# PHASE-MATCHED SECOND HARMONIC GENERATION IN POTASSIUM MALATE

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The linear and nonlinear optical properties of the organic crystal potassium malate (KM) are investigated. High birefringence and a broad transmission range combined with a rather large nonlinear optical susceptibility were found in this material. Phase-matched second harmonic generation is possible down to about 488 nm of fundamental wavelength.

## 1. Introduction

It has been shown recently that several organic crystals can be used for efficiently generating UV radiation by second harmonic generation (SHG) or sum frequency mixing (SFM) [1–4] thus replacing "classic" SHG crystals. Because of their low symmetry, crystals of complex organic molecules usually show a variety of nonvanishing coefficients of the nonlinear optical susceptibility tensor, so that phase matching in SHG or SFM easily can be achieved. Here we report about some linear and nonlinear optical properties of potassium malate (KM), which, because of its large birefringence, is a good candidate for efficient second harmonic generation in a wide frequency range.

Crystals of potassium malate (COOK · CHOH · $CH_2$ · COOH × 1.5 $H_2O$) can be grown from a racemic aqueous solution. The crystal contains two molecules per unit cell and belongs to the monoclinic point group *m* (earlier investigations favoured group 2 symmetry [5,6], but point group *m* must be concluded from the symmetry of the nonlinear susceptibility tensor as will be shown later).

In monoclinic crystals only one principal axis of the dielectric susceptibility tensor (usually chosen as *B*-axis) is fixed to the crystal axes. In point group *m* crystals the two others lie in the mirror plane and usually show up frequency dispersion.

In the case of KM no such dispersion throughout the transparent wavelength region of the crystal was found. The orientation of the principal dielectric axes *A* and *C* in the mirror plane of the crystal with respect to the crystallographic axes is shown in fig. 1. The dielectric and crystallographic axis *B* is perpendicular to the mirror plane.

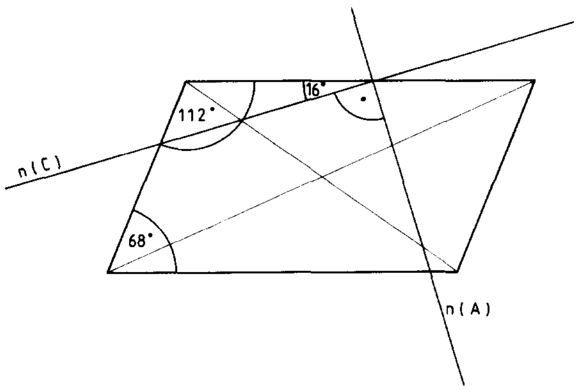


Fig. 1. Orientation of the principal axes of the dielectric tensor to the crystal axes. *B* is perpendicular to the shown mirror plane.

## 2. Linear optical properties

The indices of refraction in KM were measured in the visible and near UV range of the spectrum using the prism method. Two prisms were cut for this purpose, the orientations of which were chosen such that at minimum deviation angle the light polarization in-

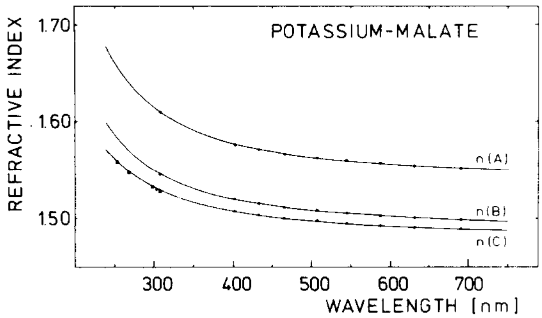


Fig. 2. Dispersion of the principal indices of refraction in potassium malate. o = measured values, □ = values gained from phase matching measurements, – = Sellmeier fit.

side the prisms was parallel to the $B$ and $C$ axes or $A$ and $B$ axes, respectively. By chosing the appropriate polarization all components of the dielectric tensor were measured for different wavelengths of some metal vapour lamps and a frequency-doubled dye laser.

The wavelength dependence of the principal indices of refraction is shown in fig. 2. The dots indicate the direct measured values, the open squares are values gained by phase-matched SHG measurements discussed later. The full lines represent a Sellmeir fit [7] to the experimental values. The constants for the Sellmeir's equations as derived from a least square fit to the experimental data are listed in table 1.

Absorption measurements carried out on a Beckman Acta IV spectrometer showed that KM is transparent in the region between about 240 and 1300 nm. This, together with the rather large birefringence and the only slight increase of the index of refraction towards the absorption limit, shows that KM is a rather good material for phase-matched SHG in the near UV region.

Table 1
Coefficients for a Sellmeir fit to the principal indices of refraction in potassium malate $n^2 = a + b\lambda^2/(\lambda^2 - c^2)$ as derived from a least square fit

| | $a$ | $b$ | $c$ |
|---|---|---|---|
| $n(A)$ | 1.542 | 0.8299 | 0.1419 |
| $n(B)$ | 1.470 | 0.7473 | 0.1343 |
| $n(C)$ | 1.339 | 0.8519 | 0.1195 |

## 3. Nonlinear optical properties

The nonvanishing coefficients of the tensor of the second order nonlinear susceptibility (furtheron referred to as SHG tensor) in KM were determined using the Maker-fringe method [8]. The light of a flashlamp-pumped dye laser which could be tuned throughout the visible range of the spectrum was used as fundamental wavelength, the generated second harmonic light was detected by a solar blind photomultiplier tube and recorded by means of standard boxcar technique. Fundamental and second harmonic polarization could be arbitrarily chosen using a polarization rotator and suitable prism polarizers.

The Maker-fringe method makes use of the interference between coherence length and crystal thickness, the latter of which can be varied by either translation of a wedge-shaped crystal or rotation of a plane-parallel crystal slab. From the resulting interference structure of the generated second-harmonic signal coherence length's and relative magnitudes of the coefficients of the SHG tensor can be determined. For our measurements we used the rotation method on three crystal slabs each oriented perpendicular to a different one of the three principal axes of the susceptibility tensor. As fundamental wavelength 630 nm was used.

In point group $m$ the polarization at the second harmonic wavelength can be described by the equations:

$$P_A^{2\omega} = d_{11}E_A^2 + d_{12}E_B^2 + d_{13}E_C^2 + 2d_{15}E_AE_C ,$$

$$P_B^{2\omega} = 2d_{24}E_BE_C + 2d_{26}E_AE_B ,$$

$$P_C^{2\omega} = d_{31}E_A^2 + d_{32}E_B^2 + d_{33}E_C^2 + 2d_{35}E_AE_C .$$

Applying the Maker-fringe method using different light polarization all of the coefficients of the SHG tensor can be measured. We found that all of the $d$'s in the above equations (and only these) are different from zero which shows that KM indeed crystallizes in point group $m$. The relative magnitudes of the $d$ values are listed in table 2, here the largest one, $d_{11}$, was put to be 1.

Table 2
Relative magnitudes of the coefficients of the SHG tensor

| $i,k$ | 11 | 12 | 13 | 15 | 24 | 26 | 31 | 32 | 33 | 35 |
|---|---|---|---|---|---|---|---|---|---|---|
| $d_{ik}$ | 1 | 0.09 | 0.1 | 0.38 | 0.21 | 0.08 | 0.1 | 0.38 | 0.6 | 0.04 |

## 4. Phase matching properties

Efficient second harmonic generation can be only achieved by phase matching of the fundamental and second harmonic waves. As can be derived from the indices of refraction and the nonvanishing coefficients of the SHG tensor type I and type II phase matching for second harmonic generation is possible in KM, type I in the wavelength region between 499 and more than 1000 nm of fundamental wavelength, type II only at wavelengths above 670 nm. In type I phase matching, where the polarization of the second harmonic wave is parallel to the $C$-axis and that of the fundamental lies in the $A$-$B$-plane the phase match angle measured with respect to the $B$-axis is given by:

$$\theta_m = \arcsin\left[\frac{n_c^{-2}(2\omega) - n_a^{-2}(\omega)}{n_b^{-2}(\omega) - n_a^{-2}(\omega)}\right]^{1/2} .$$

This dependence is shown in fig. 3, where also some experimentally found angles are indicated (dots). These measured values were used to calculate the corresponding values $n_c$ in the UV region (see fig. 2).

The short wavelength limit for phase matching (also the point where noncritical phase matching is possible) can be put to shorter wavelengths by cooling the crystal. This temperature dependence was measured by cooling a crystal cut perpendicular to the $B$-axis in a temperature controlled cryostat and tuning the dye laser through the point of noncritical phase matching for the respective temperatures. The results are shown in fig. 4, a wavelength of about 488 nm for noncritical phase matching can be achieved by cooling to liquid nitrogen temperature.

In order to get an estimate for the efficiency of KM as nonlinear crystal, a comparison of the SHG intensity from KM and KDP was performed under equal conditions. An evaluation of this measurement yields:

$$d_{31}(\mathrm{KM}) = 1.4 d_{36}(\mathrm{KDP}) \pm 20\% ,$$

a value which shows that KM can be twice as efficient as KDP in second harmonic generation near the short wavelength limit and even more at longer wavelengths ($d_{32} = 3.8 d_{31}$).

In conclusion we can say that the linear and nonlinear optical properties of potassium malate show that this organic crystal is a promising candidate for efficient UV generation by either SHG or SFM.

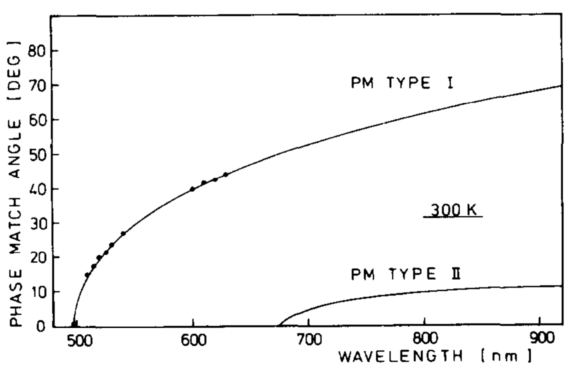


Fig. 3. Phase match angle for second harmonic generation in potassium malate. ○ = experimental values, – = calculated from the refraction index.

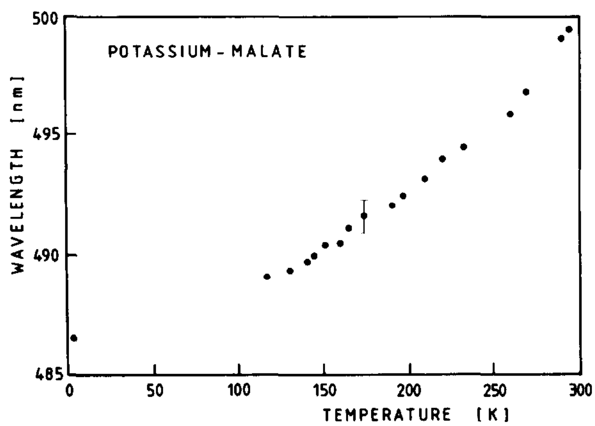


Fig. 4. Temperature dependence of the short wavelength limit for phase-matched SHG in potassium malate.

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