East European Journal of Physics. 4. 140-144 (2021)
DOI: 10.26565/2312-4334-2021-4-18 ISSN 2312-4334

X-RAY INDUCED LIGHT EMISSION OF YTTRIUM OXIDE†

Sergiy Kononenko, Oganes Kalantaryan, Vitaliy Zhurenko, Volodymyr Chishkala, Sergii Lytovchenko, Ruslan Skyba
V.N. Karazin Kharkiv National University
4 Svobody Sq., Kharkov, 61022, Ukraine
**Corresponding Author: sergiy.i.kononenko@gmail.com*

Received October 1, 2021; revised November 17, 2021; accepted November 19, 2021

The paper presents the experimental results of light radiation from Y_2O_3 ceramics caused by X-rays with energy up to 50 keV. The samples were made from commercial Y_2O_3 nanopowder by pressing and subsequent sintering in air at different temperatures from 1300 to 1500°C. Some samples sintered at 1500°C were additionally annealed at 1000°C for 10 hours. X-ray diffraction analysis of all samples did not reveal differences in the crystal structure that could be explained by heat treatment during sintering and annealing. The spectra of light emission in the wavelength range of 250-750 nm showed the presence of radiation from the electronic transitions of YO structures on the background of the luminescence of trivalent yttrium oxide. The presence of such lines of YO systems were observed also for the powder, which allows us to conclude that these structures appear on the surface of the crystallites during production. As the sintering temperature of the sample increased, the intensity of optical radiation increased. A significant difference in the effect of both temperature and sintering (annealing) time on the intensity of light emission of yttrium oxide was revealed. The intensity of the luminescent band, which is associated with the self-trapped exciton, increased with increasing thermal contribution (to estimate the contribution, we introduced a parameter equal to the product of temperature and the time of thermal action). The increase in spectral intensity in the second, third, fourth, and fifth line systems (especially for the system of lines with a maximum of λ=573.5 nm) considerably exceeded the one for self-trapped exciton. Our experimental results on the second, fourth and fifth systems of lines, which coincide well with the molecular lines YO, suggest that the heat treatment of the samples sintered from pressed Y_2O_3 powder leads to an increase in YO structures on the surface of the crystallites.

Keywords X-ray light emission, yttrium oxide, spectrum, YO structure, powder sintering.
PACS: 78

Development of new technologies is associated with the use of materials basing on wide class of inorganic refractory compounds (oxides, carbides, nitrides, borides and others), which, in addition to high melting temperatures, have high resistance, high fire-resistant and anti-corrosion properties in combination with important electrophysical and optical characteristics [1–2]. The sintering process is of particular importance for powder formation of ceramics. Herewith powder consolidation technologies can be divided into two main methods. The first is the molding of a material pressed at room temperature followed by sintering; the second, called sintering under pressure, is the simultaneous pressing and sintering of powders [1].

In most materials, including ceramics, physical and mechanical properties depend on the homogeneity of structure and density. As a rule, with increasing porosity, these characteristics decrease. The initial powders of ceramics of different fractions are subjected to different methods of shaping and heating at different rates. The larger the size of ceramic specimen, the slower it is necessary to raise the temperature during sintering, sometimes up to 0.1÷10 degree per minute, to suppress nonuniform heating processes caused by low thermal conductivity of oxides: nonuniform solidification contraction of ceramics on the surface and in the middle of specimen. At nonoptimal heating rate, ceramics with a large number of macro- and microdefects (pores, macro-and microcracks, dislocations) are formed. For small samples (laboratory) the rate of temperature rise can be much higher.

Among a wide class of ceramics, yttrium oxide (Y_2O_3) is of particular interest. This material has many applications, such as a supplement component in the processing of ceramic materials, substrates for semiconductor films, optical windows and doped with rare earth components elements for lasers and so on [3]. Structural stability in combination with unique mechanical properties also permits to consider Y_2O_3 as an interesting material for other applications. Its optical properties have been widely studied in terms of its use as a host matrix material for doping with rare earth ions such as samarium, erbium, gadolinium and europium for luminescence applications [see, for example, 4-6]. As for pure yttrium oxide, its optical properties have been less studied, nevertheless, in recent years a number of works has paid attention to its luminescent properties in connection with new possibilities of using as active elements of solid-state lasers [7-8] and luminophores [9].

Due to spectroscopic study (spectroscopy is the most versatile remote monitoring tool) astronomers have revealed presence of YO-components in various astrophysical sources. That is why YO-molecule spectrum is of considerable astrophysical interest because it is one of the main features in the spectra of cool star atmosphere [see, for example, 3-4]. Note that the presence of isolated YO-lines in the spectra of sintered ceramics of Y_2O_3 samples was confirmed in a number

---

† ***Cite as:*** S. Kononenko, O. Kalantaryan, V. Zhurenko, V. Chishkala, S. Lytovchenko, and R. Skyba, East. Eur. J. Phys. **4**, 140 (2021), https://doi.org/10.26565/2312-4334-2021-4-18

of works [12-13]. The authors [12] identified series of narrow bands that are located in the blue (435–510 nm), orange (515–640 nm), red (645–700 nm), and infrared (785–840 nm) spectral ranges as most pronounced in the spectra of commercially available powder and Y_2O_3 ceramics. They assumed that these series are emitted by bound YO-radicals, which are a part of the surface structure of yttria crystals. In our earlier experimental work [13], we also paid attention to the fact that isolated YO molecular lines were observed in the spectrum of ceramics sintered from yttrium oxide (sintering of the samples compacted from pure Y_2O_3 nanopowder).

This paper deals with an experimental study of X-ray light emission of Y_2O_3 (nanopowder and ceramics) making an emphasis on changes in spectral series which are responsible for YO band systems depending on heat treatment of the samples.

EXPERIMENT

The experiment were done with commercially available yttrium powder «ITO-Lyum», consisting of pure Y_2O_3 (purity of the powder was approximately 99.9828 %). The samples were produced by compaction procedure of the powder. «ITO-Lyum» powder hitch with mass of 1 g were placed inside the cylindrical pressform with a diameter of 10.8 mm. A hydraulic press worked in the following regime: the pressure inside the pressform was grown from 0 up to the value of 3000 kgf per cm^2 (327.5 MPa) during 1 minute without an additive exposure at maximum pressure. So pressed cylindrical pellets of 10 mm in diameter and approximately 3 mm thickness were prepared. Thermal treatment was performed in commercial electric furnace «Naberthem LHT 04/18». To avoid possible penetration of impurities into the sample (contamination by volatile oxides from the furnace) we used special a container made from the same yttrium oxide ceramics. Sintering was carried out in in air atmosphere. The heat treatment cycle included the following stages (see Fig. 1): 1) slow increase of the temperature during approximately 3 h (the average rate was 8÷10 °C per min) up to sintering temperature 1300 °C (sample #1), 1400 °C (sample #2), 1500 °C (sample #3); 2) sintering at this temperature for 1 h; 3) cooling to room temperature for 4 h in an air atmosphere. Some of the samples were additionally annealed at 1000 °C for 10 h, followed by cooling for the same time (the sample #4). It is generally accepted that sintering of yttrium oxide ceramics begins at temperatures of about 700 °C [15] (Fig. 1 shows the area (filled by gray color) that corresponds to the most efficient sintering process).

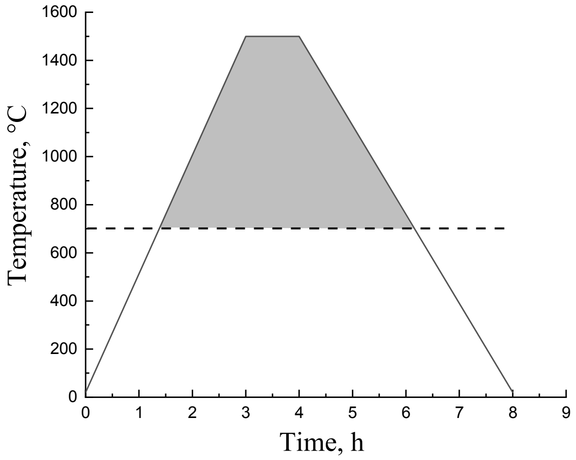


Figure. 1. Typical heat treatment shown by the example of the sample T=1500 °C.

The samples were examined by some diagnostics: X-ray diffraction analysis (XRD) and Scanning electron microscopy (SEM). Light emission excited by X-ray irradiation was studied on spectrometric complex (see details in [13]). X-ray vacuum tube source operated at voltage of up to 50 kV. Spectra were measured by grating monochromator at wavelength range of 250–750 nm. The measuring channel was calibrated with taking into account corresponding spectral sensitivity of the apparatus.

RESULTS AND DISCUSSION

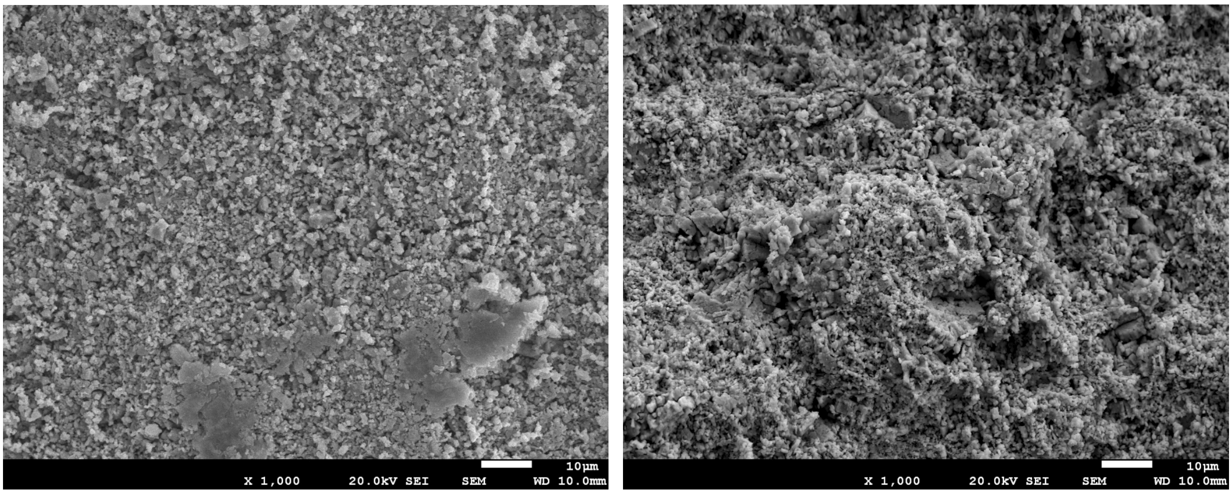
X-ray diffraction

X-ray diffractometer DRON-4-07 (Cu-Kα radiation with applying Ni selectively absorbing filter, diffracted radiation was registered by a scintillation detector) was applied for crystallographic analysis of the samples. X-ray diffraction pattern showed presence of single-phase and cubic yttrium oxide (space group No. 206). No traces of other phases were found within the sensitivity of the method. XRD demonstrated that the samples #1-4 were almost identical; no significant differences were found in the pattern.

The lattice parameters were slightly higher than database (ICDD PDF-2 International database). The distribution of the intensities of the diffraction lines corresponded to a polycrystalline non-textured state.

Scanning electron microscopy

SEM-examination of our ceramics was done by means of commercial Scanning Electron Microscope JEOL JSM-7001F. Fig. 2 shows the morphology of Y_2O_3. The prepared samples showed good morphology and homogeneity with grains of nano- and micro- sizes. We have seen that the images for plane surface and fresh cleavage demonstrated no noticeable differences. SEM-study of the the samples #3 and #4 demonstrated minor differences in the images before and after additional 10 h annealing, which indicates the absence of significant changes in the structure of Y_2O_3 ceramics associated with long heating. Also, no significant difference was found on the surfaces and fresh cleavage of the additionally annealed sample.



a b

Figure. 2. SEM-image of Y_2O_3 (sample #3, T=1500 °C): *a* is plane surface, *b* is fresh cleavage.

Luminescence measurements

Figure 3 shows typical light emission spectra induced by X-ray irradiation for powder and ceramics, sintered at 1500 °C (sample #3). To compare the spectra for different samples and experimental conditions, we performed the normalization to the maximum value of the first band, which is usually associated with self-trapped exciton (STE) [16]. As it could be seen, the spectra contained one wide band and four systems of lines, which we have already observed earlier [13]. The maxima of the first band lied near 350 nm, the other maxima of line systems were 487 nm, 545 nm, 573.5 nm and 670.5 nm. It should be noted that the spectrum observed for ceramic sample #3 was also similar to the spectra for samples #1, #2 and #4.The origin of light generation of the bands has been already discussed [13]. We only note that the first broad band is associated with an exciton [16], while the second, fourth, and fifth systems of lines are identified with good accuracy as lines of molecular yttrium oxide [17]. The origin of the third peak has not yet been established and requires further research. As for the doublet in the region 314–316 nm, its identification turned out to be difficult, since it did not correspond to any known radiation from up-to-date atomic and molecular spectral databases.

As can be clearly seen from Fig. 3 for the spectra of the powder that was not subjected to heat treatment, the lines associated with YO molecule system of lines are small, except for a peak at approximately λ=573.5 nm. For samples that were heat treated, the situation changed. The emission peaks of YO molecules have increased significantly compared to the maximum of the STE band. Heat treatments with the temperatures at which the samples were sintered hardly led to a significant increase in the size of Y_2O_3 crystallites, and, consequently, to an increase in the maximum of the band associated with STE light emission. The significant increase in YO systems of lines is apparently associated with a significant increase in the number of YO structures on the crystal surface.

The processes of sintering and annealing of powder ceramics strongly depend on both temperature at which these processes effectively occur and on the time of exposure of the sample to these temperatures. As we mentioned above, yttrium oxide the sintering and annealing processes begin to proceed effectively at temperatures above 700 °C [15]. We took into account the influence of these factors on the properties of the samples under study by applying such a parameter as temperature multiplied by the time of exposure of a given temperature to the sample (some analogy of the energy contribution parameter). We calculated the value of this parameter for our samples and plot the dependences of the maximum values of the light intensities for 5 band systems on the energy contribution parameter during heat treatment (Fig. 4).

As it can be seen from the figure, with an increase of the energy contribution parameter, the intensity of the line systems associated with YO structures increases. The last points for all experimental curves, corresponded to the sample #5 sintered at a temperature of 1500 °C with additional annealing at a temperature of 1000 °C, tend to influence slightly the YO line system light emission.

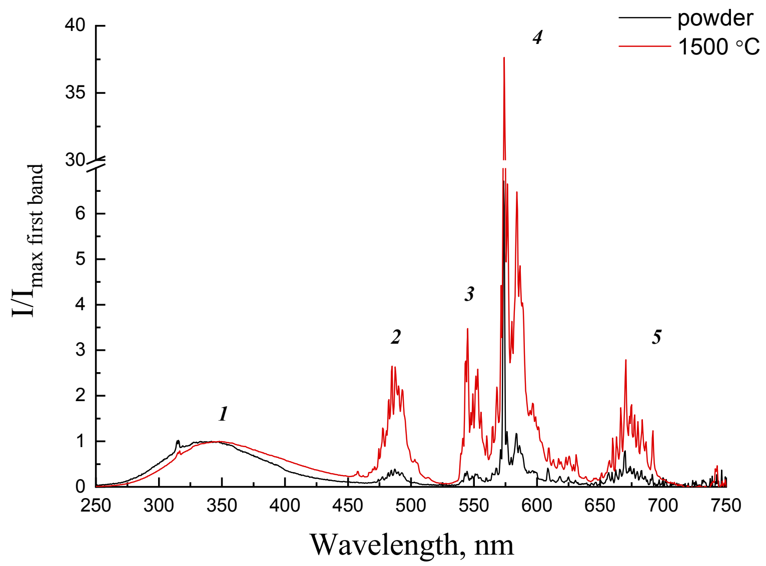


Figure 3. X-ray luminescence spectra of yttrium oxide powder and ceramic sample (sintering temperature of 1500 °C).

The numbers from 1 to 5 indicate the wavelength ranges of the corresponding first band and systems of lines (vertical bars are shown to guide eye, it indicate the borders of the bands).

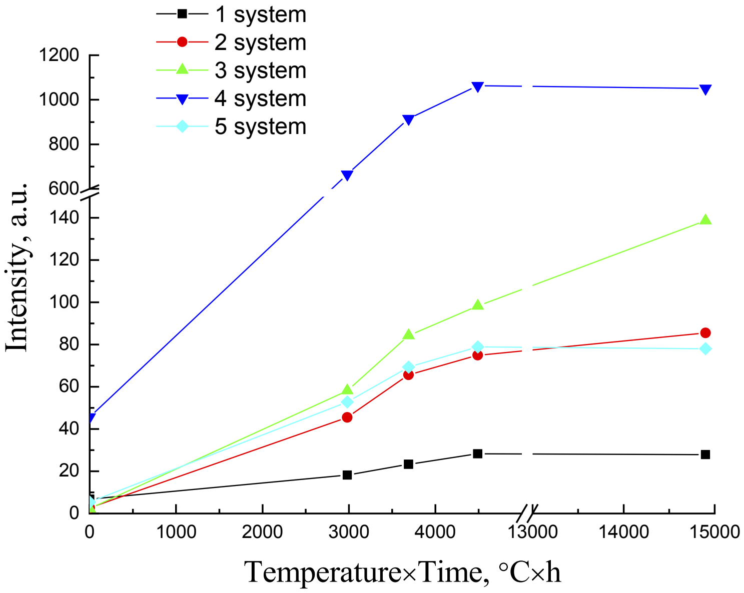


Figure 4. Luminescence light intensity as function of sintering temperature multiplied by time for different wavelength bands of Y_2O_3 spectra.

CONCLUSIONS

The performed study of the light emission from the powder and sintered ceramics exposed to X-ray irradiation up to 50 keV made it possible to conclude the following. As shown by X-ray structural analysis, as a result of sintering and annealing, Y_2O_3 crystal lattice does not change, and new types of the crystal lattice are not formed. Meanwhile, the luminescence measurements revealed that besides light emissions associated with Y_2O_3 band systems corresponded to self-trapped exciton decay (generation of radiation in the entire volume of ceramics), there were intensive YO band systems (molecular character of the spectral lines pointed out on light emission from molecule structures on surface of the crystallites). The linear structure of the YO spectra suggests that YO structures are weakly bound to Y_2O_3 crystal structure. The influence of the sintering temperature on peak maximum intensities, which allows us to talk about growth of energy contribution to the Y_2O_3 pellet, leads to an increase in the intensity of the band and systems of lines associated with YO structures. The presence of YO structures on the surface of the initial ITO-LUM powder, which is clearly seen on the spectra, makes it possible to draw a conclusion about the synthesis of these structures during production process of Y_2O_3 powder. It should be noted that the number of these structures on the surface of Y_2O_3 crystallites increasing with heat treatment process.

Acknowledgment

The authors consider it their duty to thank Bogdan Mazilin for his help in preparing the samples being studied.

ORCID IDs

Sergiy Kononenko, https://orcid.org/0000-0001-6060-2589; **Volodymyr Chishkala**, https://orcid.org/0000-0002-8634-4212
Vitaliy Zhurenko, https://orcid.org/0000-0002-4738-094X; **Oganes Kalantaryan,** https://orcid.org/0000-0002-5625-6908
Sergey Lytovchenko, https://orcid.org/0000-0002-3292-5468

REFERENCES

[1] M.I. Alymov, V.S. Shustov, A.S. Ustuhin, E.V. Evstratov, Composites and Nanostructures, **3**, 5 (2012), http://www.issp.ac.ru/journal/composites/2012/CN_03_2012.pdf (in Russsian).
[2] X. J. Song, H. Z. Cui, L. L. Cao, Transactions of Nonferrous Metals Society of China, **26**, 1878 (2016), https://doi.org/10.1016/S1003-6326(16)64265-6
[3] V.H. Mudavakkat, V.V. Atuchin, V.N. Kruchinin, A. Kayani, C.V. Ramana, Optical Materials, **34**, 893 (2012), https://doi.org/10.1016/j.optmat.2011.11.027
[4] R. Srinivasan, N.R. Yogamalar, J. Elanchezhiyan, R.J. Joseyphus, A.C. Bose, Journal of Alloys and Compounds, **496**, 472 (2010), https://doi.org/10.1016/j.jallcom.2010.02.083
[5] L. Mariscal-Becerra, R. Vázquez-Arreguín, U. Balderas, S. Carmona-Téllez, H. Murrieta Sánchez, and C. Falcony, Journal of Applied Physics, **121**, 125111-1 (2017); https://doi.org/10.1063/1.4979209
[6] W. Wang, P. Zhu, Optics Express, **26**, 34820 (2018), https://doi.org/10.1364/OE.26.034820
[7] A. Ikesue, Y. L. Aung, T. Taira, T. Kamimura, and K. Yoshida, Ann. Rev. Mater. Res. **36**, 397 (2006), https://doi.org/10.1146/annurev.matsci.36.011205.152926
[8] V. V. Osipov, V. A. Shitov, R. N. Maksimov, V. I. Solomonov, K. E. Luk'yashin, and A. N. Orlov, Photonics, **12**, 318 (2018). https://doi.org/10.22184/1993-7296.2018.71.3.318.334
[9] 9. V. V. Osipov, A. V. Ishchenko, V. A. Shitov, R. N. Maksimov, K. E. Lukyashin, V. V. Platonov, A. N. Orlov, S. N. Osipov, V. V. Yagodin, L. V. Viktorov, and B. V. Shulgin, Opt. Mater. **71**, 98 (2017), https://doi.org/10.1016/j.optmat.2016.05.016
[10] A. Bernard and R. Gravina, The Astrophysical Journal Supplement Series, **44**, 223 (1980).
[11] M. Singh and J. P. Chaturvedi, Astrophysics and Space Science, **135**, 1 (1987).
[12] V. V. Osipov, A. V. Rasuleva, and V. I. Solomonov, Optics and Spectroscopy **105**, pp. 524–530 (2008), https://doi.org/10.1134/S0030400X08100068
[13] O. Kalantaryan, V. Zhurenko, S. Kononenko, R. Skiba, V. Chishkala and M. Azarenkov, in: *2020 IEEE 10th International Conference Nanomaterials: Applications & Properties (NAP)*, 2020, pp. 01NP03-1-01NP03-5, https://doi.org/10.1109/NAP51477.2020.9309672
[14] O. Kalantaryan, S. Kononenko, E. Barannik, V. Zhurenko and V. Chishkala, in: *2021 IEEE 11th International Conference Nanomaterials: Applications & Properties (NAP)*, 2021, pp. 1-4, https://doi.org/10.1109/NAP51885.2021.9568608
[15] Joanna R. Groza, NanoStmchmd Materials, **12**, 987 (1999), https://doi.org/10.1016/S0965-9773(99)00284-6
[16] A. Lushchik, M. Kirm, Ch. Lushchik, I. Martinson, G. Zimmerer Journal of Luminescence, **87**, 232 (2000), https://doi.org/10.1016/S0022-2313(99)00271-9
[17] K.P. Huber, G. Herzberg, *Molecular spectra and molecular structure, IV. Constants of diatomic molecules, vol. 4* (Springer Science+Business Media, New York, 1979), pp. 19-24.

ЛЮМІНЕСЦЕНЦІЯ ОКСИДУ ІТРІЮ, СПРИЧИНЕНА РЕНТГЕНІВСЬКИМ ОПРОМІНЕННЯМ

С. Кононенко, О. Калантар'ян, В. Журенко, В. Чішкала, С. Литовченко
Харківський Національний університет ім. В.Н. Каразіна
61022, Україна, м. Харків, пл. Свободи, 4

Наведено результати експериментальних досліджень світлового випромінювання кераміки Y_2O_3, спричиненого рентгенівським випромінюванням з енергією до 50 кеВ. Зразки виготовлялися з комерційного нанопорошку Y_2O_3 методом пресування та подальшого спікання в атмосфері повітря за різних температур від 1300 до 1500°C. Деякі зразки, спечені за температури 1500°C, додатково відпалювалися за температури 1000°C протягом 10 годин. Рентгеноструктурні дослідження всіх зразків не виявили відмінностей у кристалічній структурі, які могли бути пов'язані з температурною обробкою під час спікання та відпалу. Спектри світлового випромінювання в діапазоні 250-750 нм показують наявність випромінювання від електронних переходів YO структур на тлі люмінесценції оксиду тривалентного ітрію. Наявність такого випромінювання було зафіксовано і для порошку, що дозволяє зробити висновок щодо виникнення цих структур на поверхні кристалітів у процесі виробництва. Зі зростанням температури спікання зразка інтенсивність оптичного випромінювання зростала. Виявлено суттєву відмінність впливу як температури, так і часу спікання (відпалу) на інтенсивність люмінесценції та світіння оксидів ітрію. Інтенсивність люмінесцентної смуги, яка пов'язується із самозахопленим екситоном, зі зростанням теплового вкладу зростала (для оцінки вкладу ми в роботі запровадили параметр, що дорівнює добутку температури на час теплового діяння). Зростання інтенсивності випромінювань у другій, третій четвертій і п'ятій системах ліній (особливо для системи ліній з максимумом λ=573,5 нм) помітно перевищувало таке для само захопленого екситону. Отримані нами експериментальні результати щодо другої, четвертої та п'ятої систем ліній, які добре збігаються молекулярними лініями YO, дозволяють припустити, що теплова обробка зразків кераміки, спеченої з пресованого порошку Y_2O_3, призводить до збільшення YO структур на поверхні кристалітів.

Ключові слова: рентгенівська емісія світла, оксид ітрію, спектр, YO структура, запікання порошків.