Raman gains of ADP and KDP crystals*

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In this paper, the Raman gain coefficients of ammonium dihydrogen phosphate (ADP) and potassium dihydrogen phosphate (KDP) crystals are measured. By using a pump source of a 30-ps, 532-nm laser, the gain coefficients of ADP and KDP are 1.22 cm/GW, and 0.91 cm/GW, respectively. While for a 20-ps, 355-nm pump laser, the gain coefficients of these two crystals are similar, which are 1.95 cm/GW for ADP and 1.86 for KDP. The present results indicate that for ultra-violet frequency conversion, the problem of stimulated Raman scattering for ADP crystal will not be more serious than that for KDP crystal. Considering other advantages such the larger nonlinear optical coefficient, higher laser damage threshold, and lower noncritical phase-matching temperature, it can be anticipated that ADP will be a powerful competitor to KDP in large aperture, high energy third-harmonic generation or fourth-harmonic generation applications.

Keywords: ADP, KDP, stimulated Raman scattering, gain coefficient

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1. Introduction

Potassium dihydrogen phosphate (KDP) crystal has been widely used as a nonlinear optical (NLO) material in inertial confinement fusion (ICF) equipment. For ultra-violet (UV) frequency conversion, the transverse stimulated Raman scattering (TSRS) is a critical limiting factor for enhancing output energy and conversion efficiency. In the past several decades, many researchers have focused on the Raman properties of KDP crystals.[1–6] In fact, some ICF equipment, like the National Ignition Facility (NIF) of America, have used a partially deuterated KDP (DKDP) crystal to relieve the TSRS problem.[7]

In recent years, many advantages have been found in ammonium dihydrogen phosphate (ADP) crystal as compared with KDP crystal, such as larger nonlinear optical (NLO) coefficient, higher laser damage threshold, and bigger angular acceptance. Nevertheless, the stimulated Raman scattering (SRS) characteristics of ADP-type crystals must be evaluated first for practical applications. The spontaneous Raman scattering and SRS effect of ADP crystal have been reported before,[8,9] and the pump wavelength is visible (532 nm) or near infrared (1064 nm). In the present paper, by comparing the SRS property at third-harmonic generation (THG) wavelength of Nd:YAG laser (355 nm), we find that the UV Raman gains are very close for ADP and KDP crystals, further confirming the application potential of ADP-type crystals in UV NLO fields.

2. Spontaneous Raman scattering

Single crystals of ADP and KDP are grown from $NH_4H_2PO_4$ and KH_2PO_4 solution using the rapid crystal growth method.[10] In the growth process, the velocity of temperature-reduction is maintained to be 0.1 °C/day. The crystal rotated in the mode of "forward-stop-backward" with a speed of about 77 rpm.[11] The pristine crystals are carefully cut along the *a*, *b*, and *c* axes, each with a size of 17 mm×17 mm×14 mm with a precision of 1′, the specimens are then optically polished.

The experiments of spontaneous Raman scattering are conducted with a HR800 Raman spectrometer (France), the pump wavelength λ_p is 633 nm, and the results are shown in Fig. 1. The information about the spectral line near 920 cm^{-1} is also listed in Table 1. It attributes to the symmetrical vibration of $[PO_4]$ tetrahedron group. It can be seen that the line width $\Delta\Omega_{R(ADP)} = 28\ cm^{-1}$ and $\Delta\Omega_{R(KDP)} = 23\ cm^{-1}$. Compared with KDP, ADP exhibits a more intense and broader Raman line.

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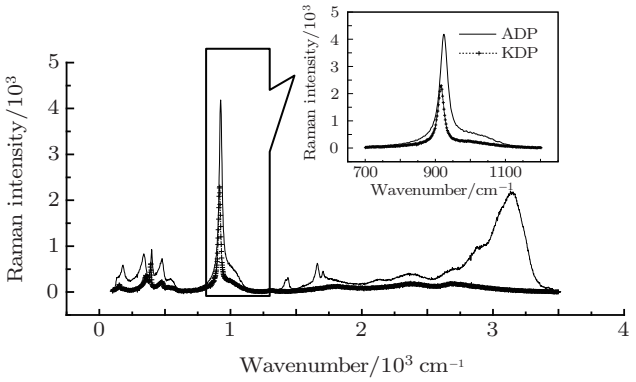


Fig. 1. Room temperature spontaneous Raman scattering spectra of ADP and KDP crystals. The inset shows the details in a range from 700 cm^{-1} to 1200 cm^{-1}, in which the solid line denotes ADP crystal and the dotted line denotes KDP crystal, respectively.

For steady state stimulated Raman scattering (SRS), the gain coefficient g_{SS} is determined by the Raman properties of a nonlinear medium[12]

$$g_{SS} = \frac{\lambda_p \lambda_s^2 N}{\hbar c \pi n_s^2 \Delta\Omega_R} \left(\frac{d\sigma}{d\Omega}\right), \quad (1)$$

where N is the number of scattering centers (here, $N_{ADP} = 0.944 \times 10^{22}$ molecules/cm^3, $N_{KDP} = 1.035 \times 10^{22}$ molecules/cm^3), λ_p and λ_s are the pump and Stokes wavelengths ($\lambda_p = 633$ nm, $\lambda_{s(ADP)} = 730.14$ nm, $\lambda_{s(KDP)} = 671.96$ nm), n_s is the refractive index at $\lambda_s (n_{s(ADP)} = 1.5202$ at 672.32 nm, $n_{s(KDP)} = 1.5060$ at 671.96 nm) and $d\sigma/d\Omega$ is the Raman scattering cross section. Thus, referencing to Table 1 the steady state Raman gain coefficients of ADP and KDP crystals at 633-nm pump condition can be calculated, and the result of $g_{SS(ADP)}$ is 1.58 times larger than that of $g_{SS(KDP)}$. On the other hand, the value of the product $(d\sigma/d\Omega)(\Delta\Omega_R)^{-1}$ can be characterized as a peak intensity Σ_{peak} in the measured spontaneous Raman scattering spectrum[12]

$$\Sigma_{peak} \propto (d\sigma/d\Omega)(\Delta\Omega_R)^{-1}. \quad (2)$$

From Table 2 and Eq. (2), it follows that

$$\Sigma_{peak(ADP)}/\Sigma_{peak(KDP)} = 1.76.$$

by using Eqs. (1) and (2), the result of $g_{SS(ADP)}/g_{SS(KDP)}$ can be obtained to be 1.58.

Table 1. Raman spectroscopic parameters of ADP and KDP crystals.

Material	Raman freq./cm^{-1}	Raman linewidth/cm^{-1}	Scattering cross section/a.u.
ADP	924	28	100[a]
KDP	916	23	46.5

[a]The scattering cross section of ADP crystal is set as the integral intensity of the spectral line near 920 cm^{-1}, and its reference value is 100.

3. Stimulated Raman scattering

The apparatus of the stimulated Raman scattering experiment is shown in Fig. 2. The light source is a mode-locked Nd:YAG laser (PY61C-10 type, Continuum), which supplies 1064-nm, 40-ps laser pulses with a repetition rate of 10 Hz. B is a frequency converter system, which can produce 532-nm or 355-nm laser. PP1 and PP2 are Glan–Taylor prisms which provide smooth variation of pump energy. F1 and F2 are two integral diaphragms. A beam compression system is marked by T, which consists of two convex lenses to increase the energy intensity of pump light by compressing the diameter of light spot. Then the laser beam is transmitted into the Raman medium (D), i.e., ADP or KDP crystal. The component S is a beam splitter which connects to an energy meter (LPE-1C). For the SRS spectrum measurement, we use the spectrometer probe (P) and a USB fiber optic spectrometer (HR4000CG-UV-NIR, Ocean Optics Inc.) with a receiving screen. The spectrometer has a wavelength resolution of 0.2 nm, and its sensitivity is 60 photons/count at 600 nm around.

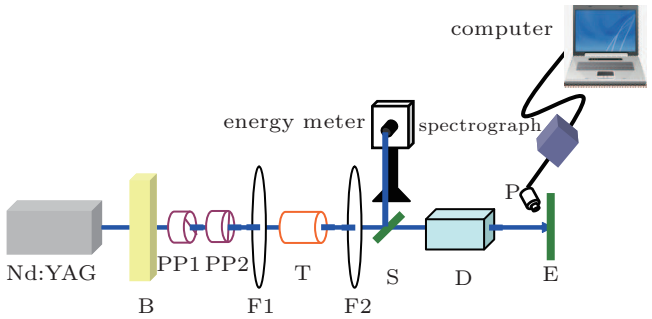


Fig. 2. (color online) SRS experimental set-up composed of (B) frequency converter system, (PP1, PP2) Glan–Taylor prisms, (F1, F2) diaphragms, (T) beam compression system, (S) beam splitter, (D) Raman medium, (E) screen, and (P) spectrometer probe.

The polarization geometry is $Z(XX)Z$. When the image like Fig. 3 is observed by the spectrometer, the input pump intensity is considered to be the threshold of the first Stokes line. This judging method is exactly the same as that described in Ref. [13]. In our SRS experiments, the durations of the pump laser τ_p are 30 ps for 532 nm, and 20 ps for 355 nm. The phonon relaxation time $T_R = (\pi c \Delta\Omega_R)^{-1} = 0.366$ ps (ADP) and 0.461 ps (KDP), where c is the velocity of light. So the steady state SRS condition $\tau_p \gg T_R$ is fulfilled in our experiments, and the steady state Raman gain coefficient could be calculated from the measured pump thresholds.

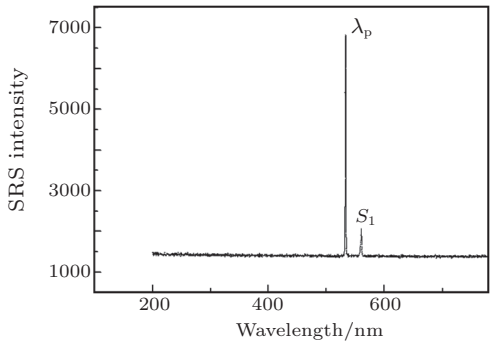


Fig. 3. Stimulated Raman scattering spectrum featuring the occurrence of the first Stokes line S_1 when the pump wavelength is 532 nm.

In the steady state case, if there is no pump depletion, then the solution for the Stokes intensity is exponential[14]

$$I_S(l) = I_S(0)\exp(g_{ss}I_p l), \tag{3}$$

where $I_S(0)$ is the intensity of the Stokes wave at the input end face, g_{ss} is the Raman gain coefficient, I_p is the intensity of the pump light, and l is the length of interaction between the laser and Raman medium. When the pump intensity I_p reaches the SRS threshold I_{th}, the exponential value of Eq. (3) will meet $G = g_{ss}I_L l = 25$.[14] From this equation, the steady state Raman gain coefficient g_{ss} can be calculated, and the results are shown in Table 2. It can be seen that for both of the crystals the Raman gain coefficient decreases with the increase of pump wavelength. At visible waveband (532 nm, 633 nm) $g_{ss(ADP)}$ is obviously larger than $g_{ss(KDP)}$, while at ultra-violet waveband (355 nm) $g_{ss(ADP)}$ is close to $g_{ss(KDP)}$.

Table 2. Values of Raman gain coefficient g_{ss} of ADP and KDP crystals.

Pump wavelength/nm	$g_{ss(ADP)}$	$g_{ss(KDP)}$	$g_{ss(ADP)}/g_{ss(KDP)}$	Origin
355	1.95	1.86	1.05	stimulated Raman scattering
532	1.22	0.91	1.34	stimulated Raman scattering
633	–	–	1.58	spontaneous Raman scattering

4. Discussion

At room temperature, both ADP and KDP crystals have the same point group D_{2d}, which belongs to space group $I\bar{4}2d$ (see Fig. 4). But the bonds in the structures of these two crystals are very distinct, which can be seen in Fig. 5.[15] The hydrogen bonds (dashed lines in Fig. 5), which link the neighboring $(H_2PO_4^-)$ groups, and the chemical bonds inside $(H_2PO_4^-)$ groups (solid lines between P, O, and H atoms in Fig. 5), are very similar in these two isomorphs, i.e., the numbers, lengths, strengths, directions of the bonds in the two groups are approximately the same. However, the bond strengths between the

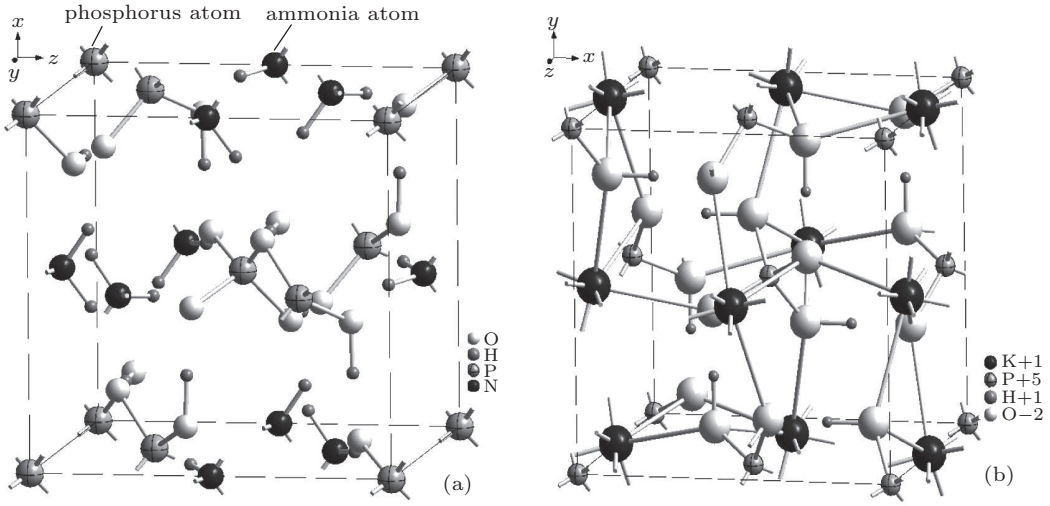


Fig. 4. Spatial structures of ADP crystal (a) and KDP crystal (b).

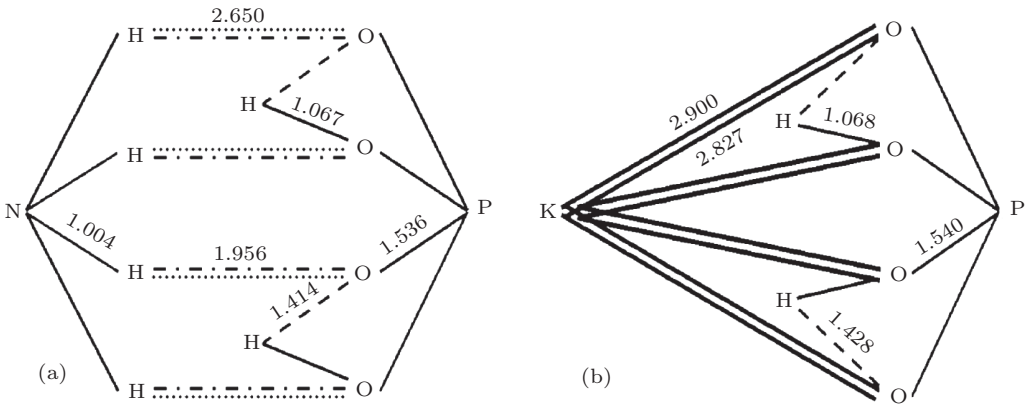


Fig. 5. Bond structures of ADP (a) and KDP (b) crystals,[15] All of the chemical bonds are represented by different kinds of lines labeled with bond length (Å).

adjacent anions ($H_2PO_4^-$) and cations (NH_4^+, K^+) are very different, while the bond number and bond direction are still analogous. The strong K–O ionic bond is substituted with a weaker N–H$\cdots$O hydrogen bond in ADP structure than in KDP. Such a difference in structure makes a larger Raman mode frequency of ADP than that of KDP (see Table 1), which could be responsible for slowing down the dephasing processes and reducing the homogenous linewidth.[12,16]

5. Conclusions

In this paper, the Raman gain coefficients of ADP and KDP crystals are compared with each other. The results show that although in the visible waveband $g_{ss(ADP)}$ is obviously larger than $g_{ss(KDP)}$, for the ultra-violet THG wavelength of Nd:YAG laser (355 nm) $g_{ss(ADP)}$ is almost the same as $g_{ss(KDP)}$. From the variation trend we can speculate that at the FHG wavelength 266-nm $g_{ss(ADP)}$ is very likely to be smaller than $g_{ss(KDP)}$, which needs more experiments to be confirmed. The present research results show that in the UV light region the SRS effect of ADP is comparable to or even weaker than that of KDP. The present research results also show that, as a powerful competitor to KDP crystal, ADP crystals could be used in large aperture THG or FHG processes.

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