Available online at www.sciencedirect.com
ScienceDirect
Radiation Measurements 42 (2007) 746–750
Radiation Measurements
www.elsevier.com/locate/radmeas

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 $NH_4H_2PO_4$ (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.

Keywords: KH_2PO_4 (KDP); $NH_4H_2PO_4$ (ADP); Self-trapped exciton; Time-resolved luminescence; Excitation spectra

1. Introduction

Nonlinear optical crystals of potassium and ammonium di hydrophosphates—KH_2PO_4 (KDP) and $NH_4H_2PO_4$ (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).

1350-4487/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.radmeas.2007.02.004

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 $7 \times 7 \times 1\,mm^3$ 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 $h\nu = 7.3$ 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 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 $h\nu = 9.7$ 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 eV), both PL bands (at 2.6 and 4.7 eV) are characterized by the decay kinetics with the identical parameters: $\tau_1 =$ 7 ns, $\tau_2 = 15$ 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: $\tau_1 = 1.7$ ns, $\tau_2 = 7$ ns, the pedestal contribution is 80–85%.

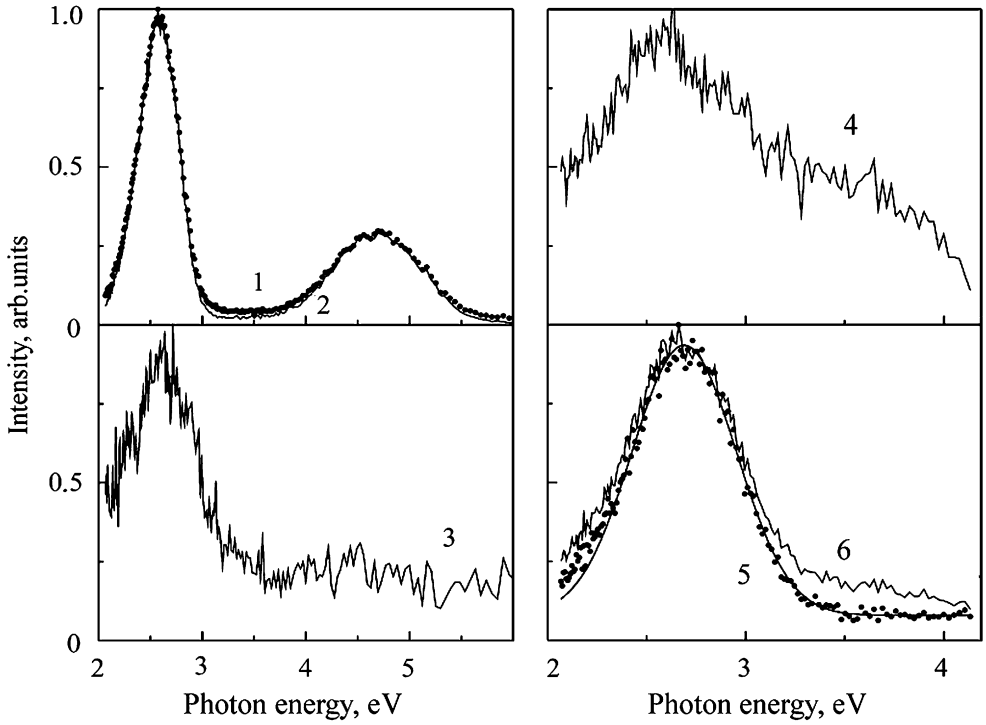

Fig. 1. Normalized spectra of the (1, 6) time-integrated, (2, 4) fast, and (3, 5) slow components of the PL of ADP at $T = 8$ K and $h\nu = 7.4$ eV (1–3) and 6.2 eV (4–6).