOOK OF LASER SCIENCE AND TECHNOLOGY

VOLUME IV: OPTICAL MATERIALS
PART 2: PROPERTIES

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HANDBOOK OF LASER SCIENCE AND TECHNOLOGY

VOLUME III: OPTICAL MATERIALS
PART 1: NONLINEAR OPTICAL PROPERTIES/RADIATION DAMAGE

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Section 1
Nonlinear Optical Properties

1. NONLINEAR OPTICAL PROPERTIES

1.1. NONLINEAR OPTICAL MATERIALS

S. Singh

INTRODUCTION

When a material substance is subjected to electromagnetic radiation, the electrons of the medium tend to be polarized. In the electric dipole approximation, this effect is characterized by an induced polarization, $\mathbf{P}_j^{(1)}$, or the electric dipole moment per unit volume of the medium phenomenologically by the linear relation:

$$\mathbf{P}_j^{(1)}\omega = \epsilon_o \chi_{jk}^{(1)}(\omega) E_k(\omega) \qquad (C \cdot \mathrm{m}^{-2} \text{ in MKS units}) \tag{1}$$

where E_k is a component of the electric field strength associated with the incident radiation, ϵ_o is the permittivity of free space having the value of 8.854×10^{-12} C · V^{-1} · m^{-1} in MKS units or $(^1/_4\pi)$ stat$C$·statV^{-1}·cm^{-1} in CGS (esu) units, and $\chi_{jk}^{(1)}(\omega)$, a second-rank tensor for anisotropic media, is a complex quantity which is responsible for the familiar optical phenomena of absorption, emission, reflection, and refraction. Thus,

$$\chi_{jk}^{(1)}(\omega) = \chi_{jk}^{'(1)}(\omega) + i\chi_{jk}^{''(1)}(\omega) \tag{2}$$

The index of refraction, $n(\omega)$, and dielectric constant, $\epsilon(\omega)$, of a medium are related to the real part of the susceptibility by:

$$n_{jk}^2(\omega) = \epsilon_{jk}^{(\omega)}/\epsilon_o = 1 + \chi_{jk}^{'(1)}(\omega) \quad \text{(MKS units)} \tag{3}$$

$$= \epsilon_{jk}(\omega) = 1 + 4\pi\chi_{jk}^{'(1)}(\omega) \text{ (CGS units)} \tag{4}$$

The absorption constant, $\alpha(\omega)$, is related to the imaginary part of the susceptibility as:

$$\alpha(\omega) = (\omega/c)\chi_{jk}^{''(1)}(\omega) \qquad (\mathrm{m}^{-1},\text{MKS}) \tag{5}$$

$$= (4\pi\omega/c)\chi_{jk}^{''(1)}(\omega) \; (\mathrm{cm}^{-1},\text{CGS}) \tag{6}$$

The number of independent components of the dielectric tensor, ϵ_{jk} (or the linear susceptibility tensor $\chi_{jk}^{(1)}$), for different crystal classes and for isotropic media are given in Table 1.1.1.

For large values of the optical fields, such as those associated with intense radiation from lasers, the induced polarization in a medium is no longer a linear function of E. In order to describe the nonlinear optical effects which can occur under such conditions, it is convenient to expand **P** as a power series in the electric field, E, and magnetic field, H, and their time and space gradients present in the nonlinear medium.[1-3] Thus, for a lossless nonmagnetic medium one can write qualitatively:

Table 1.1.1
FORM OF THE DIELECTRIC TENSOR ϵ_{jk} (OR FIRST-ORDER SUSCEPTIBILITY TENSOR $\chi^{(1)}_{jk}$) FOR VARIOUS CRYSTAL CLASSES

Cubic and isotropic system	$\begin{bmatrix} \epsilon_{11} & 0 & 0 \\ 0 & \epsilon_{11} & 0 \\ 0 & 0 & \epsilon_{11} \end{bmatrix}$
Tetragonal, trigonal, and hexagonal systems	$\begin{bmatrix} \epsilon_{11} & 0 & 0 \\ 0 & \epsilon_{11} & 0 \\ 0 & 0 & \epsilon_{33} \end{bmatrix}$
Orthorhombic system	$\begin{bmatrix} \epsilon_{11} & 0 & 0 \\ 0 & \epsilon_{22} & 0 \\ 0 & 0 & \epsilon_{33} \end{bmatrix}$
Monoclinic system (unique axis oy)	$\begin{bmatrix} \epsilon_{11} & 0 & \epsilon_{13} \\ 0 & \epsilon_{22} & 0 \\ \epsilon_{13} & 0 & \epsilon_{33} \end{bmatrix}$
Triclinic system	$\begin{bmatrix} \epsilon_{11} & \epsilon_{12} & \epsilon_{13} \\ \epsilon_{21} & \epsilon_{22} & \epsilon_{23} \\ \epsilon_{31} & \epsilon_{32} & \epsilon_{33} \end{bmatrix}$

$$\begin{aligned} \mathbf{P}_j(\omega_\sigma) = \epsilon_0[&\chi_{jk}(\omega_\sigma)E_k(\omega_\sigma) + \chi_{jkl}(\omega_\sigma)K_k(\omega_\sigma)E_l(\omega_\sigma) \\ &+ g_1\chi_{jkl}(-\omega_\sigma;\omega_1,\omega_2)E_k(\omega_1)E_l(\omega_2) - g_2 i\chi^{H}_{jkl}(-\omega_\sigma;\omega_1,\omega_2)E_k(\omega_1)H_l(\omega_2) \\ &+ g_3 i\chi_{jklm}(-\omega_\sigma;\omega_1,\omega_2)E_k(\omega_1)K_l(\omega_2)E_m(\omega_2) \\ &+ g_4\chi_{jklm}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)E_k(\omega_1)E_l(\omega_2)E_m(\omega_3) \\ &+ g_5\chi^{HH}_{jklm}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)E_k(\omega_1)E_l(\omega_2)H_m(\omega_3) \\ &+ g_6\chi^{H}_{jklm}(-\omega_\sigma;\omega_1,\omega_2,\omega_3)E_k(\omega_1)E_l(\omega_2)H_m(\omega_3) + \ldots] \end{aligned} \tag{7}$$

where j, k, l, m . . . are Cartesian subscripts obtained by the Einstein summation convention of repeated indexes j, k, l, m . . . $= x, y, z$, and g_1, g_2, g_3 . . . g_6 are degeneracy factors arising from intrinsic permutation symmetry. The frequencies (having both positive and negative values) satisfy the relation:

$$\omega_\sigma = \omega_1 + \omega_2 + \omega_3 + \ldots \tag{8}$$

In Equation 7, $\mathbf{P}(\omega)$, $E(\omega)$, and $H(\omega)$ are the Fourier complex amplitudes at ω. Thus,

$$\mathbf{P}(\mathrm{r,t}) = (1/2)[\mathbf{P}(\omega)\exp i(\mathrm{k}\cdot\mathrm{r} - \omega \mathrm{t}) + c\cdot c] \tag{9}$$

$$E(\mathrm{r,t}) = (1/2)[E(\omega)\exp i(\mathrm{k}\cdot\mathrm{r} - \omega \mathrm{t}) + c\cdot c] \tag{10}$$

$$H(\mathrm{r,t}) = (1/2)[H(\omega)\exp i(\mathrm{k}\cdot\mathrm{r} - \omega \mathrm{t}) + c\cdot c] \tag{11}$$

Also,

Table 1.1.2
NONLINEAR OPTICAL PROCESSES[9,11]

Susceptibility	Optical process	Ref.
$\chi_{jkl}(-2\omega;\omega,\omega)$	Second harmonic generation (SHG) (g = 1/2)	12
$\chi_{jkl}(0;\omega,-\omega)$	Optical rectification (OR) (g = 1/2)	13
$\chi_{jkl}(-\omega;0,\omega)$	Linear electrooptic or Pockel's effect (EO) (g = 2)	14
$\chi_{jkl}(-\omega_p \pm \omega_s;\omega_p,\omega_s)$ $\omega_r + \omega_p = \omega_s$	Parametric (sum) or difference mixing (PG) (g = 1)	15—23
$\chi_{jkl}(\omega_i)$	Optical activity and frequency mixing	24, 25
$\chi_{jklm}(-3\omega;\omega,\omega,\omega)$	Third-harmonic generation (THG) (g = 1/4)	26—28
$\chi_{jklm}(-2\omega;0,\omega,\omega)$	Electric-field-induced second-harmonic generation (FISHG) (g = 3/4)	26, 28
$\chi_{jklm}(-\omega_4;\omega_1,\omega_2,\omega_3,\omega_4)$	Three-wave sum mixing (g = 3/2)	
$\chi_{jklm}(-\omega;\omega,0,0)$	Quadratic electrooptic or DC kerr effect (g = 3/4)	50, 51
$\chi_{jklm}(-\omega;\omega,\omega,-\omega)$	Optic-field induced birefringence or self-focusing (g = 3/4)	29, 30
$\chi_{jklm}(\omega_s;\omega_p,-\omega_p,\omega_s)$	Optical kerr effect (g = 3/2)	48
$\chi_{jklm}(\omega_2 - 2\omega_1;\omega_1,\omega_1,-\omega_2)$	Three wave mixing (TWM) (g = 3/4)	28, 52
$\text{Im}\chi_{jklm}(-\omega_s;\omega_p,-\omega_p,\omega_s)$	Stimulated Raman, Brillouin, and electronic Raman scattering (SRS, SBS, SERS) (g = 3/2)	39—47
$\text{Im}\chi_{jklm}(-\omega;\omega,\omega_p,-\omega_p)$	Two-photon absorption and inverse Raman effect (g = 3/2)	35, 37, 38
$\text{Im}\chi_{jklm}(-\omega;\omega,\omega,-\omega)$	Two-photon absorption (single frequency) (g = 3/4)	31—34, 36
$\text{Im}\chi_{jklmnl}(-\omega;\omega,\omega,\omega,-\omega,-\omega)$	Three consecutive photon absorption (g = 15/4)	49

$$
\left.\begin{aligned}
E(-\omega) &= E^*(\omega) && \text{(a)}\\
\omega_{-j} &= -\omega_j && \text{(b)}\\
K_{-j} &= -K_j^* && \text{(c)}\\
K &= n\omega/c && \text{(d), } c \text{ being the velocity of light in vacuum}
\end{aligned}\right\} \quad (12)
$$

The nonlinear optical susceptibilities, χ_{jkl}, χ_{jklm}, and higher-order ones give rise to a large variety of nonlinear optical phenomena. A number of these susceptibility tensors and the types of optical processes associated with them are listed in Table 1.1.2. Also included in the table are the relevant references and the degeneracy factors. Review articles and introductory texts on nonlinear optical effects can be found in References 3 to 11.

More than a decade has elapsed since the last publication of the author's chapter on nonlinear optical materials in Reference 54. Since then, the number of nonlinear materials measured has more than doubled. In the present revised chapter this compilation is brought up to date through 1982. In addition, at the suggestion of the editor, Dr. M. Weber, data on third-order optical susceptibilities are also included.

SECOND-ORDER POLARIZATION AND ITS SYMMETRY PROPERTIES

For the general case of monochromatic waves of angular frequencies ω_1, ω_2 . . . ω_r

incident upon a medium, the jth Cartesian component of the induced polarization density, $\mathbf{P}_j^{(r)}$, at the frequency $\omega_\sigma = \omega_1 + \omega_2 + \ldots + \omega_r$ due to the rth order nonlinear susceptibility, $\chi^{(r)}$ can be written as:

$$\mathbf{P}_j^{(r)}(\omega_\sigma) = \epsilon_o\left[\sum_{\alpha_1 \ldots \alpha_r} g(-\omega_\sigma)\chi_{j\alpha_1 \ldots \alpha_r}\{-\omega_\sigma;\omega_1,\omega_2 \cdots \omega_r E_{\alpha 1}(\omega_1)E_{\alpha 2}(\omega_2)\cdots E_{\sigma_r}(\omega_r)\}\right] \quad (13)$$

where g is a degeneracy factor arising from the number of distinguishable permutations of the frequencies. The summation is carried over all of the distinct sets of $\omega_1, \omega_2 \ldots \omega_r$.

For the specific case of SHG, $\omega_1 = \omega_2 = \omega$ and $g = 1/2$, the second-order polarization at the harmonic frequency 2ω is given by:

$$\mathbf{P}_j^{(2)}(2\omega) = \epsilon_o \sum_{k,l}(1/2)\chi_{jkl}(-2\omega;\omega,\omega)E_k(\omega)E_l(\omega) \quad (14)$$

There is a considerable amount of confusion in the literature about the relation between induced nonlinear polarization and nonlinear susceptibility. The following convention is adopted here to avoid this confusion. The second-order nonlinear coefficient is denoted by $d_{jkl}^{(2)}$ and is related to the second-order nonlinear susceptibility tensor $\chi_{jkl}^{(2)}$ by:

$$\chi_{jkl}^{(2)} = 2\, d_{jkl}^{(2)} \quad (15)$$

In order to express the induced nonlinear polarization due to various second-order nonlinear processes, $\chi_{jkl}^{(2)}$ in Equation 13 is replaced by 2 $d_{jkl}^{(2)}$. Thus, in the case of SHG, the induced polarization at the harmonic frequency 2ω given by Equation 14 is expressed as:

$$\mathbf{P}_j^{(2)}(2\omega) = \epsilon_o \sum_{k,l} d_{jkl}^{(2)}(-2\omega;\omega,\omega)E_k(\omega)E_l(\omega) \quad (16)$$

Similarly, the induced polarizations associated with other second-order processes are expressed in terms of d by using the proper g values from Table 1.1.2.

The SHG coefficient d_{jkl} is a $3 \times 3 \times 3$ third-rank tensor. Since the order in which the electric field components are written in the right hand side of Equation 16 is of no significance, the ds satisfy the permutation symmetry:

$$d_{jkl}(-2\omega,\omega,\omega) = d_{jlk}(-2\omega;\omega,\omega) \quad (17)$$

This property is similar to that of the piezoelectric tensor (by virtue of which an electric polarization is produced in a medium when it is subjected to a stress). By analogy with the piezoelectric tensor, for convenience it is possible to write the nonlinear optical tensor, $d_{jkl}^{(2)}$, in a contracted form which reduces the maximum number of independent SHG tensor elements to 18. In the contracted form, the symmetric suffixes k and l are replaced by a single suffix, m, that takes the values 1 to 6. The relation between the contracted and uncontracted elements can be expressed by:

$$d_{jm} = d_{jkl}\,;\ m = \begin{cases} k & \text{if } k = l \\ g - (k + l) & \text{if } k \neq l \end{cases} \quad (18)$$

Thus, the relation between m and kl is