



Article

# Exciton Luminescence and Optical Properties of Nanocrystalline Cubic Y<sub>2</sub>O<sub>3</sub> Films Prepared by Reactive Magnetron Sputtering

Anatoly Zatsepin<sup>1</sup>, Yulia Kuznetsova<sup>1,\*</sup>, Dmitry Zatsepin<sup>1,2</sup> , Chi-Ho Wong<sup>3,4</sup>, Wing-Cheung Law<sup>3</sup> , Chak-Yin Tang<sup>3</sup> and Nikolay Gavrilov<sup>5</sup>

<sup>1</sup> Institute of Physics and Technology, Ural Federal University, 620075 Ekaterinburg, Russia

<sup>2</sup> Institute of Metal Physics, Ural Branch of Russian Academy of Sciences, 620108 Ekaterinburg, Russia

<sup>3</sup> Department of Industrial and Systems Engineering, The Hong Kong Polytechnic University, Hong Kong

<sup>4</sup> Research Institute for Advanced Manufacturing, The Hong Kong Polytechnic University, Hong Kong

<sup>5</sup> Institute of Electrophysics, Ural Branch of Russian Academy of Science, 620049 Ekaterinburg, Russia

\* Correspondence: iu.a.kuznetsova@urfu.ru

**Abstract:** This paper presents a comprehensive study of the energy structure, optical characteristics, and spectral-kinetic parameters of elementary excitations in a high-purity nanocrystalline cubic Y<sub>2</sub>O<sub>3</sub> film synthesized by reactive magnetron sputtering. The optical transparency gaps for direct and indirect interband transitions were determined and discussed. The dispersion of the refractive index was established based on the analysis of interference effects. It was found that the refractive index of the Y<sub>2</sub>O<sub>3</sub> film synthesized in this study is higher in order of magnitude than that of the films obtained with the help of other technologies. The intrinsic emission of Y<sub>2</sub>O<sub>3</sub> film has been discussed and associated with the triplet–singlet radiative relaxation of self-trapped and bound excitons. We also studied the temperature behavior of the exciton luminescence of Y<sub>2</sub>O<sub>3</sub> for the first time and determined thermal activation barriers. The optical energy and kinetic parameters of cubic Y<sub>2</sub>O<sub>3</sub> films were analyzed in comparison with those of the monoclinic films of yttrium oxide. The main difference between the optical properties of cubic and monoclinic Y<sub>2</sub>O<sub>3</sub> films was established, which allowed for a supposition of their application prospects.

**Keywords:** nanocrystalline Y<sub>2</sub>O<sub>3</sub> films; magnetron sputtering; luminescence; excitons; optical absorption; interband transitions; refractive index; thermal activation barriers



**Citation:** Zatsepin, A.; Kuznetsova, Y.; Zatsepin, D.; Wong, C.-H.; Law, W.-C.; Tang, C.-Y.; Gavrilov, N. Exciton Luminescence and Optical Properties of Nanocrystalline Cubic Y<sub>2</sub>O<sub>3</sub> Films Prepared by Reactive Magnetron Sputtering. *Nanomaterials* **2022**, *12*, 2726. <https://doi.org/10.3390/nano12152726>

Academic Editors: Shiliang Mei, Xiaoyan Liu, Bobo Yang and Dezhen Shen

Received: 28 June 2022

Accepted: 1 August 2022

Published: 8 August 2022

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Thin film oxides play an important role in emerging technologies such as photonics; micro-, nano-, and opto-electronics; as well as alternative energy sources [1,2]. Rare-earth oxides represent a promising group of multifunctional materials since they exhibit significant optical properties which are useful for commercial employment: high dielectric constant (~12–16), optical transparency over a relatively wide spectral range, and low phonon energy (up to 600 cm<sup>-1</sup>) [3]. Additionally, rare-earth oxides can be successfully involved in the manufacturing of laser devices, optical fibers, light-emitting diodes, high-frequency diodes, etc. [4]. One of the actively studied materials in this category is yttrium oxide (Y<sub>2</sub>O<sub>3</sub>), which is considered as a suitable host matrix for ionic dopants (including rare-earth and transition-metal ions) in order to construct and develop solid-state optical devices [5–7].

Three structural Y<sub>2</sub>O<sub>3</sub> polymorphs are currently known: cubic, monoclinic, and hexagonal, which are commonly referred to as C-, B-, and A-type structures, respectively [8]. Among these crystal structures, cubic Y<sub>2</sub>O<sub>3</sub> is the most stable phase under normal conditions (room temperature and atmospheric pressure). The optical properties of a cubic Y<sub>2</sub>O<sub>3</sub> host in various modifications (bulk crystal, transparent ceramic, nanoparticles) have

recently been studied in sufficient detail (e.g., see Refs. [9–12]). It has been found for bulk crystalline  $Y_2O_3$  that the intrinsic luminescence of such a host matrix is associated with excitons and optically active defects. Additional interesting results concerning the interactions between excitons and ionic dopants have been reported as well. The energy transfer from self-trapped excitons to rare-earth ions in  $Y_2O_3$  nanoparticles was discovered, and the quenching model of intrinsic luminescence in  $Y_2O_3$  was proposed in Refs. [12,13]. As for the film-based morphology of yttrium oxide, data concerning the energy gap and the refractive index of  $Y_2O_3$  were reported in Refs. [14,15] for radio frequency magnetron sputtering synthesis technology, electron beam deposition [16], thermal evaporation [17], and atomic vapor deposition techniques [18]. At the same time, the systematic studies on the emission properties of  $Y_2O_3$  films are almost non-existent. It is for this reason that this is still one of the most challenging problems in this area of research since the information about the complex properties of the  $Y_2O_3$  host matrix is highly essential for the onward development of functional materials for commercial applications.

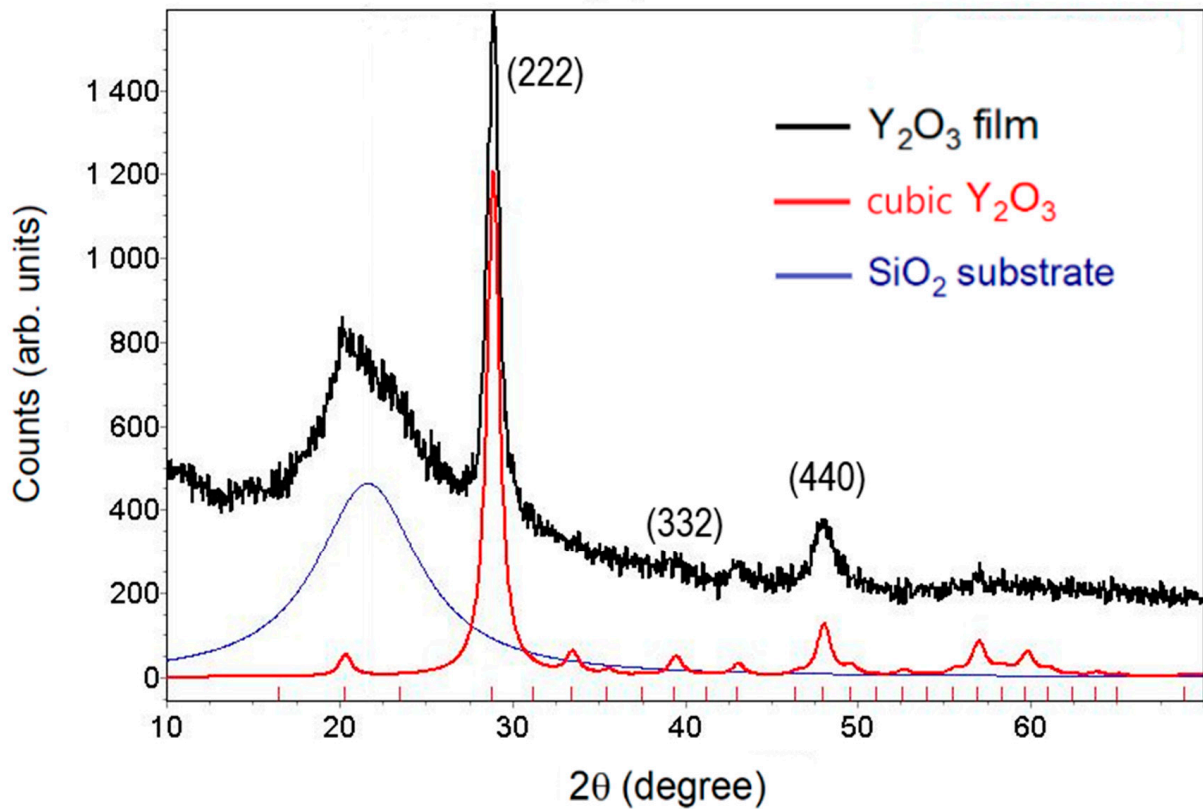
The purpose of the current study is to discover the optical properties of  $Y_2O_3$  thin films synthesized by reactive magnetron sputtering. We aimed to accomplish the following research tasks: to obtain high-purity films with low defectiveness; to study their energy structure and fundamental optical characteristics, including the spectral-kinetic parameters of elementary excitations; to compare our  $Y_2O_3$  data with similar films synthesized by other technologies; and finally, to establish the influence of structural factors on the optical, energy, and kinetic parameters of nanocrystalline  $Y_2O_3$  films. The data obtained will provide the necessary groundwork for the onward development of thin-film  $Y_2O_3$  materials.

## 2. Materials and Methods

$Y_2O_3$  film was deposited onto a silica glass substrate using the dc-pulsed mode (50 kHz, 10  $\mu$ s) of the reactive magnetron sputtering technology. Before the deposition process, the silica glass substrate was cleaned in an acetone solvent using an ultrasonic bath for 20 min, followed by drying in air. A target with a 40 mm diameter and a 2 mm thickness was yielded by employing the cold pressing procedure on metallic yttrium powder at 30 MPa. The magnetron, the sputtered target, and the substrate were placed in a vacuum chamber pumped down to  $6.6 \times 10^{-3}$  Pa with the help of a turbomolecular pump. Sputtering was carried out at 30 W magnetron power for 8 h, in an argon–oxygen atmosphere with a total pressure of 0.4 Pa and an oxygen volume concentration of less than 30%. The temperature of the substrate was maintained at  $400 \pm 25$  °C during the deposition procedure. After deposition, the sample was cooled down to room temperature in a vacuum chamber with a pressure of  $10^{-5}$  Torr. The thickness of the  $Y_2O_3$  film was estimated to be at ~800 nm; it was determined by employing the ball-abrasion method with the help of the Calotest device (CSM Instruments SA, Peseux, Switzerland).

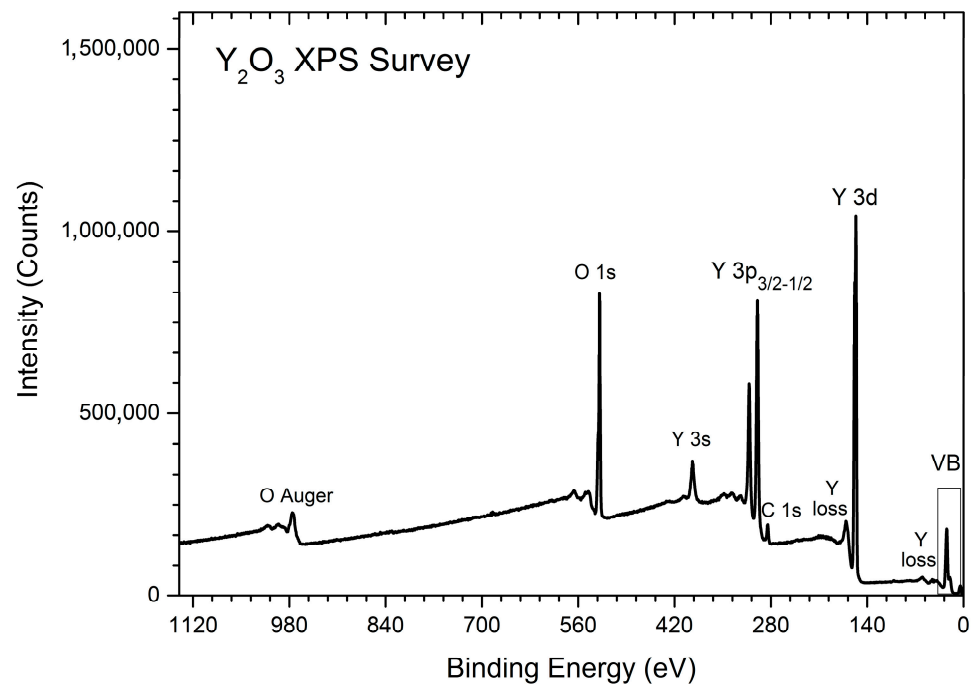
The structural-phase analysis of the sample under study was performed by means of an X-ray diffraction technique using the XPertPro MPD diffractometer with  $Cu K\alpha = 1.5405$  Å radiation. The processing of diffraction patterns was performed using the TOPAS 3 full-profile analysis program, taking into account the presence of a predominant orientation of crystallites (texture) in the material under the study. The diffraction pattern shown in Figure 1 can be identified based on one crystalline phase—the cubic  $Y_2O_3$  (Ia-3 space group) with a lattice parameter of  $a = 10.73$  Å. Plane (111), which is parallel to the surface, was found to be the preferred orientation. The wide diffused peak observed in the pattern is due to the silica glass substrate. No diffraction and reflection associated with the monoclinic modification of  $Y_2O_3$  were found. The average size of 10 nm for the coherent scattering  $D$  was obtained from the Scherrer equation  $D = \frac{k\lambda}{\beta \cos \theta}$ , where  $\lambda$  is the wavelength of the X-ray,  $k$  is a constant equal to 0.89,  $\theta$  denotes the Bragg angle, and  $\beta$  is the half-width of the line profile [19]. The average microstrain  $\langle \epsilon \rangle$  of the film was found to be  $7.4 \times 10^{-3}$  as  $\langle \epsilon \rangle = \frac{\beta \cot \theta}{4}$  [20]. In the Scherrer method used, the crystallite size and the magnitude of the microstrain were determined separately from the same (222) peak without considering the instrumental broadening. In this case, the obtained values of  $D$  and  $\langle \epsilon \rangle$  are the lower bound

on the crystallite size and the upper bound on the microstrain, respectively. The theoretical density of the film was determined to be at  $4.86 \text{ g/cm}^3$  using the equation  $\rho = \frac{ZM_w}{NV}$  [21], where  $Z$  is the number of formula units per unit cell,  $M_w$  is the molecular weight,  $V$  denotes the volume of unit cell, and  $N$  is Avogadro's number.



**Figure 1.** X-ray diffraction pattern of the  $\text{Y}_2\text{O}_3$  film. Reflexes were identified in accordance with JSPDS No. 43-1036 Standard Card for the cubic phase of  $\text{Y}_2\text{O}_3$ . A wide diffused peak is formed due to the silica glass substrate.

A chemical purity inspection of the sample under study was carried out using a ThermoScientific K-alpha Plus XPS spectrometer, which was equipped with a monochromatic micro-focused Al  $K\alpha$  X-ray source and had 0.05 at.% element sensitivity [22]. Operating pressure in an analytic chamber during a fast-wide scan (survey spectroscopy, 200 eV pass energy mode of a  $180^\circ$  hemispherical energy analyzer) was higher than  $3.2 \times 10^{-6}$  Pa. A dual-channel automatic charge compensator was applied to exclude the charging of our sample under XPS analysis because of the loss of photoelectrons. We performed pre-run-up procedures, including the standard degassing of the sample and analyzer, binding energy scale inspection, and re-calibration (when needed). In addition, we employed sputter-cleaned Au ( $4f_{7/2}$  band), Ag ( $3d_{5/2}$  band), and Cu ( $2p_{3/2}$  band) with built-in XPS Reference Standards according to the ISO 16.243 XPS International Standard and the XPS ASTM E2108-00 Standard. We used the built-in electronic database of ThermoScientific XPS spectrometer (ThermoFisher Scientific Waltham, Massachusetts, USA), the NIST XPS Standard Reference Database [23], and the Handbook of Monochromatic XPS Spectra: The Elements of Native Oxides [24] to precisely identify the survey spectrum structure (see Figure 2).



**Figure 2.** XPS Survey spectrum identification of the  $Y_2O_3$  sample under study.

As can be seen in Figure 2, the most intensive peaks belong to yttrium and oxygen, which are the components of yttrium oxide. Carbon contamination (3.97 at.%) exists in the survey spectrum of the inspected  $Y_2O_3$  sample, which is due to the well-known ability of  $Y_2O_3$  to absorb CO and  $CO_2$  species from the atmosphere (e.g., see Ref. [25]) and the general comments of ThermoScientific on the XPS study of yttrium oxide [26]. The measured O/Y ratio gives the value of 1.50, which is very close to the O/Y ratio = 1.51 of cubic  $Y_2O_3$  [25]. The obtained value is dissimilar to the O/Y ratio = 1.46 of monoclinic  $Y_2O_3$  reported in Ref. [27]. The XPS analysis of the survey spectrum confirms the formation of cubic high-purity  $Y_2O_3$  film.

### 3. Results and Discussion

#### 3.1. Interference and Refractive Index

Figure 3 shows the optical transmission spectrum of  $Y_2O_3$  film. The well-discernible interference extremes observed in the range of the optically transparent film indicate the high uniformity of the film and the clear-cut boundary between the film and the substrate. In order to determine the spectral dependence of the refractive index, we employed Swanepoel's method [28] based on the analysis of interference effects. This method allowed for the construction of the upper  $T_M$  and lower  $T_m$  envelopes of the spectrum, which are shown in Figure 3 by the red and blue lines, respectively.

The values of the upper and lower "envelopes" are substituted in order to perform calculations of the refractive index  $n(\lambda)$ :

$$n(\lambda) = \sqrt{N(\lambda) + \sqrt{N(\lambda)^2 - n_s^2}} \quad (1)$$

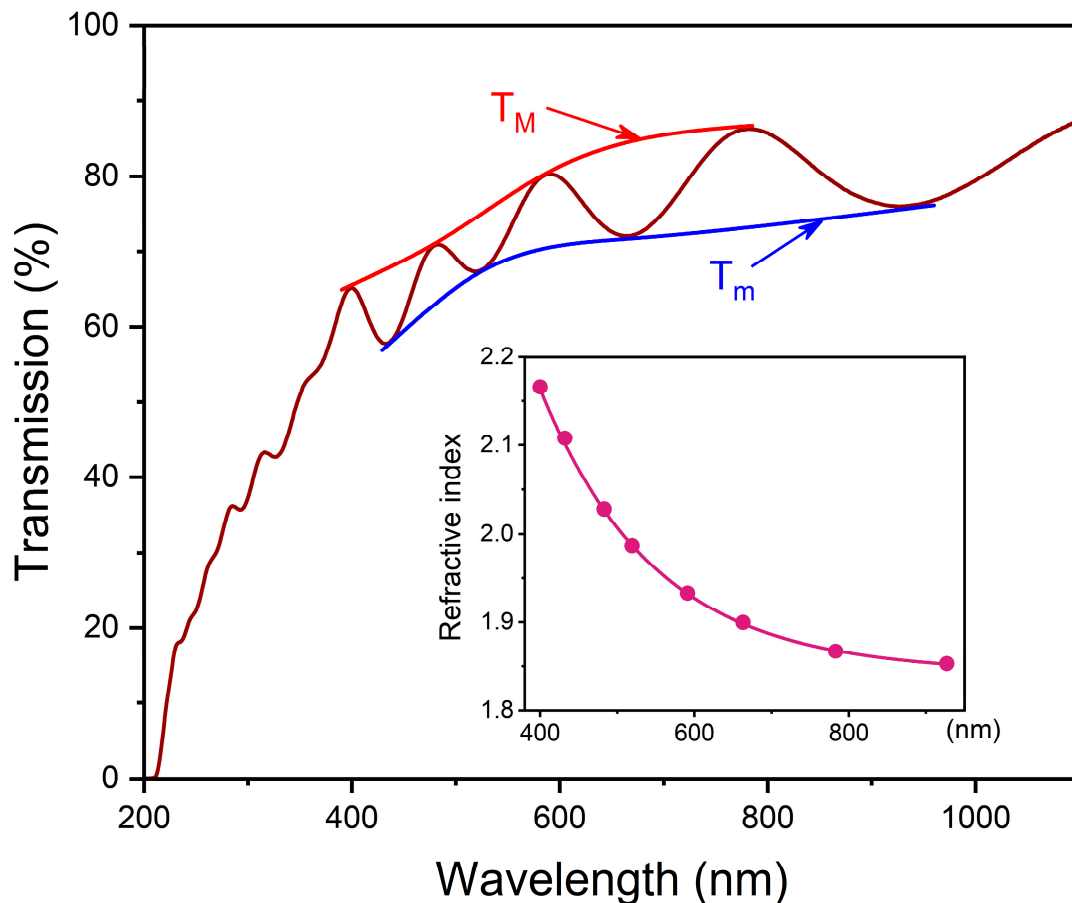
$$N(\lambda) = 2n_s \frac{T_M(\lambda) - T_m(\lambda)}{T_M(\lambda) \cdot T_m(\lambda)} + \frac{n_s^2 + 1}{2} \quad (2)$$

where  $N(\lambda)$  is the calculated intermediate value;  $n_s$  denotes the refractive index of the substrate ( $n_s = 1.452 - 1.469$  for silica glass in the studied spectral range);  $T_M(\lambda)$  and  $T_m(\lambda)$  are the upper and lower "envelopes" of the optical transmission spectrum, respectively. The measured refractive index for the wavelengths corresponds to interference extrema

and is represented by the circles in the inset of Figure 3. Spectral dependence  $n(\lambda)$  can be described using the simplified Cauchy equation (see violet line in the inset of Figure 3) [29]:

$$n(\lambda) = n_0 + \frac{A}{\lambda^2} \quad (3)$$

where  $A = 6.1 \times 10^4 \pm 0.1 \times 10^4$  is a constant and  $n_0 = 1.783 \pm 0.005$  denotes the refractive index when  $\lambda \rightarrow \infty$ . The mean of refractive index dispersion is  $D = n_F - n_C = 0.117 \pm 0.005$  where  $n_F$  and  $n_C$  are the refractive indexes at 486.1 nm and 656.3 nm, respectively.



**Figure 3.** Optical transmission spectrum of  $\text{Y}_2\text{O}_3$  film (brown line). Red and blue lines show the upper  $T_M$  and lower  $T_m$  envelopes of the spectrum, respectively. Inset shows dispersion of the refractive index obtained by Swanepoel's method [28]. The error of the refractive index is  $\pm 0.005$ .

In the targeted range of the spectrum, magnetron-sputtered cubic  $\text{Y}_2\text{O}_3$  film produces a higher refractive index when compared with that for  $\text{Y}_2\text{O}_3$  films synthesized with the use of other methods. For example, the refractive indices of cubic  $\text{Y}_2\text{O}_3$  films synthesized by means of radio frequency magnetron sputtering [15], electron beam deposition [16], and thermal evaporation [17] in the range of 400–800 nm are  $n = 1.95 - 1.91$ ,  $n = 1.93 - 1.89$ , and  $n = 1.82 - 1.72$ , respectively. In addition, the  $\text{Y}_2\text{O}_3$  film inspected in our study exhibits a relatively high dispersion of the refractive index, which is larger in order of magnitude than that reported in the literature for other  $\text{Y}_2\text{O}_3$  films. It is known that refractive index is related to the porosity and packing density of a material [30]. One can estimate the porosity ( $P$ ) and packing density ( $P_d = 1 - P$ ) of the film using the known Lorentz–Lorenz expression [31]:

$$\frac{n^2 - 1}{n^2 + 1} = \frac{n_b^2 - 1}{n_b^2 + 2} (1 - P) \quad (4)$$

where  $n$  and  $n_b$  denote the refractive index of the film and the bulk material, respectively. Assuming that the refractive index value of bulk yttria is  $n_b = 1.937$  at 590 nm [32], and accounting for experimental data obtained for the film, the porosity of the film was estimated to be  $P = 0.003$ . The obtained value is smaller in order of magnitude than the value determined for films prepared by the electron beam deposition technique [16]. We believe that the increased refractive index value of our film is due to its high packing density.

Based on the spectral dependence of the refractive index, the thickness of  $Y_2O_3$  film can be determined as follows:

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_2 n_1 - \lambda_1 n_2)} \quad (5)$$

where  $n_1$  and  $n_2$  are refractive indices at wavelengths  $\lambda_1$  and  $\lambda_2$ , which correspond to the maxima (minima) of the neighboring interference observed in the transmission spectrum. Using several pairs of interference extrema, the average thickness of  $Y_2O_3$  film is  $812 \pm 5$  nm. The film thickness value obtained analytically is close to that declared during the synthesis stage (800 nm—ball-abrasion method). In the next stage of our research, we pay attention to the optical absorption of  $Y_2O_3$  film.

### 3.2. Energy Gaps and Interband Transitions

Figure 4 shows the spectral dependence of the absorption coefficient in the tails of the region of the density of states, which was analyzed using the following expression for the Urbach rule [33]:

$$\alpha(h\nu) = \alpha_0 \cdot \exp\left(\frac{h\nu - E_0}{E_U}\right) \quad (6)$$

where  $\alpha_0$  is a constant,  $E_0$  denotes the coordinate of the crossing point of the so-called “crystal-like” Urbach rule, and  $E_U$  is the Urbach energy denoting the measure of the overall structural disorder of the system under study (static and dynamic) [34]. The Urbach absorption edge is formed by optical transitions between the localized electronic states. The  $E_U$  is a measure of the overall disorder of the material in our study. Based on the principle of equivalence and additivity of static (“frozen” phonons) and dynamic (“thermal” phonons) disorders, the Urbach energy reflects both the intrinsic irregularities of the lattice (i.e., defects, impurities, deviations from stoichiometry, etc.) and the thermal effects induced by the electron–phonon interaction [35,36].

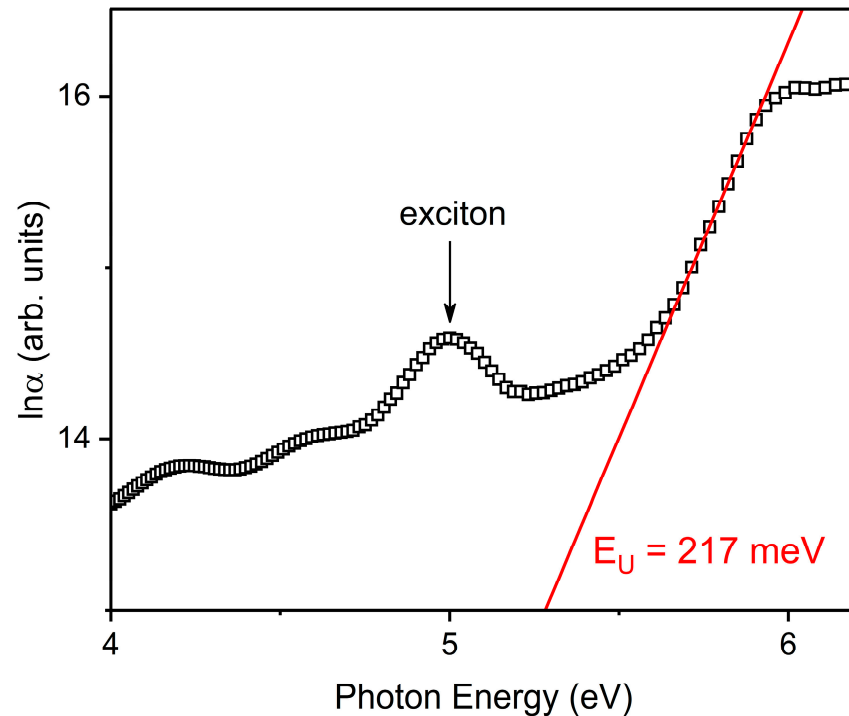
The inverse slope of the linear range of  $\ln \alpha(h\nu)$  dependence refers to  $E_U = 217 \pm 2$  meV (Figure 4). We have to note that the exact value of the Urbach energy was unknown for  $Y_2O_3$ . We compared the obtained  $E_U$  value with that of other materials in the same family of rare-earth oxides—cubic gadolinium oxide films [37]. In our recent study, the Urbach energy of the  $Gd_2O_3$  film was  $483 \pm 2$  meV, and the intrinsic defects had significantly higher concentrations, which ensured a higher degree of structural disorder. As for the  $Y_2O_3$  film, the Urbach energy was smaller, which indicates a relatively lower degree of total structural atomic disorder. In this case, a comparison of the Urbach energy for the  $Gd_2O_3$  and  $Y_2O_3$  films at room temperature gave a relatively good estimation of the total structural disorder, which is a combination of static and dynamic (phonon) disorders.

The analysis of the fundamental absorption edge was performed with the help of the Tauc equation [38,39]:

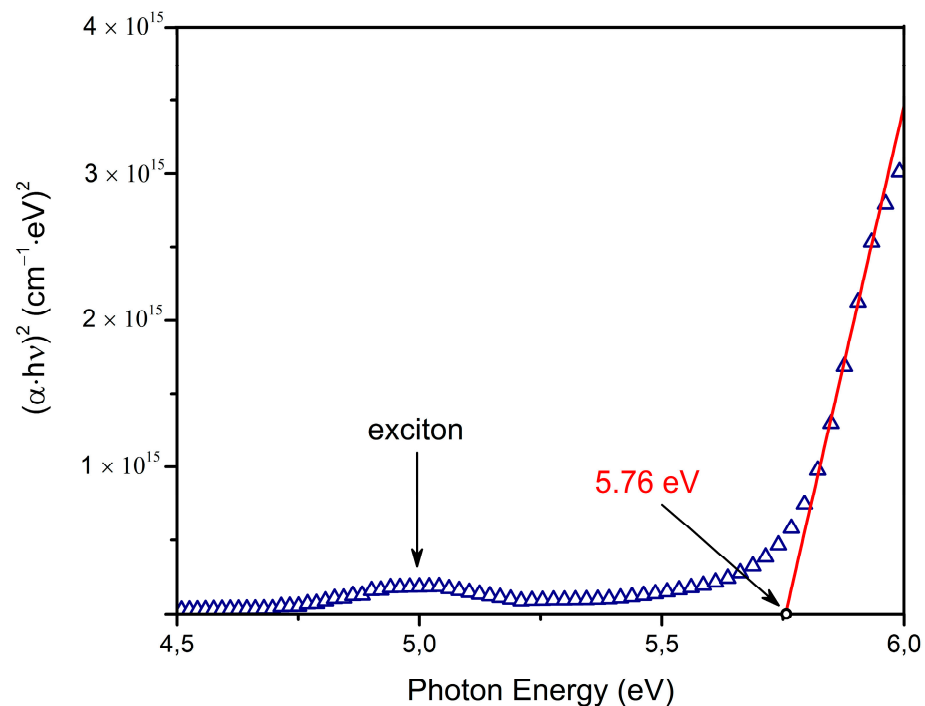
$$(\alpha \cdot h\nu)^n = A \cdot (h\nu - E_g) \quad (7)$$

where  $A$  is a constant;  $\alpha$  denotes the absorption coefficient;  $h\nu$  is the photon energy;  $E_g$  denotes the optical transparency gap, and  $n$  is the exponent which depends on the type of transitions. We studied direct allowed transitions at  $n = 2$ . The corresponding energy gap was determined by extrapolating the linear range of the  $(\alpha \cdot h\nu)^2$  function to the intersection with the abscissa axis, as shown in Figure 5. On the one hand, the measured optical transparency gap is 5.76 eV, which is very close to the value of the optical transparency gap for the  $Y_2O_3$  film synthesized by means of radio frequency magnetron

sputtering ( $E_g = 5.79$  eV) [14]. On the other hand, the optical transparency gap of our sample is slightly larger than that for the  $Y_2O_3$  film synthesized by employing atomic vapor deposition ( $E_g = 5.60$  eV) [18].



**Figure 4.** Spectral dependence of the absorption coefficient in the Urbach coordinates of the  $Y_2O_3$  film. Red line shows an approximation of the linear range of  $\ln \alpha(h\nu)$  dependence. The Urbach energy  $E_U$  was derived from Equation (6). The accuracy of  $E_U$  calculation is  $\pm 2$  meV.

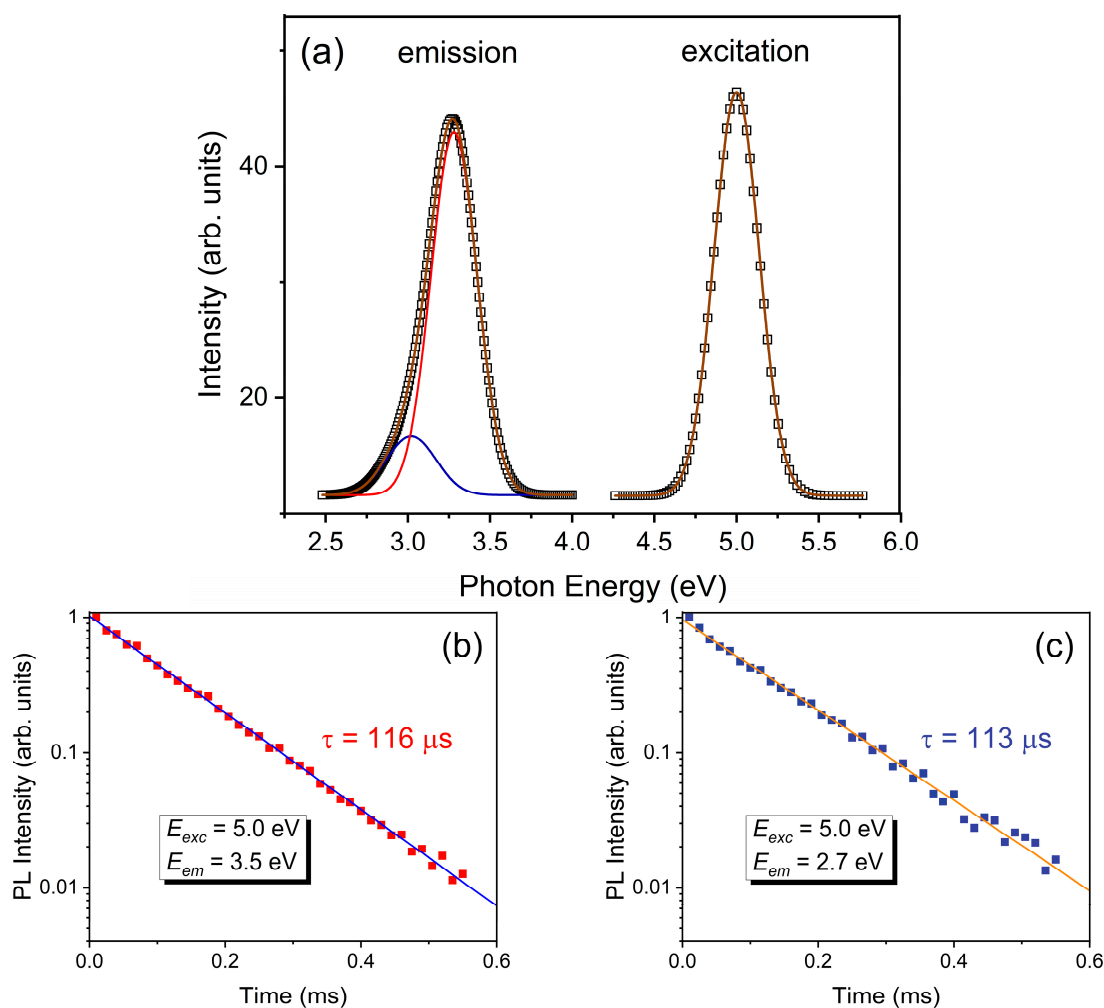


**Figure 5.** Optical absorption spectra of the  $Y_2O_3$  film, shown in Tauc coordinates for direct allowed interband transitions. Arrows indicate the corresponding optical transparency gap with a  $\pm 0.01$  eV accuracy. The band with its maximum at 5.0 eV is associated with exciton absorption.

A band with its maximum at 5.0 eV was found in the absorption spectra (see Figures 4 and 5). We believe that the origin of this band is associated with exciton absorption. It is known that for the bulk cubic  $Y_2O_3$ , a self-trapped exciton is formed by means of photon absorption and with an energy level of 6.0 eV [9]. As for  $Y_2O_3$  nanoparticles with an average size of 10 nm, the exciton absorption band exhibits at 5.9 eV [40]. However, there are no data concerning the optical properties of excitons in  $Y_2O_3$  thin films. The exciton absorption band of  $Y_2O_3$  film is shifted to a low-energy region if compared with bulk materials and nanoparticles. The luminescent properties of excitons in  $Y_2O_3$  film will later be studied in more detail.

### 3.3. Room-Temperature Exciton Emission

Figure 6a shows the emission spectrum of the  $Y_2O_3$  film under an excitation energy of 5.0 eV at room temperature. This emission spectrum is represented by the superposition of two bands whose maxima are located at 3.3 eV (FWHM = 0.3 eV) and 3.0 eV (FWHM = 0.3 eV). The excitation spectra of these two emission bands are similar to each other, and they produce one band with its maximum at 5.0 eV (FWHM = 0.3 eV). The locations of the excitation spectra were carefully calibrated. Otherwise, an overlapping of the spectra might have occurred.



**Figure 6.** Room-temperature emission and excitation spectra of  $Y_2O_3$  film. Red and blue lines show emission bands associated with radiative recombination of bound exciton and self-trapped exciton, respectively (a). Emission decay curves were measured at  $E_{em} = 3.5 \text{ eV}$ ,  $E_{exc} = 5.0 \text{ eV}$  (b) and  $E_{em} = 2.7 \text{ eV}$ ,  $E_{exc} = 5.0 \text{ eV}$  (c). The accuracy of the emission lifetime was  $\pm 3 \mu s$ .



For cubic  $Y_2O_3$  in different morphologies (bulk crystal, transparent ceramic, nanoparticles), the luminescence at 3.4–3.5 eV is related to the radiative de-excitation of self-trapped excitons (*STE*) [9,11,12,41,42]. We believe that the dominant emission band located at 3.3 eV is also associated with the *STE* radiative recombination in  $Y_2O_3$  film, and the spectral position of this band is shifted to the low-energy region when compared to bulk and low-dimensional cases. As for the second emission band, it is located at 3.0 eV, and the low-intensity luminescent band observed in the cubic  $Y_2O_3$  is associated with the radiative recombination of the bounded exciton (*BE*), which was localized in the anion vacancy center of the *F*-type [11,42]. Thus, we believe that emission bands located at 3.3 eV and 3.0 eV are associated with *STE* and *BE*, respectively.

Figure 6b,c show the decay curves of exciton emission. The measurements were carried out by monitoring the emission wavelengths at the tails of the bands in order to avoid their overlap. The decay curves of both emission bands are single-exponential, and the emission lifetimes are 116  $\mu$ s ( $E_{em} = 3.5$  eV) and 113  $\mu$ s ( $E_{em} = 2.7$  eV). A large Stokes shift and slow luminescence decay kinetics indicate that the observed luminescence bands are associated with triplet–singlet radiative transitions. Triplet emission is usually characterized by a flare-up process because it overcomes the thermal activation barrier of the intersystem crossing (*ISC*) from a high-energy singlet state ( $S_1$ ) to a low-energy triplet state ( $T_1$ ) [43,44]. In the next section, we discuss our study of the temperature behavior of exciton-related emission.

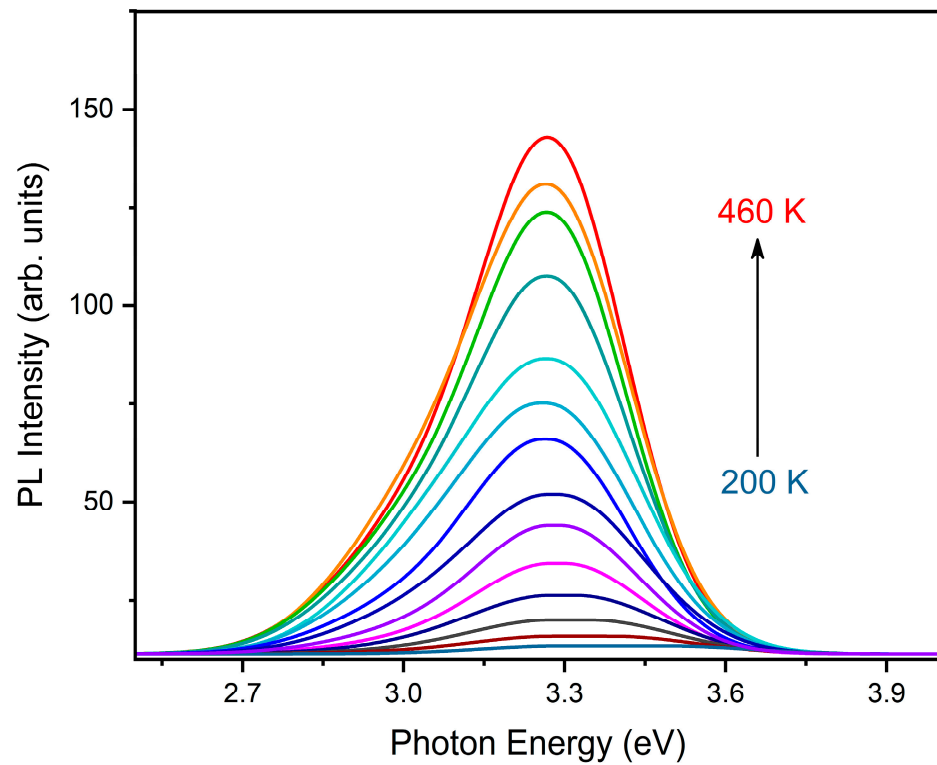
### 3.4. Temperature Behavior of Exciton Emission: Activation Barriers

The temperature-dependent emission spectra of  $Y_2O_3$  film excited by 5.0 eV are shown in Figure 7. It can be seen that emission appears at  $\sim 200$  K, where its intensity increases with temperature growth. The maxima of bands have no significant changes in their energy locations and FWHMs. It can be seen that the temperature broadening of emission bands is absent, and this indicates a relatively weak exciton–phonon interaction. As a consequence, it produces a high-efficiency radiative relaxation. No new luminescence bands were found at low temperatures, which can be associated with singlet–singlet radiative transitions. This phenomenon probably occurs due to the small thermal activation barrier of the singlet–singlet non-radiative transition. Normalized temperature dependences of integrated intensities of luminescence bands whose maxima are located at 3.2 eV (*STE*) and 3.0 eV (*BE*) are shown in Figure 8. It can be noted that *BE*-related emission flares up at high temperatures and quenches at low temperatures. Hence, the thermal activation barriers of flare-up emission and luminescence quenching for *STE* and *BE* are certainly different.

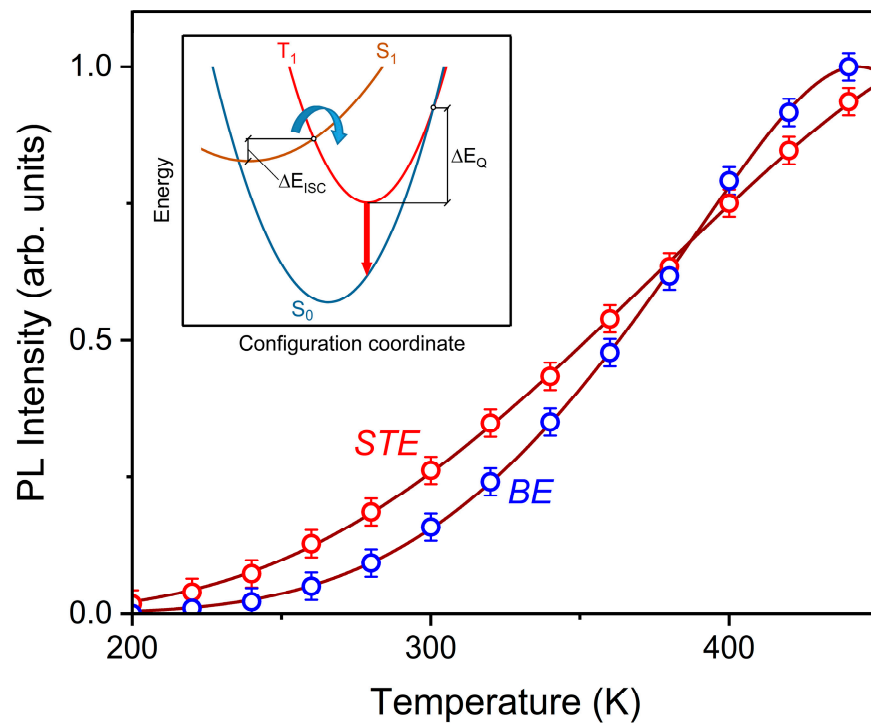
In order to determine thermal activation barriers, we analyzed the temperature dependences of emission using the following analytical expression, which takes into account flare-up emission and luminescence quenching [43]:

$$I(T) = \frac{I_0}{\left\{1 + C_1 \exp\left(\frac{\Delta E_{ISC}}{kT}\right)\right\} \cdot \left\{1 + C_2 \exp\left(\frac{-\Delta E_Q}{kT}\right)\right\}} \quad (8)$$

where  $I_0$  is the maximum luminescence intensity if the quantum effects yield *ISC* and radiative recombination is equal to 1;  $C_1$  and  $C_2$  are kinetic factors of *ISC* and the triplet radiative transition, respectively;  $\Delta E_{ISC}$  is the thermal activation barrier of *ISC*;  $\Delta E_Q$  denotes the thermal activation barrier of emission quenching. Our experimental data are shown in Figure 8. The values of  $\Delta E_{ISC}$  and  $\Delta E_Q$  during *STE* emission are 131 meV and 482 meV, respectively. In contrast, the values of  $\Delta E_{ISC}$  and  $\Delta E_Q$  during *BE* emission are 189 meV and 412 meV, respectively (an accuracy of  $\pm 2$  meV).



**Figure 7.** Temperature-dependent emission of  $\text{Y}_2\text{O}_3$  film excited by 5.0 eV, with a temperature range of 200 K–460 K.



**Figure 8.** Normalized temperature dependences of emissions associated with self-trapped exciton (STE) and bound exciton (BE) in  $\text{Y}_2\text{O}_3$  film. The circles are experimental data, whereas the lines are approximated by Equation (8). The inset shows a configuration coordinate diagram explaining the meaning of the thermal activation barriers  $\Delta E_{ISC}$  and  $\Delta E_Q$  of the intersystem crossing and emission quenching.

The *BE* emission is characterized by a larger flare-up barrier and a lower quench barrier when compared with the *STE* emission. The differences between these two thermal activation barriers are related to the non-identical adiabatic potential curves of *STE* and *BE*. A configuration coordinate diagram is shown in the inset of Figure 8. Symbols  $S_0$ ,  $S_1$ , and  $T_1$  denote the singlet ground state, singlet excited state, and triplet excited state, respectively. A combination of factors, i.e., the emission energy, flare-up barrier, and quench barrier (*BE* versus *STE*), probably suggest that the triplet term of *BE* is more preferably shifted to the left side of the inset in Figure 8. The proposed model for the configuration curves assumes that the barrier of the singlet–singlet non-radiative transitions is very low since no new bands can be detected in the emission spectra even at liquid helium temperatures.

### 3.5. The Role of Structural Factors in the Formation of Optical, Energy, and Kinetic Parameters: Comparison of Cubic and Monoclinic $Y_2O_3$ Films

Comparative characteristics of the optical parameters of cubic and monoclinic  $Y_2O_3$  films are shown in Tables 1 and 2. The monoclinic  $Y_2O_3$  film was synthesized using a similar technology, as described in Section 2; however, during the preparation of metallic yttrium powders, target sputtering sodium was used as an additive [45]. The purpose of adding sodium was to stabilize the monoclinic  $Y_2O_3$  phase. The addition of alkali ions in rare-earth oxides is mainly used in order to create non-stoichiometry in the oxygen sublattice, which promotes the formation of the monoclinic  $Y_2O_3$  phase [27,46]. The phase analysis performed confirms that the synthesized film is pure and has a monoclinic structure, and the average size of coherent scattering is 13 nm. We have highlighted the key features in Tables 1 and 2.

**Table 1.** Fundamental optical parameters of cubic and monoclinic nanocrystalline  $Y_2O_3$  films.  $E_g$  is the optical transparency gap;  $E_U$  denotes Urbach energy;  $n$  is the refractive index in the  $\lambda = 400\text{--}900$  nm range. Parameters of the monoclinic  $Y_2O_3$  film were taken from Ref. [45].

Parameter	Cubic $Y_2O_3$	Monoclinic $Y_2O_3$
$E_g$ , eV	$5.76 \pm 0.01$	$6.10 \pm 0.01$
$E_U$ , meV	$217 \pm 2$	$515 \pm 2$
$n$ ( $\lambda = 400\text{--}900$ nm)	2.165–1.859	1.621–1.532

**Table 2.** Spectral-kinetic parameters of elementary excitations in cubic and monoclinic nanocrystalline  $Y_2O_3$  films.  $E_{exc}$  and  $E_{em}$  are the maxima of excitation and emission bands, which are associated with self-trapped exciton (*STE*) and bound exciton (*BE*);  $\tau$  is the lifetime of an excited state;  $\Delta E_{ISC}$  and  $\Delta E_Q$  are the thermal activation barriers of intersystem crossing and emission quenching, respectively. Parameters of the monoclinic  $Y_2O_3$  film were taken from Ref. [45].

Excitation	Parameter	Cubic $Y_2O_3$	Monoclinic $Y_2O_3$
STE	$E_{exc}$ , eV	$5.00 \pm 0.02$	$4.96 \pm 0.02$
	$E_{em}$ , eV	$3.20 \pm 0.02$	$3.13 \pm 0.02$
	$\tau$ , $\mu$ s	$116 \pm 3$	$113 \pm 3$
	$\Delta E_{ISC}$ , meV	$131 \pm 2$	$47 \pm 2$
	$\Delta E_Q$ , meV	$482 \pm 2$	$193 \pm 2$
BE	$E_{exc}$ , eV	$5.00 \pm 0.02$	$4.96 \pm 0.02$
	$E_{em}$ , eV	$3.00 \pm 0.02$	$2.85 \pm 0.02$
	$\tau$ , $\mu$ s	$113 \pm 3$	$129 \pm 3$
	$\Delta E_{ISC}$ , meV	$189 \pm 2$	$80 \pm 2$
	$\Delta E_Q$ , meV	$412 \pm 2$	$151 \pm 2$

Monoclinic  $Y_2O_3$  film has a higher optical transparency gap than its cubic counterpart. The degree of atomic structural disorder is higher for monoclinic film and can be considered as evidence by the corresponding values of Urbach energy. This feature is likely due to the presence of defects in the monoclinic structure caused by sodium impurities embedded

during fabrication. The refractive index of the cubic  $Y_2O_3$  film is higher than that for monoclinic film because of the higher density of the cubic  $Y_2O_3$  film.

The cubic  $Y_2O_3$  film shows stronger emission energy for the exciton-related luminescent bands than the monoclinic polymorph of the  $Y_2O_3$  film (see Table 2). Differences between the thermal activation barriers of *STE* and *BE* emission are similar to each other in terms of structural polymorphs: *BE* emission is characterized by a larger flare-up barrier and a lower quench barrier when compared with *STE*. As suggested above, this can be traced to the adiabatic potential curves of *STE* and *BE*. It is important to note that the thermal activation barriers of cubic  $Y_2O_3$  in these two cases are relatively high when compared to those of its monoclinic counterpart.

In addition to exciton luminescence, the emission in the region of 3.4–3.8 eV is registered in the monoclinic  $Y_2O_3$  film, which is associated with point defects in the anionic sublattice. Hence, the intensity of defect-related luminescence is comparable to the intensity of exciton-related luminescence. The formation of optically active defects in the monoclinic polymorph is due to the embedded sodium (impurity), which stabilizes the phase. In turn, no optically active intrinsic defects have been found in the high-purity cubic  $Y_2O_3$  film, and luminescence occurs only due to the radiative relaxations of excitons.

Both cubic and monoclinic  $Y_2O_3$  films have certain advantages and disadvantages. The film in a cubic structure has a lower optical transparency, but it shows a higher refractive index when compared with the monoclinic film. The exciton-related luminescence of cubic  $Y_2O_3$  has a much higher quenching barrier, but it also flares up at higher temperatures as compared with the monoclinic  $Y_2O_3$  film. In addition to exciton luminescence, the monoclinic  $Y_2O_3$  film is characterized by defect-related emission, which is absent in the cubic polymorph. All these features should be considered when developing  $Y_2O_3$ -based thin-film materials for specific applications.

#### 4. Conclusions

High-purity nanocrystalline  $Y_2O_3$  film on a silica glass substrate was synthesized by employing the dc-pulsed mode of the reactive magnetron sputtering technique. This film has a cubic single-phase final structure, with a thickness of 800 nm and coherent scattering in the range of 10 nm. Comprehensive studies of the energy structure, optical characteristics, and spectral-kinetic parameters of the elementary excitations of  $Y_2O_3$  film were performed.

Based on the interference effects of the optical transmission spectrum, the dispersion of the refractive index of  $Y_2O_3$  film was determined. It was found that the refractive index ( $n = 2.165$ – $1.859$ ,  $\lambda = 400$ – $900$  nm) of the studied film is higher than that of films synthesized by other methods. Parameters of the band energy structure of  $Y_2O_3$  film were determined with the use of optical absorption spectroscopy. An analysis of the Urbach absorption edge showed a relatively low degree of structural atomic disorder for the cubic film in comparison to the film with a monoclinic structure. The optical transparency gap of the direct interband transitions was 5.76 eV.

Emissions at 3.3 eV and 3.0 eV in the  $Y_2O_3$  film were associated with the triplet–singlet radiative de-excitation of self-trapped and bound excitons, respectively. It was found that the spectral positions of the exciton-related emission bands were shifted to the low-energy region when compared with the known bulk and low-dimensional  $Y_2O_3$  morphologies. The temperature behavior of exciton luminescence in  $Y_2O_3$  was studied for the first time. The thermal activation barriers of intersystem crossing and emission quenching were determined. It was established that the thermal activation barriers of both the flare-up and the quenching of exciton luminescence take on significantly higher values for cubic  $Y_2O_3$  film when compared with its monoclinic counterpart.

The influence of structural types on the optical, energy, and kinetic parameters of  $Y_2O_3$  nanocrystalline films was identified and discussed. The main features of the difference between the optical properties of cubic and monoclinic  $Y_2O_3$  films determine the prospects

for their practical use. The results obtained allow us to move a step forward to further develop optical materials that are based on  $Y_2O_3$  thin-film polymorphs.

**Author Contributions:** Conceptualization, supervision, writing—review and editing, methodology, A.Z.; investigation, writing—original draft, Y.K.; investigation, writing—review and editing, D.Z.; investigation, writing—original draft, funding acquisition, C.-H.W.; investigation, writing—original draft, W.-C.L.; investigation, writing—original draft, funding acquisition, C.-Y.T.; methodology, validation, N.G. All authors have read and agreed to the published version of the manuscript.

**Funding:** The work was supported by the Ministry of Science and Higher Education of the Russian Federation (Ural Federal University Program of Development within the Priority-2030 Program, project № 4.38).

**Data Availability Statement:** Exclude this statement.

**Acknowledgments:** We thank the Research Institute for Advanced Manufacturing and the Industrial Centre of The Hong Kong Polytechnic University for support.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. David, S.P.; Soosaimanickam, A.; Sakthivel, T.; Sambandam, B.; Sivaramalingam, A. *Thin Film Metal. Oxides for Displays and Other Optoelectronic Applications*; Springer: Berlin/Heidelberg, Germany, 2020.
2. Tarancón, A.; Pryds, N. Functional Oxide Thin Films for Advanced Energy and Information Technology. *Adv. Mater. Interfaces* **2019**, *6*, 1900990. [[CrossRef](#)]
3. Yoshimoto, K.; Masuno, A.; Ueda, M.; Inoue, H.; Yamamoto, H.; Kawashima, T. Low phonon energies and wideband optical windows of  $La_2O_3$ - $Ga_2O_3$  glasses prepared using an aerodynamic levitation technique. *Sci. Rep.* **2017**, *7*, 45600. [[CrossRef](#)] [[PubMed](#)]
4. Hossain, M.K.; Hossain, S.; Ahmed, M.H.; Khan, M.I.; Haque, N.; Raihan, G.A. A Review on Optical Applications, Prospects, and Challenges of Rare-Earth Oxides. *ACS Appl. Electron. Mater.* **2021**, *3*, 3715–3746. [[CrossRef](#)]
5. Petry, J.; Komban, R.; Gimmler, C.; Weller, H. Simple one pot synthesis of luminescent europium doped yttrium oxide  $Y_2O_3:Eu$  nanodiscs for phosphor converted warm white LEDs. *Nanoscale Adv.* **2022**, *4*, 858–864. [[CrossRef](#)]
6. Chawarambwa, F.L.; Putri, T.E.; Kamataki, K.; Shiratani, M.; Koga, K.; Itagaki, N.; Nakamura, D. Synthesis of  $Yb^{3+}/Ho^{3+}$  co-doped  $Y_2O_3$  nanoparticles and its application to dye sensitized solar cells. *J. Mol. Struct.* **2021**, *1228*, 129479. [[CrossRef](#)]
7. Chávez-García, D.; Sengar, P.; Juárez-Moreno, K.; Flores, D.L.; Calderón, I.; Barrera, J.; Hirata, G.A. Luminescence properties and cell uptake analysis of  $Y_2O_3:Eu$ , Bi nanophosphors for bio-imaging applications. *J. Mater. Res. Technol.* **2021**, *10*, 797–807. [[CrossRef](#)]
8. Zinkevich, M. Thermodynamics of rare earth sesquioxides. *Prog. Mater. Sci.* **2007**, *52*, 597–647. [[CrossRef](#)]
9. Lushchik, A.; Kirm, M.; Lushchik, C.; Martinson, I.; Zimmerer, G. Luminescence of free and self-trapped excitons in wide-gap oxides. *J. Lumin.* **2000**, *87–89*, 232–234. [[CrossRef](#)]
10. Oliveira, T.C.D.; Silva, M.S.D.; Jesus, L.M.D.; Sampaio, D.V.; Santos, J.C.A.D.; Souza, N.R.D.S.; Silva, R.S.D. Laser sintering and radioluminescence emission of pure and doped  $Y_2O_3$  ceramics. *Ceram. Int.* **2014**, *40*, 16209–16212. [[CrossRef](#)]
11. Fukabori, A.; Yanagida, T.; Pejchal, J.; Maeo, S.; Yokota, Y.; Yoshikawa, A.; Ikegami, T.; Moretti, F.; Kamada, K. Optical and scintillation characteristics of  $Y_2O_3$  transparent ceramic. *J. Appl. Phys.* **2010**, *107*, 073501. [[CrossRef](#)]
12. den Engelsens, D.; Fern, G.R.; Ireland, T.G.; Harris, P.G.; Hobson, P.R.; Lipman, A.; Dhillon, R.; Marsh, P.J.; Silver, J. Ultraviolet and blue cathodoluminescence from cubic  $Y_2O_3$  and  $Y_2O_3:Eu^{3+}$  generated in a transmission electron microscope. *J. Mater. Chem. C* **2016**, *4*, 7026–7034. [[CrossRef](#)]
13. den Engelsens, D.; Fern, G.R.; Ireland, T.G.; Silver, J. Cathodoluminescence of  $Y_2O_3:Ln^{3+}$  ( $Ln = Tb, Er$  and  $Tm$ ) and  $Y_2O_3:Bi^{3+}$  nanocrystalline particles at 200 keV. *RSC Adv.* **2018**, *8*, 396–405. [[CrossRef](#)]
14. Hua, C.; Li, C.; Guo, J.; Yan, X.; Liu, J.; Chen, L.; Wei, J.; Hei, L. Optical properties of cubic and monoclinic  $Y_2O_3$  films prepared through radio frequency magnetron sputtering. *Surf. Coat. Technol.* **2017**, *320*, 279–283. [[CrossRef](#)]
15. Mudavakkat, V.H.; Atuchin, V.V.; Kruchinin, V.N.; Kayani, A.; Ramana, C.V. Structure, morphology and optical properties of nanocrystalline yttrium oxide ( $Y_2O_3$ ) thin films. *Opt. Mater.* **2012**, *34*, 893–900. [[CrossRef](#)]
16. Wiktorczyk, T.; Biegański, P.; Serafińczuk, J. Optical properties of nanocrystalline  $Y_2O_3$  thin films grown on quartz substrates by electron beam deposition. *Opt. Mater.* **2016**, *59*, 150–156. [[CrossRef](#)]
17. Shvets, V.A.; Kruchinin, V.N.; Gritsenko, V.A. Dispersion of the Refractive Index in High-k Dielectrics. *Opt. Spectrosc.* **2017**, *123*, 728–732. [[CrossRef](#)]
18. Wang, W.C.; Badylevich, M.; Afanas'Ev, V.V.; Stesmans, A.; Adelman, C.; Van Elshocht, S.; Kittl, J.A.; Lukosius, M.; Walczyk, C.; Wenger, C. Band alignment and electron traps in  $Y_2O_3$  layers on (100)Si. *Appl. Phys. Lett.* **2009**, *95*, 132903. [[CrossRef](#)]
19. Scherrer, P. Bestimmung der Größe und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen, Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen. *Math. Phys. Kl.* **1918**, *1918*, 98–100.

20. Warren, B.E. *X-ray Diffraction*; Addison Wesley Publishing, Co.: London, UK, 1969.
21. Schlecht, W.G. Calculation of Density from X-ray data. *Am. Mineral.* **1944**, *29*, 108–110.
22. Detailed Description of ThermoScientific K-Alpha Plus XPS Spectrometer. Available online: [https://xpssimplified.com/kalpha\\_surface\\_analysis.php](https://xpssimplified.com/kalpha_surface_analysis.php) (accessed on 26 April 2022).
23. Naumkin, A.V.; Kraut-Vass, A.; Gaarenstroom, S.W.; Powell, C.J. *NIST XPS Standard Reference Database 20*; Web-Version 4.1; US Government ASTM: West Conshohocken, PA, USA, 2012. [CrossRef]
24. Crist, B.V. *Handbook of Monochromatic XPS Spectra: The Elements of Native Oxides*; John Wiley & Sons: Hoboken, NJ, USA, 2000; p. 548.
25. Zhang, X.; Li, Z.; Peng, Y.; Su, W.; Sun, X.; Li, J. Investigation on a novel CaO-Y<sub>2</sub>O<sub>3</sub> sorbent for efficient CO<sub>2</sub> mitigation. *Chem. Eng. J.* **2014**, *243*, 297–304. [CrossRef]
26. ThermoScientific XPS: Knowledge Base. 2013–2022. Available online: <https://www.thermofisher.com/ru/ru/home/materials-science/learning-center/periodic-table/transition-metal/yttrium.html> (accessed on 27 March 2022).
27. Pengfei, Y.; Kan, Z.; Hao, H.; Mao, W.; Quan, L.; Wei, Z.; Chaoquan, H.; Weitao, Z. Oxygen vacancies dependent phase transition of Y<sub>2</sub>O<sub>3</sub> films. *Appl. Surf. Sci.* **2017**, *410*, 470–478. [CrossRef]
28. Swanepoel, R. Determination of the thickness and optical constants of amorphous silicon. *J. Phys. E Sci. Instrum.* **1983**, *16*, 1214–1222. [CrossRef]
29. Jenkins, F.A.; White, H.E. *Fundamentals of Optics*; McGraw-Hill: New York, NY, USA, 1981.
30. Lei, P.; Dai, B.; Zhu, J.; Chen, X.; Liu, G.; Zhu, Y.; Han, J. Controllable phase formation and physical properties of yttrium oxide films governed by substrate heating and bias voltage. *Ceram. Int.* **2015**, *41*, 8921–8930. [CrossRef]
31. Gorman, B.P.; Petrovsky, V.; Anderson, H.U.; Petrovsky, T. Optical characterization of ceramic thin films: Applications in low-temperature solid oxide fuel-cell materials research. *J. Mater. Res.* **2004**, *19*, 573–578. [CrossRef]
32. Nigara, Y. Measurement of the optical constants of yttrium oxide. *Jpn. J. Appl. Phys.* **1968**, *7*, 404. [CrossRef]
33. Urbach, F. The long-wavelength edge of photographic sensitivity and of the electronic Absorption of Solids. *Phys. Rev.* **1953**, *92*, 1324. [CrossRef]
34. Vainshtein, I.A.; Zatsëpin, A.F.; Kortov, V.S. Specific features of the Urbach rule manifestation in vitreous materials. *Glass Phys. Chem.* **1999**, *25*, 67–74.
35. Dow, J.D.; Redfield, D. Toward a unified theory of Urbach's rule and exponential absorption edges. *Phys. Rev. B* **1972**, *5*, 594–610. [CrossRef]
36. Sumi, H.; Toyozawa, Y. Urbach-Martienseen Rule and Exciton Trapped Momentarily by Lattice Vibrations. *J. Phys. Soc. Jpn.* **1971**, *4*, 342–358. [CrossRef]
37. Kuznetsova, Y.A.; Zatsëpin, D.A.; Zatsëpin, A.F.; Gavrilov, N.V. Energy gaps, refractive index and photon emission from point defects in copper-doped Gd<sub>2</sub>O<sub>3</sub> nanocrystalline films. *J. Alloys Compd.* **2022**, *904*, 163872. [CrossRef]
38. Tauc, J. *Amorphous and Liquid Semiconductors*; Plenum: New York, NY, USA, 1974.
39. Mott, N.F.; Davis, E.A. *Electronic Processes in Non-Crystalline Materials*; Oxford University Press: Oxford, UK, 1979.
40. Adam, J.; Metzger, W.; Koch, M.; Rogin, P.; Coenen, T.; Atchison, J.S.; König, P. Light emission intensities of luminescent Y<sub>2</sub>O<sub>3</sub>:Eu and Gd<sub>2</sub>O<sub>3</sub>:Eu particles of various sizes. *Nanomaterials* **2017**, *7*, 26. [CrossRef] [PubMed]
41. Fukabori, A.; An, L.; Ito, A.; Chani, V.; Kamada, K.; Yoshikawa, A.; Ikegami, T.; Goto, T. Correlation between crystal grain sizes of transparent ceramics and scintillation light yields. *Ceram. Int.* **2012**, *38*, 2119–2123. [CrossRef]
42. Novosad, S.S.; Novosad, I.S.; Bordun, O.M.; Kostyk, L.V.; Bordun, I.O.; Tuzyak, O.Y. The Influence of Europium Impurity on the Recombination Luminescence in Y<sub>2</sub>O<sub>3</sub>. *Acta Phys. Pol. A* **2018**, *133*, 806–810. [CrossRef]
43. Zatsëpin, A.F.; Biryukov, D.Y. The temperature behavior and mechanism of exciton luminescence in quantum dots. *Phys. Chem. Chem. Phys.* **2017**, *19*, 18721–18730. [CrossRef]
44. Meng, G.; Shi, Y.; Wang, X.; Wang, W.; Wang, S.; Ji, M.; Hao, C. New insight into the ultra-long lifetime of excitons in organic-inorganic perovskite: Reverse intersystem crossing. *J. Energy Chem.* **2018**, *27*, 1496–1500. [CrossRef]
45. Kuznetsova, Y.A.; Zatsëpin, D.A.; Zatsëpin, A.F.; Gavrilov, N.V. Temperature-dependent luminescence of intrinsic defects and excitons in nanocrystalline monoclinic Y<sub>2</sub>O<sub>3</sub> films. *J. Lumin.* **2022**, *250*, 119102. [CrossRef]
46. Dhananjaya, N.; Nagabhushana, H.; Nagabhushana, B.M.; Rudraswamy, B.; Shivakumara, C.; Chakradhar, R.P.S. Effect of Li<sup>+</sup>-ion on enhancement of photoluminescence in Gd<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> nanophosphors prepared by combustion technique. *J. Alloy. Compd.* **2011**, *509*, 2368–2374. [CrossRef]