

The effect of deuteration-levels in solution and temperature on the segregation coefficient of deuterium content in rapid-grown $K(D_xH_{1-x})_2PO_4$ crystals using Raman spectroscopy

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Picture of crystal

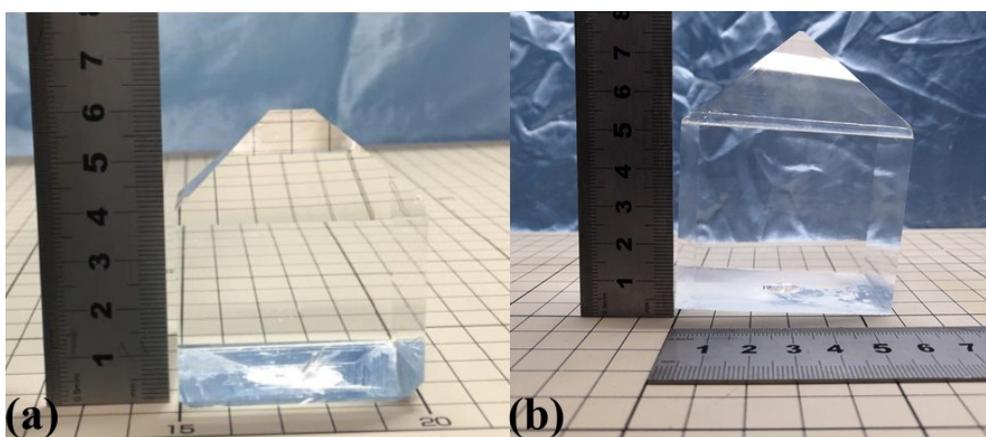


Fig. S1 (a) Picture of KDP; (b) Photograph of 98% DKDP.

Raman spectra

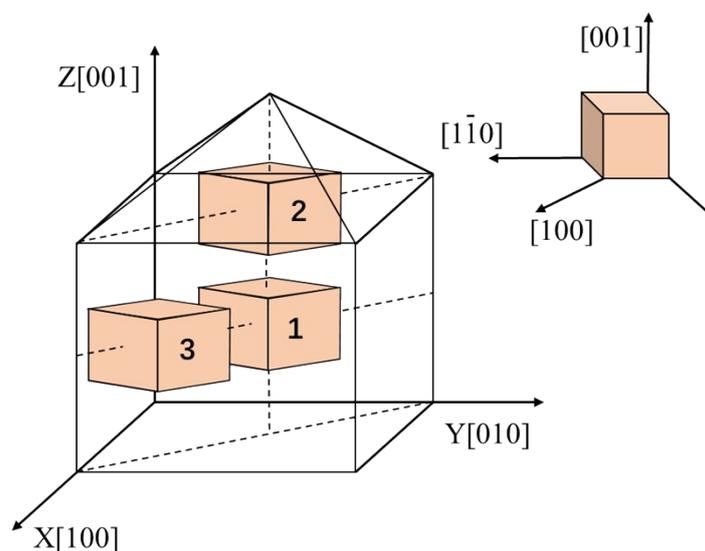


Fig. S2 Cutting diagram of DKDP samples performed for measurement; inset was cutting schematic for the crystal samples.

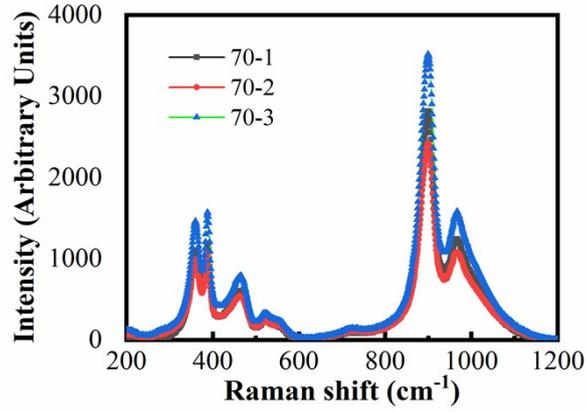


Fig. S3 Raman spectrum of 70% DKDP crystals.

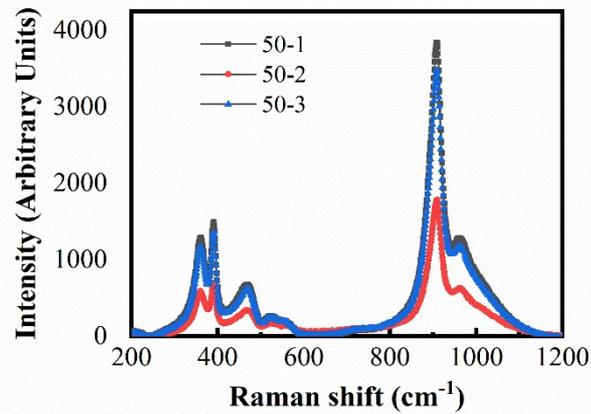


Fig. S4 Raman spectrum of 50% DKDP crystals.

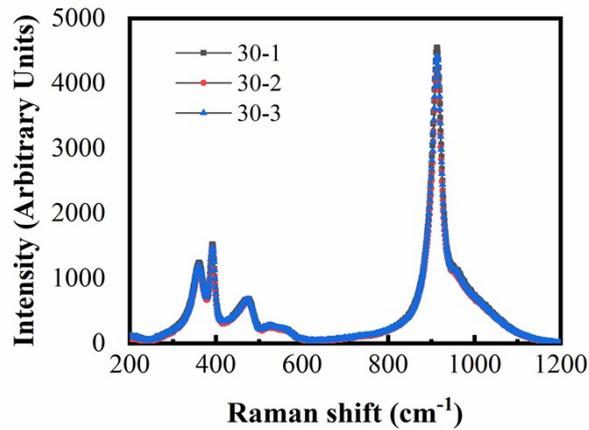


Fig. S5 Raman spectrum of 30% DKDP crystals.

Table S1. The deuterium content at different positions of the crystals.

Crystal & size/mm ³	Position	Temperature/°C	Dc/%
70%	1	46.8	50.56

63×51×70	2	45.2	50.32
	3	41.5	50.05
50% 53×56×49	1	47.3	26.76
	2	46.0	25.72
	3	43.2	28.22
30% 47×45×80	1	57.4	14.4
	2	55.8	14.4
	3	53.4	14.4

The segregation coefficient of deuterium of point seed rapid growth method depends on the temperature and the deuterium content in the solution, as the crystal grows, the temperature of the system will decrease, but the deuterium content in the solution will slightly increase. Therefore, the segregation coefficient will also change at different positions of the crystal, as shown in Table S1. For 70% DKDP and 30% DKDP, D_c in each position of the crystal is basically the same, the overall difference is not large. For 50% DKDP, the deuterium content of sample 3 increased slightly. This may be because the deuterium content in the solution will increase as the crystals grow. In this case, the fluctuation of the deuterium content in the solution has a greater effect on the coefficient, this is consistent with the trend in Fig. 4.

Raman peak assignments

KDP crystal belongs to point group D_{2d} , lattice vibration mode are the following:¹

$$\Gamma=11A_1+11A_2+13B_1+13B_2+24E \quad (1)$$

The Raman(R) and infrared(IR) active optical phonon modes are:¹

$$\Gamma_{\text{vib}}=11A_1(\text{R})+13B_1(\text{R})+12B_2(\text{R, IR})+23E(\text{R, IR}) \quad (2)$$

Raman spectrum measured from KDP single crystal as shown in Fig. S6.

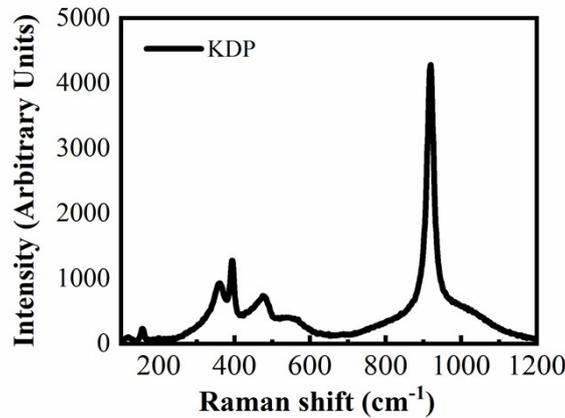


Fig. S6 Raman spectrum measured from KDP single crystal.

The H_2PO_4^- anion with the C_{2v} symmetry mainly has four characteristic vibrational modes as an

asymmetrical P(OH)₂ stretching vibration(ν_1), an in-plane P(OH)₂ bending vibration(ν_2), a PO₂ bending vibration(ν_3) and an in-plane PO₂ symmetrical stretching vibration(ν_4). Compared with results from previous literature,²⁻⁴ it is easy to determine the three internal vibration models of the H₂PO₄⁻ in KH₂PO₄ as 916cm⁻¹ (ν_1), 361cm⁻¹ (ν_2) and 1085 cm⁻¹(ν_4). 916 cm⁻¹(ν_1) belong to the symmetry species A₁. 156 cm⁻¹, 361 cm⁻¹(ν_2), 475 cm⁻¹(ν_2) and 569 cm⁻¹(ν_4) correspond to the symmetry species B₁, where 156 cm⁻¹ is the translation mode of K⁺ (T(K)).⁵ 393 cm⁻¹(ν_2) and 1085 cm⁻¹(ν_4) belong to the symmetry species B₂. 119 cm⁻¹(T(K)) and 569 cm⁻¹(ν_4) correspond to the symmetry species E. The Raman peaks measured from KDP are listed in the Table S2.

Table S2. Raman peaks measured from KDP(cm⁻¹).

Symmetry species	Wavenumber/cm ⁻¹	Assignment
A ₁	916	ν_1
B ₁	156	T(K)
	361	ν_2
	475	ν_2
	569	ν_4
B ₂	393	ν_2
	1085	ν_4
E	119	T(K)
	569	ν_4

Notes and references

1. P. Zhao, H. Xia, Z. Ling, P. Wang, Y. Su and Z. Zhang, *SPECTROSC SPECT ANAL*, 2007, **27**, 292-294.
2. F. Rull, A. Del Valle, F. Sobron and S. Veintemillas, *J RAMAN SPECTROSC*, 1989, **20**, 625-631.
3. Y. Tominaga, *Ferroelectrics*, 2010, **401**, 65-71.
4. G. Lu, H. Xia, J. Guan, S. Zhang, Y. Chen and Y. Zhou, *Chinese Journal of Light Scattering*, 2002, **14**, 4.
5. I. Kanesaka and C. Watanabe, *J RAMAN SPECTROSC*, 1998, **29**, 153-157.