Supporting Information

Single-crystalline Fibers of Deuterated Potassium Dihydrogen Phosphate

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Material

High purity KDP microcrystals dedicated for production of research grade KDP crystals for high power laser applications, D_2O (Aladdin, 99.9 atom % D) and ultrapure water were used for growth of the DKDP single-crystalline fibers.

Crystal growth

The glass bottle and glass slide were washed with hydrochloric acid, and then ultrasonicated in ultrapure water for 30 min with an ultrasonic machine to remove possible insoluble particles and metal ions. 7.5 g of KDP, 13.8 g of D_2O, 1.2 g of ultrapure water were mixed together to prepare a DKDP solution containing 85% deuterium, which was superheated above 80 °C for 24 hours. Similarly, 7.5g KDP, 12.3g D_2O, and 2.7g ultrapure water were used to prepare a DKDP solution containing 75% deuterium. The deuterium content of the solution was calculated based on the formula $D\% = \frac{D\ (\mathrm{mol})}{D\ (\mathrm{mol}) + H\ (\mathrm{mol})}$. The glass slide was placed in a vacuum dryer, and then the superheated DKDP solution was dropped on the glass slide, and the vacuum dryer was evacuated to rapidly evaporate the solution to obtain the single-crystalline fibers. The final humidity of the vacuum dryer was less than 10% and the room-temperature is about 25 °C.

The crystals on the glass sheet have two different phases including monoclinic single-crystalline fibers, tetragonal single-crystalline fibers, and tetragonal bulk crystals respectively. The three crystals are identified easily under the microscope due to their different morphologies. A large number of DKDP monoclinic phase crystals were selected under the microscope for XRD polycrystalline diffraction experiments.

X-ray diffraction structural analysis

The X-ray diffraction (XRD) data and spectra of DKDP single crystal microstructures were collected on Bruke smart Apex II X-ray diffractometer using graphite-monochromated MoKa radiation (l = 0.71073 Å). The molecular structures and packing arrangements are obtained by direct computation methods and then refined by full-matrix least-squares technique on F^2 using SHELX algorithm. For the purpose of comparison, XRD spectra of the single-crystalline DKDP fibers and fine-ground DKDP crystal powder were recorded using a commercial polycrystalline X-ray diffractometer equipped with a diffracted beam monochromator set for Cu KR radiation (λ = 1.54056 Å) in the 2θ range from 10 ^{0} to 90 ^{0} with a step size of 0.0216048 ^{0} and scan speed of 10 ^{0}/min.

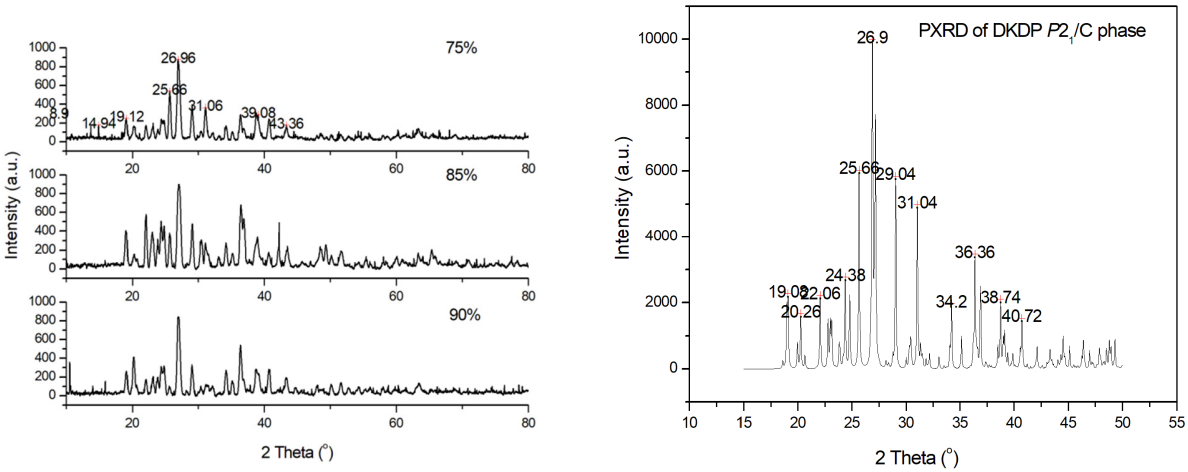

Figure 1. (left) PXRD spectra of the monoclinic DKDP single-crystalline fibers grown in different deuterium-content solution of 75%, 85% and 90%. (right) the theoretical calculated PXRD spectrum based on the structural data file of the monoclinic DKDP single-crystalline fiber.

Scanning electron microscope imaging

Scanning electron microscope (ZEISS Microscopy) images were collected for observation of the surface morphology of the crystals. The samples were platinum-sprayed before measurement.

Raman spectrum measurement

The deuterium content of the crystal was estimated by the Raman spectra. Raman spectrum measurement was conducted on a laser micro-Raman spectrometer (LabRAM HR 800) with an excitation wavelength of 531.92 nm at room temperature. The measured spectral range was from 800 to 1100 cm^{-1}.

The Raman spectra were used to estimate the deuterium content using the method described in the text. The mean and standard deviation of the deuterium content of DKDP tetragonal single-crystalline fibers were analyzed based on multiple measurements. The result is shown in Fig. S2.

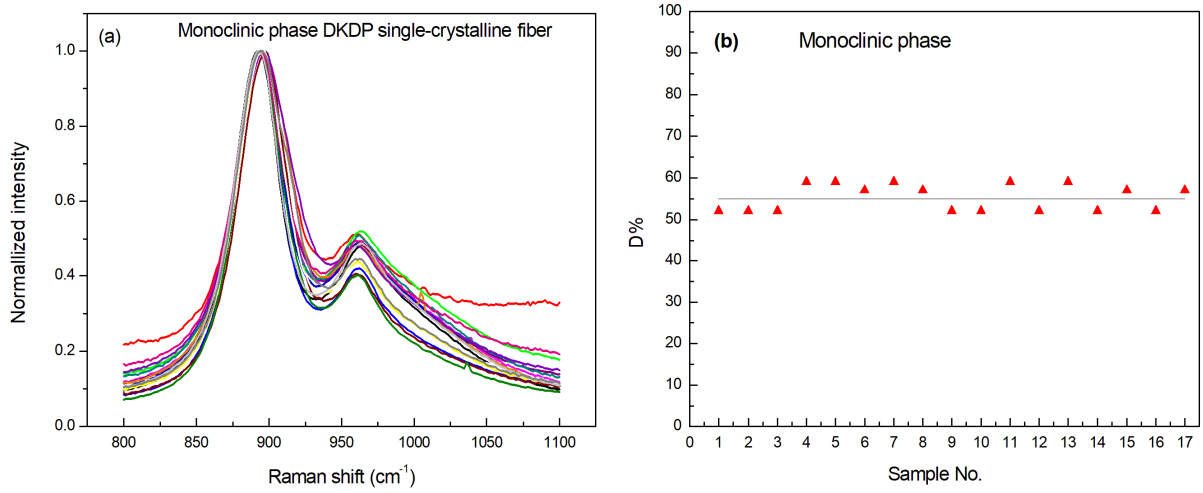

Figure 2. The deuterium content analysis of DKDP monoclinic single-crystalline fibers based on Raman spectra (a) from multiple fiber samples grown in solution containing 75% deuterium (b). The solid line is the average value of the deuterium-content. The average of the deuterium-content in the monoclinic fiber crystal is 55%.

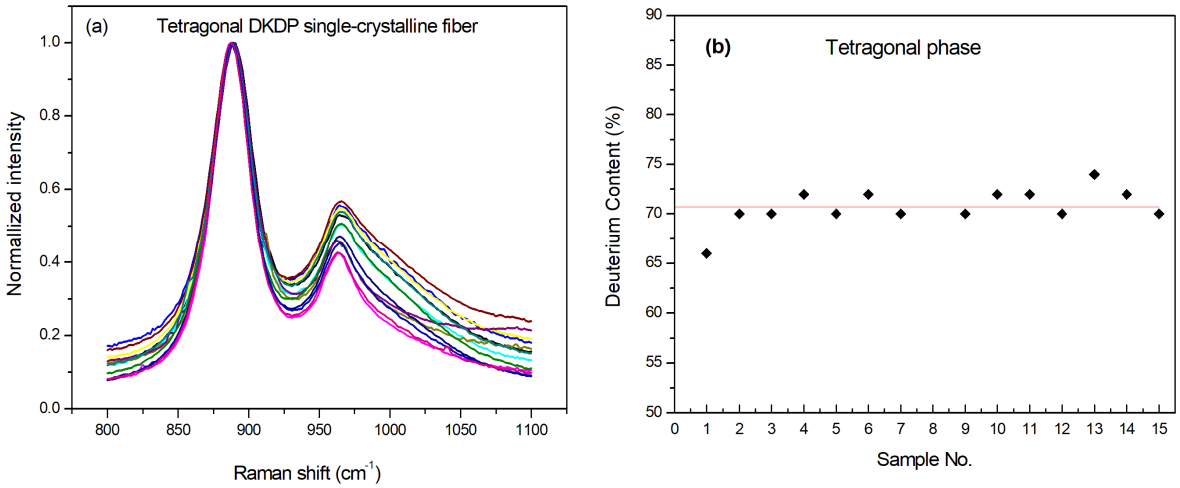

Figure 3. The deuterium content analysis of DKDP tetragonal single-crystalline fibers based on data from seven fiber sample grown in solution containing 85% deuterium. The solid line is the average value of the deuterium-content. The average of the deuterium-content in the tetragonal fiber crystal is about 70.7%.

Nonlinear optical measurement

To investigate the SHG of the tetragonal KDP microstructures, a CW 1064 nm Nd:YAG laser was used as the pump source (Maxphotonics Co., Ltd.). The output of the laser has a diameter of 2 mm. The pump light was first purified by a broadband polarizing beam splitter (PBS) cubes and then injected into a 100 X microscope objective which launches the pump field through the entrance facet of the micro-structure under investigation. Both the entrance and exit facets of the microstructures were not polished, and this resulted in about 12% coupling efficiency at each facet (a rough estimate based on the input and output power as a weak laser pumping without signal output). At the exit of the microstructure a laser-grade 1064 nm locking filter stops the residual pump laser and the second-harmonic generation (SHG) light was collected and focused onto a CCD camera by a microscope objective (10 X). The SHG spectrum was collected by a PMT grating spectrometer.

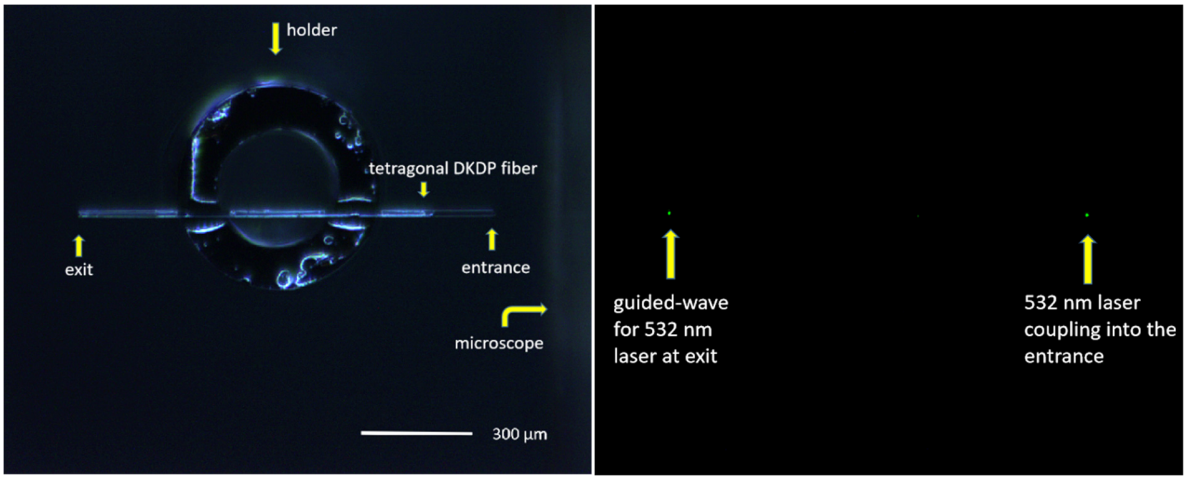

Figure 4. The optical guided-wave for 532 nm laser. The 532 nm laser was coupled to the entrance of a DKDP tetragonal

single-crystalline fiber by a 100 X microscope on the right of the picture. No light leakage occurs during the propagation of the laser along the c-axis of the fiber.