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A luminescence and absorption spectroscopy study of KH_2PO_4 crystals doped with Tl^+ ions

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ABSTRACT

We report experimental study on luminescence and optical properties of single crystals KH_2PO_4 (KDP) doped with Tl^+ ions (KDP:Tl) carried out at 10–480 K. The 4.5 eV photoluminescence (PL) of KDP:Tl originates from radiative electronic transitions $^3P_1 \rightarrow {^1S_0}$ in the Tl^+ ions upon excitation by UV-photons, X-rays, and electron beam. This luminescence can be induced by direct photoexcitation, or through the recombination process with participation of the lattice defects located in the vicinity of Tl^+ ion. These excitation mechanisms lead to different temperature behavior of the luminescence intensity. The PL excitation spectra of KDP crystals containing a small amount of the Tl^+ ions (0.001–0.008 wt.%) comprises peaks at 5.7–5.8, 6.9, and 7.3–7.4 eV, corresponding subsequently to the *A*-, *B*- and *C*-optical transitions in Tl^+. The PL time response has single-exponential behavior with an average lifetime of $\tau = 280 \pm 8$ ns. Under exposure to ionizing radiation (X-rays, or electron beam) the intensity of the Tl^+ luminescence increases depending on the exposure time. The origin of this phenomenon was associated with creation of defects in the hydrogen sublattice of KDP.

1. Introduction

Potassium dihydrogen phosphate KH_2PO_4 (KDP) in the crystalline form is a well known optical material, which was successfully used in many areas of applications, including nonlinear and integrated optics, laser technology. This material is successfully utilized in many kinds of optical devices such as non-linear optical elements, electro-optical polarizers, solid state detectors and transformers of radiation, operating in a broad spectral range from the middle infrared to the vacuum ultraviolet (VUV) spectral regions [1]. It is important that dihydrogen phosphate crystals (in particular, KDP) are a very unique inorganic material with a high content of hydrogen ions (protons) in the crystal lattice. In this regard, KDP holds great promise for use in radiation detectors of neutrons. Many research works last 30 years were devoted to studying the luminescent properties of KDP in the visible and ultraviolet (UV) spectral ranges, see e.g. [2]. These results show that KDP at temperatures below 20 K exhibits an intense intrinsic luminescence, which however is subject to thermal quenching when heated. The main reason is related to the thermal creation of defects in the hydrogen sublattice of KDP, which are the centers of an efficient non-radiative recombination for free electrons and holes [3,4].

In this connection, many research works have been focused on a study of the doped KDP crystals. However, the concentration of intrinsic defects in the hydrogen sublattice is far exceed possible concentration of any impurity in KDP. This makes extremely inefficient any transfer of energy from the matrix to the impurity at temperatures above 20 K. The thallium impurity in KDP seems to be the only dopant, which able to accept the energy transferred after non-radiative recombination of electrons and holes at the defects in the hydrogen sublattice of KDP [5].

The thallium impurity ion is known as an activator that forms s^2 centers in cubic alkali halide crystals [6–8]. Owing to the large optical transparency band ($E_g \approx 8.8$ eV), KDP is a unique noncubic host system, where the s^2 centers of Tl^+ ion can exhibit several UV-absorption bands, which allow study of various interactions between the impurity ion and the host lattice [7,9]. Until today, Tl^+ center in KDP is the only center type s^2 in the non-cubic host-lattice, where are possible all the $s^2 \rightarrow sp$ transitions corresponding to *A*, *B*, and *C* absorption bands in alkali halide crystals [5].

In previous papers we started a detailed study of undoped KDP crystals by the means of the low-temperature luminescence and optical VUV-spectroscopy with a time-resolution [3,4,10]. Detection of practically important scintillation properties of crystals KDP:Tl [11,12] stimulated further detailed studies of this material. The present work continues theses studies and focuses on spectroscopy of the KDP crystals doped with Tl^+ ions. The main goal of this paper is to study the luminescent and optical properties

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of ferroelectric crystals KH_2PO_4:Tl over the broad temperature range (10–450 K) using the method of luminescence UV and VUV spectroscopy with a time-resolution.

2. Experimental details

Single crystals of KDP containing 0.001, 0.008, and 0.1 wt.% of Tl^+ ions were grown at the STC Institute for Single Crystals NAS of Ukraine (Kharkov, Ukraine) [11–13]. The samples measuring $7 \times 7 \times 2$ mm^3 were cut from the perfect part of the grown crystal and their surfaces were polished to the high optical quality.

The present study was carried out mainly by the means of the low-temperature luminescence VUV spectroscopy. Photoluminescence (PL) spectra in the energy range of E_m from 1.2 to 6.2 eV, PL excitation (PLE) spectra in the broad energy range of $h\nu$ from 3.7 to 15 eV (0.32 nm resolution) were measured at 10 and 293 K for these crystals at the SUPERLUMI experimental station of HASYLAB [14] using synchrotron radiation. Samples were mounted in a sample holder attached to a He-flow cryostat with vacuum not less than 7×10^{-10} Torr. At the storage ring DORIS the full width at half maximum (FWHM) of SR pulses was 130 ps with the repetition period of 192 ns. Such pulses excitation enables the recording of spectra within a time-window correlated with the arrival of SR pulses. In the present experiments we recorded time-resolved spectra within two independent time-windows (TWs) set for detection of luminescence signal within 0.5–2.3 ns (TW1) and 14–58 ns (TW2) relative to the beginning of the SR pulse. Time-integrated (TI) spectra were recorded within the full time range available between two sequential excitation pulses, viz. 192 ns. The 0.3 m ARC Spectra Pro-300i monochromator and R6358P (Hamamatsu) photomultiplier were used as a registration system. The PLE spectra were corrected to an equal number of photons incident on the sample using sodium salicylate.

The luminescence characteristics in the temperature range from 90 to 480 K were measured under excitation with either X-rays (BSW2:Cu X-ray tube with $U_a = 40$ kV and $I_a = 10$ mA), or electron beam ($E_e = 180$ keV, $I = 800$ A/cm^2, $t = 3$ ns), or UV light (400 W deuterium discharge lamp with a continuous UV emission spectrum). Spectra of the X-rays induced luminescence (XRL), spectra of the pulsed cathodoluminescence (PCL), and decay kinetics of PCL were recorded by the means of the MDR-23 monochromator, the FEU-106 photomultiplier, operating in a photon counting mode, and the digital TDS-1030 oscilloscope. All measurements were performed in vacuum (residual gas pressure 10^{-4} Pa). The sample chamber was a quick response vacuum cryostat with quartz windows, which made it possible to control the sample temperature in the range of 80–500 K.

3. Experimental results and discussion

3.1. UV and VUV spectroscopy of Tl^+ ion in KDP

Fig. 1 shows the optical absorption spectra of KDP:Tl measured at room temperature. The different curves represent the absorption spectra of KDP:Tl crystals with different concentrations of the Tl^+ ions. The single absorption band at 5.76 eV (FWHM = 0.27 eV) dominates in the optical absorption spectra over the energy region from 1.2 to 6.2 eV. The band intensity depends strongly on the Tl^+ impurity concentration. The label '*A*' depicts the absorption band corresponding to the *A*-band of Tl^+ centers measured in alkali halide crystals for the impurity positions of the O_h symmetry. Bearing this in mind, the 5.76 eV absorption band in KDP:Tl can be assigned to a direct photoexcitation of the Tl^+ impurity ion.

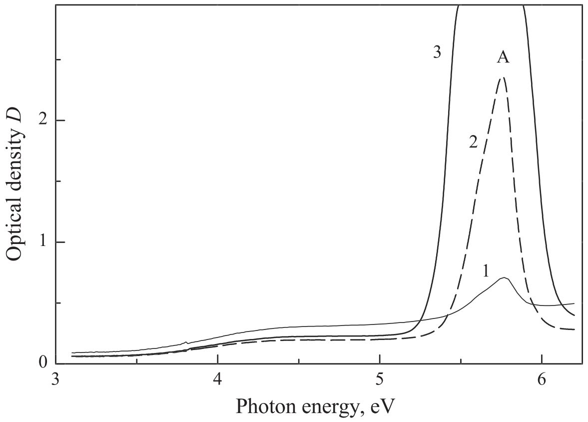

Fig. 1. The optical absorption spectra of KDP:Tl for the Tl^+ concentrations of 0.001 – (1), 0.008 – (2), and 0.1 wt.% – (3) measured at 293 K.

Discussing the luminescence of KDP:Tl, we present in figures only the time-integrated PL and PLE spectra. Although in each case, we have measured all the spectra (TW1, TW2 and TI), but in each case they were identical in the profile. All the presented PL and PLE spectra were normalized in intensity to unity at the maximum.

Fig. 2 shows the PL emission spectra of KDP:Tl under excitation with the 5.75 eV photons (the *A*-band excitation) measured at 10 and 293 K. A Stokes-shifted luminescence band was observed in the energy interval of 3.50–5.0 eV. The luminescence intensity of this band depends on the concentration of thallium ions in the same way as the absorption spectra: the higher the concentration, the greater the intensity. However, the band shape does not depend on the concentration of thallium ions in the entire investigated concentration range. In this regard, Fig. 2 shows only the luminescence spectra for KDP:Tl (0.001 wt.%).

At 10 K the PL emission band has almost a Gaussian shape with a maximum at 4.50 eV and FWHM of 0.32 eV. The low-temperature band-shape does not depend on the excitation energy value. On heating to room temperature the PL emission intensity decreases by a factor of about eight. In contrast to the low-temperature case, at room temperature the band-shape and its energy position depend on excitation energy, Figs. 2 and 3. Depending on the excitation energy, the position of the PL band is red- or blue-shifted from its low-temperature position, and bandwidth is broadened to FWHM of 0.55–0.58 eV, Table 1. Decomposition shows a low intensive sub-band at 3.9–4.25 eV, which position and intensity depend on both the temperature and excitation energy. Its contribution to

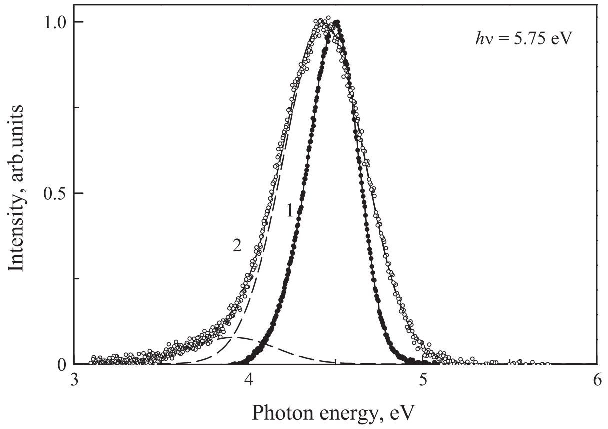

Fig. 2. The photoluminescence spectra of KDP:Tl (0.001 wt.%) at 10 – (1) and 293 K – (2). The spectra were normalized in intensities to unity at the maximum. Dashed lines show the principal Gaussians, solid lines are the results of approximation, open and black circles depict the experimental data.