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CHEMILUMINESCENCE Y_3O_2: Bi^{3+} INDUCED BY NITROGEN OXIDE

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ABSTRACT

The investigation of the processes occurring on their surfaces in the presence of a well-spread, oxygen-containing gaseous medium using luminescence methods is relevant. This article presents data on the patterns of chemiluminescence excitation in the Y_3O_2:Bi^{3+} crystalline phosphorus in the nitrous oxide (N_2O) flow. The kinetic, temperature and spectral characteristics of the chemiluminescence were studied. A gradual mechanism of chemiluminescence excitation was studied. The practical value of this study is that its results can be used to develop fundamentally new luminescent methods for the qualitative and quantitative determination of oxygen-containing impurities in gases and to prepare monographs and teaching aids in chemical physics.

Keywords: Crystalline Phosphorus, Nitrous Oxide, Luminescence Kinetics, Luminescence Spectrum, Yttrium Oxide

INTRODUCTION

Chemiluminescence (CL) is a process of luminescence triggered by chemical reactions. The chemiluminescence probe phthalhydrazides have been intensively studied and widely applied in blood detection, ROS detection, biological imaging, and reporter genes. CL is based on the production of electromagnetic radiation observed when a chemical reaction gives an electronically excited intermediate, which either luminesces (direct CL) or donates its energy to another molecule responsible for emission (indirect or sensitized CL). CL coupled with flowinjection (FICL) has the advantages of rapidity, sensitivity, a wide linear range and easy to realize automation and, therefore, is considered as a fast analysis tool in the field of pharmaceutical analysis and environmental monitoring.

Chemiluminescence (CL) flow methods generally use a Teflon or glass spiral reactor placed in front of the photosensor was the CL reaction is intended to be developed from the sample plug injected in the flow system. However, the CL emission is produced as the sample plug is carried out through the system to waste, so it's difficult to get that the signal is developed when the plug just fills the spiral cell. Therefore, it is not easy at all to get the maximum possible signal/sensitivity.

There has been significant interest recently in exploring the mechanism of chemiluminescence, with several theoretical studies exploring the reaction in models representing firefly dioxetanone.[1,2]

Nitrogen oxides (NOx sum of nitrogen oxide (NO) and nitrogen dioxide (NO_2))[3] are mainly emanated as by-products of combustion and are involved in the formation and destruction of ozone (O_3), thus they play the main role in determining the air quality in urban environments.[4] Bi3+-doped rare-earth aluminate and gallate garnets, where a Bi^{3+} ion substitutes for a trivalent rare-earth ion, can be considered as perspective materials for scintillators due to an intense and fast Bi3þ-related emission.[5]

Crystalline phosphors with the Y_3O_2 matrix are among the most important ones in lighting applications. Doped with Eu^{3+}, Tb^{3+}, Bi^{3+} ions, these crystalline phosphors are widely used in light-emitting panels and

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plasma devices for cathode-, ion-, or photo-excitation.[6] The presence of active gas particles in the residual atmosphere of such devices can significantly affect the course of luminescence excitation, stimulation and quenching in the present crystalline phosphors. Therefore, the investigation of the processes occurring on their surfaces in the presence of a well-spread, oxygen-containing gaseous medium using luminescence methods seems relevant.

EXPERIMENTAL

The experiments were performed using a high vacuum device, the main components of which are described in "Experimental installation phosphors luminescence excitation, stimulation and extinguishing by atomic and molecular beams".[7] Nitrous oxide N_2O (99.9%) was used as an oxygen-containing gas; it shows a low binding energy of the oxygen atom O in the N_2O molecule (1.7 eV and 3.6 eV in the $O(^3P)$ and $O(^1D)$ states, respectively).[8]

The flow of N_2O molecules, with a density up to $j_{N_2O} \sim 10^{20}$cм$^{-2}\cdot$c^{-1}, could be applied on a finely dispersed trivalent bismuth-doped polycrystalline yttrium oxide $Y_3O_2:Bi^{3+}$ sample, preliminarily cleaned using a long (~ 2 hours) high-temperature (T~700K) heating in high vacuum (~ 10^{-6} Pa) (Specific surface 2.3m^2/g. Particle size 2-5 μm. Bi activator content 0.05 at.%. Synthesized at the State Institute of Applied Chemistry, RF). The temperature of the sample applied as a thin layer $(h \leq 0.2\ mm)$ on the substrate heater could be maintained constant, with an accuracy of ≤ 1%, or changed rapidly (<10 s) using an electronic regulator of the heater current.[7] The luminescence of this crystalline phosphorus sample was recorded photoelectrically through a cassette with light filters using the FEU 84-3 photomultiplier tube. Due to the low intensity, the luminescence spectrum was recorded in a photon-counting mode using a high-aperture monochromator, MDR-206 (LOMO), with the H-7467-1 HAMAMATSU photon-counting head attached to the exit slit. It was controlled by the RS through the RS-232C serial interface. The recorded spectrum was programmatically corrected taking into account the instrument function of the measurement path recorded for the "black body" radiation (SI-6.5-50 lamp, T = 2854K).

RESULTS AND DISCUSSION

When the flow of N_2O molecules was applied on the surface of the heated $Y_3O_2:Bi^{3+}$ sample, a weak but detectable chemiluminescent radiation occurred in the typical activator band 380 <λ<640 nm. Fig.-1 (*1, 2*) shows the kinetic curves of the $Y_3O_2:Bi^{3+}$ chemiluminescence in N_2O flow at different temperatures. A weak initial flash is associated with N_2O adsorption on the F^+_s-type centers or atoms of the excessive Y_3O_2:Bi metal.[9] A subsequent increase in luminescence after 3-4 hours ended with a stationary intensity level, which remained unchanged throughout the experiment (several days).

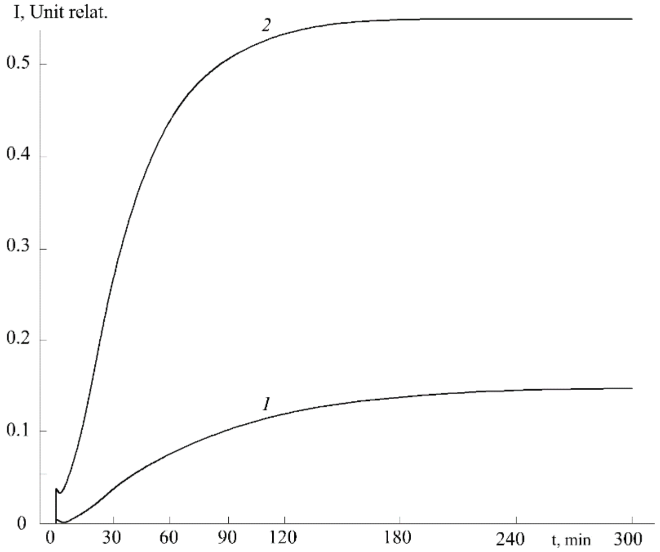

Fig.-1: Kinetics of $Y_3O_2:Bi^{3+}$ Chemiluminescence Buildup (Band 380–640 nm) in N_2O Molecule Flow ($j_{N_2O} = 1.4 \cdot 10^{20}$ cm$^{-2}\cdot$s^{-1}). Sample Temperature 615K (*1*), 685 K (*2*)

The study of the dependence of the intensity I of the Y_3O_2:Bi^{3+} luminescence on the flow density j_{N_2O} of N_2O molecules using the method of concentration-time cycles (Fig.-2) showed that luminescence intensity I (*j*) increased proportionally to the square of the flow $j^2_{N_2O}$.

The luminescence intensity of Y_3O_2:Bi^{3+} in N_2O flow increases monotonously with the temperature (Fig.-3). In this case, the found values of the activation energy E_a vary from $E_a = 0.26$ eV ($T \leq 600K$) to $E_a = 0.78$ eV ($T \geq 600K$).

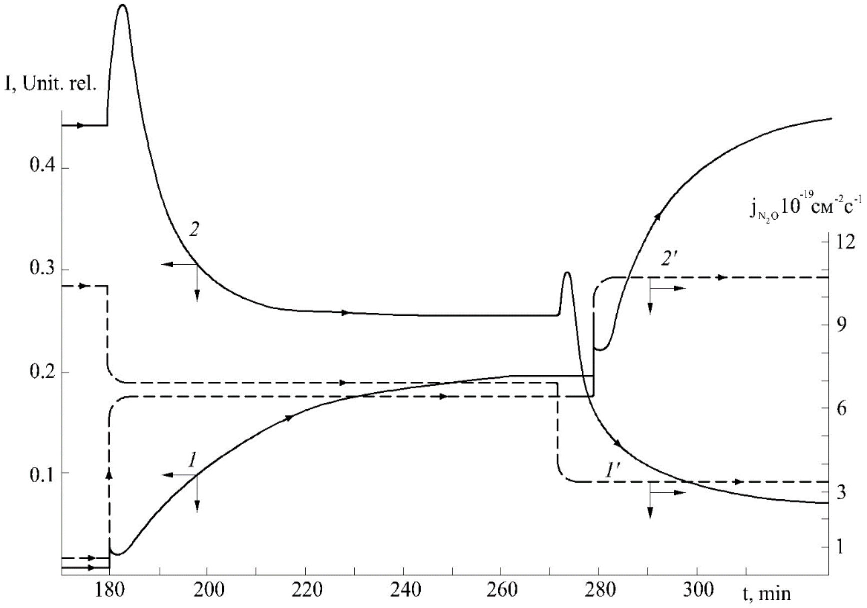

Fig.-2: Kinetics of the Y_3O_2:Bi^{3+} Chemiluminescence Intensity Relaxations with a Gradual Increase (*1*) or Decrease (*2*) in N_2O Molecule Flow j_{N_2O} (1′ and 2′-Kinetics of Changes in j_{N_2O}). Emission Band of the Sample 380-640 nm, Temperature 673 K.

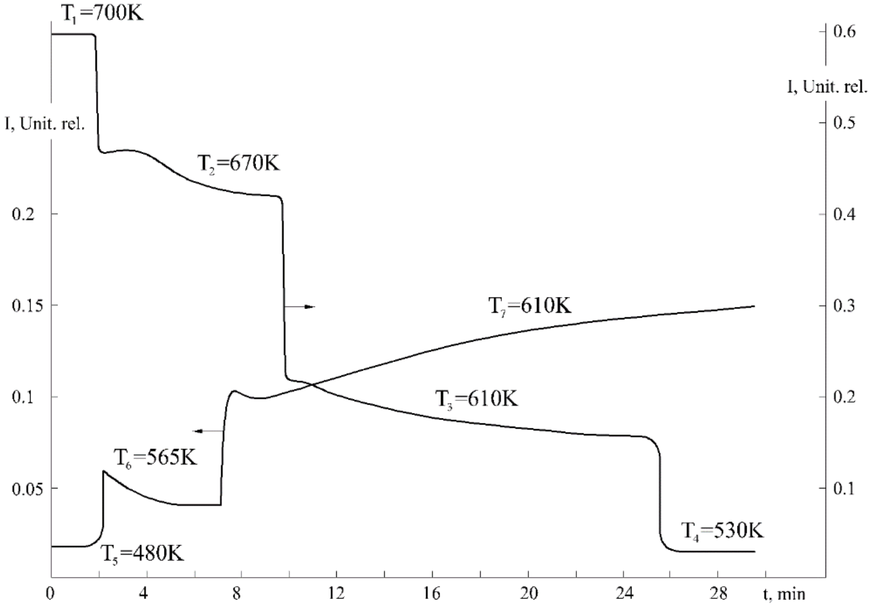

Fig.-3: Fragments of the Temperature-Time Cycle of Intensity I (t, T) of Y_3O_2:Bi^{3+} Chemiluminescence Excited by N_2O Flow ($j_{N_2O} = 1.2 \cdot 10^{20}$ cm^{-2}·s^{-1}) in the 380-640 nm Band

The Y_3O_2:Bi^{3+} chemiluminescence spectrum in nitrous oxide (Fig.-4) recorded in the photon counting mode (Fig.-4) corresponds to the allowed transitions in the trivalent bismuth ion $Bi^{3+}\left({}^3P_1 \rightarrow {}^1S_O + hv\right)$. Maxima at 410 nm and 499 nm can be associated with the Bi^{3+} ion, replacing the Y^{3+} cation in the positions with spatial symmetry S_6 and C_2, respectively.[10,11]

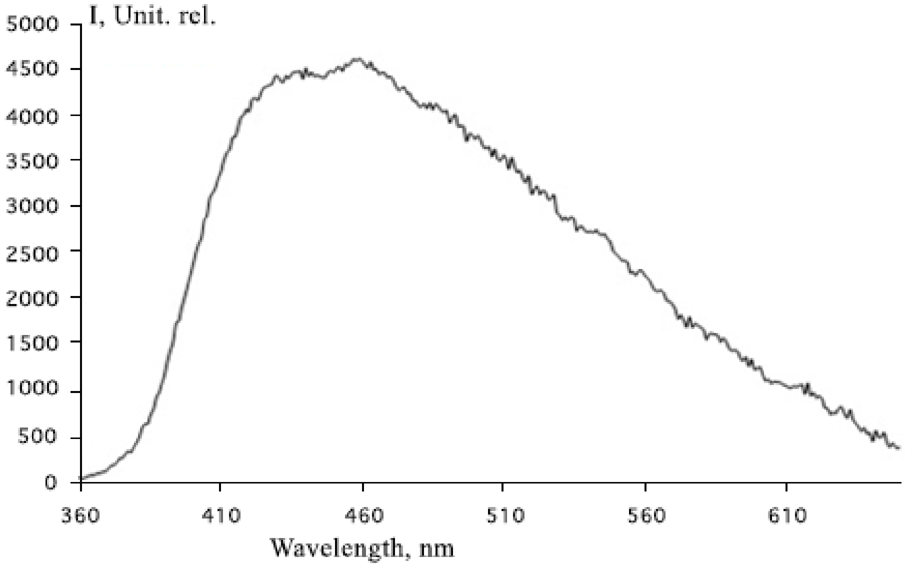

Fig.-4: Y_3O_2:Bi^{3+} CL spectrum at T = 635K in Nitrous Oxide ($j_{N_2O} = 1.2 \cdot 10^{20}$ $cm^{-2} \cdot s^{-1}$)

The interaction between Y_3O_2:Bi^{3+} phosphorus and the oxygen-containing gas N_2O is associated with luminescent radiation (intensity ~ 10^3–10^5 quanta·$cm^{-2} \cdot s^{-1}$) which remains steady, without noticeable changes, for many hours (Fig.-1). The radiation can be related, in our opinion, to the process of stoichiometric completion of the Y_3O_2:Bi surface, i.e. additional oxidation of Y atoms, since Y_2O_3 oxide contains excessive yttrium in large amounts.[12]

$$2Y + 3\left(N_2O\text{-}L\right) \xrightarrow{k,B} Y_2^{3+}O_3^{2-} + 3L + 3N_2 + \left(h\nu\right). \tag{1}$$

Where L – the symbol for the adsorption center of the crystalline grid; N_2O-L – nitrous oxide molecule adsorbed on the L center; *k* – reaction rate of yttrium oxidation; B – quantum yield of the process (1); *hv* – symbol of the photon emission act.

In this process, the accumulation of adsorbed N_2O-L near Y atoms can be initiated by the fact that the processes

$$\begin{gathered} N_2O\left({}^1\Sigma\right) \rightarrow N_2\left({}^1\Sigma\right) + O\left({}^3P\right), \\ 2N_2O\left({}^1\Sigma\right) \rightarrow 2N_2\left({}^1\Sigma\right) + O_2\left({}^3\Sigma\right), \end{gathered} \tag{2}$$

are spin-forbidden, while the process:

$$3N_2O\left({}^1\Sigma\right) \rightarrow O\left({}^3P\right) + O_2\left({}^3\Sigma\right) + 3N_2\left({}^1\Sigma\right) \tag{3}$$

is spin-allowed (Wigner rule) and exothermic.

A model of the Y_3O_2:Bi luminescence excitation micro-mechanism due to the oxidation of excessive Y, most likely, includes the following elementary processes: 1) adiabatic approach to the therm of the electronically excited state of Y_3O_2; 2) subsequent relaxation to the therm of the ground (ionic) state of $Y_2^{3+}O_3^{2-}$ with non-radiative energy transfer to the activator ion (Bi^{3+}); 3) the act of luminescence – radiative relaxation: $Bi^{3+}\left({}^3P_1 \rightarrow {}^1S_O + hv\right)$.

Lack of lattice oxygen in Y_2O_3 contributes to a long-term process of additional oxidation of Y excess metal, getting to the surface diffusely.[13,14] The luminescence intensity according to (1) is proportional to the oxidation rate *k* and quantum yield *B*.

$$I = Bk[Y]^2[N_2 - O]^3 \tag{4}$$

(expressions in square brackets – surface concentrations of the reagents).

The concentration of N^e electronically excited luminescence centers (Bi^{3+} ions) is determined by the rates of their generation G, $cm^{-2}\cdot s^{-1}$ and relaxation $\Gamma = \Gamma_1 + \Gamma_2$, s^{-1}, where Γ_1 is the rate of radiative relaxation, Γ_2 is the rate of non-radiative relaxation. The value of Γ_2 is determined both by the speed of the intra-center non-radiative relaxation Γ_3 and the surface concentration of nitrous oxide molecules $[N_2O – X]$, coordinated with the luminescence centers X (Bi^{3+}), as oxygen and oxygen-containing gases are effective catalysts for internal and inter-combination conversions in electronically excited molecules.[15-17] In addition, we take into account that quenching can occur in acts of impact interaction of N_2O with luminescence centers X

$$\Gamma_2 = \Gamma_3 + \chi[N_2O - X] + \sigma \cdot j_{N_2O} \tag{5}$$

where χ – constant of the rate of quenching with the adsorbed nitrous oxide molecules; σ – shock quenching cross-section of excited centers with N_2O molecule flow, density j_{N_2O}.

From the balanced equation:

$$\dot{N}^e = G - \Gamma N^e \tag{6}$$

in steady-state $\dot{N}^e = 0$, we get:

$$G = \Gamma N^e \tag{7}$$

The yield η is, by definition, equal to:

$$\eta = \frac{\Gamma_1}{G/N^e} = \frac{\Gamma_1 N^e}{\Gamma N^e} \tag{8}$$

In N_2O flow, the CL yield is equal to:

$$\eta = \frac{1}{1 + \Gamma_1^{-1}(\Gamma_3 + \chi[N_2O - X] + \sigma \cdot j_{N_2O})} \tag{9}$$

The CL intensity in N_2O flow is equal to:

$$I = \frac{k[Y]^2 \cdot [N_2O - L]^3}{1 + \Gamma_1^{-1}(\Gamma_3 + \chi[N_2O - X] + \sigma \cdot j_{N_2O})} \tag{10}$$

Since at high j_{N_2O} flow and high-temperature T of the sample the concentration $[N_2O\text{-}L]$ is proportional to the j_{N_2O} flow density, and at low yield η the rate of non-radiative relaxation Γ_2 significantly exceeds the speed of the radiative Γ_1, the quadratic dependence I (j_{N_2O}) observed in the experiment qualitatively follows from (10).[18,19]

The fact that the stationary Y_2O_3:Bi luminescence in N_2O is mainly associated with the oxidation of substoichiometric Y on the surface, is also confirmed by the fact that there is no hysteresis in the dependence I (j_{N_2O}), taken from the increase and decrease in the j_{N_2O} flow of N_2O molecules (Fig.-2). This cannot be expected in slow diffusive processes of atomic oxygen penetration into the volume, which should lead to luminescence quenching and, consequently, to irreversibility in dependences I (j_{N_2O}).[20] Concentrations of O-L atoms appearing on the Y_2O_3 surface during N_2O dissociation (such dissociation can occur only with the participation of "biographical" defects such as F_S-centers or, more likely, F_S^+-centers) are so small that they cannot cause significant quenching of Bi^{3+}-centers in volume.[21]

CONCLUSION

Major stages of the studied Y_3O_2:Bi^{3+} luminescence buildup in this approach are: 1) accumulation of N_2O-L molecules on the surface; 2) their partial dissociation on defects such as anion vacancies (F_S^+-

centers); 3) oxidation of excessive surface yttrium atoms with the emission of light quanta. In this case, the mechanism of the CL excitation includes: 4) an adiabatic approach of the yttrium oxide molecules, newly formed during oxidation on the surface, to an electronically excited state; 5) relaxation on the therm of the ground (ionic) state of yttrium oxide molecules with non-radiative energy transfer to the activator ion (Bi^{3+}); 6) radiative relaxation of the ion $Bi^{3+}\left({}^3P_1 \rightarrow {}^1S_O + h\nu\right)$. The Y_3O_2:Bi^{3+} luminescence type described above can be of practical use for the qualitative and quantitative determination of nitrous oxide in gases.

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