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Optical Second-Harmonic Generation in Benzophenone

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Introduction Versatile and efficient sources of blue light are of fundamental importance for various applications including optical data storage [1,2], ophthalmologic or other medical techniques [3], and laser displays [4 to 6]. In spite of the rapid development of blue laser diodes [7,8] and concurrent physical principles like optical upconversion [9], the optical second-harmonic generation [10] (SHG) still is one of the most important methods to achieve intense coherent blue light with a good optical beam quality [11].

From symmetry aspects, SHG is only possible in crystals belonging to one of the 20 point groups which lack a center of symmetry [12]. Furthermore, to meet phase matching aspects in homogeneous crystals, refractive indices for the fundamental and the generated harmonic wavelength must be of identical size [13,14], optical birefringence is necessary.

Here we discuss the properties of benzophenone ($C_{13}H_{10}O$), an organic crystal, which excellently meets the described conditions.

Crystal Properties Crystals of benzophenone can be grown from the melt (melting point approximately 48°C) [15]. The crystal structure is orthorhombic with point symmetry 222. This forces the material to be optically biaxial with the axes of the indicatrix fixed to the three mutually perpendicular symmetry axes of the crystal. Theoretical studies revealed – due to the conjugated bonds – a good second order nonlinear optical polarizability [16].

Optical Absorption For optical applications in general – and especially for SHG – the material considered must be transparent in the wavelength region of interest. Measurements of the optical absorption in benzophenone show a region of excellent transparency spanning from 390 to 1700 nm. Depending on light polarization – parallel or perpendicular to the crystallographic c-axis – two typical spectra are found. The experimental results are sketched in Fig. 1.

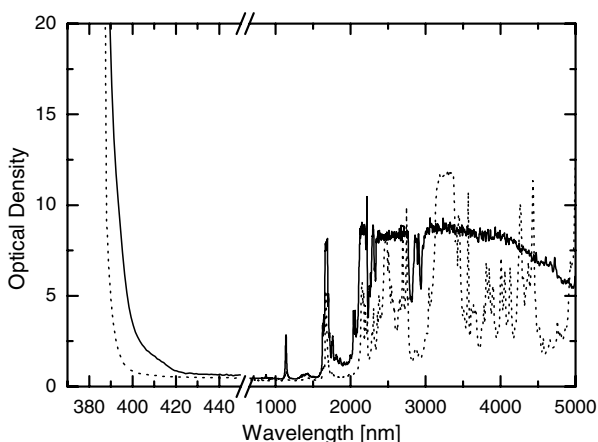


Fig. 1. Optical absorption in benzophenone. Full line: light polarization perpendicular to the crystallographic c-axis (nearly identical for polarization parallel to a- or b-axis, respectively), dotted line: polarization parallel to the c-axis. The expanded wavelength scale around 400 nm shows the difference in the onset of the fundamental absorption for the two polarizations

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Table 1

Parameters for the Sellmeier description of the refractive indices of benzophenone. Usual ordering of the indices is used (subscript 1 denotes the highest, 3 the lowest index value)

index	A_i (10^{13} m^{-2})	λ_i (10^{-7} m)
n_1	6.411	1.758
n_2	6.081	1.696
n_3	7.586	1.296

Refractive Indices The principal refractive indices were measured between 400 and 1100 nm using the prism method and various light sources. Applying the standard ordering for the refractive indices of biaxial crystals, the highest index n_1 corresponds to light polarization parallel to the crystallographic a-axis, n_2 to the b-axis, the lowest index n_3 to the c-axis.

The experimental values can be accurately described by a two parameter Sellmeier fit

$$n_i^2 - 1 = A_i / (\lambda_i^{-2} - \lambda^{-2}). \quad (1)$$

with the parameters listed in Table 1. Using this Sellmeier description, the complete wavelength dependence of the three refractive indices can be calculated; this dependence – together with the experimental data – is sketched in Fig. 2.

Nonlinear Optical Properties Due to the point symmetry 222 the tensor of the SHG nonlinear optical susceptibility for benzophenone can be written as

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{pmatrix} \quad (2)$$

with only three nonzero elements. Using a modified Maker fringe technique [17], we determined the size of these elements to be $d_{14} = (4 \pm 2) \text{ pm/V}$, $d_{25} = (1.4 \pm 1) \text{ pm/V}$, $d_{36} = (0.3 \pm 0.1) \text{ pm/V}$. The measured values do not obey the so-called Kleinman symmetry condition [18]. This might be due to the expressed polarization dependence of the optical absorption (Fig. 1). With the already discussed ordering of the dielectric axes, phase matching is possible for d_{25} and d_{36} , respectively. The birefringence is large enough to facilitate second harmonic generation of light throughout the complete visible range. Efficiencies are comparable to e.g. KDP ($d_{36}^{\text{KDP}} \approx 0.46 \text{ pm/V}$ [19]).

Conclusion The linear and nonlinear optical properties of benzophenone show that this material is a promising candidate for nonlinear optical applications. It can be utilized for second harmonic generation at fundamental wavelengths between 800 and 1700 nm with tensor elements that are in the order of magnitude of those for KDP.

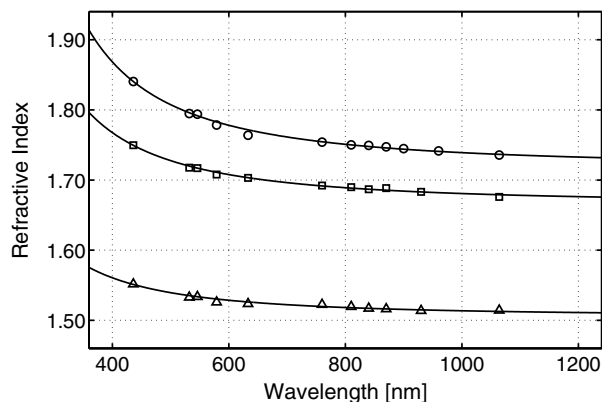


Fig. 2. Refractive indices of benzophenone, Sellmeier fit (full lines) to the experimental values (markers). Upper curve: n_1 , light polarization parallel to the crystallographic a-axis; middle: n_2 , b-axis; lower: n_3 , c-axis

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