

Luminescence of the hydrogen bonded crystals

I.N. Ogorodnikov^{a,*}, M. Kirm^b, V.A. Pustovarov^a

^a*Ural State Technical University, 19, Mira Street, 620002 Ekaterinburg, Russia*

^b*Institute of Physics, University of Tartu, 142, Riia Street, 51014 Tartu, Estonia*

Received 18 December 2006; accepted 1 February 2007

Abstract

A complex investigation of the dynamics of electronic excitations in the hydrogen bonded crystals of potassium and ammonium dihydrophosphates— KH_2PO_4 (KDP) and $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP)—is performed by the means of the low-temperature time-resolved vacuum ultraviolet (VUV) optical luminescence spectroscopy with subnanosecond time resolution and with selective photoexcitation by synchrotron radiation. For KDP and ADP crystals, data on the kinetics of the photoluminescence (PL) decay, the time-resolved PL spectra (2–6.2 eV), and the time-resolved excitation PL spectra (4–24 eV) at 8 K were obtained. The intrinsic character of the PL of KDP (5.2 eV) and ADP (4.7 eV), which is caused by the radiative annihilation of self-trapped excitons (STEs), is ascertained. Possible channels of generation and decay of relaxed and unrelaxed electronic excitations in KDP and ADP crystals are discussed.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: KH_2PO_4 (KDP); $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP); Self-trapped exciton; Time-resolved luminescence; Excitation spectra

1. Introduction

Nonlinear optical crystals of potassium and ammonium dihydrophosphates— KH_2PO_4 (KDP) and $\text{NH}_4\text{H}_2\text{PO}_4$ (ADP)—are used in short-wavelength laser technology and nonlinear and integrated optics (Rashkovich, 1991). Crystalline KDP is an ferroelectric with the Curie temperature $T_c = 123$ K, whereas ADP is an antiferroelectric with $T_c = 148$ K. Below T_c , KDP and ADP belong to the orthorhombic system with the point symmetry group. Both crystals have similar lattices, which consist of phosphate groups of two types with different orientations. Each PO_4 group is linked with four neighbouring PO_4 groups by hydrogen bonds. Hydrogen bonds play an important role in the migration of electronic excitations and the energy transfer between phosphate groups. The low energy tails of fundamental absorption (FA) of KDP and ADP are located at 180 nm in the vacuum ultraviolet (VUV) spectral range. Therefore, despite the long-term investigations and wide practical application of KDP and ADP, only a few works

are known (Baldini et al., 1972; Saito et al., 1974) in which these materials were studied by the means of the optical VUV spectroscopy.

The main goal of the present study was to investigate the dynamics of electronic excitations and luminescence in KDP and ADP crystals using a low-temperature VUV luminescence and optical spectroscopy with time resolution upon selective excitation with synchrotron radiation.

2. Experimental details

The time-resolved photoluminescence (PL) spectra (2–6.2 eV), the time-resolved PL excitation spectra (3.5–24 eV), and the time-resolved PL decay kinetics were studied at the SUPERLUMI station of HASYLAB using selective excitation with synchrotron radiation. Time-resolved spectra were measured in a time window with width Δt , delayed with respect to the beginning of the excitation pulse by δt . In this study, we performed simultaneous measurements in two time windows: a fast component ($\delta t_1 = 1.2$ ns, $\Delta t_1 = 12$ ns) and a slow component ($\delta t_2 = 230$ ns, $\Delta t_2 = 167$ ns). Simultaneously, time-integrated PL spectra were recorded. The other experimental details were the same as reported by us earlier (Ogorodnikov et al., 2004).

* Corresponding author. Tel.: +7 343 375 4711; fax: +7 343 374 3884.

E-mail address: ogo@dpt.ustu.ru (I.N. Ogorodnikov).

We used KDP and ADP single crystals of high optical quality grown at Issyk-Kul State University (Karakol, Kyrgyzstan). The samples were prepared in the form of plane-parallel plates $7 \times 7 \times 1 \text{ mm}^3$ in size with polished laser-quality surfaces oriented perpendicular to the crystallographic axis c .

3. Results and discussion

Excitation of ADP crystals by photons with energies in the vicinity of the low energy tail of FA at 8 K leads to the occurrence of intense PL mainly in two Gaussian bands at 2.6 eV (full-width at half-maximum (FWHM) = 0.47 eV) and 4.7 eV (FWHM = 0.93 eV) (Fig. 1). Heating to temperatures above 20 K leads to similar thermal quenching of both bands. Comparison of the time-resolved PL spectra (Fig. 1) indicates that the PL bands related to the fast and time-integrated components have similar shapes; the PL of ADP at 8 K is mainly due to the fast component (time window Δt_1), and the contribution of the slow component is relatively small.

The excitation spectrum of the PL band at 4.7 eV is located in the FA region of ADP (Fig. 2). The low energy falloff of the excitation spectrum of the fast component (time window Δt_1) coincides with the low energy tail of FA of ADP and the excitation has highest efficiency at $h\nu = 7.3 \text{ eV}$. The optical absorption coefficient of ADP at this energy is about 2000 cm^{-1} (Baldini et al., 1972). With a further increase in $h\nu$ to 9.3 eV, the efficiency of excitation of the 4.7 eV PL band decreases by more than a factor of 10, remaining at this level up to $h\nu = 22 \text{ eV}$. Saito et al. (1974) showed that the energy range from 8.5 to 9 eV corresponds to the beginning of interband transitions in ADP.

The excitation spectrum of the slow component of the 4.7 eV PL band (time window Δt_2) has another shape. In the vicinity of the low energy tail of FA, the excitation spectrum is a wide band peaked at $h\nu = 9.7 \text{ eV}$ (Fig. 2).

The 2.6 eV PL band of ADP crystals is efficiently excited at 8 K both in the region of optical transparency and in the FA region. The bands peaked at 5.2, 6.2, and 9.7 eV are dominant in the excitation spectrum (Fig. 2). In the FA region, the excitation spectrum of the 2.6 eV PL band has the same shape as that for the slow component of the 4.7 eV PL band (Fig. 2). Upon excitation in the transparency region, the character of the 2.6 eV PL band of ADP changes. In this case, the contribution of the slow component to the PL is dominant (Fig. 1). The PL spectrum of the slow component is a band peaked at 2.7 eV (FWHM = 0.62 eV) with a shoulder at 2.2 eV. In addition to these bands, the PL spectrum of the fast component contains a weak band near 3.5 eV (Fig. 1).

The PL decay kinetics includes two fast exponential components with time constants τ_1 and τ_2 in the nanosecond time-range and superposition of relatively slow components in the micro- and millisecond time-ranges, which manifests itself as a constant-level background (pedestal) in our measurements (Fig. 3). The numerical values of the kinetics parameters depend on $h\nu$. Upon photoexcitation in the region of creation of free excitons ($h\nu = 7.4 \text{ eV}$), both PL bands (at 2.6 and 4.7 eV) are characterized by the decay kinetics with the identical parameters: $\tau_1 = 7 \text{ ns}$, $\tau_2 = 15 \text{ ns}$, the contribution of the pedestal to the total optical sum is 10–15%. Upon excitation in the transparency region, the decay kinetics of the 2.6 eV PL band has another parameters: $\tau_1 = 1.7 \text{ ns}$, $\tau_2 = 7 \text{ ns}$, the pedestal contribution is 80–85%.

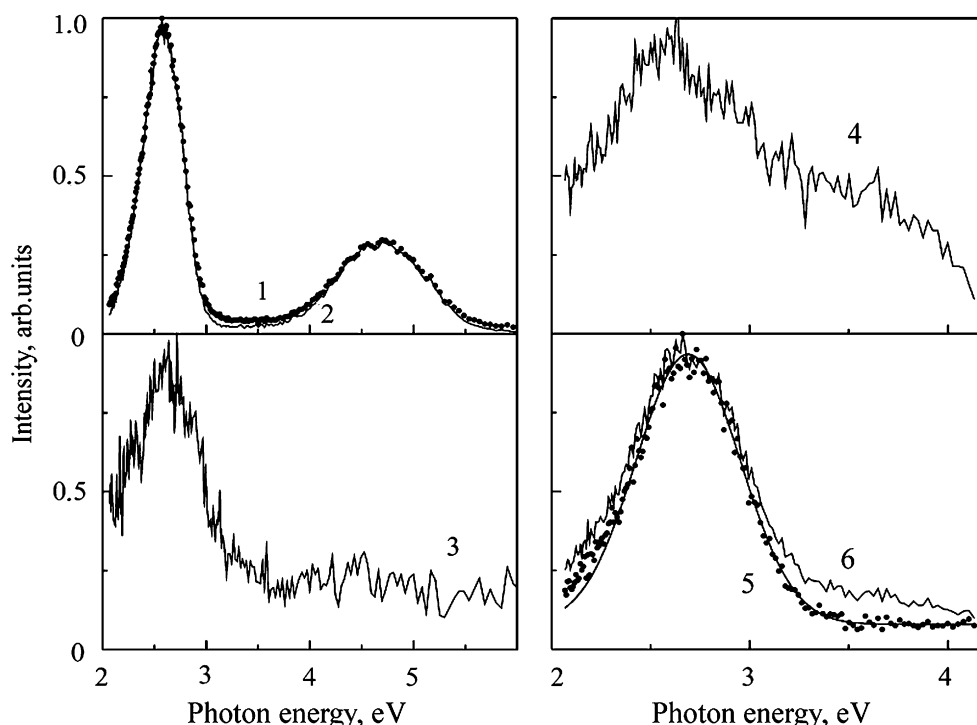


Fig. 1. Normalized spectra of the (1, 6) time-integrated, (2, 4) fast, and (3, 5) slow components of the PL of ADP at $T = 8 \text{ K}$ and $h\nu = 7.4 \text{ eV}$ (1–3) and 6.2 eV (4–6).

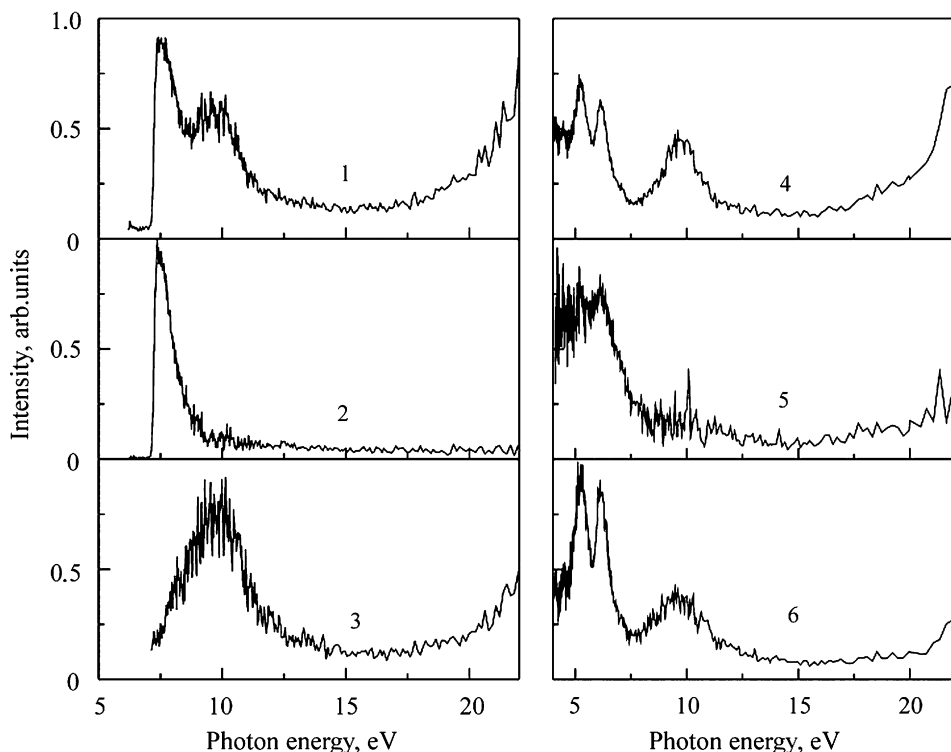


Fig. 2. Normalized excitation spectra of the (1, 4) time-integrated, (2, 5) fast, and (3, 6) slow components of the (1–3) 4.7 eV, and (4–6) 2.6 eV PL bands of ADP at $T = 8$ K.

Analysis of our results (Figs. 1 and 2), the data of Ogorodnikov et al. (2001, 2003, 2004) and Diéguez et al. (1984) showed that, at temperatures below 50 K, PL bands at 2.5–2.6 eV and PL bands at 4.7–5.2 eV with similar properties are observed in the PL spectra of undoped KDP and ADP crystals. At low temperatures, these bands are dominant both in the PL spectra upon photoexcitation in the FA region and in the X-ray induced luminescence spectra. The temperature quenching of both bands in the spectra of ADP and KDP crystals occurs in the same way above 20 K. Ogorodnikov et al. (2001, 2003, 2004) showed that these PL bands in KDP have an intrinsic origin. Similarity of these systems leads us to the opinion that the 2.6 and 4.7 eV PL bands in the ADP crystals can have similar origin. Let us to discuss this in more details.

The low-temperature broadband luminescence of ADP crystals at 4.7 eV has the following characteristic features: a large (2.6 eV) Stokes shift, the absence of selective photoexcitation bands in the transparency region of ADP, the excitation of PL only in the FA region of ADP, the highest efficiency of photoexcitation near the low energy tail of FA, the presence of exponential components in the PL decay kinetics, the absence of luminescence ‘freezing’ upon cooling to 8 K, and no direct correlation between the luminescence and the presence of particular defects in ADP crystals. The large value of the Stokes shift and the wide luminescence band unambiguously indicate the local character of the luminescence, strong electron–phonon interactions, and the significant lattice relaxation on localization of electronic excitations. Such features are characteristic of the luminescence due to the radiative annihilation of

self-trapped excitons (STEs). Ogorodnikov et al. (2003, 2004) revealed previously an STE luminescence with similar properties in KDP, which belongs to the same family as ADP. The characteristics of the 4.7 eV PL band of ADP (Figs. 1–3) correlate well with the characteristics of the STE luminescence band of KDP (Ogorodnikov et al., 2004). Thus, the low-temperature PL band of ADP at 4.7 eV has also the same origin arising from the radiative annihilation of STEs.

The similarity of the PL spectra of ADP and KDP crystals is due to the features of their crystallographic and electronic structure. Crystallographically, these are isomorphous crystals. At temperatures below the Curie point, the electronic structure of ADP and KDP crystals is determined mainly by the anionic H_2PO_4 group. Saito et al. (1974) and Stasyuk and Stetsiv (1991) showed that the upper occupied molecular orbitals of this anionic group, whose energy positions correspond to the top of the valence band of ADP and KDP, are formed from almost pure $2p\pi$ oxygen orbitals, while the lowest unoccupied orbitals, corresponding to the bottom of the conduction band, are formed of $1s$ hydrogen orbitals. The electronic transition with the lowest energy in the H_2PO_4 group is due to the transfer of an electron between these levels. Baldini et al. (1972) and Saito et al. (1974) suggested an excitonic origin of the low energy tail of the FA band of ADP and KDP. Low-temperature experiments revealed self-trapping of holes with formation of $[\text{H}_2\text{PO}_4]^0$ -radicals (so-called *B*-radicals) in ADP and KDP crystals (Diéguez et al., 1984; Stevens et al., 1999). The existence of self-trapped holes is a strong evidence in favor of self-trapping of excitons in these crystals since self-trapped

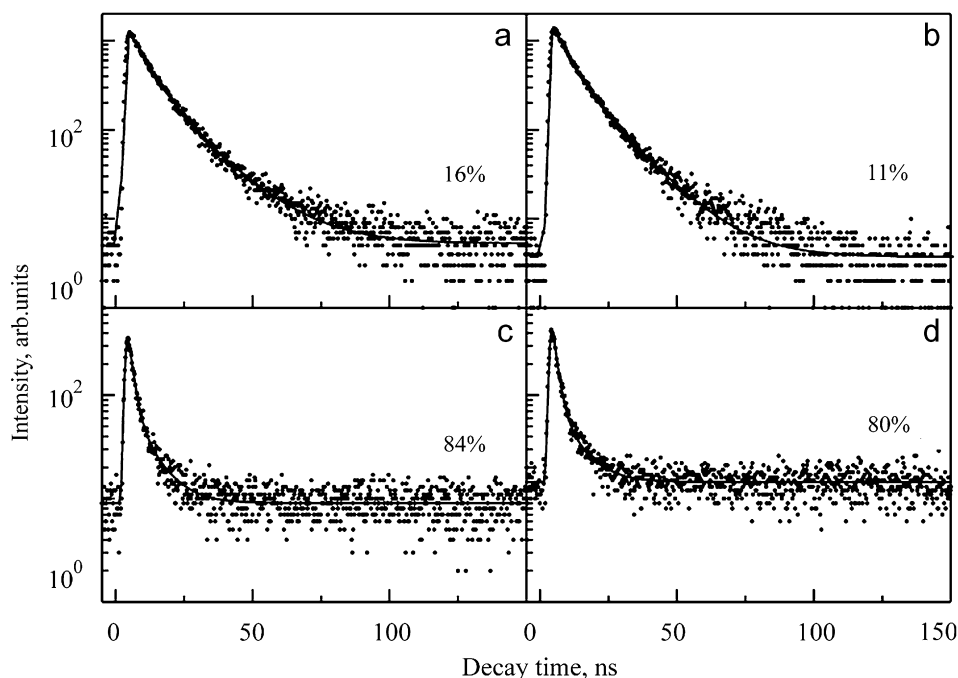


Fig. 3. The PL decay kinetics at (a) 4.7 and (b, c, d) 2.5 eV for an ADP crystal at $T = 8$ K and $h\nu =$ (a, b) 7.4, (c) 6.2, and (d) 5.2 eV. The contribution (in %) of the background to the total optical sum is noted.

holes can serve as hole nuclei for STEs. Formation of STEs may occur not only via self-trapping of free excitons formed upon photoexcitation in the intrinsic absorption but also as a result of recombination of electrons at self-trapped holes. The radiative annihilation of such STEs leads to a characteristic broadband luminescence with a large Stokes shift. This is the reason for the identical nature of the 4.7 eV PL bands of ADP and KDP crystals.

4. Conclusions

We attribute the fast component of the PL band at 4.7 eV to dipole-allowed radiative singlet–singlet transitions in STEs. The decrease in the excitation efficiency of the fast PL component at $h\nu > 7.3$ eV is due to the increase in the non-radiative energy loss as a result of the migration of free excitons. The intensity of triplet–singlet radiative transitions in ADP is lower than in KDP. Therefore, the slow-component band manifests itself rather weakly in the PL spectra, while, in the excitation spectra, the very weak band of triplet excitons expected below the energy gap E_g is not resolved against the background of competing processes. In our opinion, the excitation band at 9.7 eV is due to the formation of geminate electron-hole pairs as it has been clearly established even for free exciton formation through such process in solid Kr (Kisand et al., 2003). Such pairs are formed at the interband transitions with the lowest energies, i.e., upon excitation of photons with energies equal to or slightly exceeding E_g . It is noteworthy that the temperature-independent auto-ionization of excitons may lead to the formation of electron-hole pairs with energies below E_g in the region of formation of free excitons. The holes in these

pairs have a large translational mass and can be self-trapped to form *B*-radicals. The recombination of electrons at the *B*-radicals finally results in the formation of a lower excited triplet STE state. Therefore, the slow PL component at 4.7 eV tentatively assigned to the subsequent radiative annihilation of such STEs. But it cannot be completely excluded that this component is resulting from some other recombination process. With a further increase in the excitation energy above E_g , a paired electron acquires a kinetic energy sufficient to overcome the Coulomb barrier of the heavy hole. After the decay of such pair at 8 K, the released electron becomes localized at available trapping centres and the hole becomes self-trapped. This leads to a decrease in the PL excitation efficiency above 9.7 eV due to the accumulation of charge carriers available at trapping centres (Fig. 2). Diéguez et al. (1984) showed that, at temperatures of about 70 K, thermally induced detrapping of *B*-radicals, accompanied by thermally stimulated luminescence occurs in KDP and ADP crystals. The peak of thermally stimulated luminescence at 70 K is due to the recombination of holes at the electron centres. The spectrum of thermally stimulated (hole recombination) luminescence consists of a band peaked at 3.5 eV (Diéguez et al., 1984).

Along with the *B*-radicals, preexisting intrinsic lattice defects (so-called *A*-radicals $[\text{HPO}_4]^-$) are also present in KDP and ADP crystals. An *A*-radical is a hole localized at a $2p\pi$ oxygen orbital in the vicinity of a hydrogen vacancy. In our opinion, the PL band at 2.6 eV of ADP crystals is due to the recombination of electrons at the *A*-radicals. The following arguments are in favour of this hypothesis. The *A*-radicals, being intrinsic lattice defects, are present in any nominally undoped ADP and KDP crystals. In the FA region, the excitation

spectrum of the 2.6 eV PL band is the same as for the recombination mechanism of excitation of the slow STE PL component (Fig. 2). The PL spectrum does not contain any bands typical for the hole recombination luminescence. The local level of the hole centre of the *A*-radical is formed near the level of the hydrogen vacancy by splitting off of states at the top of the valence band to the conduction band. The local level of the self-trapped hole in the *B*-radical has the same partial electronic structure. This circumstance is responsible for the identical character of electron recombination at *A*- and *B*-radicals, which leads to the generation of an electronic excitation: a hole at the $2p\pi$ orbitals of oxygen and an electron at the $2s$ levels of hydrogen, which form a state at the conduction band bottom. The differences in the positions of the hole centres (*A*- and *B*-radicals) on the energy scale and the presence of a hydrogen vacancy in the vicinity of an *A*-radical cause the differences in the lattice relaxation and, therefore, to the different Stokes shifts observed for the luminescence bands at 2.6 and 4.7 eV.

The centres causing the 2.6 eV PL band when excited in the transparency region of ADP crystals (Fig. 1) have another nature. Indeed, the luminescence centres based on the cation vacancies (including *A*-radicals) generally do not show any excitation bands in the transparency region of a crystal. As discussed earlier, the spectral parameters of the 2.6 eV PL band upon excitation in the transparency region (Fig. 1) differ from those for the case of excitation in the fundamental absorption (FA) region (Fig. 1). The PL decay kinetics is also different for these two cases (Fig. 3). The model considering a luminescence centre excited in the transparency region of a crystal as a hydrogen vacancy associated with a heterovalent impurity yields the most adequate results. The undoped crystals of the KDP family always contain unintentional impurities of the iron group and the compensation of an excess charge upon introduction of heterovalent impurities occurs by formation of a corresponding number of hydrogen vacancies in the vicinity of an impurity. The results (Kuanyshev et al., 1999) of studies of the PL from ADP and KDP crystals doped with heterovalent

impurities with different concentrations are in favour of this model for luminescence centres.

Acknowledgement

The work was supported by RFBR (05-02-16530).

References

- Baldini, G., Cottini, M., Grilli, E., 1972. Ultraviolet reflection and absorption of KH_2PO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$ crystals. *Solid State Commun.* 11, 1257–1260.
- Diéguez, E., Cabrera, J.M., Agulló López, F., 1984. Optical absorption and luminescence induced by X-rays in KDP, DKDP, and ADP. *J. Chem. Phys.* 81, 3369–3374.
- Kisand, V., Kirm, M., Negodin, E., Sombrowski, E., Steeg, B., Vielhauer, S., Zimmerer, G., 2003. Creation of free excitons in solid krypton investigated by time-resolved luminescence spectroscopy. *J. Phys.: Condens. Matter.* 15, 2023–2032.
- Kuanyshev, V.T., Ogorodnikov, I.N., Kidibaev, M.M., 1999. Problems in Spectroscopy and Spectrometry. Urals State Technical University, Ekaterinburg. 2, 49–51 (in Russian).
- Ogorodnikov, I.N., Pustovarov, V.A., Shulgin, B.V., Kuanyshev, V.T., Satybaldieva, M.K., 2001. Low-temperature time-resolved vacuum ultraviolet luminescent spectroscopy of KDP crystals with defects. *Opt. Spectrosc.* 91 (2), 224–231.
- Ogorodnikov, I.N., Kirm, M., Pustovarov, V.A., Cheremnykh, V.S., 2003. Low-temperature time-resolved vacuum ultraviolet spectroscopy of self-trapped excitons in KH_2PO_4 crystals. *Opt. Spectrosc.* 95 (3), 385–389.
- Ogorodnikov, I.N., Kirm, M., Pustovarov, V.A., Cheremnykh, V.S., 2004. A time resolved luminescence spectroscopy study of self-trapped excitons in KH_2PO_4 crystals. *Radiat. Meas.* 38 (3), 331–334.
- Rashkovich, L.N., 1991. KDP-family Single Crystals. Hilger, Bristol.
- Saito, S., Wada, K., Onaka, R., 1974. Vacuum ultraviolet reflection spectra of KDP and ADP. *J. Phys. Soc. Japan* 37, 711–715.
- Stasyuk, I.V., Stetsiv, R.Ya., 1991. Electronic states and optical effects in the hydrogen bonded crystals KDP. *Izv. Akad. Nauk SSSR. Ser. Fiz.* 55, 522–525 (in Russian).
- Stevens, K.T., Garces, N.Y., Halliburton, L.E., Yan, M., Zaitseva, N.P., De Yoreo, J.J., Catella, G.C., Luken, J.R., 1999. Identification of the intrinsic self-trapped hole center in KD_2PO_4 . *Appl. Phys. Lett.* 75 (11), 1503–1505.