Water dissolution ultra-precision polishing of KDP crystal and its precision cleaning

Yuchuan Chen, Hang Gao*, Xu Wang and Xiaoji Teng

School of Mechanical Engineering, Key Laboratory for Precision and Non-traditional Machining Technology of Ministry of Education, Dalian University of Technology, Dalian, Liaoning, 116024, China
Email: pacocyc@163.com
Email: hanggao4187@126.com
Email: wx382935877@163.com
Email: tengxiaoji1983@163.com
*Corresponding author

Abstract: KDP crystal is a kind of excellent electro-optic material used in many laser facilities, which is also widely acknowledged to be extremely hard to machine. In this work, we developed a process to finish KDP crystal to a precision and clean engineering specimen. A micro-nano water dissolution principle and its planarisation mechanism in the machining process are illustrated, which turns the disadvantaged deliquescent property of KDP crystal into the driving force for ultra-precision polishing of the crystal. Micro emulsion fluid with nano water nuclei can precisely control the material removal and realise the selective polishing, thus forming a super smooth and precise surface. Then a subsequent cleaning process developed specially for this ultra-precision polishing method helps to get rid of the polishing fluid, and finally reduces the residue off the crystal to a clean and tidy surface with 1.964 nm rms roughness for engineering application.

Keywords: KDP crystal; water dissolution mechanism; ultra-precision polishing; precision cleaning; FTIR spectrum.


Biographical notes: Yuchuan Chen is currently a PhD candidate majoring in Mechanical Manufacturing at the Key Laboratory for Precision and Non-traditional Machining Technology of Ministry of Education of Dalian University of Technology. His research interests include the ultra-precision machining of optical crystal, subsequent cleaning process and the laser induced damage investigation of these crystals.

Hang Gao is a Professor of Mechanical Engineering at the Key Laboratory for Precision and Non-traditional Machining Technology of Ministry of Education of Dalian University of Technology, Dalian, China. He has extensive research experience in precision and ultra-precision machining process and especially in the work of ultra-precision polishing of KDP crystal and other hard-brittle
materials. He has published more than 100 papers and publications. He is now an active member of the International Committee of Abrasive Technology (ICAT) and also serving as the Chief Editor of International Journal of Abrasive Technology (Far East Area).

Xu Wang is a Doctoral student at the Key Laboratory for Precision and Non-traditional Machining Technology of Ministry of Education of Dalian University of Technology. He has expertise in the ultra-precision machining of KDP crystal with computer controlled optical surfacing (CCOS) technology.

Xiaoji Teng has done a lot of exploration work in the precision cutting technology of optical element especially the soft brittle KDP crystal. He is currently pursuing his Doctor’s degree at the Key Laboratory for Precision and Non-traditional Machining Technology of Ministry of Education of Dalian University of Technology.

1 Introduction

KDP single crystal, which in nature is a kind of soluble inorganic salt, has both disadvantages for machining such as deliquescent, extremely soft, brittle and thermally sensitive, and advantages as excellent nonlinear electro-optic switches and frequency conversion devices such as Pockels cells and second-harmonic generation in laser-based inertial confinement fusion (ICF) research (Brereton, 2013; Lin et al., 2013; Hurricane et al., 2014). However, these distinct properties also make it extremely difficult for KDP crystals to obtain a flawless surface.

In the preliminary phase of study, researchers concentrated on finishing of the KDP crystal using traditional methods, such as precision grinding and polishing. Optical polishing method of large diameter KDP crystals surface to sub-nanometres roughness was developed by Yoshida, etc. (Kozlowski et al., 1991). The surface finishing of KDP crystals was conducted using specially prepared lapping plate and slurry of diamond powder in oil. In 1999, Namba and Katagiri showed a new possibility to get optical surfaces on KDP crystals by ultra-precision grinding. The surface roughness of 0.553 nm rms was obtained by the ultra-precision surface grinding without polishing process (Namba and Katagiri, 1999).

Nowadays, single point diamond turning (SPDT) technology and magnetorheological finishing (MRF) are considered state-of-the-art for processing KDP crystal plates to large aperture. Hou et al. (2006) used SPDT technology to process large size KDP crystal (320 × 320 mm) and the rms roughness was reduced to about 5 nm. With the efforts of researchers, surface quality of the KDP crystals processed by SPDT had been increased and the surface roughness reached less than nanometres or so in partial region (Lahaye et al., 1999; Fu et al., 2011). MRF technology was employed to process KDP directly or as a succeeding technology to remove the micron ripples left by SPDT method. Plenty of research work has been done and a super smooth surface with roughness 1.06 nm rms was achieved (Menapace et al., 2009; Zeng et al., 2012).
Water dissolution ultra-precision polishing of KDP crystal

Research group from Dalian University of Technology had concentrated on the water deliquescence machining of KDP crystal. Gao et al. (2010) and Wang et al. (2010) proposed an abrasive-free polishing technology and invented water-in-oil micro emulsion dispersion fluid and achieved a scratch-free polished KDP surface with roughness lower than 2 nm. Wang et al. (2015) further studied the principle and incorporated the computer controlled optical surfacing (CCOS) technology in the machining process. This method realised the precision control of material removal and greatly improved the surface figure and quality.

However, finished crystal without immediately cleaning will easily impact the optical performance of optical element and even pollute the whole beamline (Thomas et al., 1992), which degrades the output of the optical system (Li et al., 2013). Cleaning technology, especially super smooth surface cleaning technology, is not only an essential part in ultra-precision machining and super smooth surface processing (Zhang et al., 2007), but also a critical problem affecting the function and subsequent engineering applications of the ultra-precision devices.

Few literatures have reported about the subsequent cleaning of the machined precision KDP surface. So in this work, we developed a process to finish KDP crystal to a precision and clean engineering specimen. A water dissolution principle and its planarisation mechanism in the machining process are illustrated. Then a subsequent precision cleaning process is developed specially for this ultra-precision polishing method, which helps to get rid of the polishing fluid, and finally reduces the residue off the crystal to a clean and tidy surface with 1.964 nm rms roughness for engineering application.

2 Materials and methods

The KDP crystal sample used in the abrasive-free water dissolution ultra-precision polishing were all cut with a dimension of $30 \times 30$ mm and the polishing device was a ZYP200 polisher. The principle of apparatus for polishing KDP crystals is shown in Figure 1. During polishing, the work table with the polishing pad rotates along its axis at $\omega_1$ and the carrier with KDP samples rotates at $\omega_2$. The combination of the effect is that the KDP sample performs a planetary motion and finally achieves planarisation of whole surface. The polishing fluid used in the process is a kind of micro emulsion dispersion we developed earlier, where the water content of non-aqueous fluid is 10%–20%. Samples are polished for 20 minutes to get rather good surface integrity.

The KDP crystal samples after micro-nano water dissolution polishing were instantly soaked up of solution on the surface with a filter paper and then wiped softly and carefully with lens tissue. Afterwards, samples were grouped for the preparation of cleaning. These KDP samples were then put into different cleaning agents respectively and cleaned in an ultrasonic cleaner for 5 minutes. The whole process was carried out in dry and sealed environment. To evaluate the machining effect and cleaning result of micro-nano water dissolution finished KDP crystals, the samples were analysed with a Fourier transform infrared spectrometer (FTIR) operating in reflectance mode, an Olympus metallographic microscope, and a ZYGO white light interferometer.
3 Results and discussion

3.1 Mechanism of micro-nano water dissolution machining

Deliquescence property of KDP crystal poses a great challenge in the machining and storage processes. Because KDP crystal has a solubility of 33 g in water at the temperature of 25°C, its deliquescence behaviours can easily occur with the change of the surrounding temperature and the relative humidity during the subsequent treatment such as polishing, cleaning, and coating. However, the ultra-precision polishing method takes advantage of this phenomenon and turns the disadvantage deliquescence property into the driving force for machining KDP crystal. And here, we introduce the micro-nano water dissolution polishing.

The basic mechanism of this ultra-precision polishing method for KDP crystal is shown in Figure 2. The key factor that contributes to the material removal of KDP in the polishing process is the water and it has been confined and minimised to nano-sized balls (Wang et al., 2010). In this fluid, nano scale water droplets are caged in a non-ionic
Water dissolution ultra-precision polishing of KDP crystal

27

surfactant, forming water micelles evenly distributed in an oil-based solvent. The micro emulsion dispersion is a rather stable three phase system. During this polishing process, the micro-nano water-in-oil structures in the recessed region keep in their shape for the absence of any relative movement between the crystal and polishing pad. Meanwhile, the water micelles are dispersed in the organic solvent that neither dissolves nor reacts with the KDP surface, respectively. Therefore, the KDP surface is protected by the organic solvent from coming into direct contact with the water droplets, which are trapped in micro-micelles. While in the polishing area, at the points of contact areas between the polishing pad and KDP crystal, the water micelles are deformed by the shear force created between the polishing pad and KDP crystal, and the water droplets are released and are able to dissolve the asperities on the KDP crystal surface. Then the dissolution layer is formed and soon removed by the mechanical friction and the flow of the polishing fluid. Meanwhile, in the valleys of the KDP surface where the polishing pad does not directly contact the KDP crystal, the water micelles stay rather stable and no dissolution action happens. Thus, the selective removal of material is achieved by ensuring that micro dissolution behaviours only take place at the asperities. The planarisation mechanism of the ultra-precision polishing results in more precise and accurate control of the material removal rate.

3.2 Surface investigation of polished KDP crystal

During the ultra-precision polishing process, the sample surfaces were all bathed in the polishing fluid. So the machined surface was covered with solution when the polishing process completed. Because the subtle friction force of wiping with filter paper and lens tissue on the surface, the residual polishing solution breaks down into tiny liquid globules and randomly distributed on the whole crystal surface. Under a microscopic view, distribution of residue on polished KDP crystal surface is shown in Figure 3. The oil-based polishing solution, due to its strong hydrophobic property, is quite difficult to be removed from the surface. Surface without wiping covers a large amount of residual polishing chemicals. By the reason of viscosity and surface tension, the solution will aggregate automatically into larger liquid droplets, leaving a thin fluid film on the whole surface. The existence of small droplets after simple cleaning treatment seriously impacts the optical property of KDP crystal and makes it impossible in subsequent use.

However, in this ultra-precision polishing process, the size of water nuclei was minimised to nano scale and the oil-based fluid did not react with KDP, so we could precisely control the material removal of the polishing and achieve ultra-precision machining of KDP crystal surface. The surface morphology after the ultra-precision polishing is shown in Figure 4. The surface rms and Ra roughness reached to 2.676 nm and 2.102 nm respectively, which indicated that the polished surface was a super smooth surface. While the peak to valley (PV) value stayed as high as 41.538 nm, which was influenced by the residue attaching to the machined surface. This was concluded from the spikes and stains in particular region which can be seen from the ZYGO oblique plot and the cross-section profile. More measurements were conducted on the polished surface and the surface morphology data of testing areas are shown in Table 1. This showed that the distribution and the formation of the residue on the surface were much the same, and also proved that the polished surface was a super smooth and ultra-precision surface with high quality but contaminated with polishing residue. The residual pollution after the
micro-nano water dissolution polishing covers the real surface and affects the optical performance of KDP crystal, and thus has to be removed.

**Figure 3** Distribution of residue on polished surface

**Figure 4** The morphology of crystal surface after the ultra-precision polishing (see online version for colours)
Table 1  Surface morphology data of testing areas

<table>
<thead>
<tr>
<th>No.</th>
<th>rms (nm)</th>
<th>Ra (nm)</th>
<th>PV (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.676</td>
<td>2.102</td>
<td>41.538</td>
</tr>
<tr>
<td>2</td>
<td>2.527</td>
<td>1.998</td>
<td>46.611</td>
</tr>
<tr>
<td>3</td>
<td>2.765</td>
<td>2.124</td>
<td>48.420</td>
</tr>
<tr>
<td>4</td>
<td>2.783</td>
<td>2.237</td>
<td>37.840</td>
</tr>
<tr>
<td>5</td>
<td>3.981</td>
<td>3.149</td>
<td>41.696</td>
</tr>
</tbody>
</table>

Figure 5 is FTIR spectrogram of the KDP surface of pure crystal and polished but uncleaned sample. The presence of the peaks in the infrared spectrum is caused by the changes of molecular energy level when it absorbs energy from different wavelength bands. It is obvious that the spectrum of pure crystal is smooth and there is no evident peak at high wavenumbers section, while the peaks at low wavenumbers zone are reflections of molecular structure of the crystal itself. These peaks are the characteristic peaks of a substance and the corresponding wavenumbers are characteristic frequencies. The large wide peak at 3,500 cm\(^{-1}\) indicates that there is hydroxyl (–OH) on the surface of uncleaned crystal; the deep ‘W’ shaped doublet around 2,900 cm\(^{-1}\) and the presence of several weak peaks at between 1,400 cm\(^{-1}\) and 1,500 cm\(^{-1}\) indicate clearly the existence of methyl (–CH\(_3\)), methylene (–CH\(_2\)–), and methyne (≡CH), etc. It can be concluded from the comparison of surface infrared spectra of the pure crystal and the uncleaned sample that the substance left on the uncleaned crystal surface must have organics with methyl (–CH\(_3\)). Hence, the residual components on crystal surface after the micro-nano water dissolution ultra-precision polishing must be organic chemicals with C and H.

Figure 5  Surface FTIR spectra comparison between pure crystal and polished but uncleaned crystal (see online version for colours)

FTIR analysis shows that the residual components on the polished crystal surface are organic chemicals with –CH\(_3\) and –OH groups, i.e. mostly the polishing fluids.
3.3 Precision cleaning of processed KDP crystal

Based on the elaborate analysis above, surface contaminants were mainly organic ingredients. Polishing fluid made up the most of them and the chemical composition of which is known. The unknown parts were organic chemicals with –CH₃ and –OH groups which could be concluded into the same bracket as organics. Besides, the whole ultra-precision polishing process was carried out in the clean room and no dust or particle was detected on the polished crystal surface. So, according to the principle of the dissolution in the similar chemical structure, a set of environment friendly organic cleaning agents, such as toluene of hydrocarbons, ethanol of alcohols species and Novec™ 71 series of hydrofluorothers, were selected to perform the cleaning process, which were all strong organic solvent with good compatibility and volatility, that is, they could dissolve the organic chemicals but do not react with KDP crystal. However, in order to overcome the intermolecular forces and hydrogen bonding at the interface between KDP crystal and residual chemicals, high frequency ultrasonic aided vibration cleaning was introduced on account of the heavy vibration force that will do harm to the precision surface.

Figure 6 Polished surface cleaned with toluene

Through analysing of the surface topography and the component of the residue on the crystal surfaces after cleaning with these different agents, it is gained that toluene cleaned crystal surface stands out with no liquid residue and obvious damage or deterioration, and a satisfied clean surface is acquired. The cleaning effect is shown in Figure 6 and the FTIR spectra comparison between pure crystal and the toluene cleaned surface is shown in Figure 7. It can be seen that the hydroxyl (–OH) peak at high wavenumbers and hydrocarbon functional group peaks, such as methyl (–CH₃), methylene (–CH₂–), and methyne (≡CH) peaks, at low wavenumbers on the spectrum of uncleaned crystal surface disappeared and the spectrum of toluene cleaned crystal become identical with that of the pure crystal. Corresponding characteristic peaks on the spectra curves are the same to the generation positions and there is no new generated peak, which indicates that surface is clean and without residue after cleaning with toluene solvent. White light interferometer
result indicates that the crystals surface roughness and PV value are reduced to 1.964 nm and 18.935 nm after toluene cleaning (Figure 8). The little improvement in surface roughness and dramatic decrease in the PV value tell the fact that the chemical residue on the polished surface are removed and the real ultra-precision crystal surface comes out.

**Figure 7** FTIR spectra of pure crystal and toluene cleaned crystal (see online version for colours)

![FTIR spectra](image)

**Figure 8** Surface topography of KDP crystal cleaned with toluene (see online version for colours)

![Surface topography](image)

### 4 Conclusions

A micro-nano water dissolution principle and its planarisation mechanism in the ultra-precision polishing process were illustrated. Micro emulsion fluid with nano water nuclei can precisely control the material removal and realise the selective polishing, thus forming a super smooth and precise surface, which was verified in the experiment and a 2.676 nm rms roughness surface was achieved. Analysis indicated that the residue on the surface of KDP crystal after micro-nano water dissolution ultra-precision polishing were chemical compounds consisted of C and H elements. A subsequent cleaning process was developed specially for this ultra-precision polishing method, which could eliminate the
surface residue. Finally, a clean and tidy surface with 1.964 nm rms roughness, 18.935 nm PV and without contaminants for engineering application was acquired.

Acknowledgements

This work is supported by National Natural Science Foundation of China (Grant No. 51135002), Science Fund for Creative Research Groups (Grant No. 51321004).

References

