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Host and defect-related luminescence in Rb₂KTiOF₅ oxyfluoride crystals irradiated by fast electrons

A V Kozlov and V A Pustovarov

Institute of Physics and Technology, Ural Federal University, 19 Mira Str., 620002, Yekaterinburg, Russia

E-mail: A.V.Kozlov@urfu.ru

Abstract. The paper presents a comparative analysis of RKTF crystals (full name single crystals Rb_2KTiOF_5), and RKTF+e crystals, single crystals irradiated on a cyclotron by fast electrons Rb_2KTiOF_5. The crystals were grown by slow solidification method. The study was conducted at a temperature from 7 to 400 K for various types of optical and radiation effects. Spectra of photoluminescence (PL) and X-ray excited luminescence (XRL) in region of 1.5-5.5 eV, time-resolved pulse cathode-luminescence (PCL) spectra, the temperature depending of the XRL, luminescence decay kinetics were studied. Single crystal RKTF are transparent from microwave up to the edge of the long-wave fundamental absorption (near UV range). We detected three luminescence bands for RKTF, in the visible spectral region, that were attributed to radiative annihilation of intrinsic excitons (2.25 eV), recombinaion-type luminescence (2.1 eV) and luminescence of higher $TiOF_5$ complexes (1.9 eV), for all emission bands characterized by great (~1.5-1.8 eV) Stokes shift. The exponential component with lifetime of approximately 19 μs was found in the PCL decay kinetics at 2.25 eV. In the crystal RKTF+e we detected new luminescence bands 2.6 eV and 3.2 eV and the disappearance of the RKTF luminescence bands. Stokes shift of the band 3.2 eV of the RKTF+e crystal is much smaller and is equal to 0.7 eV. Excitation of the band 3.2 eV occurs in the field of crystal transparency, which indicates the defective nature of the glow. PCL decay kinetics at 2.0 and 2.5 eV has a complex nature and consists of at least two components with a life time of 0.5 ms and 6 ms, that significantly more in comparison with RKTF. Irradiation by fast electrons of crystals Rb_2KTiOF_5 led to entirely new optical properties and suppression of self-luminescence of the crystals.

1. Introduction

The family of complex oxifluorides, which, in particular, include single crystals RKTF, in recent years has been actively studied for a number of reasons: First of all, the presence of strong distortion of M-(O, F) (M=Ti in case of RKTF crystals) tetrahedron or octahedron in the crystal lattice, which is due to different degrees of ionicity in metal-oxygen and metal-fluorine bonds. Various distortions of the crystal lattice caused by this phenomenon have an impact on nonlinear coefficients. As a result, oxifluorides can be interesting as nonlinear optical materials.

The relevance of Rb2KTiOF5 crystals in nonlinear optics is also confirmed by the structural similarity with the KTiOPO₄ (KTP) crystals. The material has a high optical damage, a very good optical nonlinearity and thermal stability, as a result, it is widely used in the production of lasers, such as Nd:YAG and other neodymium-doped lasers. In both crystals (KTP [6] and RKTF [7]), titanium

ions are located in the acentric positions in octahedral environments. Rubidium addition in substitution of potassium ions $KTiOPO_4$ crystals was studied in a recent paper [8]. The RKTF crystal contains both the rubidium and potassium cations.

The anion sublattice of transition metal oxyfluorides is usually represented by the octahedral groups [metal$O_{6-x}F_x$], where «metal» is the transition metal ion (W, Mo, Nb, Ti; x=3, 4, 5) [1–5]. The subject of this paper is a particular case of transition metal oxyfluorides, where «metal»=Ti, x=5.

At room temperature the RKTF crystals have the cubic modification of G_0, the space group Fm3m, Z=4, the anion sublattice of this crystal is completely disordered [1, 9, 10]. Upon cooling, a series of low-temperature phase transitions to the more low-symmetry modifications of Rb_2KTiOF_5 with G_i, where i=positive integer is successively manifested. The first phase transition to the low-temperature tetragonal modification $G1$ (the space group $I4/m$, Z=10) occurs at T=215 K [12, 13].

In G_0-RKTF, the amount of fluorine ions is five times more than oxygen ions [7]. This is significantly more than that in some other oxyfluorides, for example in $K_3WO_3F_3$ the amount of fluorine and oxygen ions is the same [11], which can cause new properties of RKTF.

Currently, there are no papers devoted to the study of optical and luminescent properties of the irradiated RKTF single crystals. For non-irradiated Rb_2KTiOF_5 single crystal the optical properties are known only for the high-temperature G_0 phase. The optical transparency range at the 5% level covers the 0.3–9.0μm spectral range (sample thickness d=0.85mm, room temperature), optical bandgap energy E_{go}=3.9 eV, average refractive index n≈1.8 for λ≈5 μm and photoluminescence (PL) emission spectra (1.2-3.7 eV) [7]. However, the PL excitation (PLE) and reflection spectra were not presented in [7]. Some preliminary results on low-temperature luminescence spectroscopy of Rb_2KTiOF_5 single crystals were the influence of fast electron irradiation on the luminescence-optical properties of the crystals RKTF. Earlier, the work was published, where a similar effect was produced by fast electrons on crystals $K_3WO_3F_3$ [15], this led to the emergence of a new 3.2 eV emission band having a complex kinetics, different temperature dependence and a different origin than the main emission band.

The aim of this work is optical and luminescent spectroscopy of pure (RKTF) and irradiated by fast electrons (RKTF+e) single crystals in a wide temperature range from 7 to 380 K. Comparative analysis of the obtained experimental data. determination of the nature of luminescence in both samples, and the influence of irradiation by fast electrons was carried out.

2. Experimental details

The $G0$-Rb_2KTiOF_5 crystals of optical quality (size: 6×8×1.5 mm^3) were grown at Institute of Geology and Mineralogy, Novosibirsk, Russia (Siberian Branch of the Russian Academy of Sciences) by slow solidification method. The grown samples were certified by the XRD analysis by the method of Debye-Scherrer. The process of growing and certification of samples is described in more detail in [7].

The samples were irradiated with fast electrons at the linear accelerator UR-10C at the Ural Federal University (E=10 MeV, fluence 1·10^{17} e/cm^2).

Crystals are transparent in a wide region from the infrared region (9 μm) to medium-wave ultraviolet region (300 nm), possess the band gap around 3.9 eV and have phase transition at a temperature 215 K. It should be noted, that in earlier researches the presence of two mixed disordered positions of O/F was revealed.

Pulse electron accelerator Radan-303A type (average energy E=120 keV, pulse duration about 1 ns, pulse frequency 100 Hz) was used for measurements of pulse cathodoluminescence (PCL) and PCL decay kinetics. The 0.3 m–ARC Spectra Pro-300i monochromator equipped with either a MCP–PMT detector or cooled CCD-camera were used as a registration system. PCL measurements were carried out in Institute of Physics University of Tartu (Estonia).

The part of optical and luminescence measurements were carried out at laboratory of the Solid State Physics Ural Federal University, Yekaterinburg. The photoluminescence emission (PL) and photoluminescence excitation (PLE) spectra were recorded using a 400W deuterium discharge lamp DDS–400, two the double-prism DMR–4 type monochromators and a R6358–10 Hamamatsu type photomultiplier tube (PMT). The yellow-green lumogen–luminophore with a known quantum yield in

the energy range studied, was used to normalize the PLE-spectra to an equal number of photons incident on the sample. The luminescence measurements were carried out using a vacuum cryostat with a pressure of residual gases lower than 5×10^{-4} Pa.

X-ray excited luminescence (XRL) spectra was recorded using the MDR-23 grating monochromator and PhEU-106 photomultiplier tube. A portable URS-55A X-rays source (Cu anode, 30 kV, 10 mA) was used for luminescence excitation.

3. Experimental results and discussion

The results of measurements of PL for RKTF crystals are shown in figure 1 and 2. The PL spectra contain one broad complex band in the 2.2 eV region with a Stokes shift of 2.0 eV. This emission can be effectively excited only in the region of the long-wave edge of the fundamental absorption or in the area of interband transitions (figure 3 and 4). In the area of transparency of crystals in the spectrum of the excitation PL there are no selective band. With the decrease in temperature, the output of PL increases sharply. At T=7 K, there is a splitting of the main FL band into two components: 1.9 and 2.25 eV, which is also confirmed in the RL and PCL spectra, figures 5, 6 and 7, respectively.

It should be noted, that with increasing temperature, there is a shift of the main band in the excitation spectrum of FL in the low-energy region, and this shift correlates with the low-energy displacement of the edge of the fundamental absorption of the crystal. Such behavior of the photoluminescence properties is characteristic of self-luminescence in crystals of the tungstates or molybdates. The intrinsic luminescence of tungstates is usually attributed to the radiative relaxation of excitons-like excitations localized on WO_6 octahedra or the WO_4 tetrahedra [16].

Based on all the above properties of the studied PL and by analogy with the properties of PL crystals of tungstates and molibdates we can say that the PL in the RKTF samples is associated with the luminescence of autolocalized excitons, so that is not associated with point lattice defects or impurity centers. We do not have the results of a study of the temperature dependence of the absorption spectrum (the so – called Urbach's rule) but based on the absorption spectrum measured at room temperature, we can estimate the energy of interband transitions E_g~4.2–4.3 eV. This value is quite typical for crystals of complex tungstates and molibdates [17].

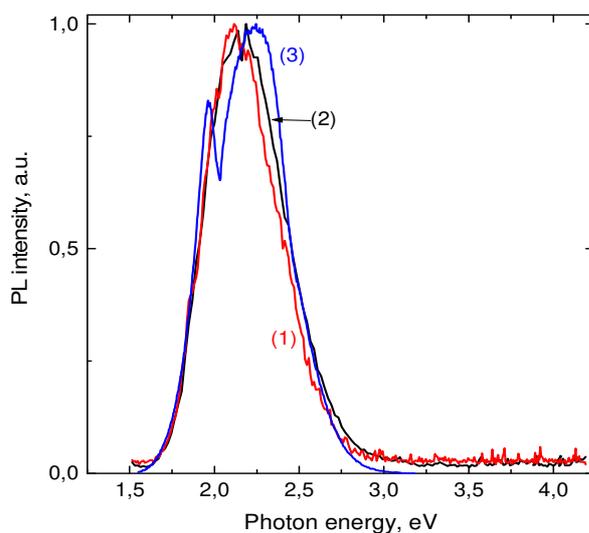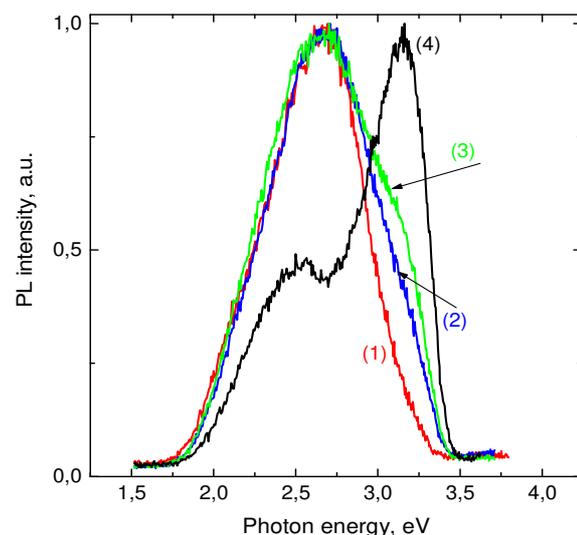**Figure 1.** The PL spectra of Rb2KTiOF5 crystals measured at T=295 (1), 95 (2), 7 K (3). E_{exc}=4.2 eV.

Figure 2. The PL spectra of Rb2KTiOF5+e crystals measured at T=85 K. E_{exc}=4.8 (1), 4.33 (2), 4.6 (3), 4.17 (4) eV.

After irradiation with fast electrons, for the crystals RKTF+e, was discovered significant changes in the spectra of FL. First, the 2.2 eV bands of pure unirradiated crystal are absent. That is, when irradiated with fast electrons, new radiation-induced defects are created, own glow (glow of autolocalized exciton) disappears, however, two new bands 2.6 and 3.16 eV were found, with high intensity, at a temperature of liquid nitrogen. Each of the bands has a selective maximum in the excitation spectrum (figure 4).
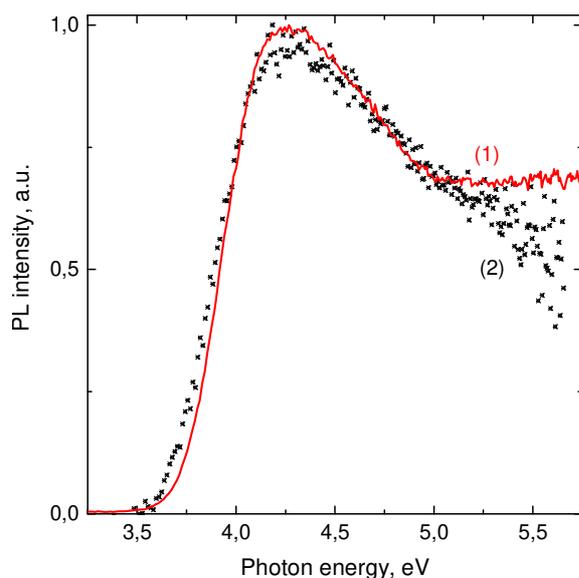
Figure 3. The PLE spectra of Rb_2KTiOF_5 crystals measured at T=295 (1), 95 K (2). E_{emis}=2.25 eV.

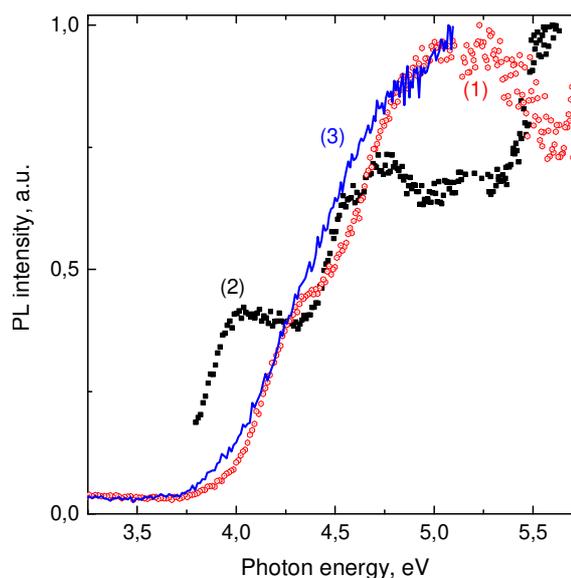**Figure 4.** The PLE spectra of Rb_2KTiOF_5+e crystals measured at T=85 K. E_{emis}=2.65 (1), 3.2 (2), 2.12 eV (3).

Band of 3.16 eV is excited in the transparency region of the crystal on the border of the fundamental absorption edge, the peak is at 4.0 eV (Stokes shift of 0.85 eV), band 2.6 eV is excited in the region of the fundamental absorption edge and the interband transitions (Stokes shift of 2 eV or more).

For these bands it was not possible to detect the output of x-rays, in contrast to the band 2.2 eV, this may indicate that the process of excitation of x-rays is superficial, and at the depth of penetration of x-rays there are processes of nonradiative recombination.

In figure 5, the RL spectra of a pure non-irradiated RKTF crystals measured at different temperatures are presented. As well as the PL spectra, the presented RL spectra are characterized by a broad complex band in the 2.2 eV region, the output of the RL drops significantly with increasing temperature. The band 1.9 eV is also detected in the RL spectra. Further study showed that this band has a different temperature dependence of the output of the RL, which confirms the complex shape of the main band.

On PCL spectra (figure 6 for a pure sample and figure 7 for the irradiated sample) measured in different time windows, similar to the PL changes under the influence of fast electrons are observed. Thus, for RKTF, the results are fully correlated with the above spectra of PL and RL. The PCL spectra measured at room temperature in different time windows 0-3 ms (figure 6, curve 1) and 0.1–3 ms (figure 6, curve 2) clearly show the difference between the two bands. It can be observed that the low-energy band is more pronounced in the PCL spectra of the slow component. This is confirmed by measurements of the decay kinetics of PCL in these bands, (figure 8). In the region of 2.25 eV the

decay kinetics of ICL is monoexponential, τ=19 μs. At 1.8 eV, the decay time is much longer (micro-millisecond range).

The separation of this radiation band into two components is due to electronic transitions in TiOF5 octahedra with different local distortions.
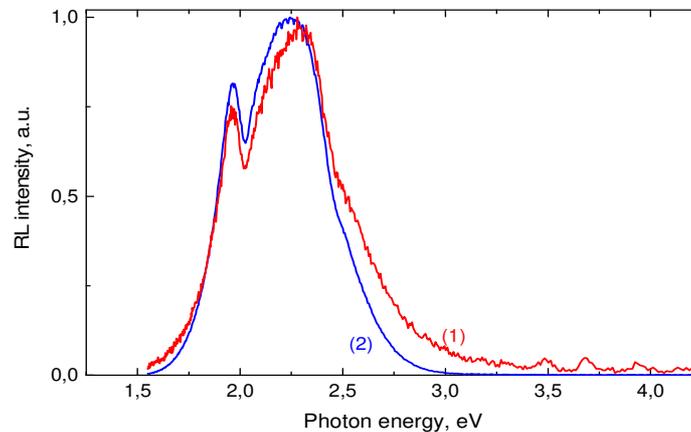

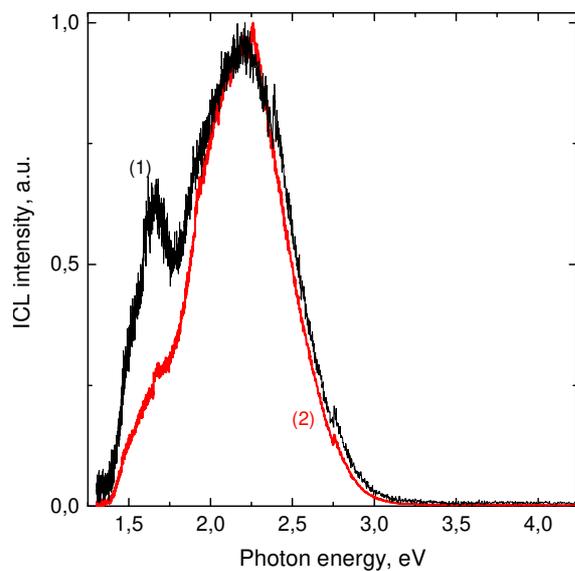**Figure 5.** RL spectra of Rb$_2$KTiOF$_5$ at T=295 (1) and 7 K (2).

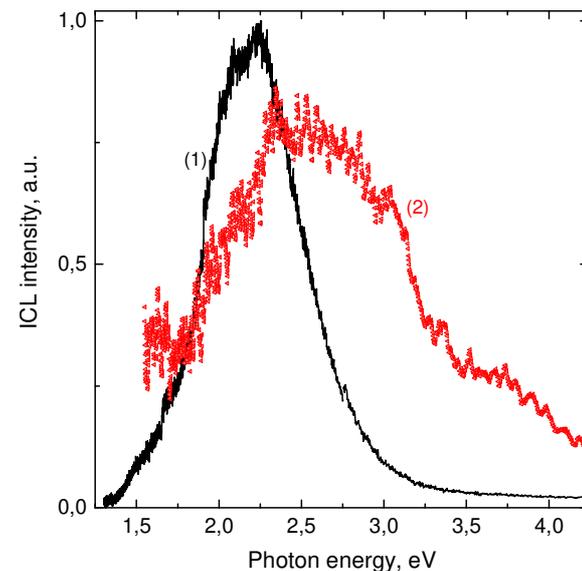**Figure 6.** The time-resolved PCL spectra of Rb$_2$KTiOF$_5$ crystals, T=7 K. Time windows 0–3 (1) and 0.1–3 ms (2).

Figure 7. The time-resolved PCL spectra of Rb$_2$KTiOF$_5$ crystals, T=7 K. Time windows 0–2 ms (1) and 0–32 ns (2).

After irradiation of the crystals RKTF+e with fast electrons in PCL spectra at the following changes happened: first, a 3.2 eV band appeared (it is also visible in the PL spectrum at T=85 K), in the window 0-32 ns there is a redistribution of intensities in favor of this band, which indicates a faster kinetics (this is also confirmed in figure 3). The parameters of the decay kinetics in this band cannot be determined. Secondly, the 1.8 eV band observed in figure 6 disappeared. Thirdly, the resulting decay kinetics (figure 9) are approximated with sufficient approximation by at least 3 exponents (the approximation formula and the resulting values τ are presented in table 1 and 2 of figure 9 for curves 1

and 2, respectively), approximately equal to 0.5, 3-4 and 10-14 µs, while in the pure sample, the kinetics is monoexponentially.

Figures 10 and 11 show the temperature dependences of the luminescence yield. Both crystals are characterized by a significant increase in the intensity of the PL yield with a decrease in temperature, but the pure sample has a two-stage quenching process, apparently, this is due to the overlap of the PL bands of different centers of luminescence.
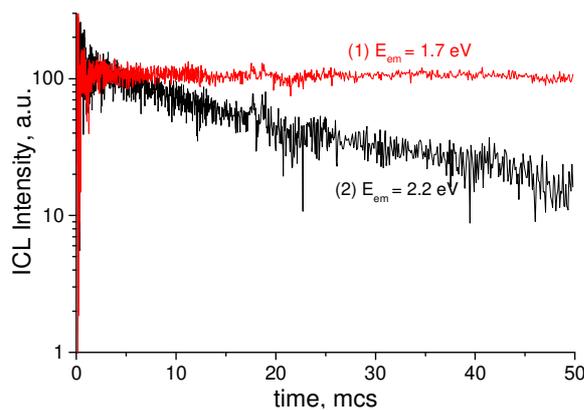

Figure 8. PCL decay kinetics of Rb_2KTiOF_5 measured at T=7 K. E_{emis}=1.7 (1), 2.2 eV (2).

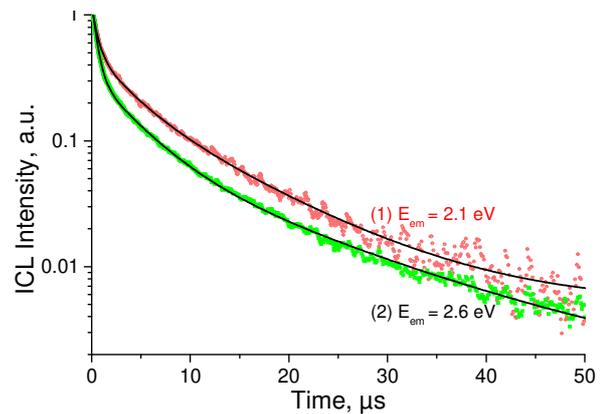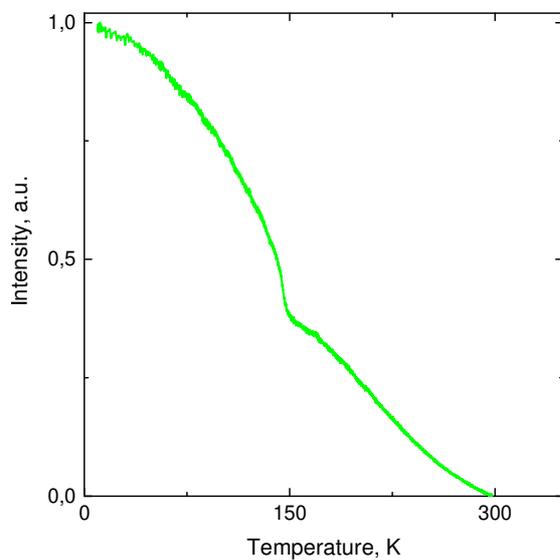**Figure 9.** PCL decay kinetics of $Rb_2KTiOF_5+e^-$, measured at T=7 K. E_{emis}=2.1 (1), 2.6 eV (2).

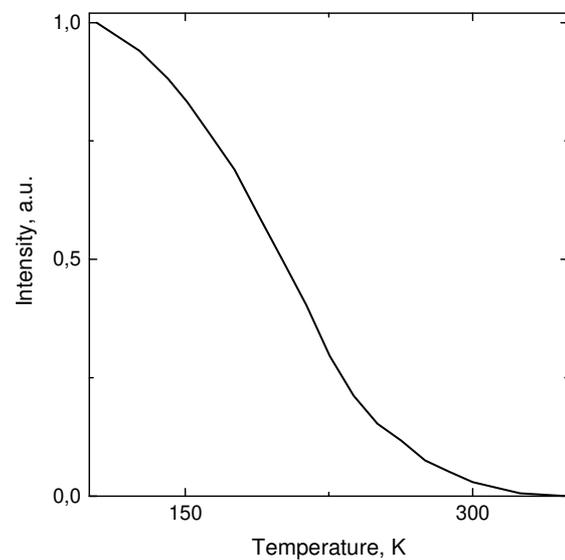**Figure 10.** Temperature dependence of PL output in Rb_2KTiOF_5: E_{exc}=4.2 eV, E_{emis}=2.2 eV.

Figure 11. Temperature dependence of PL output in $Rb_2KTiOF_5+e^-$ E_{exc}=4.75 eV, E_{emis}=2.65 eV.

And quenching begins almost immediately from the temperature of liquid helium. In an irradiated sample, the quenching process is one-stage and apparently begins at temperatures slightly below the liquid nitrogen temperature. This once again confirms the hypothesis about the different nature of PL irradiated and pure sample.

4. Conclusion

The aim of this research work was comparative analysis of luminescent properties of large RKTF single crystals of optical quality, that was grown using slow solidification method; namely, pure samples, and samples irradiated with fast electrons. For this purpose, the methods of luminescent spectroscopy were used, besides the results of PL, PLE, RL, and PCL, decay kinetics and temperature dependences of the luminescence yield were obtained.

The broadband luminescence in the region of 2.2 eV with a Stokes shift of 2.0 eV was detected for the pure sample. This glow in its properties, for both crystals of tungstates and molybdates, belongs to luminescence of self-trapped excitons. The luminescence is formed by electron transitions in the $TiOF_5$ octahedra, characterized by the presence of various crystal lattice distortions.

At the same time, there is no band in the irradiated sample. However, two new bands 2.6 and 3.16 eV were found, each of them has a selective maximum in the excitation spectrum. The band of 3.16 eV is excited in the transparency region of the crystal on the border of the fundamental absorption edge, the peak at 4.0 eV (Stokes shift of 0.85 eV), band 2.6 eV excited in the region of the fundamental absorption edge and the interband transitions (Stokes shift of 2 eV or more). These differences were confirmed in the spectra of RL, PCL and in the kinetics of luminescence decay.

Thus, irradiation of the crystal by fast electrons, creating new defects of the crystal structure by the mechanism of shock displacement, on the one hand, extinguishes the luminescence of the STE, creating an alternative channel of the charge carrier flow. On the other hand, it induces new point defects, manifested as the centers of luminescence. The variation of the fast electron fluence allow to control the concentration of radiation-induced defects.

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