EXCITATION OF THE FLUORESCENCE OF TUNGSTATES IN THE REGION OF THE FUNDAMENTAL ABSORPTION USING SYNCHROTRON RADIATION

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Fluorescent tungstates of metals of group II of the periodic system, used, in particular, as x-ray luminophors, belong to the class of self-activated crystallophosphors based on salts of oxygen-containing acids, which, as a rule, are derivatives of d-transition metals — tungsten, molybdenum, niobium, tan-talum, zirconium. It is suggested that the centers of fluorescence are anionic complexes, formed by these elements [1,2].

Very little is as yet known about the energy structure of the luminophors under consideration. There are data on the widths of the forbidden zone E_g only for calcium tungstate: an investigation of the spectrum of excitation of the phosphorescence of CaWO₄ in the interval of energies 4-14 eV led to the conclusion [3] that the quantity E_g is equal to 6-6.5 eV. At an energy of the quanta of exciting radiation exceeding $2E_g$, an increase in the yield of static fluorescence was observed, interpreted as a consequence of photon amplification.

In this work we discuss the results of a measurement of the spectra of excitation of static fluorescence of calcium and cadmium tungstates within a broader range of energies (3-30 eV). In particular, these measurements permitted the detection of certain peculiarities of the influence of quenching agents, as well as chemical and heat treatment of the tungstates, on their fluorescence.



Fig. 1. Spectra of excitation of static fluorescence of $CaWO_4$, produced by precipitation from solution (1) and calcined, followed by washing with water (2) and supplementary treatment with hydrochloric acid and ammonia (3).

In the region of 10-30 eV, excitation was performed with synchrotron radiation, the source of which was an electronic amplifier at 680 MeV. A VMR-2 monochromator with a normal drop was used. A chamber for measuring fluorescence and reflection was set up at its exit.

The relative quantum yield of the fluorescence was determined by measuring the intensity of the fluorescence of the investigated luminophor relative to the intensity of the fluorescence of sodium salicylate, the quantum yield of which, at least up to 35 eV, does not depend on the energy of the photons of the exciting light [4]. Sodium salicylate was set up in the place of the luminophor. The signals were recorded successively with a FÉU-19A photomultiplier. In each measurement, the signal of a pickup of the number of electrons on the orbital was used as the supporting signal. After amplification with a preamplifier, the signal was sent from the FÉU to an amplitude—time transformer with output on a digital voltmeter.

In the region of 5.5-14 eV, the measurements were performed on a vacuum monochromator according to the Sey-Namiok scheme.

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UDC 535.37





 η_k rel. units



Fig. 3. Spectra of excitation of static fluorescence of $CaWO_4$ (1) and $CdWO_4$ (2).

The source of excitation was a capillary hydrogen lamp. Optical separation of the signals with synchronous recording of the supporting signal from sodium salicylate and the signal from the investigated sample on an ÉPP-09 was carried out. Two FÉU-29 photomultipliers were used as the light receivers. A SZS-22 light filter was set up in front of the photomultiplier, which recorded the fluorescence of the investigated sample.

Measurements in the long-wave region (3-5.9 eV) were performed on the QR-50 spectrophotometer from Shimadzu with an integrating sphere.

The precipitated calcium tungstate possesses comparatively weak photoluminescence. As a result of its calcination with a flux (CaCl₂) at 1000°C, the yield of fluorescence in the investigated re-

gion of energies of the quanta increased 3-4-fold (Fig. 1). In the case of excitation with x rays, the increase in the yield of fluorescence reached 10-20-fold [5]. This corresponds to the assumption [3] that not every WO_4 group is capable of serving as a center of luminescence.

The presence of relatively inactive layers on the surface of tungstates is characteristic, which leads to the appearance of a deep "dip" in the excitation spectra beyond the edge of the fundamental absorption at E > 7-8 eV (Figs. 1 and 2). The quantum yield of the fluorescence in this region (beginning with E = 6.3 eV) is substantially increased (doubled at E > 10 eV) as a result of the removal of the surface layer of calcined CaWO₄ by its successive treatment with hydrochloric acid and ammonia (Fig. 1).

Figure 2a cites the spectra of excitation of the fluorescence of $CaWO_4$ with an impurity of $P_2O_7^{4-}$, which is a quenching agent, and without it. Quenching, like the influence of surface treatment, has an effect beginning with a quantum energy of 6.3 eV, which evidently corresponds to the width of the forbidden zone of $CaWO_4$. Moreover, quenching is also observed in the long-wave portion of the excitation spectrum, which can be explained by inactive (or relatively inactive) absorption of the exciting radiation by the centers of quenching. This effect is manifested to an even greater degree when antimonate is introduced into $CaWO_4$ (Fig. 2a), as well as pyrophosphate into $CdWO_4$ (Fig. 2b). In the short-wave region the quenching action of the impurity, evidently associated with migration losses of energy, begins (as in the case of introduction of $P_2O_4^{4-}$) at 6.3 eV in the first of these two cases and at 5.9 eV in the second. Probably the latter quantity corresponds to the width of the forbidden zone of $CdWO_4$.

We measured the spectra of excitation of static fluorescence of $CaWO_4$ and $CdWO_4$ in the region of quantum energies up to 30 eV, using a synchrotron radiation (Fig. 3). It should be noted that the spectrum of excitation of the fluorescence of $CaWO_4$ in the interval 6-40 eV was obtained earlier [6] by the use of several sources of ultraviolet radiation; however, the greater dispersion of the experimental points in this work does not permit reliable establishment of the positions of individual maxima in the spectrum.

A steep rise in the spectral curve of the excitation of $CaWO_4$ begins at a quantum energy of 13-15 eV, somewhat exceeding twice the width of the forbidden zone. Possibly this rise corresponds to the beginning of photon amplification. The further shape of the curve can be explained by the appearance of high-energy electronic and exciton states or plasmons, responsible for the more effective energy transfer along the lattice than the electron—hole pairs and low-energy excitons. This probably also explains the fact that the yield of x-ray and cathode luminescence of tungstates and other luminophors based on salts of oxygen-containing acids is several times lower than might have been expected from calculations similar to [7], which were based on the assumption that the energy transmitters are thermolyzed electrons and holes.

In the region of energy greater than 25 eV, in crystals of calcium salts, transitions from the levels of the Ca²⁺ framework, formed by 3p-states of this cation, appear, which is confirmed by a calculation of the energies of these states, performed on an electronic computer in [8] (let us note that the energy of the M_{II,III}-level of the free Ca atom is 25.4 eV [9]). The reflection maxima in the region of 25-27 eV were detected experimentally in calcium sulfide, oxide [10], and fluoride [8]. Evidently they also occur in the reflection spectrum of CaWO₄. A decrease in the depths of penetration of the exciting radiation and a corresponding increase in the losses of energy near the surface correspond to it. This also explains the presence of a dip in the excitation spectrum of CaWO₄ in the region of 26 eV. A sharp maximum at 23 eV may be associated with the formation of a cationic exciton (cf. [11]) or a plasmon.

In the excitation spectrum of the fluorescence of cadmium tungstate, a dip in the region of 18-20 eV may also be associated with transition from the level of the shell of the cation or from the lower level of the valence zone, genetically related to the cadmium ion (according to certain data, the energy of the $N_{IV,V}$ -level of the free cadmium atom is equal to 17.1 eV [12]).

For a more reliable interpretation of the mechanism of excitation at individual maxima, it is necessary to calculate the zone structure and perform measurements of the reflection spectrum of single crystals of the corresponding tungstates in the region of the fundamental absorption.

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