

## EXCITON X-RAY INDUCED LUMINESCENCE OF $Y_2O_3$ POLYCRYSTALS SINTERED FROM THE NANOPOWDER<sup>†</sup>

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The paper is devoted to the changes in the X-ray luminescence spectra of nanoscale  $Y_2O_3$  ceramics, namely the radiation associated with a self-trapped exciton. Additional heat treatment (annealing) of ceramic samples leads to changes in the exciton band of the spectra. These are a change in the shape and shift of the maximum of this band. Long-term irradiation of the samples by X-ray photons with an energy of 60 keV also led to changes in the exciton band. A theoretical model based on experimental data explains the changes in the spectra. The energy source of luminescence in this case is photoelectrons formed by energetic photons. Traps for these electrons are formed on the surface of submicrocrystals. Changes in the surface-to-volume ratio of crystals, as well as the frequencies of excited phonons and excitons are the basis for changes in the X-ray luminescence spectra of  $Y_2O_3$  ceramics.

**Keywords:** X-ray irradiation; exciton luminescence; yttrium oxide; spectrum; powder sintering

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### INTRODUCTION

Recently, the number of  $Y_2O_3$  studies both from a fundamental point of view and with regard to application in important technical tasks, has grown significantly. At first the largest share of yttrium oxide consumed was in the production of such phosphors, which can emit shades of red on electron beam displays (for example, television screens). The scope of other applications is gradually increasing. Yttrium oxide is also used in high-power lasers, in energy-saving white LEDs, to increase the strength and durability of aluminum and magnesium alloys, in specialized types of glass and optical lenses, in various electrical and gas sensors, in high-quality ceramics [1].

$Y_2O_3$  ceramics is the basis of a family of phosphors that differ in the elements with which the matrix is doped. In recent years, white light-emitting diodes (W-LED) have replaced traditional light bulbs and fluorescent lamps due to their high luminous efficiency, long working time, energy saving, high reliability, high reproduction index and environmental friendliness [2].

Over the past few decades, mono- and polycrystalline ceramics have been in great demand due to their excellent chemical and physical stability with high transparency over a wide range of wavelengths. They are used for military use and in the semiconductor industry, for example, as components of transparent armor, window domes, and plasma etching chambers [1, 2]. This study focuses on transparent  $Y_2O_3$  ceramics, which have been attractive as a medium for use in tomorrow's high-power lasers and luminescent materials due to their higher thermal conductivity with lower thermal expansion compared to  $Y_3Al_5O_{12}$  (YAG). Therefore,  $Y_2O_3$  is selected as the main material for solid-state lasers [3]. Solid-state ceramic lasers have a wide range of applications in industry, medicine and the military. This research paper presents the production of vacuum-sintered  $Y_2O_3$  ceramics synthesized by the coprecipitation method [3].

New directions of use of this compound should be noted separately. It turned out that the addition of yttrium nanoparticles to lubricants significantly reduces friction in mechanisms and can be recommended as a Lubricant Automotive Application [4].

The luminescence spectra of  $Y_2O_3$  upon excitation by various types of ionizing radiation are well known. The most powerful band in the spectra is the radiation associated with self-trapped exciton (STE) decay [5]. In our previous work, we presented results clearly indicating that additional annealing leads to changes in luminescence in this wavelength band [6]. In the same works, physical reasons were given that can lead to such an effect.

The purpose of this work is the theoretical reasoning of changes in the luminescence spectra of  $Y_2O_3$ , which are associated with additional heat treatment of the samples.

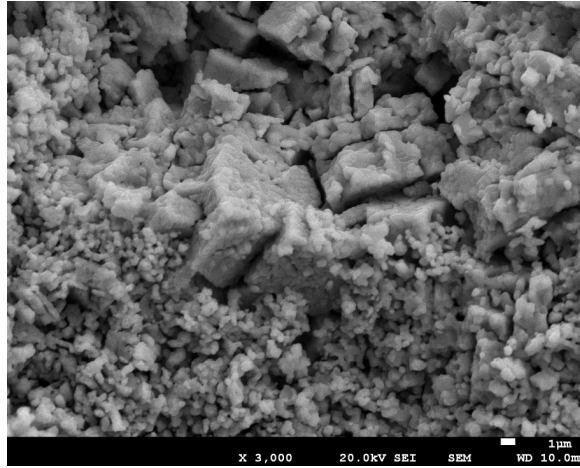
### YTTRIUM OXIDE SAMPLES FOR EXPERIMENTATION

Experimental studies of  $Y_2O_3$  exciton luminescence induced by 60 keV X-ray photons were carried out with the samples prepared by sintering technique. The detail description of the experiment and the sample preparation procedure one can find in our previous works [6-7]. The samples were ceramics with the shape of round plates (with a diameter of 10.0 mm and a thickness of 3 mm) with a fine-grained nanoscale structure. They were made from ITO LUM nanopowder by sintering

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of compacted pellets for one hour in atmospheric conditions at a temperature of  $1500^\circ\text{C}$ . Some of ceramics were additionally annealed at a temperature of  $1000^\circ\text{C}$  for 10 hours. The results of the study of these samples using an SEM- and XRD-diagnostics, given in previous works, did not reveal any difference in the structure of annealed and unannealed polycrystals. As can be seen from SEM-image on Fig. 1, the sample consists of randomly arranged sub-microcrystals of  $Y_2O_3$ . It can be seen that there are significant cavities between the crystals, which can influence a luminescence.

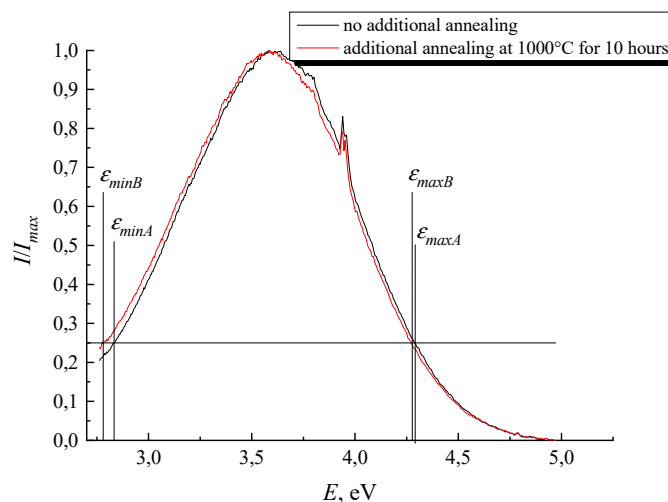


**Figure 1.** SEM-image of fresh cleavage for  $Y_2O_3$  sintered at  $T = 1500^\circ\text{C}$

The main energy channel of luminescence in this case is production of photoelectrons by X-ray photons with subsequent conversion of their energy into luminescent radiation at transitions in crystals. The ratio between the volume of the crystals in the sample and the cavities (surfaces of the crystals) is important for the luminescence output.

### EXCITON BAND LUMINESCENCE SPECTRA

It was previously shown [7] that after annealing of yttrium oxide polycrystals, the luminescence spectra due to STE recombination shifted to the long-wavelength region. This conclusion was made on the basis of the fact that the maximum of the band of the annealed sample is shifted towards longer wavelengths as compared to the case of the unannealed sample. Figure 2 shows the typical normalized luminescence spectra  $S(\varepsilon)$  in the energy range from 2.762 eV (450 nm) to 4.972 eV (250 nm), which corresponds to exciton luminescence, for two  $Y_2O_3$  samples that differ in additional annealing at  $1000^\circ\text{C}$  for 10 hours.



**Figure 2.** Normalized luminescence spectra for two  $Y_2O_3$  samples sintered at  $T=1500^\circ\text{C}$  for 1 hour without additional annealing (A) and with annealing at  $T=1000^\circ\text{C}$  for 10 hours (B).

As can be seen from the figure, the long-wave shift occurs both for the long-wave limit of the luminescence photon spectrum (with photon energy  $\varepsilon_{min}$  at the level of  $-12$  dB) and for the short-wave limit (with photon energy  $\varepsilon_{max}$ ). The calculated average photon energies lead to the same conclusion about the long-wavelength shift in the spectra for the samples with additional annealing:

$$\bar{\varepsilon} = \int_{\varepsilon_{min}}^{\varepsilon_{max}} \varepsilon S(\varepsilon) d\varepsilon \left\{ \int_{\varepsilon_{min}}^{\varepsilon_{max}} S(\varepsilon) d\varepsilon \right\}^{-1}$$

Table 1 shows the corresponding values of the average photon energy of exciton luminescence for the samples being studied.

**Table 1.** The average photon energy of exciton luminescence

No	Preparation technology of Y <sub>2</sub> O <sub>3</sub> sample	$\bar{\varepsilon}$ , eV	$\varepsilon_{min}$ , eV	$\varepsilon_{max}$ , eV
1	Sintering at $T=1500^{\circ}\text{C}$ for 1 hour without additional annealing	3.5072	2.8379	4.2862
2	Sintering at $T=1500^{\circ}\text{C}$ for 1 hour with additional annealing at $T=1000^{\circ}\text{C}$ for 10 hours	3.4738	2.7746	4.2715

A similar effect of reducing the energy and frequency of radiation photons in Y<sub>2</sub>O<sub>3</sub> with a decrease in temperature was described in detail in [8]. According to the developed theory, upon cooling, the stiffness of the crystals increases and thus the frequency of optical phonons, which are associated with excitons, increases. At the same time, the energy of the ground state of the exciton increases in proportion to the phonon energy  $\hbar\omega_u$  of its own optical mode as follows:  $E_u = S_u\hbar\omega_u$ . The energy of the excited state defines the absorption properties of Y<sub>2</sub>O<sub>3</sub> whereas the energy of ground state is responsible for the energy of photons at emission:

$$\varepsilon = \hbar\omega = E_0 - S_u\hbar\omega_u, \tag{1}$$

here  $E_0$  is the energy at the bottom of excited state. As a result, changes in the phonon energy  $\hbar\omega_u$  results in a small shift of the exciton spectrum into the long-wavelength region [8-10].

According to recent studies, annealing affects the composition, microstructure, and mechanical properties of not only single crystals, but also Y<sub>3</sub>O<sub>2</sub> films [11-14]. Therefore, the reason for the decrease in radiation energy can be, as in the case of cooling, an increase in the stiffness of microcrystals, which leads to an increase in the phonon frequency  $\omega_u$  of the optical mode. The formula for the relative change in phonon frequency follows directly from the expression (1) for relaxation energy

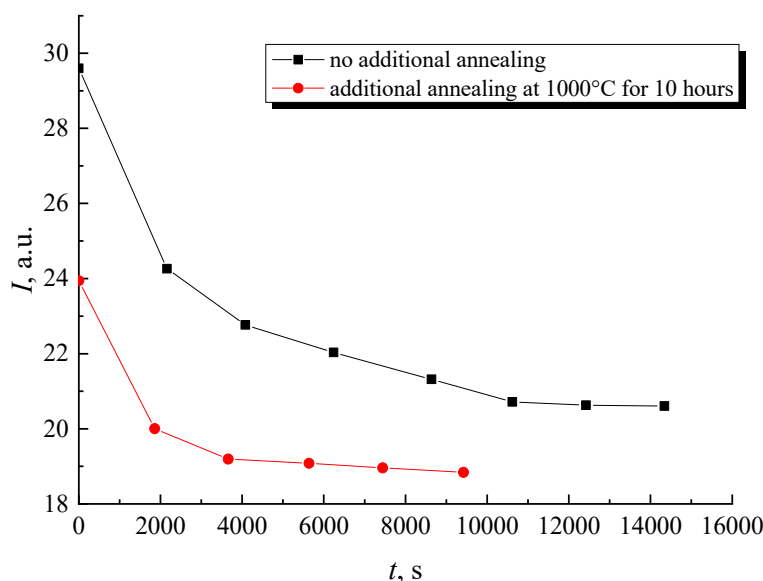
$$\frac{\Delta\omega_u}{\omega_u} = \frac{\hbar\Delta\omega}{S_u\hbar\omega_u}$$

where  $\hbar\Delta\omega$  is the change in energy of luminescent radiation photons. Using the data of table 1, we get  $\Delta\omega_u/\omega_u = 2.2 \times 10^{-2}$ .

### TIME DEPENDENCE OF THE LUMINESCENCE

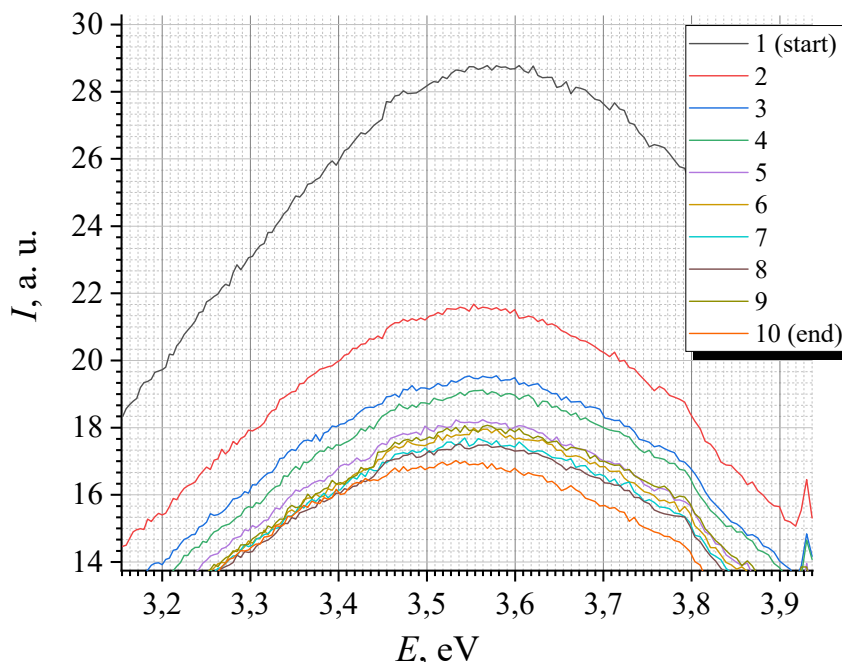
During the long-term continuous X-ray irradiation of yttrium oxide samples, the intensity of luminescence decreases sharply at first, but eventually reaches a plateau. As it is shown on Fig. 3, this feature applies to both additionally annealed and unannealed samples. As a matter of fact, the curve presented on this figure represents the dependence of exciton luminescence on the radiation dose of continuous irradiation.

Note that to plot the curves of the dependence of the exciton luminescence intensity on the irradiation time, we used data on the intensity level at a wavelength of  $\lambda=350$  nm, which corresponds to the luminescence photon energy of 3.56 eV. The reason is that the maximum of the luminescence spectrum associated with excitons did not change during the irradiation time and was always close to this value.



**Figure 3.** The dependence of luminescence intensity at  $\lambda=350$  nm (photon energy of 3.56 eV) for two Y<sub>2</sub>O<sub>3</sub> samples sintered at  $T=1500^{\circ}\text{C}$  for 1 hour without additional annealing and with annealing at  $T=1000^{\circ}\text{C}$  for 10 hours on the time of X-ray irradiation

The decrease of luminescence spectral intensity with exposure time is shown on Fig. 4. Table 2 presents the numerical values of the luminescence level, which corresponds to the spectral maximum for each of the spectra presented on Fig. 3. The average time interval between experimental data points of the spectra (cyclic scanning with dose accumulation) is about 1800 seconds.



**Figure 4.** Decrease of exciton luminescence with irradiation cycle (time) for Y<sub>2</sub>O<sub>3</sub> sample sintered at 1500°C for 1 hour without additional annealing

**Table 2.** The parameters of exciton intensity maxima

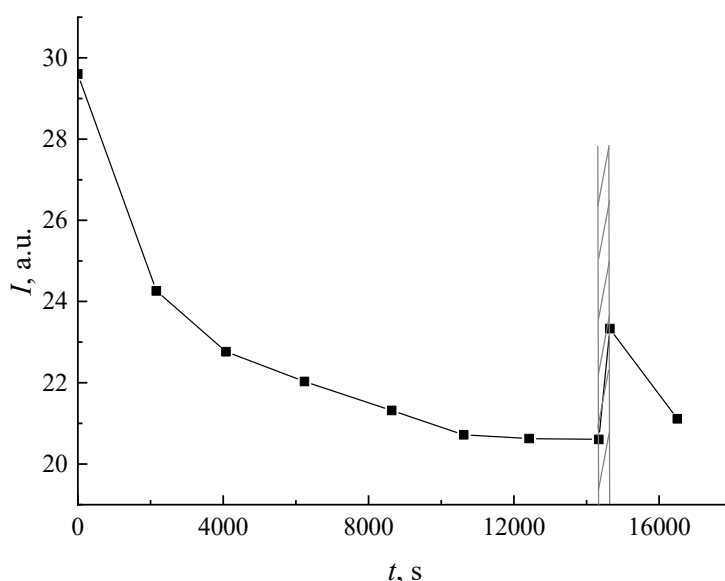
The number of cycle scanning	Photon energy at maximum, eV	Luminescence intensity at maximum, a. u.
1	3.59	28.77
2	3.56	21.59
3	3.56	19.52
4	3.56	19.12
5	3.56	18.16
6	3.56	17.95
7	3.56	17.68
8	3.56	17.48
9	3.56	18.03
10	3.54	16.94

The experimental dependences of luminescence intensity at  $\lambda=350$  nm (photon energy of 3.56 eV) for both types of Y<sub>2</sub>O<sub>3</sub> samples (see Fig. 3) were analyzed and treated by Origin program fitting procedure. The best match of the experimental data on the dynamics of the luminescence intensity with the fitting results can be achieved when using the time dependence with two exponentials:

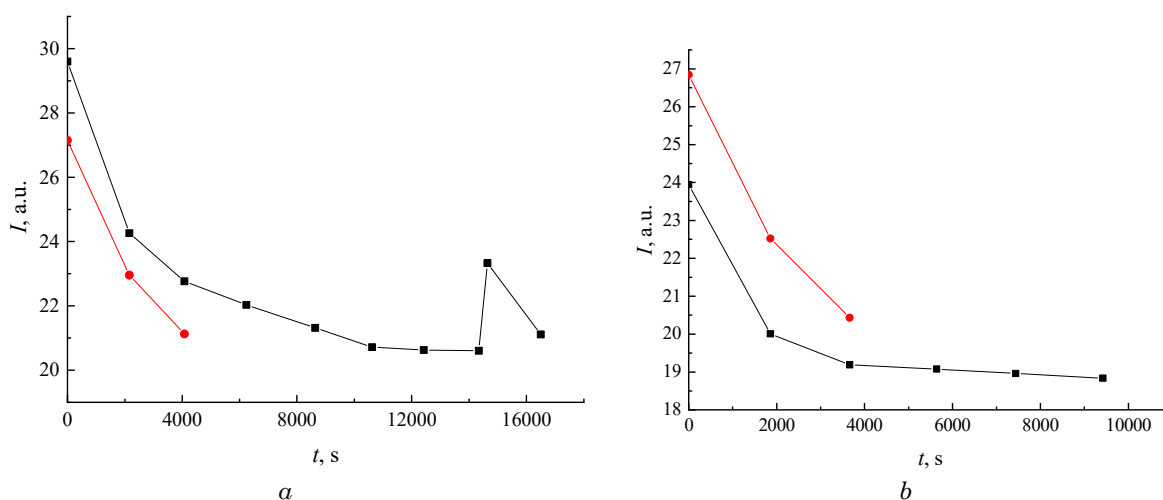
$$I(t) = I_0 - I_1 - I_2 + I_1 e^{-b_1 t} + I_2 e^{-b_2 t} = I_0 - I_1(1 - e^{-b_1 t}) - I_2(1 - e^{-b_2 t}).$$

It was suggested in [7] that the luminescence level decrease is caused by the presence of traps for photoelectrons. The results of the fitting can be interpreted by the presence of two types of traps, each of which is characterized by its capacities  $I_1$ ,  $I_2$  and the relaxation rates of trapped electrons  $b_1$  and  $b_2$ .  $I_0$  is initial value of the luminescence intensity at  $t=0$ , which decreases at  $t \rightarrow \infty$  to the smallest value due to the filling of traps. At the same time, the inequality must be fulfilled.

After termination of X-ray irradiation, the traps must be emptied, that is, the concentration of captured electrons in the traps must gradually decrease to zero. The emptying rate is determined by the same constants  $b_{1,2}$  as the relaxation rate, since the emptying process is the inverse of the trap filling process. As a result, even after a short-term termination of X-ray irradiation for 10-20 minutes upon further resumption of irradiation, a partial recovery of the luminescence level is observed, as shown, for example, for the sample without annealing on Fig. 5. This means that in this case the dependence of the luminescence intensity on the irradiation dose ceases to be a monotonic time function.



**Figure 5.** Recovery of the luminescence level upon continuation of irradiation after a brief shutdown of X-ray irradiation for  $Y_2O_3$  sample without additional annealing. The time interval without X-ray exposure is shaded.



**Figure 6.** Recovery of the luminescence level upon resumption of irradiation after a long termination of X-ray irradiation in the  $Y_2O_3$  samples: *a* is without additional annealing, *b* is additionally annealed (squares correspond to first X-ray exposure, circles – the second repeated exposure after X-ray termination).

Moreover, the recovery of the luminescence level appears to be greater the longer the time of its absence. This is associated with a higher level of trap emptying, since at  $t \rightarrow \infty$  the concentration of trapped electrons must decrease to zero. As shown on Fig. 6a, after a long termination of X-ray irradiation for the sample without annealing, there is an almost complete recovery of the luminescence intensity (see table 3). In the case of the annealed sample after long termination of X-ray irradiation, even some increase in the exciton luminescence intensity was observed during re-irradiation, as shown on fig. 6b and Table 3.

**Table 3.** The exciton luminescence intensity at maximum

Technique of sample preparation	The maximum intensity at the first exposure, a. u.	The maximum intensity at the second exposure, a. u.
No additional annealing	29.6003	27.1511
Additional annealing	23.9435	26.8464

### CONCLUSIONS

The paper presents the theoretical model of exciton luminescence of  $Y_2O_3$  ceramics sintered from nanopowder. The samples were sintered at a temperature of  $1500^\circ C$  for 1 hour, then some of them were removed from the furnace, and the others were additionally annealed at a temperature of  $1000^\circ C$  for 10 hours. Luminescence was excited by continuous X-ray radiation with energy of 60 keV.

It is shown that the effect of additional heat treatment on the luminescence spectrum in the STE region can be explained by the changes in the coupling of excitons with phonons. An increase in the frequency of phonons, which leads to a decrease in the energy of photons of STE luminescent radiation, is calculated.

The experimental results for long-term irradiation indicated a significant role of photoelectron traps formed between the surfaces of submicrocrystals in  $Y_2O_3$  samples. The intensity of luminescence initially decreases quite rapidly, but over time exponentially reaches a plateau. Temporary termination of X-ray irradiation leads to the disappearance of luminescence, and then, when turned on, its intensity becomes greater than it was at the plateau. This effect is associated with the gradual capture of photoelectrons by the traps until they are completely filled, as a result of which the luminescence level reaches a plateau. The traps should be emptied after the X-ray radiation has stopped. When the X-ray is turned on again, they are again filled with photoelectrons, which in turn leads to a decrease in the level of exciton luminescence.

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#### ЕКСИТОННА ЛЮМІНЕСЦЕНЦІЯ ПОЛІКРИСТАЛІВ $Y_2O_3$ , ЩО СПЕЧЕНІ З НАНОПОРОШКУ

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Стаття присвячена вивченню змін у рентгенлюмінесцентних спектрах нанорозмірної кераміки  $Y_2O_3$ , а саме випромінення, що пов'язане з самозахопленим екситоном. Додаткова теплова обробка (відпал) зразків кераміки призводить до змін у екситонній смузі спектрів. Це зміна форми та зсув максимуму цієї смуги. Довготривале опромінення зразків рентгенівськими фотонами з енергією 60 кеВ також призводило до змін у екситонній смузі. Теоретична модель, яка базується на експериментальних даних, пояснює зміни у спектрах. Енергетичним джерелом люмінесценції у цьому випадку є фотоелектрони утворені енергійними фотонами. На поверхні субмікрокристалів утворюються пастки для цих електронів. Зміни у співвідношенні поверхні з об'ємом кристалів, а також частот збуджених фононів та екситонів є базою для змін у спектрах рентгенлюмінесценції кераміки  $Y_2O_3$ .

**Ключові слова:** рентгенівське опромінення, екситонна люмінесценція, оксид ітрію, спектр, спікання порошку