

Complex defects in crystal scintillation materials and phosphors

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Abstract. The possibility of the existence of complex defects in pure and doped crystal phosphor discussed in work. The luminescent properties of mono- and nanocrystals of zinc tungstate, the powders of YAG with various compositions are studied. It is shown that the intrinsic defects, impurities, oxygen vacancies, the hydroxyl groups may be present in the structure of the complex defects (nanodefects). Nanodefects form during synthesis and have high efficiency of the transfer of excitation energy to the emission centres.

1. Introduction

The existing models assume uniform distribution of the lattice defects in the crystal. A defect, a dopant, is an elementary unit that possesses specific properties which do not depend on the matrix it is located in. This assumption is confirmed by the studies of radiation-induced processes in the crystal with a perfect structure and a low dopant concentration. This approach was used to establish the structure of defects of different types (emission centers in particular), the processes associated with defect migration, transformation, and transfer of excitation energy and excitation relaxation. However, crystal phosphors frequently contain large concentrations of defects, dopants; the crystal structure is complex and imperfect. Therefore, it can be assumed that defects enter these crystals in the form of complex systems during synthesis. The complexes are supposed to contain a dopant, co-dopants and intrinsic lattice defects to compensate the difference in the charge of the matrix and dopant ions, and elastic tension in the region of the dopant location. This complex is expected to be a nano-sized formation as compared to a point defect and it can be referred to as a nanodefect [1,2]. Crystal phosphors with high concentration of defects which form nanodefects can be referred to as highly imperfect phosphors. Formation of these complex defects with emission and absorption centers during synthesis is supposed to significantly affect the processes of the excitation energy transfer to emission and relaxation centers.

The key information on the formation of nanodefects and their structure available to date was obtained from the study of LiF crystals doped with polyvalent Fe, Ti, U and W ions. The

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charge of multivalent ions differs from the charge of Li replaced by these ions. To compensate the charge and elastic stresses, intrinsic defects are introduced in the vicinity of the dopant ion: interstitial ions and vacancies. Crystals containing multivalent ions are grown from the mix with ions incorporated in the mix in the form of oxides, which means that oxygen ions enter the crystal. High multivalent ion concentrations can be incorporated in the crystal in case the crystal is grown in air in the presence of LiOH in the mix. During synthesis, multivalent ions introduced in the LiF crystal with oxygen ions, OH, and intrinsic defects form nanodefects. It was experimentally shown that nanodefects contain oxygen ions [3–6], OH [7–8], interstitial ions and vacancies [2]. A nanodefect contains an emission center with O^{2-} ion in its structure and, probably, an anion vacancy [1, 9–11].

A nanodefect has a large capture cross section for charge and energy carriers. Electronic excitations captured by nanodefects are effectively transferred to the emission center. Therefore, the presence of nanodefects makes the LiF crystal containing multivalent ions an efficient converter of radiation energy into luminescence. It can be assumed that in scintillators and phosphors, which typically contain a high concentration of defects (impurity and intrinsic defects), nanodefects formed during synthesis can significantly affect radiative processes. This paper presents experimentally obtained information on the presence of nanodefects in scintillation crystals and phosphors.

2. Research Methods

The time-resolved luminescence spectroscopy were used to find out the presence of nanodefects in highly imperfect scintillator and phosphor crystals. The luminescence in the samples was excited by high-energy pulsed electron fluxes, laser radiation with λ_{exit} of 337, 266 and 355 nm and LED chip with $\lambda_{\text{exit}}=452$ nm. The density of the electron flux energy was 70 mJ/cm², the average energy of the accelerated electrons was ~250 keV and the duration of the excitation pulse was 10 ns. The pulse duration of the laser flux was 2 ns. Phosphors were excited using LED chips with an emission band at 360, 395 and 452 nm. To measure kinetic characteristics, pulse voltage was applied to the chip to generate a 70 ns flash.

In excitation by electron fluxes and laser radiation, the spectra and kinetics of luminescence decay were recorded using the PMT-84-6 photomultiplier with MDR-3 monochromator and LECROY digital oscilloscope 6030 (350 MHz). The time resolution of the measuring system was 7 ns. When excited by chip, the luminescence decay kinetics was recorded using the MDR-204 monochromator PMT "Hamamatsu 10720-20" and Tetronix DPO-3033 oscilloscope with 2 ns time resolution.

In steady-state measurements, the luminescence and excitation spectra were measured using the Agilent Cary Eclipse spectrofluorimeter, and a pulsed xenon lamp was used as a light source. The integrated luminescence spectra were recorded using the Avantes AvaSpec-3648 and AvaSpec-2048 fiber optic spectrometers in the range of 200–1100 nm.

The elemental phosphor composition was determined using the Quanta3D 200i scanning electron microscope with an energy dispersive X-ray analysis system (EDAX). The morphology of the phosphor powder was investigated with the Leica DM 6000 M optical microscope and Quanta3D 200i electron microscope.

The scintillation material samples were provided by the Institute for Scintillation Materials NAS of Ukraine. The phosphors chosen for the study were commercial samples.

3. Experimental results and discussion

3.1. Existence of nanodefects in metal tungstate crystals

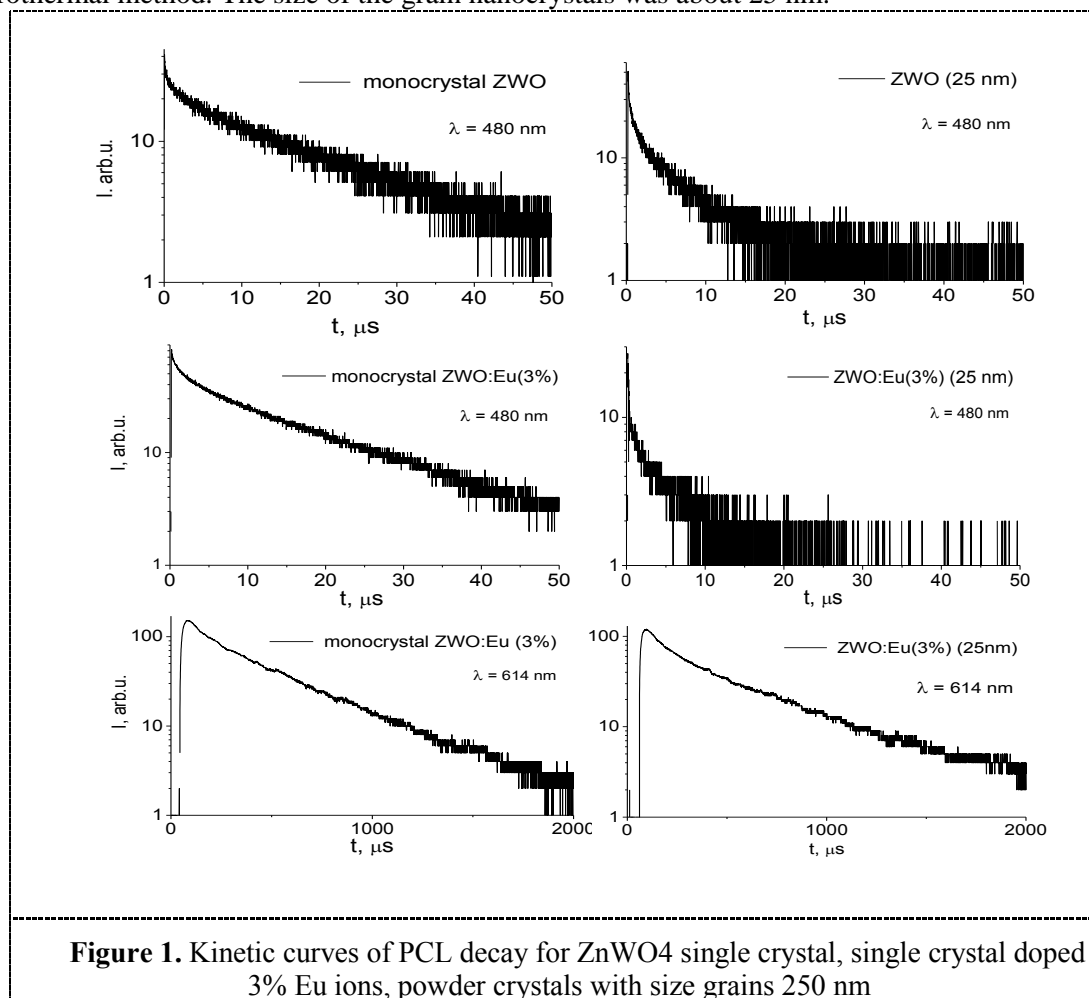
It has been found that radioluminescence of PbMoO₄, CaMoO₄, CaWO₄, PbWO₄, CdWO₄; CdWO₄-Li₂CO₃; CdWO₄-Li₂CO₃-Bi₂O₃, LiF:WO₃ and Li₂W_{0.95}Mo_{0.05}O₄ crystals and other crystals of this type

have similar spectral characteristics. The luminescence spectra of the crystals contain a band with a maximum of about 2.6 eV and half-width ~ 0.6 eV. Similar spectral-kinetic parameter values of the excited emission in oxygen-containing materials different both in the crystal lattice type and in the type of the co-dopant indicate some common features of the radiative center structure [12–14].

Tungstate and molybdate crystals are typically grown by the Czochralski method from the mix prepared by mixing Zn, Pb and Cd metal oxides with tungsten and molybdenum oxides in appropriate proportions to obtain a stoichiometric composition. The crystal grown by this method is supposed to contain numerous lattice defects, and this should affect the material characteristics. In [13], the authors suggest that highly imperfect crystals, tungstates, molybdates and polyvalent ion doped LiF crystals, contain complex defects (nanodefects) which represent a set of intrinsic lattice defects incorporated during the growth of impurity ions, including oxygen ions, OH^- .

Introduction of Li and Bi impurities in CdWO_4 crystal leads to uncontrolled changes in the light output. This suggests an indirect role of Li and Bi in the scintillation process. Doping should have an effect on the degree of intrinsic imperfection due to mutual charge compensation and, consequently, on nanodefect formation. Therefore, incorporation of the dopant impurity results in changed light output, but this change depends on the nanodefect formation associated processes during crystal growth [15,16].

The spectral-kinetic characteristics of the luminescence were studied for ZnWO_4 and $\text{ZnWO}_4\text{-Eu}$ prepared in the form of nano- and bulk crystals. Bulk crystals were grown in air by the Czochralski method, and nanocrystals were grown under microwave activation at 120°C for 30 minutes by the hydrothermal method. The size of the grain nanocrystals was about 25 nm.



In work [17] it was found that the spectra of the macro- and nanocrystal luminescence are similar in shape and position. In the ZnWO_4 crystal spectrum, a characteristic scintillation band can be observed with a maximum at 490 nm. In the $\text{ZnWO}_4\text{-Eu}$ crystal spectrum, apart from this band, a narrow band caused by europium can be observed at 614 nm in the long wavelength region [18]. However, after pulse excitation, the kinetic curves of the luminescence decay in ZnWO_4 nano- and bulk crystals are found to be distinctly different.

The kinetic curves of the luminescence decay for the studied samples are shown in Fig. 1. The investigation of the spectral-kinetic curves of the PCL decay of undoped ZnWO_4 crystals of different dispersion indicated the following results. The characteristic luminescence decay time of single crystals is 26 μs . The luminescence decay time of grain-like nanocrystals with a size of 25 nm is about $\sim 7 \mu\text{s}$. The kinetic characteristics in the main scintillation band (host luminescence) in monocrystals and nanocrystals $\text{ZnWO}_4\text{:Eu}$ change in a similar manner (Fig.1). However, the decay time in the band 614 nm caused by europium ions is weakly dependent on the morphology and size of the crystal of zinc tungstate. The decay time at band of luminescence 614 nm for mono- and nanocrystals it is about 0.4 ms.

These findings indicate that in a nanometer-sized crystal, the surface of the crystal significantly affects its radiative characteristics. When the crystal size is greater than one micrometer in diameter, the radiative characteristics remain unchanged. This occurs if the sizes of the emission complexes are comparable to those of the crystals. This assumption is supported by a weak effect of crystal sizes on the radiative characteristics of the europium centers.

3.2. *The possibility of existence of nanodefects in white LED phosphors*

LEDs with blue light converted by phosphor to visible one are the most effective sources of white light. Most commonly used phosphors are those based on yttrium aluminum garnet doped with rare earths. The phosphors are synthesized in air from the mix, a mixture of powders of at least four oxides. The crystal produced contains a high concentration of crystal defects. Therefore, it can be expected that nanodefects are formed in white LED phosphors during synthesis that determines high efficiency of blue light to white light conversion.

A set of commercial YAG phosphors taken for the study differed in the ratio of the basic elements of their composition. The studied phosphors were solid solutions of Y, Al, Gd and Ga oxides doped with Ce. All the phosphors represented powders of microcrystals or microfluxes less than 30 μm in size.

In the phosphors, the deviation from the average aluminum content does not exceed 20%, the content of yttrium changes by 4 times, and that of gadolinium changes from 0 to 12%. According to the specification, all the samples are doped with cerium. In a number of phosphors, cerium was not detected as its weak band is often overlapped by the spectral background caused by other elements present in the phosphor.

The excitation and luminescence spectra of all the phosphors were measured. Table 1 shows the results of the characteristics obtained for the excitation and luminescence spectra measured by conventional method using the Cary Eclipse spectrofluorimeter. In the table, λ_{em} , λ_{ex} , λ_{emm} , $\lambda_{\text{ex-m}}$ indicate the wavelengths of the luminescence and excitation spectra, and FWHM of the corresponding bands in electron-volt.

The kinetic characteristics of photoluminescence decay in phosphors were measured under excitation by radiation from the chip with $\lambda_{\text{ex-m}}=452 \text{ nm}$. The values of the characteristic luminescence decay times are given in Table 2. The characteristic decay times τ of all the investigated phosphors are found within 60–66 ns. An exception is the SOM-5000 phosphor; its decay time is 53 ns. The measured decay times coincide with those obtained in [19–20].

Table 1. Characteristics of the luminescence and excitation spectra of the studied phosphors.

| Phosphors | The spectral characteristics | | | | | | | |
|-------------------------|------------------------------|-----------------|------------------------------|-----------------|-----------------------------------|-----------------|------------------------------|-----------------|
| | Luminescence | | | | Excitation λ_{emm} | | | |
| | $\lambda_{\text{ex}}=340$ nm | | $\lambda_{\text{ex}}=440$ nm | | | | | |
| | λ_{emm} , nm | ΔE , eV | λ_{emm} , nm | ΔE , eV | $\lambda_{\text{ex-m}}$, nm | ΔE , eV | $\lambda_{\text{ex-m}}$, nm | ΔE , eV |
| SDL5000 | 515 | 0.396 | 515 | 0.393 | 344 | 0.257 | 446 | 0.441 |
| SDL 4100 | 532 | 0.413 | 533 | 0.403 | 341 | 0.322 | 446 | 0.457 |
| SDL 3000 | - | - | - | - | 341 | 0.273 | 453 | 0.421 |
| SDL1000 | 532 | 0.416 | 530 | 0.440 | 340 | 0.273 | 446 | 0.419 |
| SD3300 | 532 | 0.390 | 532 | 0.384 | 340 | 0.261 | 448 | 0.447 |
| MG 531 W S800 | 533 | 0.398 | 533 | 0.399 | 340 | 0.313 | 445 | 0.447 |
| MG 633 1 W S800 | 533 | 0.401 | 533 | 0.405 | 340 | 0.322 | 448 | 0.447 |
| L-2083-2-+L2085-1-S1000 | 533 | 0.408 | 533 | 0.415 | 340 | 0.332 | 446 | 0.409 |
| AWS5-90818-1 | 533 | 0.398 | 533 | 0.406 | 340 | 0.332 | 448 | 0.447 |
| EDL5100 | 511 | 0.420 | 511 | 0.411 | 340 | 0.322 | 448 | 0.447 |
| FL-4255 | 512 | 0.411 | 512 | 0.419 | 345 | 0.331 | 450 | 0.494 |
| FL-5049 | 560 | - | 564 | 0.502 | 340 | - | 480 | 0.448 |
| FL-6040 | 500 | - | 510 | 0.273 | - | - | 510 | 0.542 |

Table 2. Characteristics of the photoluminescence bands and decay times in the maxima of the luminescence bands for phosphors.

| Phosphors | Characteristics of band. $\lambda_{\text{ex-m}} = 452$ nm | | |
|---------------|---|----------|-------------|
| | $\lambda_{\text{em-m}}$, nm | FWHM, eV | τ , ns |
| AWS-5/90818-1 | 535±2 | 0.474 | 61 |
| L-2086/2W | 550±2 | 0.457 | 62 |
| MG-397/2W | 545±2 | 0.438 | 64 |
| MG-531/W | 532±2 | 0.447 | 62 |
| MG-558/2W | 537±2 | 0.457 | 65 |
| MG-571/W | 535±2 | 0.447 | 62 |
| SDL3300 | 553±2 | 0.443 | 64 |
| SDL3000 | 556±2 | 0.475 | 66 |
| SDL3400 | 550±2 | 0.455 | 65 |
| SDL4000 | 532±2 | 0.468 | 61 |
| SDL4100 | 530±2 | 0.462 | 60 |
| SDL5000 | 517±2 | ~0.450 | 53 |

The comparison of the results obtained in the study of the radiative characteristics of phosphors and their elemental composition allows the following conclusion. No direct relation of the radiation characteristics can be observed, i.e. spectral and kinetic characteristics are not related to the composition of the studied phosphors. This implies that the emission characteristics of phosphors depend not only on the elemental composition, but on the lattice defects introduced into the crystal during synthesis. Variation in the elemental composition causes changes in the defect structure of the crystal, which can result in the formation of similar type of defect and nanodefekt complexes.

4. Conclusion

The results obtained in the study of zinc tungstate based scintillation crystals imply that complex nanometer-sized defects are formed in these crystals during synthesis. The kinetic

characteristics of the luminescence of the investigated ZnWO_4 and $\text{ZnWO}_4\text{:Eu}$ crystals dramatically change for crystals which are 10 nm and less in size.

In the studied white LED phosphors, the spectral and kinetic characteristics of the luminescence in the main bands are similar irrespective of the great difference in the elemental composition of the phosphors. This suggests that the emission centers and relaxation of these centers in the studied phosphors are similar. Apparently, the radiative characteristics of the phosphor depend not only on the composition but also on the imperfection of the medium related primarily to the intrinsic defects. It may be assumed that during synthesis complex defects (nanodefects) with emission centers containing intrinsic defects are formed in the phosphor. Nanodefects cause a sharp increase in the efficiency of the transfer of excitation energy to the emission centers.

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