1.7. Nonlinear optical properties

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1.7.1. Introduction

The first nonlinear optical phenomenon was observed by Franken *et al.* (1961): ultraviolet radiation at 0.3471 μm was detected at the exit of a quartz crystal illuminated with a ruby laser beam at 0.6942 μm. This was the first demonstration of second harmonic generation at optical wavelengths. A coherent light of a few W cm^{-2} is necessary for the observation of nonlinear optical interactions, which thus requires the use of laser beams.

The basis of nonlinear optics, including quantum-mechanical perturbation theory and Maxwell equations, is given in the paper published by Armstrong *et al.* (1962).

It would take too long here to give a complete historical account of nonlinear optics, because it involves an impressive range of different aspects, from theory to applications, from physics to chemistry, from microscopic to macroscopic aspects, from quantum mechanics of materials to classical and quantum electrodynamics, from gases to solids, from mineral to organic compounds, from bulk to surface, from waveguides to fibres and so on.

Among the main nonlinear optical effects are harmonic generation, parametric wave mixing, stimulated Raman scattering, self-focusing, multiphoton absorption, optical bistability, phase conjugation and optical solitons.

This chapter deals mainly with harmonic generation and parametric interactions in anisotropic crystals, which stand out as one of the most important fields in nonlinear optics and certainly one of its oldest and most rigorously treated topics. Indeed, there is a great deal of interest in the development of solid-state laser sources, be they tunable or not, in the ultraviolet, visible and infrared ranges. Spectroscopy, telecommunications, telemetry and optical storage are some of the numerous applications.

The electric field of light interacts with the electric field of matter by inducing a dipole due to the displacement of the electron density away from its equilibrium position. The induced dipole moment is termed polarization and is a vector: it is related to the applied electric field *via* the dielectric susceptibility tensor. For fields with small to moderate amplitude, the polarization remains linearly proportional to the field magnitude and defines the linear optical properties. For increasing field amplitudes, the polarization is a nonlinear function of the applied electric field and gives rise to nonlinear optical effects. The polarization is properly modelled by a Taylor power series of the applied electric field if its strength does not exceed the atomic electric field (10^8–10^9 V cm^{-1}) and if the frequency of the electric field is far away from the resonance frequencies of matter. Our purpose lies within this framework because it encompasses the most frequently encountered cases, in which laser intensities remain in the kW to MW per cm^2 range, that is to say with electric fields from 10^3 to 10^4 V cm^{-1}. The electric field products appearing in the Taylor series express the interactions of different optical waves. Indeed, a wave at the circular frequency ω can be radiated by the second-order polarization induced by two waves at ω_a and ω_b such as $\omega = \omega_a \pm \omega_b$: these interactions correspond to sum-frequency generation ($\omega = \omega_a + \omega_b$), with the particular cases of second harmonic generation ($2\omega_a = \omega_a + \omega_a$) and indirect third harmonic generation ($3\omega_a = \omega_a + 2\omega_a$); the other three-wave process is difference-frequency generation, including optical parametric amplification and optical parametric oscillation. In the same way, the third-order polarization. governs four-wave mixing: direct third harmonic generation ($3\omega_a = \omega_a + \omega_a + \omega_a$) and more generally sum- and difference-frequency generations ($\omega = \omega_a \pm \omega_b \pm \omega_c$).

Here, we do not consider optical interactions at the microscopic level, and we ignore the way in which the atomic or molecular dielectric susceptibility determines the macroscopic optical properties. Microscopic solid-state considerations and the relations between microscopic and macroscopic optical properties, particularly successful in the realm of organic crystals, play a considerable role in materials engineering and optimization. This important topic, known as molecular and crystalline engineering, lies beyond the scope of this chapter. Therefore, all the phenomena studied here are connected to the macroscopic first-, second- and third-order dielectric susceptibility tensors $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$, respectively; we give these tensors for all the crystal point groups.

We shall mainly emphasize propagation aspects, on the basis of Maxwell equations which are expressed for each Fourier component of the optical field in the nonlinear crystal. The reader will then follow how the linear optical properties come to play a pivotal role in the nonlinear optical interactions. Indeed, an efficient quadratic or cubic interaction requires not only a high magnitude of $\chi^{(2)}$ or $\chi^{(3)}$, respectively, but also specific conditions governed by $\chi^{(1)}$: existence of phase matching between the induced nonlinear polarization and the radiated wave; suitable symmetry of the field tensor, which is defined by the tensor product of the electric field vectors of the interacting waves; and small or nil double refraction angles. Quadratic and cubic processes cannot be considered as fully independent in the context of cascading. Significant phase shifts driven by a sequence of sum- and difference-frequency generation processes attached to a $\chi^{(2)} \cdot \chi^{(2)}$ contracted tensor expression have been reported (Bosshard, 2000). These results point out the relevance of polar structures to cubic phenomena in both inorganic and organic structures, thus somewhat blurring the borders between quadratic and cubic NLO.

We analyse in detail second harmonic generation, which is the prototypical interaction of frequency conversion. We also present indirect and direct third harmonic generations, sum-frequency generation and difference-frequency generation, with the specific cases of optical parametric amplification and optical parametric oscillation.

An overview of the methods of measurement of the nonlinear optical properties is provided, and the chapter concludes with a comparison of the main mineral and organic crystals showing nonlinear optical properties.

1.7.2. Origin and symmetry of optical nonlinearities

1.7.2.1. *Induced polarization and susceptibility*

The macroscopic electronic polarization of a unit volume of the material system is classically expanded in a Taylor power series of the applied electric field **E**, according to Bloembergen (1965):

$$\mathbf{P} = \mathbf{P}_0 + \varepsilon_o(\chi^{(1)} \cdot \mathbf{E} + \chi^{(2)} \cdot \mathbf{E}^2 + \ldots + \chi^{(n)} \cdot \mathbf{E}^n + \ldots), \tag{1.7.2.1}$$

where $\chi^{(n)}$ is a tensor of rank $n+1$, $\mathbf{E}^n$ is a shorthand abbreviation for the nth order tensor product $\mathbf{E} \otimes \mathbf{E} \otimes \ldots \otimes \mathbf{E} = \otimes^n \mathbf{E}$ and the dot stands for the contraction of the last n indices of the