Study on the second-order nonlinear optical characteristics of urea L-malic acid

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The second-order nonlinear optical characteristics of a novel organic crystal, urea L-malic acid (ULMA), were studied. Both type I and type II phase-matching angles of the biaxial crystal ULMA were calculated, whose loci are in the Hobden class 9. The efficiencies of second harmonic generation (SHG) of ULMA and KDP at a fundamental wavelength of 1064 nm were compared by using the Kurtz powder method. The results showed that the nonlinear coefficient of ULMA is about 1.57 times of that of KDP. High SHG efficiencies were observed over a broad range of the spectrum when ULMA was pumped by outputs generated from an optical parameter oscillator. To our knowledge, it is the first report where continuous SHG at fundamental wavelengths from1300 to 950 nm with ULMA was achieved.

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Materials with high second-order susceptibilities are important because of their possible applications in optical switching, frequency conversion, and data storage, etc[1]. Organic materials are of interest due to their good processability, in addition to their high hyperpolarizabilities. Urea is one of the organic crystals that have been put to practical use[2,3]. It has high hyperpolarizability and broad transparency. However, it is hygroscopic, and growth of large high-quality crystals proves to be difficult. Many new organic crystals have been prepared with molecular engineering approaches and have been shown to have potential in nonlinear optical applications.

Urea L-malic acid (ULMA) is one of the derivatives of urea, which keeps the nonlinear optical property of urea with greatly reduced hygroscopicity. The chiral molecule L-malic acid was used for creating two-dimensional anionic networks held together by O–H$\cdots$O hydrogen bonds to form anisotropic acentric crystalline frameworks. Urea, the second harmonic generation (SHG) active unit, was encapsulated within the L-malic acid network to afford noncentrosymmetric inclusion complex. ULMA was designed to combine the properties of both L-malic acid and urea in order to achieve overall macroscopic optical nonlinearity enhancement[4,5]. As shown in Fig. 1, the ULMA are broadly transparent, possessing a transmission of >70% for light with incident wavelengths from 380 to 1440 nm[4,5]. So it is one of the most promising materials for nonlinear optical applications in ultraviolet (UV) region.

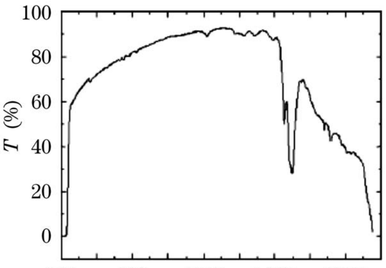

Fig. 1. Transmission curve of a 0.5-mm ULMA plate, measured using a Shimadzu spectrophotometer.

ULMA crystallizes in the monoclinic space $P2_1$. Based upon the measured data of the refractive indices[5], the phase-matching conditions for SHG at 1064-nm fundamental wavelength were computed. The results for type I and type II SHG are shown in Fig. 2. They are consistent with the class 9 phase matching according to Hobden's classification[6].

Kurtz powder method was used to evaluate the SHG efficiencies of ULMA and KDP. The schematic experimental setup is shown in Fig. 3. A Q-switched Nd:YAG laser was employed, which emitted 8-ns pulse with 10-Hz repetition rate. Samples were ground and graded by use of standard sieves to particles within 80–150 μm in diameter. They were subsequently loaded into a 1 mm quartz cell. The fundamental wave beam of Nd:YAG laser was weakly focused on the sample. Filter 2 was a narrow band passing filter (Fig. 3), whose central wavelength was 532 nm. After the fundamental beam was blocked, the second harmonic generated by ULMA was detected by a spectrometer. The combination of a half-wave plate and a polarizer was used to adjust the fundamental wave intensity and a beam splitter was used to monitor the intensity. Experiment results of SHG versus fundamental wave intensity were plotted in Fig. 4. The dots were the measured results and the lines were the second order polynomial fits. The fit results showed that the second order nonlinear coefficient of ULMA was about 1.57 times of that of KDP at 1064 nm. When the

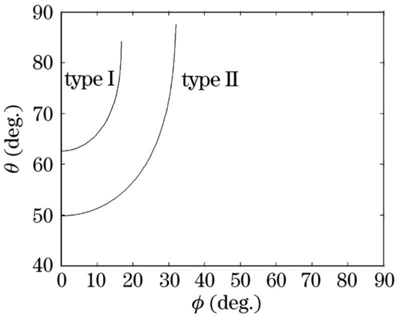

Fig. 2. Phase-matching angles of ULMA for type I and type II, plotted on the first quadrant.

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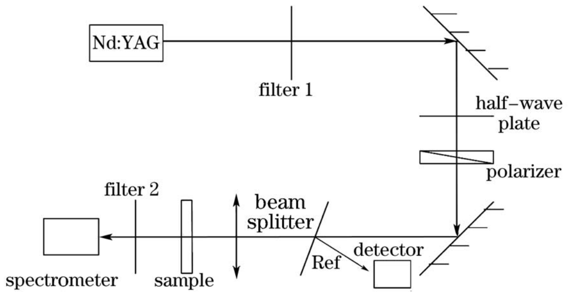

Fig. 3. Experiment setup used for study of SHG in powders.

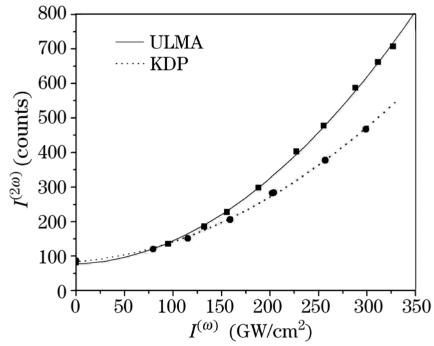

Fig. 4. Second harmonic intensity versus fundamental intensity at 1064 nm.

input intensity reached 300 GW/cm^2, the KDP powder sparkled, and later it was found adhered to the wall of the quartz cell at the focal point due to localized melting by high-energy laser incident light. On the contrary, the ULMA powder showed no detectable damage until the laser intensity reached over 500 GW/cm^2. Clearly, the ULMA has higher damage threshold than KDP.

A preliminary experiment was carried out to observe the SHG efficiencies of ULMA pumped by various fundamental waves. The experiment setup is shown in Fig. 5. An optical parameter oscillator (OPO) pumped by the third harmonic of Nd:YAG was used to generate laser pulse (6 ns at 10-Hz repetition rate) with variable wavelength. An idler of OPO was weakly focused on the ULMA powder loaded in a 10-mm quartz cell after the short wavelength was removed by a series of long wavelength passing filters. When the idler was scanned from 1300 to 900 nm, the red to blue second harmonic of ULMA was observed. A fiber spectrometer was placed at 90° from the incident laser to detect the second harmonic of the sample. The relative intensities of SH and corresponding fundamental wave energies are shown in Fig. 6. From the data we found that coefficients between the second harmonic intensity and the square of fundamental intensity are different at various wavelength. It is apparent that the nonlinear coefficients of ULMA are wavelength dependent.

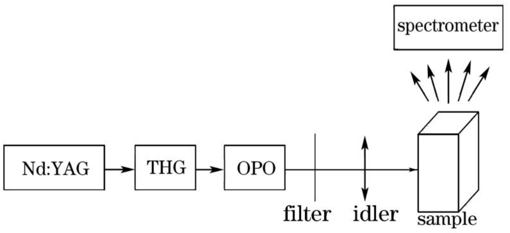

Fig. 5. Experiment setup used for observing SHG spectrum of ULMA.

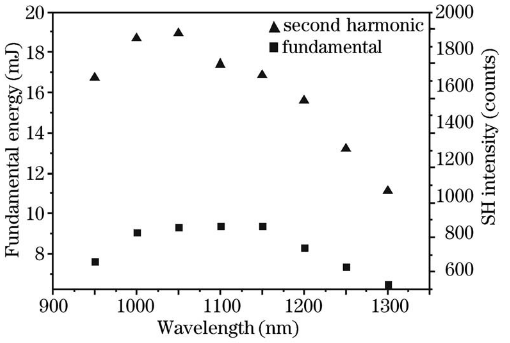

Fig. 6. SHG spectrum of ULMA.

In summary, ULMA is a type of broadly transparent crystal, possessing a transmission of >70% for incident wavelengths from 380 to 1440 nm. The crystal is biaxial, whose type I and type II phase-matching angles were calculated and were found to be in class 9 in Hobden's classification. The efficiencies of second harmonic generation (SHG) of ULMA and KDP at a fundamental wavelength of 1064 nm were compared by using the Kurtz powder method. Measurement results showed that the nonlinear coefficient of ULMA was about 1.57 times of that of KDP. The SHG experiments of ULMA at variable fundamental wavelengths were carried out. ULMA exhibited high SHG efficiency over a broad range of the spectrum and the nonlinear coefficients are wavelength dependent. To our knowledge, it is the first report where continuous SHG at fundamental wavelengths from 1300 to 950 nm with ULMA was achieved.

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