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Optical characteristics of tungsten trioxide luminescence in different matrices

The comparative research using time-resolved spectroscopy of the optical characteristics of an emission in two types phosphors: natural phosphors: ZnWO4, CdWO4, microcrystalline WO3, and artificial once: wide band gap dielectrics LiF, MgF2и BaF2 doped with tungsten trioxide were presented. Both single crystals and ceramic samples obtained in the process of high-speed radiation synthesis in air under a flux of 1.5 MeV electrons were studied. It has been established that the spectral-kinetic characteristics of the studied materials luminescence are the similarity in dielectrics, where WO3 is present as a dopant; in semiconductors (MeWO4), where tungsten trioxide is present as WO62– oxyanion and in crystal lattice of tungsten trioxide binary component. It is found that tungsten trioxide, being doped in dielectric, forms a subband of impurity states in the dielectric band gap, due to which, of spatial separation of electron-hole impurity pairs becomes possible upon optical excitation of the dielectric.

Keywords: radiation synthesis; natural phosphors, artificial phosphors, luminescence, time-resolved spectroscopy, emission center, subband.

Introduction

The wide practical use of transition metal oxides MeO (Me: W, Ti, Fe), double oxides AMeO (A: Cd, Mg, Ca, Zn), oxyfluorides AMeOF is due to the manifestation of amazing electrical, magnetic, optical properties of such materials. Their superior chemical stability, high catalytic activity, molecular and electronic flexibility are sufficient to make this material suitable for a wide range of applications including photocatalysis for water purification from contaminants, gas sensors, solar cells in electrochromic, photochromic, photoelectrochromic devices [1–7].

Among polyvalent metal oxides, tungsten trioxide WO_3 is considered to be one of the most important gas sensing materials in the world, being sensitive to many different gas species, like O_3, CO, NO, H_2S, and CH_4. Among double oxides $MeWO_4$ wolframite $ZnWO_4$ is a promising candidate in photocatalysis for the photodegradation of chemical contaminants. It has proved to be an efficient photocatalyst under both ultraviolet and visible light irradiation, or being doped with different ions, or by forming a heterostructure with different compounds such as ZnO, TiO_2, WO_3, and others. $ZnWO_4$-based catalysts have been explored toward inorganic and organic molecules [8–10].

In general, the catalysis process starts with the creation under the light irradiation of electrons (e) in the conduction band (CB) and holes (h) in the valence band (VB) of the catalyst. Holes in the VB are strongly oxidizing, while electrons in the CB are strongly reducing. The free charges, reaching the catalyst surface, are involved in the creation of free radicals, consumed in the processes of decomposition, mineralization, and oxidation of various pollutants. The efficiency of catalysis depends, in particular, on the number of charge carriers in the CB and VB, which is kept constant if spatial charge separation can be achieved or decreases, as a result, of the e-h pairs recombination.

In the present work the radiative recombination of electron-hole pairs in the materials used in catalysis is investigated. The relevance of such studies is obvious since it is free charge carriers that determine the efficiency of the realized catalytic processes.

The study of optical properties of phosphors has been carried out for several decades, however, at present; there is no consensus on the nature of the luminescence center even in the well-studied natural phosphors $MeWO_4$. According to [11–14], emission centers (EC) are octahedral oxyanion WO_6^{2-}, as components of the undisturbed crystal lattice. The luminescence spectrum presents a monoband at 2.6 eV belonging to spin-forbidden $^3T_{1u}\rightarrow{}^1A_{1g}$ triplet singlet electron transition in self-trapped excitons (STE) and is an intrinsic (fundamental) property of the crystal lattice.

An alternative interpretation of the EC nature was reported in [15, 16], where the light output in band at 2.6 eV is due to strong influence of external factors, complex technology of sample preparation, low degree of the original materials purity, high level of lattice imperfection caused by inability to maintain the specified level and defect type of the devices components. Within this concept, both the emission and excitation spectra of the emission in band at 2.6 eV belong to extrinsic defects of lattice deficit-oxygen centers WO_{6-x}. The luminescence of such material is not fundamental, and the crystal lattice is only an intermediary in the light energy transition to the local impurity center.

Obviously, without knowing the nature of the EC, there is no chance to influence on the efficiency recombination of the free charges created by the action of light in material. The lack of a unified view on the nature of emission centers, as well as the on influence of external factors on the magnitude of the light output, is obstacles to expanding the scope of practical application of these advanced materials. From the generally accepted point of view, parameters of the emission transition, such as light output, emission region, decay time of emission, excitation spectrum are determined by not only the structure of EC but also properties of matrix.

The present study is a comparative research of the optical characteristics of the W-O emission centers in in six types of phosphors: natural ones ($ZnWO_4$, $CdWO_4$crystals, WO_3 ceramics micro-powder) which are widely used in catalysis and artificial ones (wide-band gap dielectrics: LiF, MgF_2 and BaF_2, doped with tungsten trioxide). The studies were carried out using time-resolved spectrometry with nanosecond time resolution.

The aim of such comparison investigation is to figure out the nature of ECs and effect of the phosphorus matrixes on the properties of tungsten-oxygen emission centers.

Materials and research methods

In the present work, the emission properties of W-O complexes either in the form of dopant or as a component of the crystal structure were the objects of research. The wide-band dielectrics of different morphology: LiF crystal and ceramics MeF_2 (Me: Mg, Ba), doped with WO_3 (so called artificial phosphors) presented the first group of materials. The natural scintillators, the so-called self-activating materials: crystals and ceramics $MeWO_4$ (Me: Zn, Cd,) and microcrystalline ceramics powder WO_3 presented the second one.

Natural phosphors of $ZnWO_4$ and $CdWO_4$ were grown by the Czochralski method at the Institute for Single Crystals (Kharkov). The tungsten trioxide was present in the form of oxyanion WO_6^{2-}. The phosphors belong to semiconductors with a band gap not exceeding 5 eV and possess high radiation resistance and high light output.

Artificial phosphor LiF doped with tungsten trioxide WO_3 with a concentration up to 1 wt.% was grown by the Czochralski method at the State Optical Institute (Sankt Petersburg). The MgF_2 and BaF_2 doped with tungsten trioxide were synthesized under a high-energy electron beam with an ELV-6 electron accelerator created at the G.I. Budker Institute of Nuclear Physics (Novosibirsk). The maximum content of the dopant in ceramics samples was 0.5 wt. % due to the high volatility of tungsten hexafluoride WF_6.

Microcrystalline WO_3 powder was supplied by Hebei Suoy New Material Technology Co., Ltd (China) with a purity of not less than 99.5 %.

The method of synthesis by using a flux of 1.4 MeV electrons was developed, applied and described by us in [17–21]. A charge consisting of a mixture of powders with different composition and components ratio was placed in a copper solid crucible. A beam of electrons with a diameter of about 2 mm was scanned along the surface of the charge with a frequency of 50 Hz using electromagnets; the crucible with the charge was displaced relative to the beam at a rate of 1 cm/s. The duration of the radiation pulse was 2 ms, the estimated value of the synthesis temperature was ~1500 C.

Radiation-chemical processes of interaction of environmental components with the open surface of the molten charge start with the formation by electron pulses of free (non-localized) electrons (e) and holes (h) (electron-hole plasma) for a time not more than 10^{-15} s from the onset moment of the radiation pulse. Normally, the formation of a new near-order (phase transition) was initiated by an external parameter — the temperature. In the express synthesis method used, phase formation takes place in dielectric materials containing short-lived radiolysis products of high concentration (10^{22} cm^{-3}) during the radiation pulse (2 ms) with a significant time delay in temperature rise. Apparently, in such extreme conditions the phase formation was initiated by quantum fluctuations of charge density in electric and magnetic fields of electron-hole plasma. Formation of the crystalline phase occurs during the action of the radiation pulses ($\leq$ 2 ms) and subsequent annealing of ceramics at 700 C in air.

The repeatability of spectral-kinetic characteristics of synthesized materials, as well as the properties similarity of crystalline and synthesized materials of the same chemical composition testify to the possibility of using the express method developed by us for practical purposes. Its main advantages include high-speed synthesis in air without supplying thermal energy from outside, possibility of obtaining ceramics in the form of crystallites with sizes depending on radiation field parameters.

The initial imperfection of research materials was evaluated by the absorption spectra in the range of 13–3 eV with a vacuum monochromator-based spectrometer at 300 K.

Natural phosphors $ZnWO_4$ and $CdWO_4$ regardless of morphology (ceramic, crystal) reveal transparency boundaries in the form of a threshold of about 4 eV. It is assumed to be located in the region of the Urbach “tail” and refers to the absorption transition of self-trapped excitons (STE) in WO_6^{2-} oxyanion [22–27]. The band gap E_g in these materials is determined in the range from 3.2 to 4.5 eV.

The lattice structure of the binary compound WO_3 was corner-sharing WO_6 octahedron units that are capable of forming clusters of different sizes [28, 29]. These clusters are considered to be connected to each other by W-O-W or hydrogen bonds, the latter due to incorporated water. The value of the band gap depends on the degree of the anionic sublattice imperfection and is determined in the range E_g=3.25–2.7 eV. The latter value belongs to the formation with the chemical formula (WO_3 nH_2O).

Pure wide band gap crystals LiF (E_g=13.6 eV), MgF_2 (E_g=12.4 eV) and BaF_2 (E_g=10.6 eV), grown in a fluorinating atmosphere, were transparent in the $E<E_g$ region. In the LiF crystal, the WO_3 doping is accompanied by a shift of the transparency boundary towards lower energies up to 4 eV with increasing tungsten trioxide content in the lattice (Fig. 1 (a)). The absorption coefficient at 8 eV reaches the value of 100 cm^{-1}, which indicates a high level of initial lattice imperfection of the doped crystals.

Crystals $ZnWO_4$, $CdWO_4$ and ceramics samples BaF_2-WO_3 and MgF_2-WO_3 opaque in the E>3.9 eV.

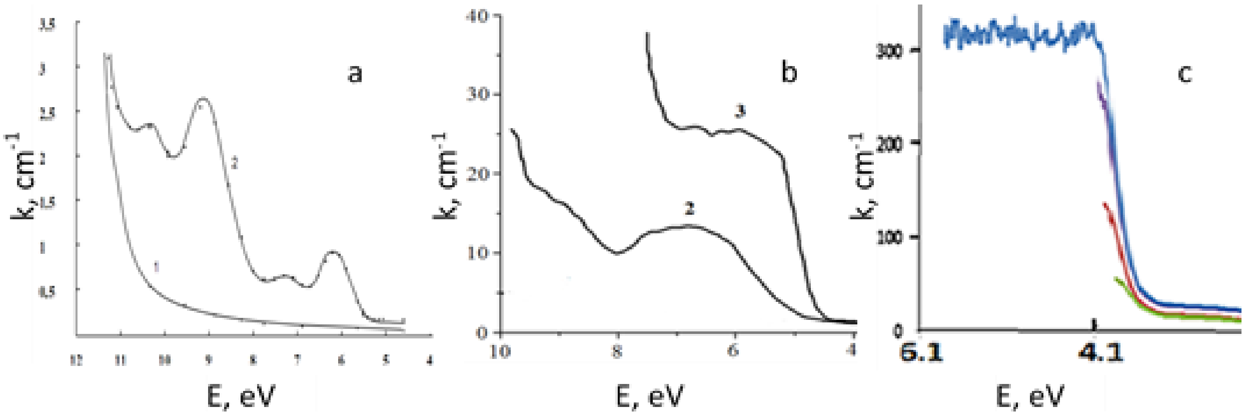

Figure 1. Absorption spectra of LiF crystals (a)(b). (a): non-doped (1), doped with WO_3 0.1 wt. % (2); (b): 0.2 wt. % (2); 0.3 wt. % (3). (c): absorption spectra of $ZnWO_4$ crystals.

All investigated materials under the action of light flux luminesced in the spectral range of 2.9–2.5 eV. The luminescence spectra were measured using two crossed MDR-204 monochromators equipped with a Hamamatsu R928 PMT for radiation detection. The integral characteristics of the luminescence were measured using an AvaSpec-2048 USB2.0 high-precision fiber optic spectrometer. Spectral-kinetic parameters of photoluminescence (PhL) and cathodoluminescence (CL) in crystals were studied in the time interval of 1.10^{-8}–1.10^{-3} s after the end of a single excitation pulse in the temperature range of 15–300 K.

Emission spectra and decay kinetics of PhL and CL were recorded on a LeGroy-WP-6030a oscilloscope.

The excitation spectra of the emission were measured in the interval of 6–1 eV at 300 K in a steady state mode with a hydrogen lamp as a source and were measured by the Agilent Cary Eclipse spectrofluorimeter.

The emission of phosphors was investigated under two types of excitation: $E_{ex}\approx E_g$ (1) and $E_{ex}>>E_g$ (2), where E_g is the band gap of the binary component WO_3.

The first condition was realized when PhL was excited by the fourth harmonic of Nd-laser (photon energy of 4.66 eV, pulse duration is 5 ns). The second condition was realized at excitation of luminescence by a pulse of 250 keV electrons with a duration of 10 ns. In both cases, researched materials luminesced in the region of 3.0–2.5 eV.

The surface structure of the synthesized samples was investigated using a scanning electron microscope Mira 3 (TESCAN). If the examined samples were dielectrics, they were coated with a conductive carbon layer using a Quorum Q150R ES sputtering system. The investigation was conducted at an accelerating voltage of 25 kV.

As an example, Figure 2 shows a picture of as-synthesized under the influence of an electron beam E=1.4 MeV, P=18 kW/cm^2 $ZnWO_4$ ceramics in the crucible and SEM images of its sample surfaces. On the surface of $ZnWO_4$ samples upon increasing the image resolution, a porous microstructure with elongated elements ranging in size from 7 to 20 μm and a thickness of approximately 7 μm are observed.

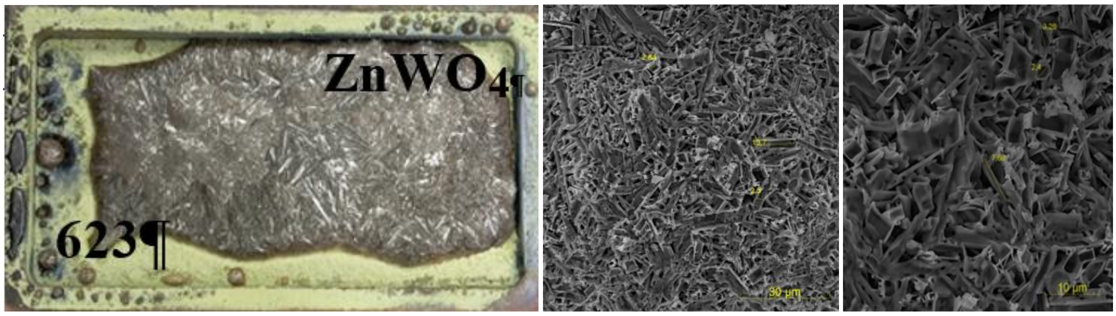

Figure 2. A picture of as-synthesized ceramics $ZnWO_4$ being in the crucible and SEM images of the surface of this ceramic sample.

X-ray diffraction patterns were collected using a Bruker D8 ADVANCE diffractometer (AXS, Berlin, Germany) equipped with a scintillation detector in step-scan mode over a diffraction angle range 2θ of 10 to 90° and CuKα radiation as the source. Sample identification utilized the Powder Diffraction File (PDF-2) database (ICDD, 2007), and indexing was performed using the EVA software (Bruker, 2007).

Figure 3 shows XRD spectra of synthesized ZnWO4 (a), and MgF2 doped with WO3 (b) samples.

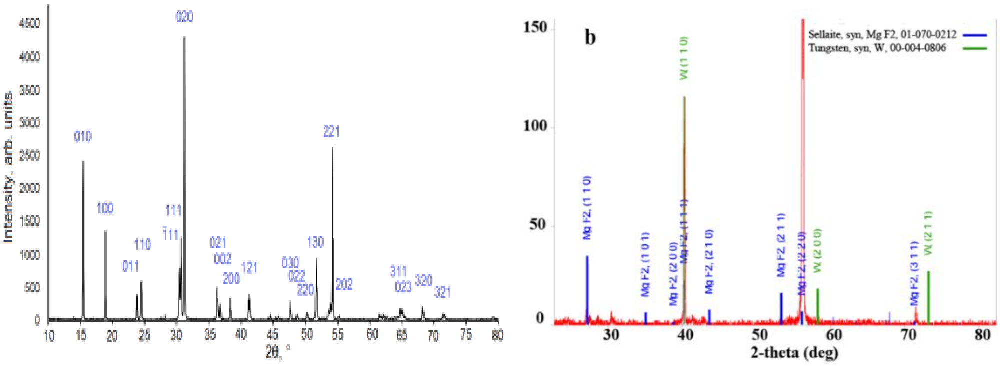

Figure 3. XRD patterns of $ZnWO_4$ ceramics sample (a) and MgF_2 doped with WO_3 (b)

Every synthesized ceramics $ZnWO_4$, $CdWO_4$, MgF_2 and BaF_2 are found to have a high degree of crystallinity, their elements composition is close to stoichiometric, and parameters similar to those ones in single crystals.

Results and Discussion

As it was previously shown [30, 31], in LiF dielectric doped with transition metal oxides (Me: Ti, Fe, W), emission in the region of 3–2.6 eV (Fig.4 (a)) occurs inertia-free with respect to a nanosecond excitation laser pulse (4.6 eV) or electron pulse (250 keV). The luminescence decay kinetics has two components: ns and μs at 270 K (Fig.4 (b)). The intensities ratio of the short and long components in band maximum is determined by the degree overlap of the bands at 3.0 and 2.6 eV.

The spectrum of the ns component is independent of the oxide type and is a band with a maximum at 3.0 eV and FWHM of 0.6–0.7 eV. The spectrum of the μs component is a monoband in the region of 2.8–2.5 eV, whose maximum position depends on the oxide type (Fig. 4 (a)).

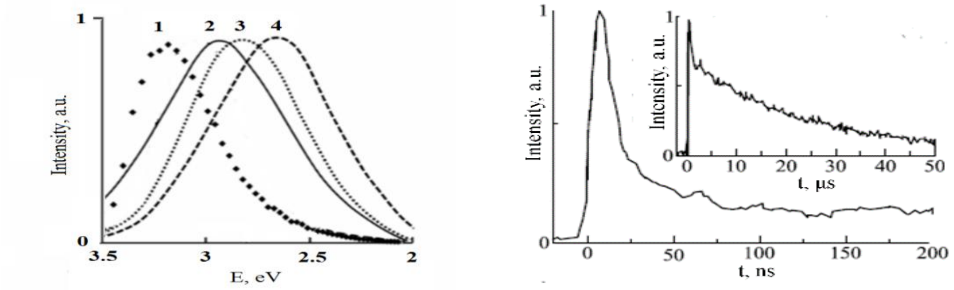

Fig. 4 (a): PhL spectra, excited by laser pulse (4.6 eV) in LiF crystals, doped with Fe_2O_3 (1, 2), TiO_2 (1, 3), WO_3 (1, 4), measured with 10 ns (1) and μs delay (2–4) relative to the end of the excitation pulse at 270 K (the spectra are normalized); (b): PhL decay kinetics at 2.6 eV in the crystal LiF-WO_3, measured with ns and μs delay (on the insert).

Below we will mainly describe the optical properties of tungsten trioxide in different matrixes.

As it turned out, luminescence at 2.6 eV can be excited in quite different materials: in dielectrics, not only LiF, but also MgF_2 and BaF_2, doped with WO_3; in natural phosphors $ZnWO_4$, $CdWO_4$, where tungsten trioxide is a structural component of the lattice; and in binary compound WO_3 (Fig. 5 (a)).

Figure 5 also shows the excitation spectra of emission at 2.6 eV in the studied materials in the range 3.8–6.2 eV.In all spectra there are thresholds in the region of 3.8–4 eV. Due to the presence of a small amount of dopant, we were able to measure the long-wavelength edge of the spectrum in the region >4 eV and establish the presence of three well-resolved bands at 6.2; 5.5 and 5 eV in spectrum of BaF_2 ceramics doped with 0.04 wt. % WO_3 (Fig. 5 (c)).

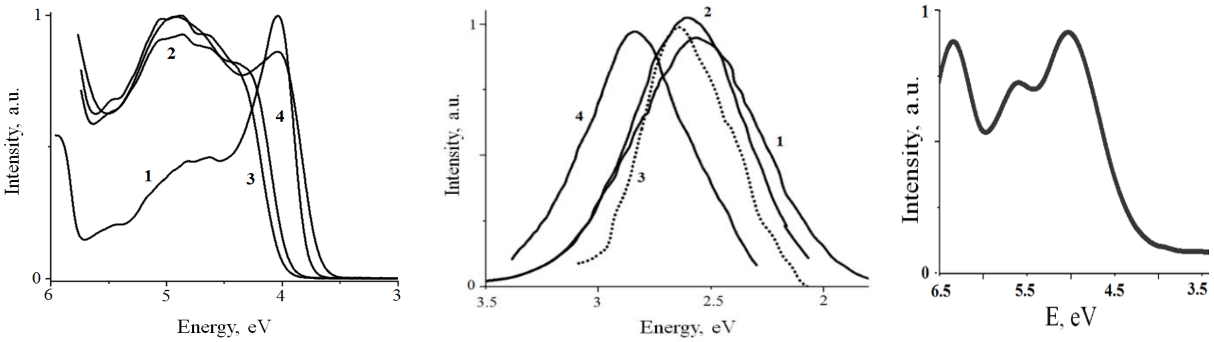

Figure 5 (a): PhL spectra, excited by laser pulse (4.6 eV) of $ZnWO_4$ ceramics samples (1); MgF_2-WO_3 (2), CL spectrum of binary compound WO_3 (3); BaF_2-WO_3 (4). (b): excitation spectra of emission at 2.6 eV in ceramics: $ZnWO_4$ (1), BaF_2-WO_3 (2), $CdWO_4$ (3) and MgF_2-WO_3 (4); (c): excitation spectrum of emission at 2.6 eV in BaF_2 ceramics doped with 0.01 wt. % WO_3.

Attempts to evaluate the role of the lattice cation in the organization of the energy structure of the EC led to the following conclusions.

It is known that at photoexcitation in the region ≥4 eV in double oxides AWO (A: Zn, Mg, Ca, Cd), which are n-type semiconductors with a band gap width of 3–5 eV, a luminescence in the region of 2.4–2.8 eV occurs; the lattice cation practically does not affect the spectral position and band half-width of the luminescence.

It turns out that this conclusion can be extended to materials of other chemical composition, provided that they contain W-O complex. So, in the double oxide Li2WO4 and in the Li2W0.95 Mo0.05 O4 system at low temperature (4.2 and 10 K, respectively), the spectrum of an intrinsic luminescence of the tetrahedral WO4 complex excited at about 5 eV consists of a band at 2.5 eV and FWHM 0.6 eV [32, 33]

In the most studied oxyfluoride K3WO3F3, belonging to the double oxides AWO6-xFx (A: K, Rb), emission at 2.6 eV with spectral and kinetic parameters similar to those in the spectrum of natural phosphorus ZnWO4 have been found [34].

Thus, the experimental data carried out by us and known from the literature confirm the calculations of theorists and indicate a minor influence of lattice cation on the formation of VB and CB in studied $MeWO_4$ semiconductor materials. Band structure of materials was formed by oxyanion orbitals. The VB top was formed by 2p states of oxygen; the bottom of the CB was formed by vacant 5d states of the polyvalent ion W. The value of the minimum energy required to excite the intrinsic luminescence in the materials is not less than E_g (3.2–4.5 eV).

Another parameter that allows estimating the degree of connection between the EC and the matrix lattice is the Stokes shift (E_{ss}). E_{ss} carries information about the value of energy losses for relaxation of the crystal lattice of the matrix in the location area of the excited EC. According to our results, the value of E_{ss} does not depend on the lattice type and is equal to 1.5–1.3 eV for EC with emission transition at 2.6 eV. Since the same value of E_{ss} is determined and in nanocrystalline powder WO_3, it becomes obvious that in this case E_{ss} does not reflect the elastic properties of the matrix containing the EC but characterizes the energy losses inside the tungsten oxide during its excitation.

In search of structure-sensitive characteristics of the luminescence, we have investigated the emission decay at 2.6 eV in various materials. It was found that in LiF matrix the emission decay time constant in the series of Fe, Ti, W oxides is equal to 180, 60 and 25 μs at 270 K and increases by a few orders of magnitude when temperature decreases. Figure 6 (a) (curves 1, 2) shows the temperature dependence of the luminescence decay time of impurity oxide centers TiO_2 and WO_3 in the LiF matrix. For the WO_3 the luminescence decay time in the low temperature region is different in ZnWO4 and LiF -WO_3 (Fig. 6 (a) (curves 2, 3)). However, it is not clear whether the lattice type or the energy position of the impurity in the lattice affects the probability of a radiative transition in the low temperature region.

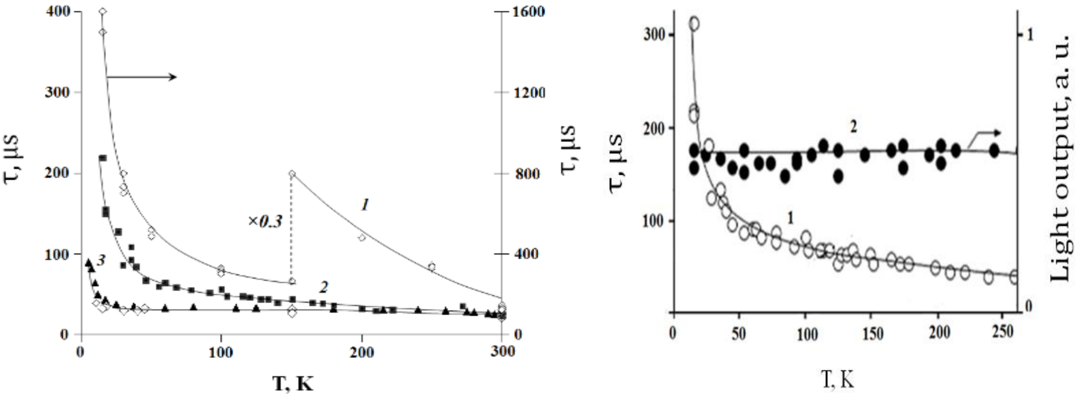

Figure 6 (a): temperature dependence of the decay time constants of PhL at 2.6 eV in LiF crystals, doped with TiO2 (1), WO3 (2), and in ceramic semiconductor ZnWO4 (3).
(In curve (3, a) black triangles are data from [35], rhombuses are data from the present studies). (b): temperature dependence of time decay constant (1), light output at 2. 6 eV (2) in LiF-WO3 crystal.

The kinetics of emission decay over time after the end of nanosecond pulse excitation splits up into three branches with different decay components and can be expressed by three exponentials:

$$J(t)=\sum A_i \exp(-t/\tau_i),$$

where A_i and τ_i are the amplitude intensity and the decay time constant of the corresponding decay time component.

Decay time constants at 270 K have the following values: τ_1=0.2 μs, τ_2= (3−4) μs and τ_3=18−20 in MgF_2-WO_3 and BaF_2-WO_3 ceramics samples, 25−35 μs in Zn and Cd tungstate ceramic samples and in LiF-WO_3 crystals. It should be noted that this peculiarity in the energy structure of luminescence centers (three-component attenuation process) is an inherent property of the emission transition at 2.6 eV and is preserved in different types of crystal lattice: in the face-centered cubic lattice (LiF), wolframite ($ZnWO_4$), rutile (MgF_2) and in the fluorite lattice (BaF_2).

The fundamental properties of the ES also include the existence of an anomalous temperature dependence of the emission decay at 2.6 eV in the low temperature region. In $MeWO_4$ semiconductors in the temperature range 5–400^0 K there are two temperature regions with different temperature dependence of the light output in the band at 2.6 eV. In the high-temperature region ($T>250^0$ K) — in the region of temperature luminescence quenching — the decrease of light output with rising T ($I_3\tau_3=f(T)$) is due to increasing probability of thermal transition of the luminescence center from the excited to the ground state accompanied with phonons emission. In the low-temperature region (5–100^0 K) in a narrow temperature range, an increasing probability of the radiative transition is observed with a constant value of light output ($I_3\tau_3\neq f(T)$). This effect is observed in the range of 4–15 K in $ZnWO_4$ crystals, in $CdWO_4$ crystals in the region of 8–20 K, and in $CaWO_4$ in the range of 10–40 K [36–38].

We found a similar effect in LiF-WO_3 and LiF-TiO_2 systems, but in a wider temperature range of 15–150 K [39, 40]. The details of the anomalous temperature dependence of the luminescence parameters at 2.6 eV in the LiF-WO_3 crystal are presented in Figure 6 (b) (Temperature quenching of luminescence in the 2.6 eV band in this material starts at T> 250 K [36, 38, 41]). For mathematical description of the observed effects, a three-level energy model emission center consisting of ground level and splitted excited level, which lower sublevel is metastable, were proposed in [38, 42].

Thus, the above-described properties of the emission at 2.6 eV in six types of phosphors indicate the absence of a connection between tungsten trioxide and the matrix and the absence of a matrix effect on the parameters of various processes: absorption, excitation and photoluminescence with the participation of this oxide.

The minimum value of photon energy required to excite the emission at 2.6 eV in $ZnWO_4$ and $CdWO_4$ is about 4.1 eV and coincides with the transparency border these materials. In binary compound WO_3 the energy of about 3.6–2.7 eV is required to excite the luminescence at 2.6 eV. According to [43–45], emission in this material is a result of electron-hole recombination.

It has been established that in natural phosphors the excitation spectrum of luminescence at 2.5–2.7 eV represents an energy continuum in the range of 4–30 eV (the range of fundamental absorption). For example, in $CdWO_4$ 2.5 eV emission excited in the region of 4.5–7 eV is the result of recombination of genetically linked electron-hole pairs in the form of molecular oxyanion self-trapped excitons. In the region of higher energies photons create free electrons and holes. During subsequent electron-hole recombination, part of the released energy is transferred to EC to excite 2.5 eV emission. The similar processes occur in $ZnWO_4$ and $CaWO_4$ [12, 46–48]. The authors estimated the absorption coefficient in the region of fundamental absorption of 5–30 eV and confirmed the correlation between these two processes: emission excitation at 2.6 eV and the value of the absorbed energy. Consequently, the presented two types of spectra (excitation and absorption) belong to the fundamental properties of natural phosphors with tungsten trioxide as the oxyanion WO_6^{2-}.

Based on our earlier studies, the introduction tungsten oxide or oxides of transition metals Fe or Ti in LiF crystal is accompanied by a loss of transparency in a wide range of 4–12 eV. The absorption spectrum of LiF crystal doped with WO_3 is a group of overlapping bands in the range of 5–12 eV (Fig. 1 (a)). It means that the oxide of polyvalent metal forms wide energy subband of the absorption states in the dielectric band gap. In this case in LiF-WO_3 under light irradiation the following sequence of events is possible.

- Due to the large width, the subband of absorbed states of dopant (Fig. 1 (a)) located close to bottom of the dielectric CB or even overlapped one.
- Photogenerated exited electron (e) of dopant transits to CB leaving a hole on the dopant ion.
- The lifetime of such free electron in the CB becomes indefinitely large, first, due to absence of a hole (h) in the VB of the dielectric, second, low probability of e-h recombination on dopant, concentration of which is not more than 1 wt.%.

Conclusion

The characteristics of PhL and CL in semiconductors $ZnWO_4$, $CdWO_4$, binary compound WO_3 and in WO_3 doped dielectric matrixes LiF, MgF_2 and BaF_2 both in single crystals and in ceramic samples were investigated using time-resolved spectrometry methods.

The similarity of spectral-kinetic parameters of emission in the region of 2.9–2.5 eV excited in all investigated materials has been established.

The parameters values of the studied emission at 300 K are given below:

1. the spectral position of the emission band peak is at 2.5−2.8 eV;

2. FWHM of emission band is 0.5−0.75 eV;
3. emission decay time is 18−30 μs;
4. three-component character of luminescence decay at 2.6 eV and coincidence of time decay constants of components in different matrixes;
5. splitting of the upper excited energy level of the luminescence center;
6. the value of the minimum energy of excitation emission at 2.6 eV is about 3.8–4.1 eV in all investigated materials;
7. the Stokes shift value of emission center is 1.5–1.3 eV;
8. no impact of the lattice cation on the optical properties of tungsten trioxide.
9. the absorption spectrum of the LiF dielectric doped with WO_3 is a set of overlapping bands in the range of 4–12 eV, which indicates the formation of a subband of absorption levels of the dopant in the forbidden band of the dielectric.

The independence of the parameters of the observed emission from the properties of the matrices in which the radiative center is located allows us to attribute the radiative transition at 2.6 eV to an interband transition in the crystal structure of the binary compound WO_3, and the characteristics of the transition — to fundamental ones.

It is found that tungsten trioxide being doped in dielectric, forms a subband of impurity states in the dielectric band gap due to which of spatial separation of electron-hole impurity pairs becomes possible upon optical excitation of the dielectric.

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Әртүрлі матрицалардағы вольфрам триоксиді люминесценциясының оптикалық сипаттамалары

Екі түрдегі люминофорлардағы сәулеленудің оптикалық сипаттамаларының рұқсат етілген уақыт бойынша спектроскопиясына салыстырмалы зерттеу ұсынылған, яғни: табиғи люминофорлар: $ZnWO_4$, $CdWO_4$, микрокристалды WO_3 және жасанды люминофорлар: кең аралықтағы диэлектриктер, LiF, MgF_2 және BaF_2 вольфрам триоксидімен легирленген. 1,5 МэВ электрон ағыны кезінде ауада жоғары жылдамдықты сәулелену синтезі процесінде алынған монокристалдар да, керамикалық үлгілер де зерттелді. Зерттелетін материалдардың люминесценциясының спектрлік және кинетикалық сипаттамалары диэлектриктердің қасиеттеріне ұқсас екендігі анықталды, мұнда WO_3 допант ретінде қатысады; жартылай өткізгіштерде вольфрам триоксиді WO_6^2 – оксианион түрінде және вольфрам триоксиді екілік компонентінің кристалдық торында болады. Вольфрам триоксиді диэлектрикте легирленген кезде диэлектриктің өту жолағында қоспа күйлерінің ішкі жолағын түзетіні дәлелденді, соның арқасында диэлектриктің оптикалық қозуы кезінде электронды-тесік қоспа жұптарының кеңістікте бөлінуі мүмкін болады.

Кілт сөздер: радиациялық синтез, табиғи фосфор, жасанды фосфор, люминесценция, уақыт-рұқсат етілген спектроскопия, жарқырау орталығы, ішкі жолақ.

Л.А. Лисицына, Г.К. Алпысова, Д.А. Мусаханов

Оптические характеристики люминесценции триоксида вольфрама в различных матрицах

Представлено сравнительное исследование с помощью время-разрешенной спектроскопии оптических характеристик излучения в двух типах люминофоров: природные люминофоры: ZnWO4, CdWO4, микрокристаллический WO3 и искусственные люминофоры: широкозонные диэлектрики, LiF, MgF2 и BaF2, легированные триоксидом вольфрама. Были исследованы как монокристаллы, так и керамические образцы, полученные в процессе высокоскоростного радиационного синтеза на воздухе под потоком электронов 1,5 МэВ. Установлено, что спектрально-кинетические характеристики люминесценции исследованных материалов имеют сходство со свойствами диэлектриков, где WO3 присутствует в качестве допанта; в полупроводниках, где триоксид вольфрама присутствует как WO62 — оксианион и в кристаллической решетке бинарного компонента триоксида вольфрама. Доказано, что триоксид вольфрама, будучи легированным в диэлектрике, образует в полосе пропускания диэлектрика подполосу примесных состояний, благодаря которой при оптическом возбуждении диэлектрика становится возможным пространственное разделение электронно-дырочных примесных пар.

Ключевые слова: радиационный синтез, природный люминофор, искусственный люминофор, люминесценция, время-разрешенная спектроскопия, центр свечения, подзона.

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