A Luminescence and Absorption Spectroscopy Study of KH_2PO_4 Crystals Doped with Tl^+ Ions

Ogorodnikov I.N., Pustovarov V.A., Mezenina N.S.,
Puzikov V.M.^{*}, Salo V.I.^{*}, Voronov A.P.^{*}

Ural State Technical University, Mira Street, 19, Ekaterinburg, 620002, Russia,

Phone: +7 (343) 3744391, e-mail: ogo@dpt.ustu.ru

^{}STC Institute for Single Crystals NAS of Ukraine, Lenin ave., 60, Kharkov, 61001, Ukraine,*

Paper presents results of a study of crystals $\text{KH}_2\text{PO}_4\text{-Tl}$ carried out by the use of both the optical absorption and time-resolved luminescent spectroscopy over the broad temperature range of 10–450 K and the excitation energy range of 4.5–18 eV. In spectra of optical absorption single isolated band (A-band) is revealed at 5.76 eV (FWHM=0.27 eV). Energy position of this peak is located in the optical transparency band of a KDP crystal. The luminescence spectra comprise of one dominating band at 4.5 eV (FWHM=0.5 eV), caused by an electron transition $^3\text{P}_1 \rightarrow ^1\text{S}_0$ (A-band). In spectra of the photoluminescence (PL) excitation are revealed the A-, B-, and C- transitions in ion Tl^+ (peaks 5.75, 6.9, 7.2 eV), and the band at 7.9 eV in the luminescence excitation spectra at $T=295$ K associated with creation of an exciton in the vicinity of the impurity center. At $T=10$ K splitting A-band in spectra of the PL excitation is revealed. For the first time the effect of increasing of intensity of the Tl -luminescence, depending on the exposure time is revealed and investigated under excitation with either X-ray radiation, or an electron beam. The paper discusses the mechanism of this effect. On the basis of experimental data the configuration diagram of the Tl -center in crystal KDP-Tl was established.

Considerable attention has been recently focused on a study of the doped luminescent materials operating in the ultraviolet (UV) and vacuum UV (VUV) spectral ranges. The KDP crystal (potassium dihydrogen phosphate: KH_2PO_4) is important ferroelectric, which is utilized in many kinds of optical devices as electro-optical polarizer, detector and transformer of radiation. In previous works [1, 2] we started an investigation of undoped KDP crystals by the means of the low-temperature time-resolved VUV spectroscopy. The present paper continues this study focused on the KDP crystals doped with thallous ions.

The Tl^+ ion is a known activator forming the s^2 -centers in cubic alkali halide crystals [3]. 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 a number of UV-absorption bands which allow study of the various interactions between the impurity ion and the host lattice [3, 4]. To date, the Tl^+ center in KDP-Tl is so far the only s^2 center in a noncubic host lattice where all the possible $s^2 \rightarrow sp$ transitions corresponding to the A, B, and C bands in alkali halides have been confirmed [5].

The present study was carried out at the Ural State Technical University and at the SUPERLUMI experimental station of HASYLAB by the means of the low-temperature luminescence VUV spectroscopy with the time-resolution. Time-resolved and steady-state photoluminescence (PL) spectra in the energy range from 1.5 eV to 6.2 eV, PL excitation spectra in the energy range from 3.7 eV to 15 eV, and the decay kinetics of PL were measured for KDP:Tl crystals at the SUPERLUMI experimental station of HASYLAB using synchrotron radiation. The 0.3 m ARC Spectra Pro-300i monochromator and either R6358P (Hamamatsu) photomultiplier, or CCD camera were used as a registration system. Single crystals of KDP containing 0.1–0.001 wt.% Tl^+ ions were grown at the STC Institute for Single Crystals NAS of Ukraine (Kharkov, Ukraine) [6].

Figure 1 shows the optical absorption spectra of KDP-Tl measured at RT. The different curves represent the absorption spectra of KDP-Tl crystals with different concentrations of Tl^+ ions. As can be seen in the figure, the single absorption band at 5.76 eV (FWHM=0.27 eV) appears in the energy region from 1.2 to 6.2 eV. The intensity of this band strongly depends on the Tl^+ concentration. Here, the label “A” signifies that the absorption band corresponds to the A-band in Tl^+ center under the O_h symmetry in alkali halides, i.e. the 5.76 eV absorption band in KDP-Tl can be assigned to a direct photoexcitation of the Tl^+ impurity ion.

Figure 2 shows the photoluminescence (PL) spectra of KDP:Tl excited with 5.7 eV photons (the A-band excitation) measured at 10 K and RT. A Stokes-shifted luminescence band is observed at 4.50 eV with almost a Gaussian band-shape and either 0.35 eV (10 K), or 0.50 eV (RT) of FWHM.

Fig. 1. The optical absorption spectra of KDP:TI for the TI^+ concentration of $1 \cdot 10^{-3}$ – (1), $8 \cdot 10^{-3}$ – (2), and $1 \cdot 10^{-1}$ wt.% – (3) measured at RT

Fig. 3. The PL excitation spectra of KDP-TI

The decomposition of the observed PL band shows two relatively weak sub-bands at 4.3 and 5.0 eV alongside with the main PL band at 4.5 eV (Fig. 2).

The PL emission band-shape at 10 K is almost independent on the exciting photon energy; however this is not true for the PL intensity. The PL excitation spectra for the 4.50 eV emission band of KDP:TI measured at 10 and 300 K are shown in Fig. 3. From Figure 3 it follows that the excitation spectrum is located mainly in the energy range from 5.5 to 7.5 eV. The set of the PL excitation bands matches well the known optical absorption bands of KDP-TI single crystals containing a small amount of thallium ions TI^+ and exhibiting five characteristic polarized absorption bands A_z , A_{xy} , B_{xy} , C_{xy} and C_z in the ultraviolet region [5]. The 4.5 eV luminescence can be induced only on the excitation of the A , B and C absorption bands associated with impurity TI^+ ions (Fig. 4). It is clearly found that the 4.50 eV band is induced under the excitation of the A -, B -, and C -absorption bands associated with impurity TI^+ ions. In this connection, the 4.50 eV luminescence band would be ascribed to a radiative transition from the $^3\text{P}_1$ excited state to $^1\text{S}_0$ ground state of TI^+ ions (A -transition) since there is a strong response on the A -absorption band of TI^+ ions.

Fig. 2. The photoluminescence spectra of KDP-TI at 10 K – (1) and RT – (2)

Fig. 4. The PL emission spectra of KDP-TI

The PL excitation spectrum changes in profile on heating. A new broad excitation band appears at RT in the energy range from 7.5 to 8.5 eV. In contrast to the low-temperature case, a profile of the PL emission band, as well as its energy position, depend on the excitation energy. This indicates that the observed PL emission band at 4.5 eV in KDP-TI is a complex band. We have found no excitation bands over the energy range of the band-to-band transitions up to 15 eV. This means that the energy transfer from the host lattice to the impurity TI^+ ions has a very insignificant efficiency, as it was found earlier by us for some other impurity ions in crystal KDP [1, 2].

The PL decay kinetics of KDP-TI under selective photoexcitation in the A -, B -, and C -bands at RT obeys a mono-exponential law with a time-constant of 280 ± 8 ns. The luminescence time-response at 10 K in our measurements appears as a pedestal, indicating a time-constant of the micro-second and millisecond time-ranges (Fig. 5).

On heating to room temperatures, the intensity of luminescence decreases by a factor of about eight, the band-width broads, and the PL band maximum exhibits a blue shift of 50 meV. Figure 6 shows a temperature dependence of the 4.5 eV PL measured over the temperature range from 80 to 450 K.

Fig. 5. The PL decay kinetics of KDP -Tl at 10 K – (1) and RT – (2)

Fig. 7. Temperature dependence of the decay-time constant of the 4.5 eV PCL emission band for KDP -Tl, symbols relate to experimental data, and the solid line is the result of approximation

The luminescence spectra under band-to-band excitations with either X-rays, or e -beam, measured over the broad energy band from 1.5 to 8 eV, comprise of the 4.5 eV PL emission band due to $^3P_1 \rightarrow ^1S_0$ radiative transition in the Tl^+ impurity ion. This means that the expectable high-energy transitions either $^3P_2 \rightarrow ^1S_0$ (B -transition), or $^3P_3 \rightarrow ^1S_0$ (C -transition) are not inherent to the Tl^+ ion in the KDP host lattice. In fact, the high-energy transitions would be expected in the PL emission spectrum at higher energies from 4.5 to 7.0 eV. One can envision that the B - and C -transitions occur through the fast nonradiative relaxations from 3P_2 - and 3P_3 -high-energy excited states onto the 1P_1 lowest excited state of the Tl^+ ion. The proper $^3P_1 \rightarrow ^1S_0$ radiative transition occurs at the later stage.

A time response of the pulsed cathodoluminescence (PCL) of KDP-Tl was measured in the microsecond decay-time range at various temperatures from 100 K to 450 K. The PCL decay kinetics of the 4.5 eV emission band obeys an exponential law. The decay-time constant of PCL is subject to shortening on heating. Figure 7 shows a temperature dependence of the decay-time constant of the 4.5 eV PCL emission band for KDP -Tl.

Fig. 6. Temperature dependence of the 4.5 eV PL emission band for KDP -Tl at $E_{ex}=5.6$ eV

Fig. 8. The exposure time-dependence of the 4.5 eV luminescence intensity of KDP-Tl at RT under excitation with X-rays, symbols relate to experimental data, and the dashed line is the result of approximation

From Fig. 7 it follows that the decay-time constant exhibits a drastic change near the ferroelectric transition temperature $T_C = 123$ K. A numerical analysis of the experimental data on $\tau(T)$ exhibit two thermally stimulated processes with activation energies of 200 meV in the vicinity of T_C , and of 60 meV at higher temperatures (Fig. 7). This result indicates clearly that the relaxed excited electronic states of the Tl^+ ions in KDP-Tl are strongly influenced by the ferroelectric local field due to surrounding ligand ions. The composite band nature may cause the peculiar behavior of the 4.5 eV band near the ferroelectric temperature.

The luminescence intensity I_0 under band-to-band excitations with either X-rays ($U_a=40$ keV), or an electron beam ($E_e=150$ keV) in KDP-Tl at RT depends strongly on the exposure time t (Fig. 8). In doing so, the luminescence intensity at 4.5 eV increases by the factor higher than 25, obeying an exponential law ($I_0(t) \sim 1-\exp(-t/\tau)$) with the time-constant $\tau = 55$ s.

Our interpretation of this phenomenon is based on the fact that band-to-band excitation creates lattice defects in the hydrogen sublattice of KDP crystal: interstitial hydrogen ions and appropriate hy-

drogen vacancies [7-9]. The hydrogen vacancies under excitation form trapped hole centers, which have an elevated cross-section for nonradiative recombination of delocalized electrons. The realizing energy can be transferred through the dipole-dipole interaction to the neighboring Tl^+ ions. This excitation of the Tl^+ ions results in radiative A -transitions, increasing the luminescence yield at the 4.5 eV emission band.

Figure 9 summarizes all the obtained data and shows the schematic configuration coordinate diagram of energy levels for Tl^+ ion in KDP lattice. For the simplicity, only discussed levels are shown.

Fig. 9. Schematic configuration coordinate diagram of energy levels for Tl^+ ion in KDP lattice. For the simplicity, only discussed levels are shown

To sum up, we obtained following basic results:

1. The luminescence of crystal KDP at the 4.5 eV emission band occurs under action of photons, X-rays radiation, an electron beam, and it is caused by radiative electron transition $^3P_1 \rightarrow ^1S_0$. Other bands of a luminescence is not observed, owing to cascade nonradiative transitions from higher excited levels onto the lowest excited state of ion Tl^+ .

2. The PL excitation spectra contain a number of peaks 5.7; 6.9 and 7.3 eV, corresponding to A -, B - and C - transitions, accordingly. Identification of bands is based on estimation of positions of these absorption bands in approach of linear compression

of energy of the excited states of a crystal field in respect of a free ion.

3. The PL decay kinetics of ion Tl^+ in KDP does not depend on excitation in A -, B -, or C -band, it is mono-exponential in profile and has a PL decay time-constant of $\tau = 280 \pm 8$ ns. A life time of the center in the excited state at $T=295$ K in KDP-Tl is comparable with that for ion Tl^+ in alkali halides.

4. Temperature dependence of luminescence yield under excitation with X-rays, measured in A -band, does not correlate with temperature dependence of the PL yield. It is connected with different mechanisms of excitation of the impurity center: a direct photoexcitation of an impurity ion and excitation of the impurity center through the recombination process under action of X-rays radiation.

5. Temperature dependence of a PCL decay time, measured in the temperature range from 80 to 450 K, is characterized by two processes; each of them has the certain energy of activation. These stages associated with both the migration and radiative relaxation stages of excitation of the Tl^+ luminescence in KDP-Tl.

6. For the first time the phenomenon, increasing the Tl^+ luminescence yield and depending on the exposure time under action of either X-rays, or e -beam, is revealed and investigated.

7. The schematic configuration coordinate diagram of energy levels for Tl^+ ion in KDP lattice was deduced on the basis of the obtained experimental data.

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