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Phase-matched third harmonic generation in ABN crystals at $\lambda = 1.064\mu\text{m}$

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Abstract

A type II phase-matched third harmonic generation in an organic single crystal of 4-aminobenzonitrile has been studied. A Q-switched, mode-locked Nd-Yag laser at $1.064\mu\text{m}$ has been used in the experiments. Direct comparison with a phase-matched type II THG from a BBO crystal shows that the UV signal in ABN is 50 times larger than in BBO.

Introduction

Organic molecules with internal charge transfer such as para-disubstituted benzene with donor/acceptor groups exhibit high hyperpolarizabilities and lead in crystal to exceptional nonlinear properties [1,2]. Despite the great interest there is in studying such materials for nonlinear optics, only few data on third order susceptibility $\chi^{(3)}$ are available. Then testing models [3,4] for such susceptibility appears uneasy.

Here, we present phase-matched third harmonic generation (THG) in a single crystal of 4-aminobenzonitrile (ABN). For ABN, NH_2 is the donor group and CN the acceptor group.

Material

4-aminobenzonitrile is distilled under vacuum and extensively zone refined (>200 passes). Single crystals are grown under vacuum by the Bridgman technique.

ABN is a monoclinic biaxial crystal [5] which has a large transparency spectral range extending down to 320nm. In addition, ABN is centrosymmetric so that no second harmonic generation can occur.

Type II_{xy} phase matching in an ABN monocrystal

Assuming the crystallographic c axis to be parallel to the dielectric z axis, the type II_{xy} phase-matched THG will be defined by a 3ω field in the (xy) plane generated with one field in the same plane (extraordinary vibration "e") and two fields along the z axis (ordinary vibration "o"). We symbolize this process by (ooe-->e).

For type II_{xy} phase-matching, the wavevector equation is therefore given by :

$$\vec{k}_{3\omega} = 2\vec{k}_z^{\omega} + \vec{k}_{xy}^{\omega} \quad (1)$$

with $\vec{k}_{3\omega}$, $\vec{k}_z^{\omega}$, $\vec{k}_{xy}^{\omega}$ wavevectors for third harmonic field, "o" fundamental and "e" fundamental fields.

To solve equation (1), we have to know indexes of refraction at the fundamental and the third harmonic wavelengths.

Using minimum deviation [6], reflectivity [6] and Brewster experiments, we were able to measure indexes with a precision of ± 0.005 .

As we used (b,c) cleaved plane to improve the surface quality, the input fundamental beam is not perpendicular to the crystal surface. So, wavevectors are not collinear and this fact was taken into account in our calculations. We found 19.7° , 18.9° and 21.7° for angles between the x axis and $\vec{k}_{3\omega}$, $\vec{k}_z^\omega$, $\vec{k}_{xy}^\omega$. The corresponding external incidence angle θ for the fundamental beam is 36.7° .

THG experimental setup

We used a Q-switched, mode-locked Nd-Yag laser at $\lambda=1.064\mu\text{m}$ giving 600Hz bursts of picosecond pulses. As we are looking for type II_{xy} phase-matching, the optimal ratio of fundamental "o" and "e" intensities is two: the polarization of the incident beam is then adjusted with a half wave plate.

A 4.5mm thick ABN crystal is oriented with a goniometric head and the phase matching angle is measured by rotating the crystal around the z axis. The THG signal at 355nm is filtered, detected with a photomultiplier (Hamamatsu R1546) and measured with a lock-in amplifier synchronized on the 600Hz laser repetition rate.

Results

Figure 1 shows the dependence of the THG signal on fundamental incidence angle. The maximum intensity is obtained for an external angle $\theta=41.7^\circ$ to be compared to the theoretical value $\theta=36.7^\circ$.

This difference is partly due to our hypothesis of the z dielectric axis parallel to the c axis : indeed, a 1° difference is measured for the optimal external angle, depending whether the sample is rotated clockwise or counterclockwise. In addition, a laser induced thermal drift of the indexes may occur.

Figure 1 : Angle tuning THG curve for type II_{xy} process in an ABN crystal. The phase-matching angle is $\theta=41.7^\circ$.

The FWHM of the THG signal dependence on external incidence angle is the external acceptance angle $\Delta\theta$. Figure 1 reads $\Delta\theta=24'$.

The log / log dependence of the observed signal versus the intensity of the fundamental beam shows the expected value of 3.

The experimental dependence of the THG signal on the polarization angle β (angle between the (xy) plane and the polarization of the incident beam onto the sample) is shown on figure 2 (crosses). Assuming nearly equal Fresnel coefficients for "o" and "e" fields, we should find a $\sin^2(\beta) \cdot \cos^4(\beta)$ dependence. Figure 2 shows that the agreement is very good.

Figure 2 : variation of the type II_{xy} THG intensity for an ABN crystal as a function of the polarization angle. The dashed line represents the theoretical curve.

Calibration

In order to evaluate the efficiency of the THG, a direct comparison is made with the THG signal given by a β -Barium Borate (BBO) crystal [7,8].

As no properly cut BBO was available, we used a type I phase-matched second harmonic generator. This crystal was rotated to generate UV by type II phase-matched THG. The maximum UV intensity was obtained for an external incidence angle $\theta=42.4^\circ$ (very close to the theoretical value $\theta=41.35^\circ$). The external acceptance angle $\Delta\theta$ is approximatively $10'$. In the same experimental conditions, the UV intensity is 50 times smaller for the BBO crystal than for the ABN crystal, both crystals being set at their optimal incidence angle.

Discussion

The walk-off angle ρ between "o" fundamental wave Poynting vector and "e" fundamental wave Poynting vector reduces the overlap between both waves, and therefore causes a drop in the UV signal. A calculation using the theoretical values for the incidence angle θ gives $\rho=4.2^\circ$ for ABN and $\rho=4^\circ$ for BBO.

These values, combined with a $220\mu\text{m}$ measurement for the radius (waist) outside the crystal of the incident beam, allow us to perform a very crude estimation for the overlapping zone between the ordinary and the extraordinary beams.

This zone can then be characterized by an effective length taken along one of the Poynting vector : 2.1mm for the ABN crystal, 2.4mm for the BBO crystal. Using the angle between this Poynting vector and the normal to the crystal surface, we can finally define some sort of effective crystal thickness : 1.9mm for the ABN crystal and 2.1 mm for the BBO crystal. It is worth noting that these values are very similar despite very different crystal thicknesses : 4.5mm for the ABN crystal, 2.5mm for the BBO crystal.

Now, for a crystal whose thickness is the effective thickness, we can solve Maxwell Equations in the approximation where the fundamental field is not affected by the nonlinear process. From this we can deduce the change in the UV signal when the equation (1) is no longer fulfilled. Finally, using Descartes laws, we can relate the change in external incident angle with the departure to equation (1) and obtain the theoretical external acceptance angle.

We found $\Delta\theta=7'$ for ABN and $\Delta\theta=10'$ for BBO to be compared to the respective experimental values $\Delta\theta=24'$ and $\Delta\theta=10'$.

For ABN, this experimental value is much too large. It seems that this discrepancy cannot be related to some intrinsic limitation, as for instance the laser divergence. Indeed, the BBO value shows that we are able to measure acceptance angles as small as $10'$. However, we should be very careful in our conclusions, the geometry of the different beams being fairly complex (non collinear wavevectors ...), unexpected effects can occur. A more comprehensive analysis is under progress to clarify this point.

In fact, we are more inclined to explain our results assuming an insufficient quality for our ABN crystal (scattering surfaces ...).

At this point, it is not worth making a precise calibration of our signal in order to determine the effective susceptibility. Prior to this, we need to use better quality crystals in order to obtain a more reliable value. We have grown new crystals and they will be checked fairly soon.

Conclusion

Third harmonic generation has been obtained in an organic crystal of 4-aminobenzonitrile at a $1.064\mu\text{m}$ fundamental wavelength.

Despite the low quality of the crystal used, assessed by an abnormally large acceptance angle, we were able to obtain a 50 times larger UV signal than in a BBO crystal. The effective lengths being equivalent for the two crystals, it seems reasonable to assume that the effective susceptibility for ABN is at least seven times larger than for BBO.

We should now rationalize this result more precisely.

Afterwards, we will investigate other THG configurations in order to gain more information on the nonlinear susceptibility tensor of the ABN crystal. This in order to monitor the influence of the crystalline condensed state on the nonlinear properties of organic molecules.

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