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Photoluminescence and light scattering in lead tungstate single crystals

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Temperature dependences of photoluminescence have been obtained for lead tungstate single crystals with stored light sum. The thermal decay effect on the photoluminescence intensity has been revealed, this effect being connected with the pair recombination interaction of the emission centers and electron traps localized in the surrounding thereof. Oscillations in the light reflection intensity have been found near 200 K. Those are supposed to be associated with the action of thermal fluctuations.

Получены температурные зависимости фотолюминесценции монокристаллов вольфрамата свинца с накопленной светосуммой. Обнаружено влияние термовысвечивания на интенсивность фотолюминесценции, связанное с парным рекомбинационным взаимодействием центров свечения и электронных ловушек, локализованных в их окружении. Обнаружены осцилляции интенсивности отражения света в области 200 K. Предполагается связь с действием тепловых флуктуаций.

Results by [1] show that the energy accumulation and transformation in $PbWO_4$ (PWO) single crystals occurs in the complexes of defects consisting of a luminescence center and an electron trap localized in its surrounding (AT complexes). During the crystal thermal activation, a paired recombination interaction arises between the AT complex components. This interaction consists in the direct transition of the electron localized on the trap to the luminescence center. It can be revealed from temperature dependences of luminescence for the crystals irradiated previously at low temperatures. The direct transitions favor the electrons released from the traps as compared to thermalized electrons arising under X-ray excitation of the crystal, because such electrons should "seek" for the empty recombination centers. Thus, during the electron transitions from the traps to the recombination centers, the recombination rate of the free charge carriers decreases, thus reducing the X-ray luminescence (XRL) intensity. The XRL intensity is recovered as the traps become emptied.

The purpose of this work was to study the AT complexes in more detail. The study of photoluminescence (PL) may provide more information on the luminescence centers and the interaction thereof with the nearest surrounding, because the photoexcitation is rather selective. That is why we have measured simultaneously the PL and thermoluminescence (TL), the PL, reflection and scattering spectra of light from the PL region. The undoped PWO crystals grown by the Czochralski technique were used. The measuring setup is presented schematically in Fig. 1. The light from the source *1* passes

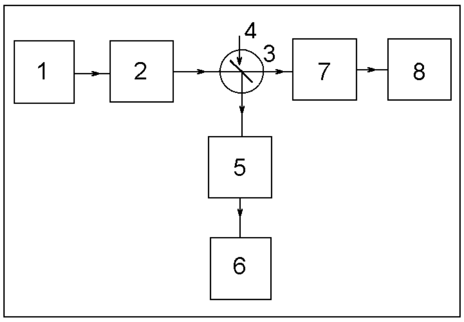

Fig. 1. Experimental setup: *1*, light source; *2*, *5*, *7*, monochromators; *3*, vacuum chamber; *4*, sample.

through the monochromator *2* into the vacuum chamber *3* and attains the sample *4*. The sample emission is recorded at the monochromator output by the photoreceiver *6*. The intensity of light passing through the crystal (transmission) is recorded using the monochromator *7* and photoreceiver *8*. As the exciting sources, a glow lamp or an LGI-21 laser (λ = 337nm) were used. Linear monochromators DMR-4 (*2* and *5*) as well as a MUM type one (7) were employed. The FEU-100 PMT in current mode were used as photoreceivers. The results were registered by two-coordinate recorders. The sample heating/cooling system provided linear heating within 100 to 600 K range. The method for combined measuring of PL and TL temperature dependences has been described in [2]. The measurements were made under 10^{-1} to 10^{-2} Torr vacuum. The samples were shaped as $15\times15\times2$ mm^3 plates. The measurement error was within ±5 %.

The PL spectrum of a PWO single crystal under laser excitation is shown in Fig. 2. It is seen to consist of several strongly overlapped bands. The main band of the highest intensity is peaked near 550 nm. Besides of that main band, there are much weaker ones in the long-wavelength region. The PL maximum position evidences the presence of defects in the anionic sublattice [3]. Fig. 3 presents the temperature dependence of PL intensity (*1*) and the TL curve (*2*). Both the dependences were measured simultaneously. Prior to the measurement, the sample was irradiated by a laser for 3–5 s at 100 K. The TL is presented by three peaks differing in intensity. The most intense low-temperature peak has a maximum at 130 K. Besides, two weak peaks at about 180 and 230 K are observed. From the initial slope of the peak at 130 K, the activation energy was determined to be 0.314±0.025 eV. For other peaks, it is impossible to determine the activation energy values due to low intensities.

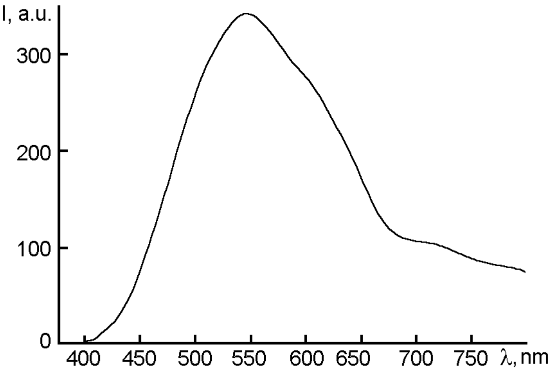

Fig. 2. PWO crystal photoluminescence spectrum.

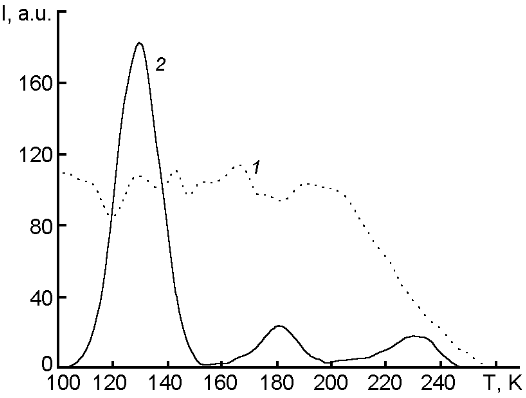

Fig. 3. Temperature dependence of PL (*1*; λ_{obs} = 550 nm, λ_{exc} = 337 nm) and TL (*2*; λ_{obs} = 550 nm) for PWO crystal.

The PL intensity temperature dependence in its plateau region contains substantial deviations from that defined by Mott formula [4]. Those deviations demonstrated as intensity minima are observed in the decay region of TL peaks. We have observed a similar phenomenon also under X-ray excitation as well as in [2, 5]. In [5], an explanation has been proposed for the nature of that fact; it has been confirmed in experiment. According to [5], each local minimum is connected with the emptying a specific kind of traps. For example, there are three such minima in the low-temperature TL peak range. The next TL peak (T_{max} = 180 K) is accompanied by two minima. The decay of the 230 K peak is masked considerably by the temperature quenching. Thus, the temperature behavior of PL and TL confirms the results by [1] and allows us to conclude the complex structure of AT complexes in PWO. In the surrounding of the luminescence centers, three groups of traps are localized presented by more that six local levels.

It is to note that, in spite of a large intensity distinctions between the 130 K TL peak and two other ones, the PL intensity changes caused by the decay thereof are essentially the same. This may be associated with different mechanisms of the thermally activated electrons from the traps to the recombination centers. In the 100 to 150 K range, the traps of which only small fraction is localized so that the direct transitions to the emission centers are possible seem to be emptied. The predominant fraction of such traps is remote, so the transition occurs across the conduction band states. For the traps corresponding to the 180 K TL peak, there is an inverse situation. It is just the direct transitions that predominate in this case. The peak with T_{max} = 230 K is located within the temperature quenching range, as it was mentioned above. Therefore, it is difficult to determine its effect on PL. The presence of thermal decay effect on the PL intensity allows to ascribe the recombination mechanism to the latter.

When measuring the PL temperature dependences, the intensity oscillations were revealed for the light reflected from the sample near 200 K (the incidence and reflection angles are equal to 45°). The temperature dependence for reflection of light from the luminescence region (λ = 550 nm) is shown in Fig. 4 (curve *1*). Within the 170–220 K temperature range, the damping oscillations of the reflection are seen to occur followed by a section where the reflection is stable; in the 275–350 K region, a reflection peak with a maximum near 300 K is observed. The intensity of light scattering at 90° to the exciting one (curve *3*) shows a structureless minimum in the same temperature range and an insignificant change near 300 K. The same features of the reflection behavior near 200 K were revealed in the spectral region of PL excitation. The distinctions were observed only near 300 K, where a structureless minimum in the temperature dependence of reflection accompanied by a transmission maximum was observed in some cases. At temperatures exceeding the ambient one, no changes were found in the reflection, transmission, and scattering intensities. It is to note that the above specific features in the temperature dependence of reflection are observed only in the region of elastic and quasi-elastic scattering. At inelastic scattering, including PL, that effect was not observed. Of interest is also the fact that the reflection remains essentially constant at the inverse temperature change from 300 K to 100 K. As the heating rate increases from 3 K/min up to 10 K/min, the reflection oscillations disappear, but the structureless minimum in the same temperature range remains. The reflection maximum at 300 K increases slightly.

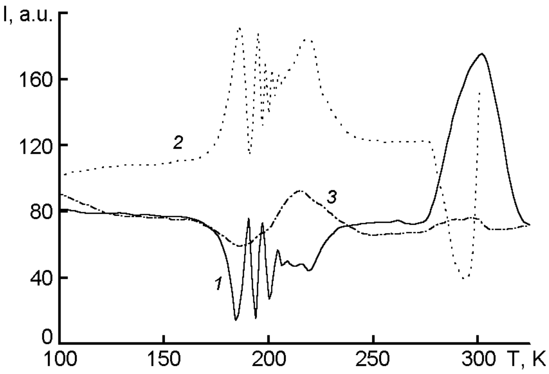

Fig. 4. Temperature dependences of intensity of reflection (*1*), transmission (*2*), and scattering (*3*) for PWO crystal.

The effect observed seems not to result from changes in the interference conditions due to the crystal heating, since in that case, the transmission should either remain constant (if the reflected waves interfere) or decrease together with the reflection (if the incident wave interferes with the reflected one). Consideration of dependences presented in Fig. 4 allows to conclude that the temperature-dependent reflection changes and scattering drop may be associated with changes in the number of active scattering centers caused by thermal fluctuations. These changes may be due to the ionization thereof under simultaneous localization of the electron on the neighboring defect. As to the absence of oscillations in the temperature dependence of scattering, this fact can be explained by distinctions in the oscillation and fluctuation character between the crystal subsurface layers (where the reflection occurs) and its volume.

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Фотолюмінесценція та світлорозсіяння у монокристалах вольфрамату свинцю

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Отримано температурні залежності фотолюмінесценції монокристалів вольфрамату свинцю з накопиченою світлосумою. Виявлено вплив термовисвічування на інтенсивність фотолюмінесценції, пов'язаний з парною рекомбінаційною взаємодією центрів світіння та електронних пасток, локалізованих у їхньому оточенні. Виявлено осциляції інтенсивності відбивання світла в області 200 К. Припускається їх зв'язок з дією теплових флуктуацій.