Recombination Processes in PbWO$_4$:Tb$^{3+}$ Crystals

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In the paper the results of investigations of X-ray excitation spectra, thermostimulated luminescence and the influence of light illumination on the thermoluminescence glow curves of pure and Tb-doped PbWO$_4$ crystals are presented. It is suggested that the F$^-$-centres are formed in PbWO$_4$ crystals at filling oxygen vacancies near Pb$^{3+}$ ions to three electrons under X-ray irradiation at 90 K. The nature of 108 K thermostimulated luminescence peak is connected with the [(WO$_3$ + F$^-$)-Pb$^{3+}$] associations. It was established that thermal or optical destruction of this peak leads to appearance of the radiative transitions of excitons localized near the [(WO$_3$ + F)-Pb$^{2+}$] complex centres.

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1. Introduction

In Refs. [1, 2] have been presented the earlier results of the research on spectral-luminescence and kinetic properties of pure and Tb-doped PbWO$_4$ crystals under optical and X-ray excitation. It was shown that the presence of Tb$^{3+}$ ions in PbWO$_4$ crystals leads to essential modifications of thermoluminescence glow curves (TL), strongly reduces slow components in scintillation impulse and photostimulated luminescence (PSL) is exhibited in this material. In the present work, we analyzed earlier and new results on the X-ray luminescence (XL) and the influence of long-wave irradiation on XL spectra and TL curves, a 75 W incandescent lamp with IKS-7 ($\lambda = 850–3500$ nm) or KS-13 ($\lambda = 630–2700$ nm) optical filters were used as the radiation source. Details of these measurements are described in Ref. [3].

2. Experimental

Samples for the investigations were prepared from pure and doped with Tb$^{3+}$ PbWO$_4$ single crystals grown in a platinum crucible under air atmosphere using the Czochralski technique. The crystals were obtained from stoichiometric melt of special purity grade PbO and WO$_3$ oxides. The Tb$^{3+}$ doping ion was introduced into the blend as Tb$_4$O$_7$ oxide. The terbium concentration in the melt was 0.01 wt%. The measurements were carried out in the temperature region 90–295 K. The XL spectra and TL curves were performed in vacuum using the monochromator of an SF-4A spectrophotometer and FEU-51 photomultiplier. To measure the TL curves, the samples were exposed to X-ray irradiation during 10 min at 90 K. X-ray excitation was provided by a URS-55A X-ray generator and Cu-target BSV-2 X-ray tube ($U = 45$ kV, $I = 12$ mA). In the study of PSL and the effect of long-wavelength radiation on XL spectra and TL curves, a 75 W incandescent lamp with IKS-7 ($\lambda = 850–3500$ nm) or KS-13 ($\lambda = 630–2700$ nm) optical filters were used as the radiation source. Details of these measurements are described in Ref. [3].

3. Results and discussion

The steady-state XL spectra of pure PbWO$_4$ crystals at 90 K are characterized with a wide composite asymmetric band peaked at 467 nm. Doping with impurity of Tb$^{3+}$ ions leads to appearance of activator luminescence lines attributed to $f$–$f$ transitions in Tb$^{3+}$ [1, 2].

Figure 1 illustrates the TL glow curves of Tb doped PbWO$_4$ sample exposed to X-ray irradiation and after an additional irradiation of the sample by the light in different spectral range through the IKS-7 and KS-13 filters, respectively. Besides a dominant peak near 115 K, a number of weak peaks in more high-temperature region are detected in the TL glow curve of Tb doped PbWO$_4$ sample (Fig. 1, curve 1). IR-light irradiation, during 1 min through the optical filter IKS-7 of preliminary X-ray irradiated sample at 90 K, gives rise of PSL flash, significantly reduces the 115 K peak and shifts its maximum to 120 K. At the same time, the slight decrease of peaks’ intensity in the range of 150–295 K is observed (Fig. 1, curve 2). Illumination by the light through the optical filter KS-13 of preliminary X-ray irradiated sample at 90 K, gives rise of PSL flash, significantly reduces the 115 K peak and shifts its maximum to 120 K. At the same time, the slight decrease of peaks’ intensity in the range of 150–295 K is observed (Fig. 1, curve 2). Illumination by the light through the optical filter KS-13 leads to bleaching of all TSL peaks, thus does not change their positions in the temperature scale (Fig. 1, curve 3).

From a difference between curves 1 and 2 (inset in Fig. 1) follows that IR illumination releases the stored light sum, which is characterized by the peak at 108 K. The analysis of this peak has shown that process of photostimulated release of stored light sum occurs behind
monomolecular kinetics. The depth of trap responsible for 108 K TSL peak was calculated using Antonov–Romanovski method [4]. This depth was found to be about 0.26 eV. PSL flash intensity decays exponentially with decays times: $\tau_1 \approx 78$ s, $\tau_2 \approx 194$ s and $\tau_3 \approx 435$ s (Fig. 2). Thermo and photo-stimulated radiative recombination of carriers occurs mainly through the centres responsible for a green emission band.

The present results on the spectral characteristics of PbWO$_4$:Tb$^{3+}$ crystals agree with the data received by other authors [5–7]. The value of depth of low temperature trap — 108 K peak ($E = 0.26$ eV) in PbWO$_4$:Tb$^{3+}$ is close to depth ($E = 0.25$ eV) of traps, which are observed in PbWO$_4$ crystals doped with La$^{3+}$ ions. The nature of the trap level is related to the (WO$_4^{3−}$–La$^{3+}$) electron centres [6, 7]. Photosensitive peak at 108 K present in TL glow curve of PbWO$_4$:Tb$^{3+}$ crystals can be also attributed to similar trap centres (WO$_4^{3−}$–Tb$^{3+}$) [2].

Doping of PbWO$_4$ with Tb$^{3+}$ ions leads to compensation of a negative charge of part of cation vacancies with activator ions, formation of the complex centres of a type (Tb$^{3+}$–V$_{Pb}$–Tb$^{3+}$), and accordingly to a deviation of defective structure of a host lattice towards surplus not compensated anion vacancies, and a correspondent increase of the (WO$_4^{3−}$–Pb$^{3+}$) centres, which are responsible for the excited states of a green-yellow emission [8].

It is known that TSL peaking near 109–115 K is observed in undoped PbWO$_4$ crystals and ceramics [9]. For the receiving of additional information about recombination processes in PbWO$_4$ at low temperatures, we investigated the influence of IR irradiation on TL glow curves of pure PbWO$_4$ crystals grown according to the method of Ref. [10] in which the intensive TSL peak at 109–115 K was observed. It was found that the behaviour of TSL peak at 109–115 K under long-wave light irradiation, in undoped PbWO$_4$ crystals, is similar to that observed in PbWO$_4$:Tb$^{3+}$ crystals.

According to Ref. [11], the radiation-induced absorption bands peaking around 3.5 eV (354 nm), 2.9 eV (427 nm), 2.4 to eV (516 nm) and 1.8 eV (688 nm) in PbWO$_4$ crystals have been attributed respectively to two different hole centres — Pb$^{3+}$ (3.5 eV) and O$^−$ (2.9 eV), and to two electron centres, namely, F$^+(V_O + e)$ or F(V$_O$ + 2e), observed near 2.4 eV and 1.8 eV, respectively. In Ref. [12] it is shown that in CaO compound anion vacancy can capture three electrons to form F$^−$-centre which is analogue of the F$^−$-centre in alkali halide crystals. Earlier, in Ref. [3] it was concluded that in YAG:Ce$^{3+}$ crystals, the doping ions form hole centres Ce$^{3+}$ and increase the concentration of matrix electronic F$^−$-centres responsible for the PSL excitation band in infrared region peaking near 940 nm. The position of the peak related to F$^−$-centres is closer to the bottom of conduction band than that of F$^−$-centres in forbidden band.

Taking into account facts that short-wave edge of transmission of IKS-7 optical filter is in higher wave spectral range (approximately at 850 nm) than position of absorption band originating from F-center (600–800 nm), and IR irradiation of preliminary X-ray excited crystal results in appearance of PSL flash, and moreover, the curve of light sum released by IR illumination is characterized by TSL peak near 108 K, it is possible to assume that this peak can be connected with the electronic F$^−$-centres.

On the basis of present results we suggested that creation of F$^−$-centres in PbWO$_4$ crystals occurs mainly near Pb$^{2+}$ at filling oxygen vacancies to three electrons. Thus the nature of 108 K TSL peak can be attributed to [(WO$_4^{3−}$ + F$^−$)–Pb$^{3+}$] associate centres. Thermal destruc-
tion of these centres leads to appearance of the radiative transitions of \((\text{WO}_2^-)^*\) excitons localized at neighboring \([\text{(WO}_3 + F)\text{--Pb}^{3+}]\) complex centres. Under light irradiation of \(\text{PbWO}_4:\text{Tb}^{3+}\) preliminary excited with X-ray quanta through the optical filter KS-13, the PSL arises in an electronic stage of recombination process as results of photostimulated delocalization electrons mainly from \(F^-\)centres on the initial stage and from \(F\)-centres on the second one.

4. Conclusions

The stored light sum in 108 K peak is released at thermal or optical bleaching. Process of photostimulated release of stored light sum occurs on monomolecular kinetics. It is assumed that the oxygen vacancies in the vicinity of \(\text{Pb}^{3+}\) can capture three electrons and form \(F^-\)centres under X-ray irradiation at 90 K in \(\text{PbWO}_4\) crystals. The nature of 108 K TSL peak is connected with the \([\text{(WO}_3 + F^-)\text{--Pb}^{3+}]\) associate centres. It was established that thermal or optical destruction of this peak leads to appearance of the radiation transitions of \((\text{WO}_2^-)^*\) excitons, which are localized near the \([\text{(WO}_3 + F)\text{--Pb}^{3+}]\) complex centres. PSL arises in an electronic stage of recombination process as results of photostimulated delocalization electrons mainly from \(F^-\)-centres on the initial stage and from \(F\)-centres on the second one.

References