Crystalline perfection and optical properties of rapid grown KH_2PO_4 crystal with chromate additive

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Abstract. Potassium dihydrogen phosphate (KDP) crystals were grown in the presence of a series of chromate (CrO_4^{2-}) additive concentrations via rapid growth method. CrO_4^{2-} made KDP crystals were coloured by yellow-green, suggesting CrO_4^{2-} had entered into the crystal lattice. The elemental analysis indicated that Cr element in KDP crystal was at ppm level. High resolution X-ray diffraction data revealed that the crystalline perfection of these as-grown KDP crystals was destroyed after CrO_4^{2-} entered into crystal lattice, embedded in the full width at half maximum was broadened and satellite peaks appeared. Additionally, the extinction ratio was decreased with rise of CrO_4^{2-} concentration. CrO_4^{2-} introduced two absorption peaks centred at 360 and 280 nm and enhanced the intrinsic absorption near 220 nm, which were at the same band positions compared with the CrO_4^{2-} or HCrO_4^- transmittance spectra. Additionally, CrO_4^{2-} could increase the size of light scattering, which was attributed to the point defects and microscopic defects by the replacement by CrO_4^{2-} at PO_4^{3-} position.

Keywords. KDP crystal; additive; CrO_4^{2-} ; crystalline perfection; optical properties.

1. Introduction

Potassium dihydrogen phosphate (KDP) crystal is a remarkable nonlinear optical crystal due to its excellent electro-optical and nonlinear optical properties (Sasaki and Yokotani 1990; Yoshida *et al* 2000). In the high power laser system for inertial confinement fusion, KDP crystal is usually applied as a frequency conversion device because of its high transmittance from the near-infrared and visible to the ultraviolet band (Garces *et al* 2001; Yang *et al* 2008). However, there often exists some anomalous absorption in the transmittance spectra which originates from impurities in KDP crystal lattice. The anomalous absorption is harmful to frequency conversion applications if the absorption band overlaps the fundamental pump or the output wavelengths. For example, metallic cations in KDP crystal lattice can introduce absorption in the band range from 210 to 215 nm for the replacement of K^+ ions (Pritula *et al* 2008).

Impurities, which are inevitable when growing KDP crystal from solution, can dramatically affect both growth and optical properties of KDP crystal. When impurities enter into the KDP crystal lattice, they can distort crystal lattice and thereby introduce local deformations and point defects, which are considered to be one of the origins that decrease crystalline perfection and optical properties (Varma and Prasad 1990; Rashkovich and Kronskey 1997; Guzman

and Kubota 2005; Zhang *et al* 2007). Nowadays, people have confirmed that metallic cationic impurities are prone to incorporation into prismatic sector of KDP crystal, especially for rapidly grown KDP crystal (Land *et al* 1999; Kubota *et al* 2004; Wang *et al* 2006). On the other hand, the influence of anionic impurities is much more sophisticated on both crystalline perfection and optical properties of KDP crystal. Some organic dye anions, such as Chicago Sky Blue, are inclined to enter into pyramidal sector of KDP crystal and make pyramidal sector coloured. We have found SO_4^{2-} is tended to enter into the pyramidal sector and SiO_3^{2-} is principally inclined into prismatic sector (Zhang *et al* 2007; Ding *et al* 2010). The sophisticated influence of anionic impurities demands further study on crystalline perfection and optical properties of KDP crystal.

In the previous work (Ding *et al* 2011), we reported interaction mechanism of CrO_4^{2-} with both (100) and (101) faces of KDP crystal, based on the structural similarities of CrO_4^{2-} to PO_4^{3-} . In the present work, we aim to describe the influence of CrO_4^{2-} on both crystalline perfection and optical properties of rapid grown KDP crystal.

2. Experimental

2.1 Growth of KDP crystals

KDP crystals were grown in a Holden Crystallizer via rapid growth method. The solutions were prepared by using

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KH_2PO_4 with analytical grade (Merck Co., Germany) and de-ionized water. The solutions were filtered through a membrane with a pore diameter of $0.22\ \mu\text{m}$ and were overheated for 24 h at 80°C in the crystallizers. The CrO_4^{2-} additive source was an analytical grade K_2CrO_4 and was inserted into the growth solution before crystal growth. The dominant configurations of CrO_4^{2-} in KDP solutions where the pH value was about 4.2 are $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_4^- , from the view of proton reaction and dimerization reaction (Ding *et al* 2011). The seed crystals, ‘point seeds’ were used for rapid growth method. The crystals were rotated in a mode of forward-stop-backward. During the crystal growth process, the solution was stirred continuously by a stirrer at a rotation rate of 77 rpm. The growth temperature range was $60\text{--}30^\circ\text{C}$.

2.2 Characterization

The elemental analysis was carried out on an inductive coupled plasma emission spectrometer (IRIS Intrepid II, America, Thermo).

Z-cut KDP crystal plates with thicknesses of 5 and 15 mm were well polished for crystalline perfection and optical measurements, respectively. The crystalline perfection was monitored by using high resolution X-ray diffraction (HRXRD) on a High Resolution X-ray Diffractometer (D5005, German, Bruker AXS) with an irradiation wavelength of $0.1541\ \text{nm}$. The tube voltage and current were 30 kV and 30 mA, respectively.

Static extinction ratio was a crucial quantitative parameter for characterizing the structural homogeneity and optical performance of KDP crystal, which was the ratio of the maximum light intensity (I_{max}) to the minimum light intensity (I_{min}). In the static extinction ratio measurement, the I_{max} and I_{min} were acquired in polarized light system.

The transmittance spectra of KDP samples in the region of $200\text{--}1700\ \text{nm}$ were measured by means of HITACHI U-3500 spectrometer.

The light scattering was observed by a laser tomography system consisting of a 532 nm 50 mW output He–Ne laser, a microscope and a camera (Wang *et al* 2001).

3. Results and discussion

3.1 Growth habits

Figure 1 illustrates photograph of these as-grown KDP crystals by using rapid growth method with various concentrations of CrO_4^{2-} additive. During the crystal growth process, no spontaneous crystallization occurred. KDP

crystals are transparent with lower CrO_4^{2-} concentrations. However, with higher CrO_4^{2-} concentrations, KDP crystals are coloured yellow-green without any colour segregation, suggesting that CrO_4^{2-} has been incorporated homogeneously into crystal lattice and the distribution coefficients of CrO_4^{2-} in both prismatic and pyramidal sectors are close to each other. The quantities of Cr element in different sectors of KDP crystals are listed in table 1, which indicates that the concentrations of Cr in both prismatic and pyramidal sectors increase with a rise of CrO_4^{2-} and the quantities of Cr element in prismatic sector were somewhat higher than those in pyramidal sector. But the difference was inconspicuous and consequently KDP crystals were grown without any colour segregation.

3.2 Crystalline perfection

In order to acquire influence of CrO_4^{2-} on crystalline perfection of KDP crystal, high resolution X-ray diffraction (HRXRD) was carried out. HRXRD curves of Z cut plates are shown in figure 2. As can be seen the peak on the HRXRD curve for pure KDP crystal is sharp without any satellite peaks, which indicates that the crystalline perfection of pure KDP crystal is excellent. The appearance of satellite peaks on HRXRD curves for KDP crystals grown with 500 and 5000 ppm CrO_4^{2-} indicates that the crystalline perfection becomes worse. According to the Cr element distribution results, we believe that the small quantity of CrO_4^{2-} in KDP crystal has caused structure distortion and spoiled the

Figure 1. Photograph of KDP crystals grown by rapid growth method with various CrO_4^{2-} concentrations.

Table 1. Cr element concentrations in different sectors of KDP crystals.

CrO_4^{2-} concentrations (ppm)	0	50	500	1000	5000	10000
Prismatic sector	7.69	9.36	12.32	19.82	26.50	41.15
Pyramidal sector	9.02	9.90	11.68	15.27	19.57	24.60

structure homogeneity. On the other hand, the full widths at half maximum (FWHM) of HRXRD curve for KDP crystals grown with 500 and 5000 ppm CrO_4^{2-} are larger than that for pure KDP, which also indicates that CrO_4^{2-} has brought structure distortion.

3.3 Static extinction ratio

As is well known, the static extinction ratio is one of the most effective ways to illustrate lattice stress in a crystal which is usually associated with optical homogeneity. A crystal with large static extinction ratio means the lattice stress is little and optical homogeneity is excellent. Because the entrance of impurity or additive into crystal lattice can

bring lattice stress, static extinction ratio accordingly can reflect the impurity effect on optical homogeneity for a crystal. Figure 3 displays influence of CrO_4^{2-} on static extinction ratio of KDP crystal. The static extinction ratio decreases rapidly and is maintained in a stable condition with the rise of CrO_4^{2-} additive. The decrease of the static extinction ratio indicates CrO_4^{2-} can bring lattice stress and destroy optical homogeneity of KDP crystal. But higher concentrations of CrO_4^{2-} additive make equivalent contributions to optical homogeneity.

3.4 Transmittance spectra

Rapid growth method allows KDP crystal to grow along both X and Z directions. As a result, such KDP crystal has pyramidal and prismatic sectors, whose transmittances are different with each other. Figure 4a shows transmittance spectra of pyramidal sector of KDP crystals grown by rapid growth

Figure 2. HRXRD curves of Z cut KDP plates grown by rapid growth method with various concentrations of CrO_4^{2-} .

Figure 3. Influence of CrO_4^{2-} on static extinction ratio of KDP crystal.

Figure 4. Transmittance spectra of KDP crystals with various concentrations of CrO_4^{2-} grown by rapid growth method: **a** pyramidal sector and **b** prismatic sectors.

method. The transmittance at the infrared region of KDP crystals grown with CrO_4^{2-} additive is approximately equal to that of pure crystal. At the UV region where the wavelength is shorter than 450 nm, two absorption peaks centred at 364 and 281 nm appear, which are at the same band positions compared with the CrO_4^{2-} transmittance in alkaline solution where only CrO_4^{2-} species exists. Additionally, the intrinsic absorption centred at 219 nm is intensified when KDP crystals were grown with CrO_4^{2-} additive. Taking consideration of that, CrO_4^{2-} can cause absorption near 219 nm, the intensified absorption at 219 nm for KDP crystals can be attributed to entrance of CrO_4^{2-} into KDP crystal lattice.

As for prismatic sector, at the UV region where the wavelength is shorter than 450 nm, the transmittance decreases rapidly and reaches to minimum at 270 nm, as can be seen in figure 4b. According to the literature (Garces *et al* 2001), the strong absorption at the UV region in KDP crystals might be caused by metallic iron impurities. When the additive concentration is 10000 ppm, an absorption peak centred at 360 nm appears, it means CrO_4^{2-} can also enter into prismatic sector.

It should be noticed that a red shift occurs for the absorption edge near 360 nm if more CrO_4^{2-} enter into KDP crystal lattice. The red shift might be ascribed to H transferring onto CrO_4^{2-} , which means partially HCrO_4^- has entered into KDP crystal lattice to replace H_2PO_4^- . We believe that the replacement of H_2PO_4^- by either CrO_4^{2-} or HCrO_4^- can bring point defects and structural stress. That might be the reason why CrO_4^{2-} causes worse crystalline perfection and lower static extinction ratio.

3.5 Light scatter

In KDP crystal, there exists some small micro-cavities that were referred to as ‘pinpoints’, which could scatter light to

be like small particles under illumination of laser (Adams *et al* 2005). The influence of CrO_4^{2-} on light scatter images of KDP crystal is shown in figure 5. It can be seen that the orientation of the light scatters are in random distribution pattern. The density of light scatter varies a little with the increase of CrO_4^{2-} additive concentration. The size of a single light scatter increases when the CrO_4^{2-} additive concentration is high. The results suggest that the incorporation of CrO_4^{2-} into KDP crystal lattice have destructed the optical integrities and increase the defect size. It must be pointed out that there are two kinds of dominant light scatter morphologies which are shown in the inserted pictures. The first kind, named as ‘multi-points scatter’, can be depicted as follows: the main scatter centre with highest brightness, after which there exists an area of glow and another subsidiary light scatter. This kind of light scatter suggests that the laser brightness was impaired. The second kind is ‘single point scatter’—there is only one scatter point after which a light shadow appears.

The density and morphology of laser light scatter is customarily associated with microscopic defects, crystalline perfection, structural and optical homogeneities and point defects in the crystal. From the above analysis, we have concluded that CrO_4^{2-} can destroy the crystalline perfection, which is adverse to the optical homogeneity. Additionally, owing to the structure similarity to PO_4^{3-} , CrO_4^{2-} could enter into crystal lattice and bring point defects as follows:

The replacement of CrO_4^{2-} or HCrO_4^- at PO_4^{3-} could bring redundant electrons at H position, which were negative H vacancies. The redundant electrons, fixed at H position, could

Figure 5. Light scatters in KDP crystals grown by rapid growth method with various concentrations of CrO_4^{2-} .

oscillate in the laser fields (Jones *et al* 1989) and facilitate rapid absorption during duration of laser pulse. As a result, the negative H vacancies enlarged the sactters and caused single point scatters.

As can be seen from the formula, CrO_4^{2-} could not only generate negative H vacancies, but also simultaneously bring positive electric charge at PO_4^{3-} positions. The positive electric charge at PO_4^{3-} positions, whose volume was relatively larger, could seize redundant and additional electrons and scatter the laser. Consequently, the sactters were displayed as multi-point scatters. Moreover, the replacement of CrO_4^{2-} or HCrO_4^- at PO_4^{3-} causes more vacancies and the microscopic defects in crystal lattice can scatter the laser towards any random orientations, which is in agreement with the light scatter results.

4. Conclusions

The growth habits, element analysis and transmittance spectra show explicit evidence that CrO_4^{2-} have entered into KDP crystal lattice. The replacement of PO_4^{3-} by CrO_4^{2-} brought more point defects and microscopic defects in crystal lattice. Consequently, CrO_4^{2-} destroyed crystalline perfection, spoiled optical homogeneity of KDP crystal and increased light scatter size.

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