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# OPTICAL SECOND HARMONIC GENERATION IN ORGANIC CRYSTALS: UREA AND AMMONIUM-MALATE

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Optical second harmonic generation (SHG) has been investigated in single-crystals of urea and ammonium-malate (AM). Phase match angle, refractive indices, and all nonvanishing coefficients of the non-linear susceptibility tensor have been measured. A comparison to KDP shows, that AM is comparable to KDP, urea much more efficient in SHG than KDP.

The measurements were performed with a flash-lamp pumped dye laser which could be tuned from 480 nm to 640 nm using different dyes (mainly coumarins and rhodamines). The crystals were grown from solution and had a typical size of 5 x 10 x 10 $mm^3$ in the case of urea and 15 x 15 x 10 $mm^3$ in the case of AM, respectively, after cutting and polishing. They could be rotated in the laser beam around a horizontal and a vertical axis, so that all desired crystal directions for the incident polarization could be achieved. For the detection of the second harmonic signal served a solar-blind photomultiplier with CsTe photocathode, the signal of which could either be displayed on an oscilloscope or be averaged by a gated integrator.

## 1. Urea ($CO(NH_2)_2$)

From powder measurements the high nonlinear optical susceptibility of urea is well known (1). Our measurements show that efficient phase-matched frequency doubling is possible over a wide spectral range. In urea (crystallographic class $D_{2d}$ ($\bar{4}2$ m)(2) ) only the three components $\chi^1_{23} = \chi^2_{31} = \chi^3_{12}$ of the nonlinear optical susceptibility tensor are non-zero; phase matched frequency doubling of type II is possible for the two equivalent components $\chi^1_{23}$ and $\chi^2_{31}$ (as the crystal is optically positive uniaxial).

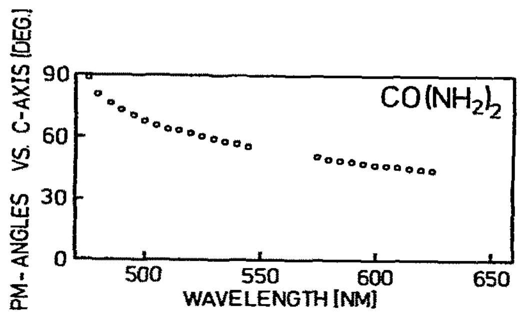


Figure 1

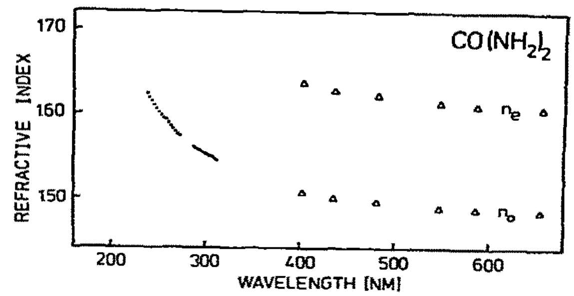


Figure 2

The measured phase match (PM) angles for these components are plotted in fig. 1; the short wavelength limit was found to be at 476 nm (fundamental beam), no long wavelength limit up to the IR absorption bands of the crystal (starting at 1.43 $\mu$m) can be extrapolated. The best efficiency for frequency doubling is achieves for a PM angle of 45$^o$, i.e. at wavelengths near 600 nm.

The refractive indices of urea in the region from 400 to 650 nm were measured by a conventional prism method (triangles in fig. 2). From these results and from the PM angles the index of the ordinary beam in the near UV region can be derived (dots in fig. 2). The wavelength dependence can be approximated by a Sellmeier equation of the form $n^2 = A+B(\lambda^2-C)^{-1}$ with A = 2.17, B = 0,014, and C = 0,028 ($\lambda$ in $\mu$m). A comparison to KDP shows that $\chi^1_{23}$ (urea) $\approx$ 3 x $\chi^3_{12}$ (KDP).

## 2. Ammonium-Malate ($NH_4$-OOC-CHOH-$CH_2$-COOH$\cdot H_2O$)

This salt of the racemic malic acid crystallizes in the monocline domatic structure (point group $C_s$ (m) ) exhibiting only one plane of reflection, perpendicular to the optical b-axis. Thus most of the quadratic terms of the dielectric polarizability tensor do not vanish.

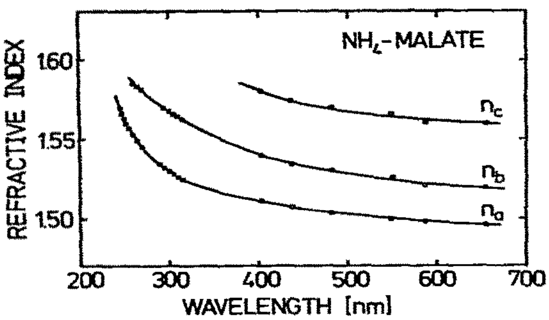


Figure 3

| Propagation direction | E (ω) | E (2ω) | observed tensor components | $\chi^i_{jk}/\chi^3_{33}$ at 600 nm |
|---|---|---|---|---|
| b | a | a | $\chi^1_{11}$ | 0.65 |
| | a | c | $\chi^3_{11}$ | 0.32 |
| | c | a | $\chi^1_{33}$ | 0.16 |
| | c | c | $\chi^3_{33}$ | 1.00 |
| c | b | a | $\chi^1_{22}$ | 0.24 |
| a | b | c | $\chi^3_{22}$ | 0.21 |

Components of the nonlinear susceptibility tensor in $(NH_4)$ malate

Table 1

In the present study, we can show for the first time that phase-matched SHG in AM is possible from 492 nm (fundamental beam) to longer wavelengths. From the PM-angle measurements in several configurations (3) we could derive two of the three refractive indices in the near UV spectral region (the refr. indices in the visible region again were directly measured). The results are plotted in fig. 3 (circles: measured by prism-method, squares: computed from the PM-angle measurements).

Measurements of the SHG intensity in highly symmetric however not phase matching directions served for determining the nonvanishing components of the nonlinear susceptibility tensor. The measured values are listed in table 1, where also the measurements' configurations are given. A comparison to KDP yields $\chi^1_{23}$ (AM)$\approx$ $\chi^3_{12}$ (KDP) (for $\chi^1_{33}$ (AM) phase-matching is possible).

In conclusion we can say that both investigated materials urea and ammonium-malate exhibit rather good doubling efficiencies so that these substances may be a useful supplement to the small number of materials, which can be used for phase-matched second harmonic generation in the near ultraviolet region

References:

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