Ultraviolet luminescence and creation of (WO$_4$)$_{3-}$-type centers under UV irradiation of PbWO$_4$ crystals doped with trivalent rare-earth ions

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Abstract. Luminescence characteristics and creation of (WO$_4$)$_{3-}$ and (WO$_4$)$_{3-}$-A$^{3+}$ centers were studied in PbWO$_4$ crystals doped with trivalent rare-earth A$^{3+}$ ions (A$^{3+}$: La$^{3+}$, Lu$^{3+}$, Y$^{3+}$, Ce$^{3+}$, Gd$^{3+}$, Eu$^{3+}$) under selective irradiation in the 3.4-5.0 eV energy range at 5-80 K. Optically created centers were detected by the TSL and ESR methods. Creation spectra of the mentioned centers were measured and the activation energies needed for their creation were calculated. It was found that both the (WO$_4$)$_{3-}$ and (WO$_4$)$_{3-}$-A$^{3+}$ centers can be created not only in the band-to-band transitions region but also in the 3.8 $\pm$ 0.4 eV range. The activation energy for their creation at T<40 K is close to zero. Under irradiation in the energy range around 3.8 eV at T>60 K, the activation energy for (WO$_4$)$_{3-}$-A$^{3+}$ centers creation varies from 10 to 25 meV, depending on the irradiation energy. A new UV emission, peaking in the 3.05-3.20 eV range, was found whose thermal quenching takes place with the same activation energy. Radiative decay of defect-related states, as well as the processes of their non-radiative decay, resulting in creation of (WO$_4$)$_{3-}$-A$^{3+}$ centers and thermal quenching of the UV emission, are considered to explain the effects observed.

1. Introduction

Single crystals of lead tungstate (PbWO$_4$) are well known as a fast and heavy scintillation material for high-energy physics experiments. Radiative and non-radiative decay of various exciton- and defect-related states under selective UV excitation at T>80 K was systematically studied for many PbWO$_4$ crystals (see, e.g., [1-4] and references therein). It was found that the radiative decay of the self-trapped and various localized excitons of the (WO$_4$)$_2$ type, arising from the regular crystal regions, is responsible for the complex blue B emission band. The complex low-temperature green G(I) emission band of undoped crystals was ascribed to excitons of the same type, but arising from the lead-deficient...
crystal regions. Photo-thermally stimulated non-radiative decay of the exciton- and defect-related states results in the appearance in the crystal lattice of various electron and hole centers. Tunneling recombination of the electron centers connected with oxygen vacancies and the hole centers connected with lead vacancies is accompanied with the green G(II) emission. It was concluded that lead and oxygen vacancies play the most important role in the optically and thermally stimulated recombination processes. Co-doping with stable trivalent rare-earth A\(^{3+}\) ions which substitute for Pb\(^{2+}\) ions in the PbWO\(_4\) crystal lattice [5] supresses the lead-deficient structure and reduces the number of the isolated vacancies [2, 6, 7]. This leads to a strong suppression of both the G(I) emission and slow (\(\mu s\text{-ms}\)) tunnelling recombination G(II) emission and to an enhancement of the fast (2-4 ns at RT) B emission. As a result, considerable improvement of scintillation characteristics of PbWO\(_4\) crystals is obtained. However, the peculiarities of the luminescence and defects creation processes in A\(^{3+}\)-doped PbWO\(_4\) crystals were not studied in detail. Therefore, the aim of the present work was to study the processes of luminescence and creation of electron (WO\(_4\))\(^{3-}\) and (WO\(_4\))\(^{3-}\)-A\(^{3+}\) centers in PbWO\(_4\); A\(^{3+}\) crystals (A\(^{3+}\): La\(^{3+}\), Lu\(^{3+}\), Y\(^{3+}\), Ce\(^{3+}\), Gd\(^{3+}\), Eu\(^{3+}\)) under their selective irradiation in the 3.4-5.0 eV energy range at 5-80 K.

2. Experimental procedure

Single crystals of PbWO\(_4\);A\(^{3+}\) were grown in Japan by Furukawa Co. Ltd from 4N purity raw material, using the Czochralski method in air with a Pt crucible and following the third crystallization method [8]. The concentration of A\(^{3+}\) ions was about 135 ppm in the melt. The crystals contain less than 1 ppm of other impurities [8] and also very few isolated (non-compensated) lead and oxygen vacancies [2-6].

Luminescence characteristics were studied with the use of the set-ups and procedures described in [1, 3]. Decay kinetics were measured with a modified Spectrofluorometer 199S (Edinburgh Instruments) under excitation with a nanosecond coaxial hydrogen-filled flashlamp (IBH) or microsecond Xe lamp (IBH) and using two single grating monochromators. The detection was performed with a IBH-04 photomultiplier module using the method of time-correlated single photon counting. A deconvolution procedure (SpectraSolve software package) was applied to extract true decay times from multiexponential approximation. Time-resolved emission spectra were measured under excitation with a Nd:YAG laser-pumped optical parametric oscillator NT 342/1/UVE (EKSPLA, Lithuania). It allows to obtain pulsed monochromatic radiation in the 0.6-6.0 eV energy range with a pulse duration of 5 ns.

Optically created centers were detected by the thermally stimulated luminescence (TSL) and electron spin resonance (ESR) methods. The TSL glow curves were measured with a heating rate of 0.2 K/s after selective UV-irradiation of a crystal for 15-30 min through a monochromator with spectral width of the slits \(\approx\) 5 nm. The spectral integrated emission of a crystal was detected with a photomultiplier or a Hamamatsu (6240) photon counting system. The ESR spectra were measured at 18 K using a ERS 231spectrometer (Germany) after irradiation of a non-oriented PbWO\(_4\);Y\(^{3+}\) crystal at different temperatures (10-80 K) with the Nd:YAG laser. After each TSL or ESR measurement the crystal was heated up to 150 K to destroy the optically created centers.

The experiments at low temperatures were carried out with the use of immersion helium cryostats and vacuum nitrogen cryostats.

3. Experimental results

3.1. Photoluminescence characteristics

In the PbWO\(_4\); A\(^{3+}\) crystals studied, besides the intense B emission, the weak ultraviolet - UV, green - G(I) and red - 1.9 eV emissions are observed (figure 1a). The position and FWHM of the UV band are slightly different in different crystals, varying from 3.05 eV to 3.20 eV and from 0.56 eV to 0.64 eV, respectively. This difference can be caused by a complex structure of this band and by its overlap with the B band. The B/UV emission intensity ratio depends on the crystal (table 1). The maximum position of the G(I) emission band varies in different crystals from 2.25 eV to 2.40 eV. The 1.9 eV emission is
different from the red emissions (1.57 eV and 1.48 eV) ascribed in [9] to complex lead-vacancies-containing centers. These centers are absent in most of the crystals studied in the present work. Under 3.85 eV excitation, the intensities of the UV, G(I) and 1.9 eV emissions are comparable (figure 1a). The intensity ratio of the UV and G(I) bands depends on the crystal (table 1).

In the excitation spectrum of the UV emission, the exciton band located at about 4.1 eV and a complex band located in the 3.50-3.95 eV range are observed (figure 1b). The 4.1 eV band appears partly due to the overlap of the UV and B emission bands. Its maximum is shifted to lower energy with respect to the exciton band located at 4.13-4.15 eV in the excitation spectra of the other emissions.

Table 1. Intensity ratios obtained from corrected emission spectra measured at 80 K under E_{exc}=3.85 eV (for the UV and G(I) emissions) and E_{exc}=4.5 eV (for the B emission). The activation energies E_q for thermal quenching of the UV emission. The activation energies E_a for the creation of the TSL peak at 97-107 K under irradiation at T_{irr}>55 K in the exciton (4.1 eV) and in the defect-related (3.7 eV) energy range.

| Crystal   | Emission intensity ratios | E_q, meV | E_a, meV |
|-----------|--------------------------|----------|----------|
| UV/G(I)   | B/UV                     | UV       | UV       | B/UV |
| PbWO_4:Lu | 1.38                     | 84       | 15       | 11   |
| PbWO_4:Y  | 1.26                     | 108      | 16       | 11   | 25   |
| PbWO_4:Ce | 1.19                     | 540      | 12       | 10   |
| PbWO_4:Gd | 0.96                     | 108      | 10       |      |
| PbWO_4:Eu | 0.84                     | 288      | 15       |      |

Thermal quenching of the UV emission takes place at much lower temperatures (T_q≈130 K, see the inset in figure 1b) as compared with the B emission (T_q≈160-180 K [1]) (T_q is the temperature where the emission intensity has decreased by a factor of 2). The activation energies E_q for thermal quenching of this emission, calculated from the lnI(1/T) dependences, are about 10-16 meV and slightly depend on the crystal (see table 1).

At 80 K the decay kinetics of the UV emission of the PbWO_4:Y^{3+} crystal consists of three components with decay times of 35 ns, 350 ns (figure 2a) and 11-14 μs (figure 2b, curve 1). The time-
resolved emission spectra, shown in the inset of figure 2a, indicate that both the ns-components arise from the 3.15 eV band. In the emission spectrum of the μs-component, the UV band located at about 3.05 eV and the G(I) band are observed (see the inset in figure 2b). The decay time of the G(I) emission (figure 2b, curve 2) is close to the value (≈20 μs) observed in other undoped crystals [3]. The time-resolved emission spectra measured at 10 K at different time gates (figure 3) also indicate that the spectra of the fast (curves 1, 2) and the slow (curves 4, 5) decay components of the UV emission are located at about 3.15 eV and 3.05 eV, respectively. At 10 K, the decay time of the slow component is about 100 μs.

A very fast weak ≈3.25 eV emission band was detected at RT in [10] and ascribed to the radiative decay of the non-relaxed self-trapped exciton state. If so, the B/3.25 eV emission intensity ratio should be sample-independent. However, this is not the case for the UV emission studied (table 1). Besides, according to [10], the intensity of the 3.25 eV emission decreases with decreasing temperature. Thus, the UV emission reported in the present paper is different from that observed before.

Figure 2. Luminescence decay kinetics in the PbWO4:Y3+ crystal measured at 80 K for the (a) 3.15 eV; (b) 3.0 eV (curve 1) and 2.35 eV (curve 2) emission bands. In the insets: (a) the emission spectra of the ns-components; (b) the emission spectrum measured at t=40 μs after the excitation pulse. Eexc=3.8 eV.

Figure 3. Time-resolved emission spectra of the PbWO4:135 ppm Y3+ crystal at 10 K. Time gates: 0-0.1 μs (curve 1), 0.1-1.1 μs (curve 2), 1-11 μs (curve 3), 10-110 μs (curve 4), and 100-1100 μs (curve 5). Excitation with the Nd:YAG laser at 3.87 K; for emission detection spectral width of slits 10 nm.

3.2. Thermally stimulated luminescence studies
Thermally stimulated luminescence of X-ray irradiated PbWO4:A3+ crystals was studied in [5, 11-15]. The TSL peaks at about 50 K and 95-110 K were ascribed to the thermal destruction of (WO4)3− and (WO4)3−-A3+ centers, respectively. The TSL intensity in the UV-irradiated crystals is weak. The characteristics of all the crystals studied are similar. In the present paper they are illustrated on the example of the PbWO4:Y3+ crystal. After irradiation at Tirr<40 K, peaks appear at 53 K and 107 K (figure 4a). They are most effectively created in the band-to-band transitions region and by about two orders of magnitude less effectively, in the 3.8 ± 0.4 eV range. The creation spectra of both TSL peaks coincide (figure 4b), and around 3.8 eV they are close to the excitation spectrum of the UV emission (compare figures 4c and 1b).
From the dependences of the TSL peak intensity on the irradiation temperature $T_{irr}$, the activation energies $E_a$ were determined for the TSL peaks creation under irradiation in the exciton (4.05 eV) and defect-related (3.7 eV) regions. For $(WO_4)_3$- centers creation, $E_a=0$ (figure 5a). At $T_{irr}<40$ K, the $E_a$ value for the creation of $(WO_4)_3^{-}-A_3^+$ centers is also close to zero (figure 5b) which means that these centers are created only at thermal destruction of $(WO_4)_3$- centers. At $T_{irr}>60$ K, $(WO_4)_3^{-}-A_3^+$ centers are created with $E_a=10-25$ meV (table 1) depending on the irradiation energy $E_{irr}$ (see the inset in figure 5b).

**Figure 4.** (a) The TSL glow curve measured after irradiation of the PbWO$_4$:Y$^{3+}$ crystal at 26 K with $E_{irr}=3.8$ eV. (b, c) Creation spectra of the TSL peaks at 53 K (solid circles) and 107 K (open circles) (normalized at 4.7 eV) measured under irradiation (b) at 26 K and (c) at 75 K.

**Figure 5.** Dependence of the TSL intensity on the irradiation temperature $T_{irr}$ measured for the TSL peaks located at (a) 53 K and (b) 107 K after irradiation of the PbWO$_4$:Y$^{3+}$ crystal with $E_{irr}=4.05$ eV (solid circles) or $E_{irr}=3.7-3.8$ eV (open circles). In the inset, dependence of the activation energy $E_a$ for the 107 K peak creation on $E_{irr}$ obtained under irradiation at $T_{irr}>55$ K.

### 3.3. Electron spin resonance studies

The ESR spectra of $(WO_4)_3$- and $(WO_4)_3^{-}-La_3^+$ centers in PbWO$_4$ crystals were studied in [16, 17] and [5, 13], respectively. The ESR characteristics of $(WO_4)_3^{-}-Lu_3^+$ centers were described in [17]. In the present paper, the ESR signals from $(WO_4)_3$- and $(WO_4)_3^{-}-Y^{3+}$ centers were detected. After irradiation of PbWO$_4$:Y$^{3+}$ with $E_{irr}=4.05$ eV at $T_{irr}<40$ K, $(WO_4)_3$- centers are mainly created, while $(WO_4)_3^{-}-Y^{3+}$ centers appear only after heating of the irradiated sample up to 60 K or after irradiation at 60-80 K (figure 6). Similar results were obtained in [5, 17] under irradiation of PbWO$_4$:A$^{3+}$ crystals with the He-Cd laser (3.82 eV). From the dependence of the ESR signal intensity on the irradiation temperature, the activation energies $E_a$ were calculated for the creation of $(WO_4)_3^{-}-Y^{3+}$ centers. Under irradiation at $T_{irr}<40$ K, the $E_a$ values are close to zero. Under irradiation at 4.05 eV in the 60-80 K temperature range, a value of $E_a=11$ meV was obtained. This value is close to the $E_a$ value obtained for...
the creation of the TSL peak at 107 K under the same irradiation conditions, as well as to the value of 
$E_q$ for thermal quenching of the UV emission in the PbWO$_4$:Y$^{3+}$ crystal (table 1).

**Figure 6.** The ESR spectra of (WO$_4$)$_3^{-}$ and (WO$_4$)$_3^{-}$-Y$^{3+}$ centers measured at 18 K after 
irradiation of the PbWO$_4$:Y$^{3+}$ crystal at $T_{irr}=20$ K 
and $T_{irr}=60$ K, respectively. $E_{irr}=4.05$ eV. The 
orientation of the magnetic field was close to the 
[100] axis of the crystal.

4. Discussion

The data obtained in [5, 17, 18] and in the present paper indicate that electron (WO$_4$)$_3^{-}$ and (WO$_4$)$_3^{-}$- 
A$^{3+}$ centers in PbWO$_4$ crystals can be created by the photons of energies 3.8 ± 0.4 eV which are about 
1 eV smaller than the band gap energy. The creation of (WO$_4$)$_3^{-}$ centers was explained before by a 
tunnelling process of the electron from an excited Pb$^{2+}$ ion [17] or by the ionisation of (MoO$_4$)$_2^{-}$ groups 
and the subsequent trapping of the released electrons at (WO$_4$)$_2^{-}$ groups [18]. However, the 
PbWO$_4$:A$^{3+}$ crystals studied do not contain the Mo impurity. In the undoped PbWO$_4$ crystals, the 
absorption in the energy range around 3.8 eV is usually ascribed to the excitons from Pb-deficient 
(e.g., Pb$_{7.5}$W$_8$O$_{32}$ [19]) crystal regions or to some defect-related centers. In [1-4] it was shown that at 
$T_{irr}>120$ K, the photo-thermally stimulated disintegration of the mentioned exciton- and defect-related 
states takes place with the activation energies of about 0.2-0.4 eV which are much larger than the 
values of $E_q$ and $E_a$ obtained in the present paper.

The UV emission band, whose excitation spectrum coincides with the creation spectrum of electron 
(WO$_4$)$_3^{-}$ and (WO$_4$)$_3^{-}$-A$^{3+}$ centers in the energy range around 3.8 eV, is relatively wide. Its 
FWHM=0.60±0.04 eV, like for the B and G(I) emission bands which both are of exciton origin. 
However, the Stokes shift (∼0.7 eV) is smaller than that observed for the other exciton emission bands 
in PbWO$_4$ crystals. The presence in the decay kinetics of the UV emission of two (fast - 35 ns and 
slow - 350 ns at 80 K) components with practically coinciding emission spectra is characteristic for an 
emission, arising from the triplet relaxed excited state (see, e.g., [20] and references therein).

We assume that the effects observed are due to the radiative and non-radiative decay of an excited 
state of some defect-related center. Under excitation around 3.8 eV, not only the radiative decay of 
this state, accompanied with the weak UV emission, but also ionisation of the defect center is possible. 
At $T_{irr}<40$ K, the electrons released into the conduction band are trapped at (WO$_4$)$_3^{-}$ groups and 
electron (WO$_4$)$_3^{-}$ centers are created with the activation energy $E_a=0$. The energy level of (WO$_4$)$_3^{-}$ is 
located at 50 meV below the bottom of the conduction band [16]. We assume that tunneling transitions 
of electrons from the (WO$_4$)$_3^{-}$ centers into the excited state of the mentioned defect center can take 
place. This process results also in the appearance of the UV emission. At $T_{irr}>60$ K, when the (WO$_4$)$_3^{-}$
centers are thermally unstable, the optically released and trapped at (WO₄)²⁻ electrons are immediately thermally released from the created (WO₄)³⁻ centers into the conduction band and retrapped at more deep (WO₄)²⁻⁻A³⁺ traps. As a result of this dynamical process, electron (WO₄)³⁻⁻A³⁺ centers are created with the activation energy which is smaller than 50 meV. This process leads to the decrease of the population of the excited state of the defect center and, consequently, to the thermal quenching of the UV emission with the same activation energy of 10-25 meV. Further studies are needed to make a justified conclusion on the origin of the defect center responsible for the effects observed and on the structure and dynamics of its excited states.

5. Conclusions
The ESR and TSL studies of PbWO₄:A³⁺ crystals (A³⁺: La³⁺, Lu³⁺, Y³⁺, Ce³⁺, Gd³⁺, Eu³⁺) irradiated in the 3.4-5.0 eV energy range at 5-80 K indicate that electron (WO₄)³⁻ and (WO₄)³⁻⁻A³⁺ centers can be created under irradiation of the crystals not only in the band-to-band transitions region but also in the energy range around 3.8 eV. The activation energies for their creation are Eₐ=0 and Eₐ=10-25 meV, respectively. Under excitation in this range, a new UV emission band peaking at 3.05-3.20 eV is found. At T>60 K, both thermal quenching of the UV emission and the photo-thermally stimulated creation of (WO₄)³⁻⁻A³⁺ centers take place with the same activation energy. The radiative and non-radiative decay of a defect-related state are proposed as possible reasons of the effects observed.

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