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New annealing method to improve KD_2PO_4 crystal quality: learning from high temperature phase transition

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The existence of the high temperature phase transition in KD_2PO_4 was confirmed by thermal analysis, dielectric analysis and Raman spectroscopy analysis. The results showed that KD_2PO_4 presented only one high temperature phase transition at about $T_{tr} = 430$ K much lower than the thermal decomposition temperature. None Raman shift attributable to dehydration product indicated that the HTPT had nothing to do with thermal decomposition. The structural change during HTPT was discussed. The much more similarity between HT-phase and tetragonal phase makes much lower temperature of HTPT in KD_2PO_4 crystal. The hydrogen-deuterium exchange can be suppressed under protective ambient which help improve the annealing temperature. New annealing method was developed by using silicone oil as protective ambient under higher temperature up to 403K, thus improved the quality of KD_2PO_4 crystal.

Introduction

Tetragonal Deuterated Potassium Dihydrogen Phosphate (DKDP) crystal is one of the feasible candidates preferred used to substitute KDP crystal as pockels cell and frequency conversion crystal due to its better electro-optic performance and weak Stimulated Raman Scattering (SRS) effect.¹ However, the Laser Damage Threshold (LDT) of DKDP crystal is much lower than KDP crystal, which limits the intensity of the laser. The damage mechanism of DKDP crystals has been adequately studied. One reason is laser induced thermal decomposition or High Temperature Phase Transition (HTPT).^{2, 3} On the other hand, thermal annealing is an effective method to improve the crystal quality and has been widely used in KDP crystal.⁴⁻¹² The higher annealing temperature, the better improvement will gain. The annealing temperature of KDP crystal is about 423K. However for DKDP crystal, the annealing temperature is usually below 363K. The reason of the low annealing temperature is also attributed to high temperature behaviors such as thermal decomposition or HTPT.¹³

Recently, several studies have reported that some KDP-family compounds (MH_2PO_4 , M = K, Cs, Rb, NH_4) such as CsH_2PO_4 and RbH_2PO_4 may show superprotonic behavior upon heating at high temperature.^{14, 15} This is associated with structural phase transition from a room temperature phase to a high temperature phase. It expands the application fields of KDP-family crystals to operate as fuel cell electrolytes at elevated temperatures.

High temperature behaviors of KDP type crystal have attracted special attention for many years due to its importance in laser induced damage, annealing and superprotonic behavior studies.

The high temperature behavior of DKDP crystal is thought same as its analog KDP crystal. Thus few attentions were paid on it. However, there are still some differences between DKDP and KDP crystal due to the isotope effect. What is more, even though large amount of results were obtained about the high temperature behaviors of KDP crystal. They are still controversial.

Considering of the lack of results on the special and controversial high temperature behaviors of DKDP crystal, further studies are necessary to fully understand them. Accordingly, the present study employs multiple methods to investigate the high temperature behaviors especially HTPT in DKDP crystal. This study may help develop a new annealing method to improve crystal quality.

Experimental

Crystal growth

DKDP crystal is usually grown by traditional growth method.¹⁶ Traditional growth is likely to obtain high quality crystals but the growth period is too long to product crystals effectively. Nowadays, DKDP crystals can be grown by rapid growth method^{17, 18} which increases productivity greatly.

Tetragonal DKDP crystals with 98% deuteration were grown from DKDP solution by rapid growth method in standard 2500 ml glass crystallizers. The crystals are transparent without any visible macroscopic defects.

Characterization techniques

Thermal analysis To determine the existence of HTPT in DKDP crystal, Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) measurements were performed by using Perkin-Elmer Diamond TGA analyzer and Mettler Toledo DSC822e analyzer respectively. The TGA and DSC measurements were performed under dry nitrogen ambient. Samples were heated by a rate of 2K/min during the measurements.

Dielectric analysis Dielectric analysis was performed by using Agilent 4294A precision impedance analyzer at 1 KHz. Specimen with size of 8.08 mm × 8.10 mm × 2.46 mm cut along the X, Y, and Z

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axis was used to determine the ϵ_{33} of DKDP crystal at different temperature. The heating rate was same as thermal analysis method.

Raman spectroscopy analysis Cubic specimens with size of 5 mm \times 5 mm \times 5 mm or smaller used for Raman measurements were carefully cut along the X, Y, and Z axis with an orientation precision of 3' where X, Y, and Z are corresponding to the crystallographic a, b and c axis, respectively. The (001) planes of these specimens were fine polished. Raman measurements were performed by using a Horiba Jobin Yvon HR 800 Raman spectroscopy. The spectra slit widths were set to maintain a resolution of approximately 1.5 cm^{-1} and a wavelength precision of 1 cm^{-1} . A laser of 6 mW was operated at 532.1 nm. The Raman spectra were collected with scattering geometry in the range from 50 to 1400 cm^{-1} to gain more information of the crystal structure. Measurements were carried in a furnace (under dry nitrogen ambient to prevent possible crystal deliquescence and hydrogen-deuterium exchange) under heating from 300 to 470 K with the step width of 10 K. The heating rate was 10 K/min and 5 min was allowed for temperature stabilization. The integration time per spectrum was 60 s. The measurements were performed 2 or 3 times to obtain sufficient intensity.

X-ray diffraction The samples with size of 8mm \times 8mm \times 2mm for XRD measurement were cut along a and c axis respectively. The samples were heated in a homemade furnace with a rate of 2K/min until 443K. Then the samples were kept at 443K for 2 hours. The heated samples were measured by using Bruker-AXS D8 ADVANCE X-ray diffractometer equipped with a diffracted beam monochromator set for Cu $K\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$) in the 2θ range 10–80°, with a step size of 0.02° and a step time of 0.2 s at room temperature.

High-resolution X-ray Diffraction (HXR) and thermal annealing The HXR was performed on a Bruker D8-discover diffractometer equipped with a 4-boune Ge (220) monochromator set for Cu $K\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$). The accelerating voltage was 40 kV, and the tube current was 40 mA. The step time and step increment were 1.0 s and 0.001°, respectively. Two (100) and (101) oriented wafers of DKDP crystal mechanically polished on both sides were used as the HXR sample with the dimension of 20mm \times 20mm \times 0.6 mm³. Then the wafers were annealed in a homemade furnace. The furnace was filled with silicone oil (viscosity 28 Pa \cdot s) as protective and heat transfer medium. Figure 1 illustrates the annealing steps. The annealing temperature was set to 393K near but lower than the detected phase transition temperature to improve the effect of annealing without phase transition. The heating and cooling rates above 353K were set less than that below 353K to ensure safety. Moreover, the cooling rates were slower to

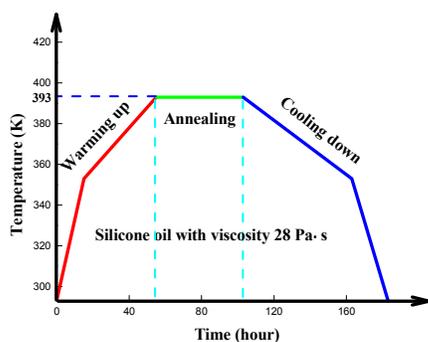


Figure 1 Annealing process for DKDP crystal.

avoid additional residual thermal stress. The samples were immersed in the silicone oil throughout the whole process and annealed for 48 hours. The annealed wafers were performed HXR again to test the effect of thermal annealing.

Results and discussion

Existence of HTPT in DKDP crystal

There are still controversies about the existence and nature of the HTPT in KDP type crystal. Eliezer Rapoport¹⁹ showed the real existence of phase transition and plotted the phase diagram of KDP crystal. J. Anand Subramony clarified the crystal structure of the high temperature phases.^{20, 21} While other evidence was interpreted as that the so called phase transitions were solely consequence of thermal decomposition.²²⁻²⁴ These controversies come from the fact that the HTPT temperature of KDP crystal is near the range of thermal decomposition. For DKDP crystal, the HTPT temperature may be far below thermal decomposition temperature due to the fact that DKDP is less stable than KDP crystal upon heating.

The existence of HTPT of DKDP crystal was studied by thermal analysis, dielectric analysis and Raman analysis. Figure 2 shows the TGA and DSC curve of tetragonal DKDP crystal. Weight loss was detected at 480K in TGA curve which indicated that thermal decomposition occurred. In the DSC curve, strong endothermic peaks can be found at 430K lower than decomposition temperature. The peak at 430K is a strong evidence of the existence of HTPT. The absent of HTPT in TGA curve shows the little weight change during HTPT process. This could be interpreted as HTPT would be a sole new phase instead of product of the thermal decomposition.

Figure 3 shows the dielectric constant of DKDP crystal in the 298-443K range. The dielectric constant was almost unchanged below 373K. It increases gradually above that and reaches the peak at 428K. Then it falls suddenly and increases gradually again above 430K. The highest value is 10143.88 more than two orders of magnitude higher than that at room temperature. The sudden change of dielectric constant can be regarded as another evidence of the existence of HTPT.

The dielectric constant gradually decreases with no peak as the temperature is down to room temperature. This indicates that the HTPT is irreversible. Although the dielectric constant returns to the same value, the sample crushed during HTPT and it never return to low temperature phase again.

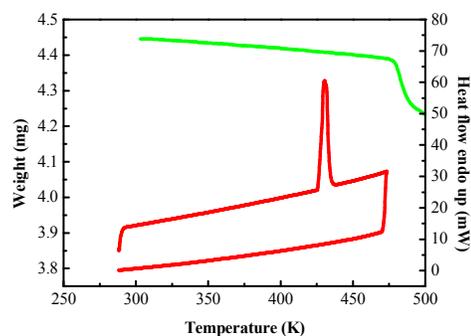


Figure 2 TGA and DSC curve of tetragonal DKDP crystal. Weight loss at 480K indicated that thermal decomposition occurred. Strong endothermic peaks at 430K temperature shows evidence of HTPT.

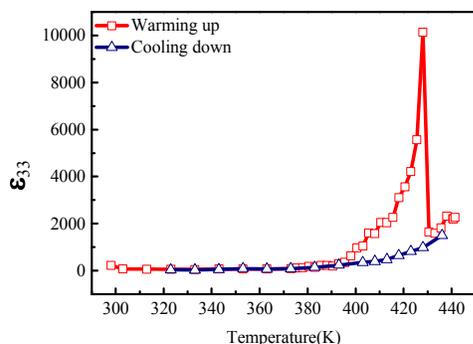


Figure 3 Dielectric constant of DKDP crystal in the 298-443K range.

High temperature behaviors of KDP crystal have been investigated by Byoung-Koo Choi²⁵ and Houda Ettoumi²⁶ with Raman spectrum. They revealed the existence and nature of HTPT in KDP crystal. Accordingly, the present study employs a Raman spectroscopic method to investigate the evolution of the Raman spectra for DKDP single crystal with the temperature rising from 300 to 470 K. Figure 4 shows the Raman spectra of DKDP crystal under different temperature. The Raman spectra did not change distinctly with the increase of temperature until 430K. Upon heating above 430K, some significant modifications in the Raman spectra were observed, which indicated the appearance of high temperature phase. As the temperature is raised from 430 to 470K, no other high temperature phase was found.

In previous work,^{27, 28} the recorded Raman spectra can be subdivided into two frequency regions by the obvious interval between them: The low frequency (50-300cm⁻¹) region of external modes, 300-1200cm⁻¹ region of PO₄ internal modes. The Raman spectrum data, relative intensities and proposed assignments of the two phases are listed in Table 1.

To understand the nature of the HT-phase transition in DKDP crystal, the Raman spectrum of probable thermal decomposition product Potassium Metaphosphate (KPO₃)₆ was measured at room temperature. The result is shown in Figure 5. The lines at 687cm⁻¹ and 1163cm⁻¹ in the spectrum of (KPO₃)₆ are characteristic frequencies of ν_s (P-O-P) and ν_s (O-P-O) internal vibrations of chains of PO₄ tetrahedra respectively.²⁹ We could no longer observe any feature attributable to dehydration products both in RT-phase and HT-phase of DKDP. Thus we can exclude the much-mentioned suggestion that the HTPT undergoes near 430K is solely a consequence of thermal decomposition.

KDP and DKDP crystals may undergo high-pressure and high temperature environment created by the laser pulse when they are operated as electro-optic switches and frequency converters. The extreme environment plays a key role in initiating the damage process. R. A. Negres³⁰ reported that laser-damaged KDP is proposed to be a mixture of KDP and KPO₃. It indicates that in the process of laser damage, the local temperature in crystals is even higher than the decomposition temperature (~453K). The higher intensity of the laser pulse, the higher local temperature will gain and vice versa. Thus the much lower phase transition temperature (T_{ir}=430K) of DKDP crystal limits its laser damage threshold much lower than KDP crystal.

Nature of HTPT in DKDP crystal

Previous research reported that tetragonal KH₂PO₄ crystal undergoes two HTPTs. HT-Phase II' and I are formed at 468K and

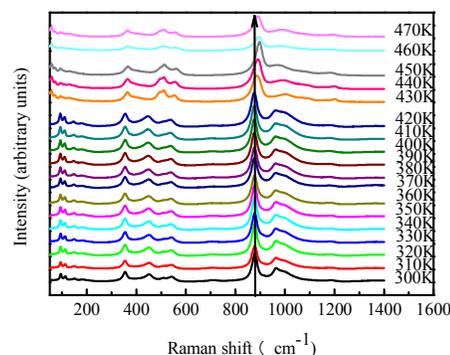


Figure 4 Temperature dependence of the depolarized Raman spectrum of DKDP crystal in the 300-470K range. Significant modifications in the Raman spectra were observed at 430K, which indicated the appearance of high temperature phase.

Table 1 The assignments of the vibration for RT-phase and HT-phase DKDP crystals.

RT-phase T=300K Raman shift (cm ⁻¹)	HT-phase T=430K Raman shift (cm ⁻¹)	Assignments
-	58w	lattice modes
-	72w	
95w	94vw	
114w	-	
150vw	-	
354s	364s	ν ₂ (δO-P-O)
450m	510s	ν ₄ (δO-P-O)
538m	553m	
878vs	886vs	ν ₁ (νP-OD)
961s	1001m	δ(OD)&ν ₃ (νP-OD)
1187w	1195w	ν ₃ (νP-OD)

In the column of relative intensities, s: strong, m: medium, w: weak, vw: very weak, ν: stretching, δ: bending.

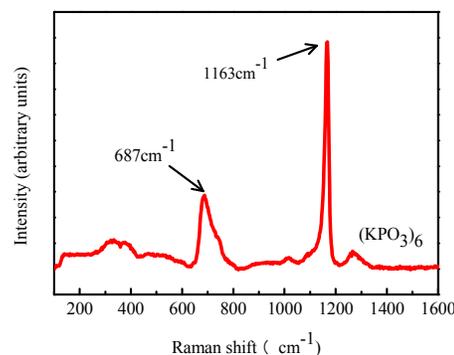


Figure 5 Raman spectra for Potassium Metaphosphate (KPO₃)₆ at room temperature.

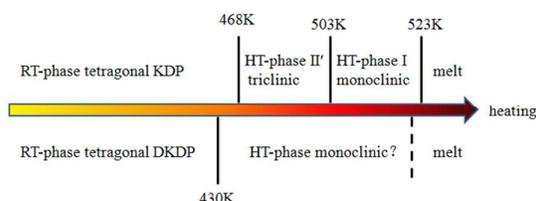


Figure 6 Thermal transformations of KDP and DKDP crystals under heating. HT-Phase II' and I are formed at 468K and 503K respectively in KDP crystal while only one HT-phase was found at 430K in DKDP crystal.

503K²⁰ respectively while heating shown in Figure 6. For DKDP, only one HT-phase was found at 480K.^{31,32} In our experiment, HT-phase transition took place at 430K much lower than 480K.

The exact crystal structure of HT-phase is still unclear due to the difficulty in the separation of HT-phase from the mother RT-phase. It is plausible that the HT-phase was regarded as monoclinic phase similar to HT-phase KDP I. Figure 7 shows the structural comparison of tetragonal DKDP and HT-monoclinic KDP crystal. The structures of tetragonal DKDP and HT-monoclinic KDP crystal are topologically similar. It is worth noting that the substitute of hydrogen by deuterium may change the structure of monoclinic phase I and make HT-monoclinic DKDP crystal more similar to tetragonal DKDP crystal. This phenomenon has been confirmed by its isomorphism room temperature monoclinic (RTM) phase DKDP crystal.³³⁻³⁶ If the tetragonal phase is sheared along <010> directions for about 8.774°, it will turn to monoclinic phase. That is where the HTPT occurs. HTPT will cause strong shear stress along 010 directions in the crystal, which lead to crystal crash.

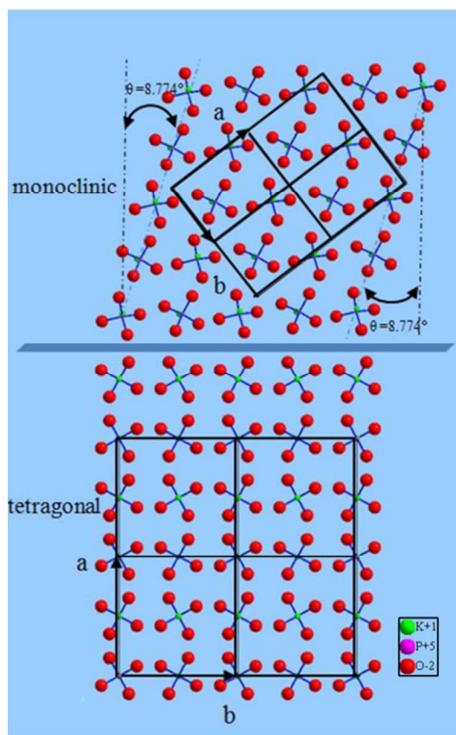


Figure 7 Structural comparison of tetragonal DKDP and HT-monoclinic KDP crystal. Hydrogen atoms and deuterium atoms are removed for clarity.

Figure 8 and Figure 9 show the XRD diagram of a-cut and c-cut DKDP crystal heated up to 443K respectively. The miller indexes of main peaks are identified and listed in Table 2. For a-cut crystal, the main peaks are all belong to {100} planes. It indicated that the main structure did not break during the HTPT. It is because the <010> direction is thin which can release the shear stress and did not cause serious broken. However, (110) plane of monoclinic phase appears in a-cut plate. It probably because the structure of (110) plane is similar to (100) plane of tetragonal phase. For c-cut plate, the highest peak is (004) plane of tetragonal phase. Much more peaks appear which indicated the serious broken of the mother phase. It is because that the shear stress along <010> direction is hard to release.

Thermal annealing

The annealing temperature of DKDP crystal is usually below 363K under air conditions which limit the effect. This is probably because of the hydrogen-deuterium exchange with the vapor in air due to isotope effect. If the crystal is protected from air, the hydrogen-deuterium exchange can be inhibited. According to Thomas Huser,³⁷ the dependence of the Raman shift of the PO_4 vibration $\nu_5(\text{PO}_4)$ on degree of deuteration is almost perfectly linear with function $D = -2.684\text{cm} \times R + 2452.6$ where D and R are the degree of

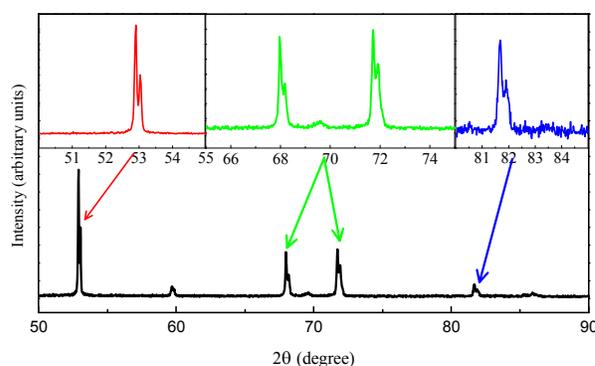


Figure 8 XRD diagram of a-cut DKDP crystal heated up to 443K.

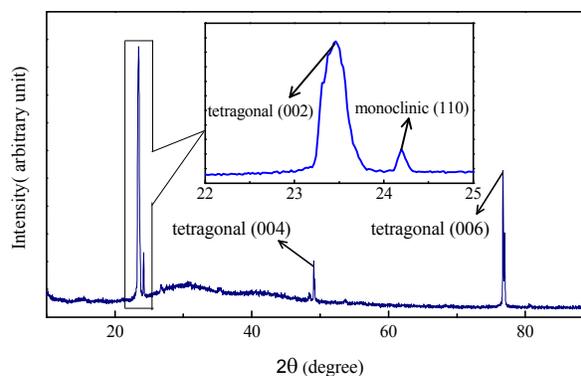
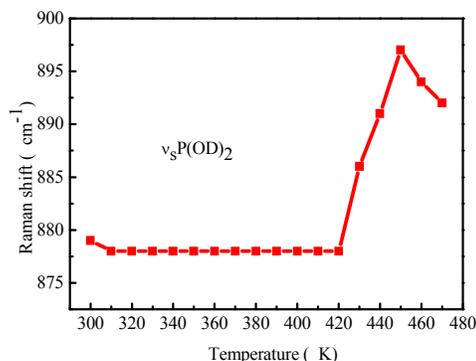


Figure 9 XRD diagram of c-cut DKDP crystal heated up to 443K.

Table 2 The identified miller indexes of main peaks

Sample	Phase	Experimental 2θ (degree)	Calculated 2θ (degree)	Identified (h k l)
a	Tetragonal	23.458	23.840	0 2 0
	Tetragonal	49.079	48.798	0 4 0
	Tetragonal	76.921	76.578	0 6 0
	Monoclinic	24.194	24.511	1 1 0
c	Tetragonal	52.901	52.577	0 0 4
	Tetragonal	67.967	68.550	0 1 5
	Tetragonal	71.804	71.492	4 4 0
	Tetragonal	59.653	58.508	0 2 4
	Monoclinic	53.037	53.040	-1 0 8
	Monoclinic	68.179	67.779	1 0 10
	Monoclinic	71.919	72.198	-2 0 10

deuteration (in %) and the spectral mean of the PO_4 vibration (in cm^{-1}) respectively. The Raman shifts of $\nu_s\text{P}(\text{OD})_2$ at different temperature are plotted in Figure 10. It shows that the Raman shift of $\nu_s\text{P}(\text{OD})_2$ is located at 878cm^{-1} at room temperature indicating that the deuterium concentration of the crystal is 96.0%. It is smaller than 98% which is calculated by the equation³⁸ $K_{\text{eff}} = 0.68 \exp(0.00382M)$, where K_{eff} and M are the effective segregation coefficient and the mole% D in the solution respectively. This is probably because the effective segregation coefficient (K_{eff}) decreases with the increase of supersaturation. The equation fits better under low supersaturation in traditional growth process. Thus in our rapid growth process under higher supersaturation, the deuteration of crystal is smaller than the one in traditional growth process. Moreover the Raman shift doesn't change until 430K, which indicates that the hydrogen-deuterium exchange is suppressed and that the HTPT occurs independently. DKDP crystal is stable until 430K under protective ambient according to the HTPT results. It indicates that protective ambient may help raise the annealing temperature of DKDP crystal.

Figure 10 The Raman shifts of $\nu_s\text{P}(\text{OD})_2$ at different temperature.

New annealing method was applied by using silicone oil as protective and heat transfer medium. HRXRD measurement was taken before and after the annealing process. The X-ray rocking curves were listed in figure 11. Before annealing, the x-ray rocking curve of (020) plane was asymmetric because of the strong stress in prism area. The shoulder at 11.89° is an evidence of low angle grain boundary. Unlike (020) plane, the x-ray rocking curve of (101) plane is symmetric without any shoulder. All these indicate that the quality of prism area is worse than pyramid area in rapid growth DKDP crystal. This is a common problem for rapid growth method.

The curve of (020) plane becomes symmetric and shoulder disappears after the process of thermal annealing. Moreover, the FWHM decreases to from $83.736''$ to $74.808''$. For (101) plane, the rocking curve is much more symmetric even though increases the FWHM. It is obvious that the high temperature thermal annealing in silicone oil can release the residual stress thus improve the crystal quality especially for prism area.

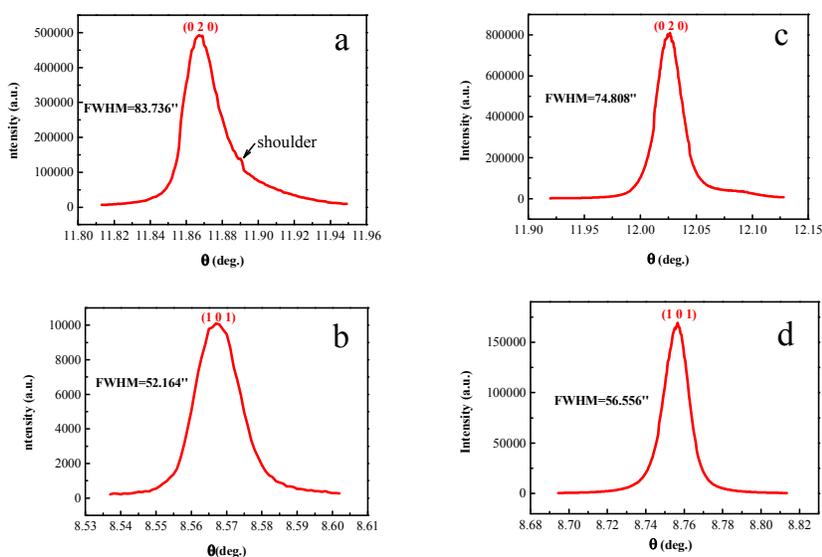


Figure 11 X-ray rocking curves of (100) and (101) slices before and after annealing process. a: (100) slice before annealing, b: (101) slice after annealing, c: (020) slice before annealing, d: (020) slice after annealing.

This new annealing method is more effective in rapid growth crystal. Generally speaking, the quality of rapid growth crystal is not as good as traditional growth crystal. A major reason is the large residual stress caused by rapid cooling rate. By releasing the residual stress through new annealing process, rapid growth crystal can get rid of its disadvantage and will be widely used as optical devices.

Conclusions

Thermal analysis, dielectric method and Raman spectroscopy analysis confirm the existence of HTPT in KD_2PO_4 . The results show strong evidence that KD_2PO_4 presents only one high temperature phase transition at about $T_{tr} = 430$ K much lower than the thermal decomposition temperature. None Raman shift attributable to dehydration product was observed in High Temperature Phase (HT-phase) of DKDP. It indicates that the HTPT had nothing to do with thermal decomposition. The structures of tetragonal DKDP and HT-monoclinic phase are similar. This makes temperature of HTPT in DKDP crystal much lower than that in KDP crystal. The ν_1 keeps constant before HTPT indicating that the hydrogen-deuterium exchange can be suppressed under protective ambient which helps improve the annealing temperature. According to the study of HTPT in DKDP crystal, new annealing method was conducted by using silicone oil as protective ambient under higher temperature up to 403K, thus improved the quality of DKDP crystal.

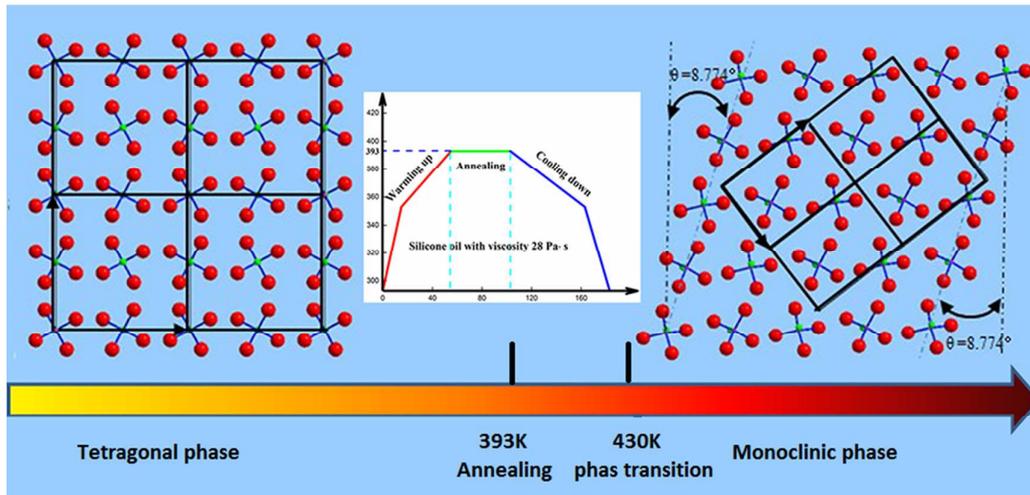
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Graphical Abstract



New annealing method was developed according to HTPT study, which improve the quality of DKDP crystal effectively.