Laser-Induced Luminescence Associated with Surface Hydroxide Groups in Al$_2$O$_3$

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Abstract—Laser-induced luminescence of OH$_s$ groups for undoped Al$_2$O$_3$ oxides of various phase compositions was excited by pulsed nitrogen laser radiation at 337.1 nm. The luminescence band at 500–650 nm assigned to hydroxide groups of Al$_2$O$_3$, actually, consists of several lines at 500–515, 553, 567, 577, 607, and 633 nm; these constituent bands can be assigned to various types of OH$_s$ surface groups. In the low-temperature phases of the $\gamma \longrightarrow \delta \longrightarrow \theta$-Al$_2O_3$ series, excitation at a wavelength of 337.1 nm gave rise to a characteristic luminescence band associated with surface hydroxide groups of Al$_2$O$_3$ that appeared at 770 nm.

Alumina is one of the most popular materials in catalysis. In most industrial catalytic processes, alumina serves as a support for active phases, which are either other oxides or transition or precious metals in the form of mononuclear or polynuclear complexes or clusters.

Luminescent methods are widely used for structural studies of surface oxo complexes of oxides [1]. Luminescence associated with OH$_s$ surface groups was described for a number of oxides, namely, Al$_2$O$_3$ [2–7], MgO [2, 8], ThO$_2$ [9], ZrO$_2$, and SiO$_2$, and for zeolites [10]. Because of the great variety of possible types of OH$_s$ centers and complex structures of transition Al$_2$O$_3$ phases, however, OH$_s$ luminescence data for Al$_2$O$_3$ are controversial. Knozinger and Jeziorowski, in their early work [2], described luminescence spectra excited at λ_{ex} = 514.5 nm for η-Al$_2$O$_3$ samples that were dehydroxylated in vacuo below 800°C. They assigned the luminescence band with peaks at 573 and 600 nm to terminal OH$_s$ groups (types Ia and Ib, respectively). The luminescence spectra measured by Shen and Suib [3] for γ-Al$_2$O$_3$, which they assigned to OH$_s$ groups, have four peaks (at 345, 375, 430, and 500 nm). Breysse et al. [4] found a luminescence band associated with OH$_s$ groups at 440–450 nm in the η-Al$_2$O$_3$ spectrum (λ_{ex} = 350–360 nm).

In this work, we study in detail the structure of the luminescence band at 500–600 nm, which is assigned to OH$_s$ groups. We also search for other possible luminescence centers associated with surface hydroxide groups in the series of γ-AlOOH $\longrightarrow$ γ-Al$_2$O$_3$ $\longrightarrow$ δ... $\longrightarrow$ θ... $\longrightarrow$ α-Al$_2$O$_3$ samples.

EXPERIMENTAL

The following undoped alumina samples were used. Sample 1 (table): γ-Al$_2$O$_3$ (Condea, SEASOL GmbH, S = 205 m^2/g, calcination temperature T_c = 630°C). Sample 5 (table): boehmite (Bm) (γ-AlOOH, Pural SB1, SEASOL GmbH, S = 250 m^2/g after 3-h activation at 550°C). The impurity levels (ppm) in sample 5 were as follows: SiO$_2$, 120; Fe$_2$O$_3$, 100; TiO$_2$, 100; and Na$_2$O, 20. The other impurities did not exceed 10 ppm.

The initial samples were subsequently heat treated. Sample numbering, together with the phase compositions and selected properties of the samples, is found in the table. We also used some samples described in our earlier work [11]: sample 9 (γ-Al$_2$O$_3$, T_c = 750°C), sample 10 (0.1% Cr/γ-Al$_2$O$_3$), and sample 11 (0.1% Fe/Al$_2$O$_3$, T_c = 750°C).

Luminescence spectra were excited by pulsed nitrogen laser radiation at 337.1 nm (AIL-3, pulse repetition frequency 97.3 Hz, pulse energy Q = 16.7 µJ/pulse, pulse duration $\tau_p \leq$ 10 ns). The spectra were recorded on an MDR-12 (LOMO, Russia) high-aperture monochromator and an LN/CCD-1100PF/UV (Princeton Instruments, the United States) camera having a spectral sensitivity range from 180 to 950 nm. Characteristic exposure times for the spectroscopic chamber were Δt = 0.5–10 s.

Samples were heated in vacuo, and luminescence spectra were recorded either directly in the vacuum chamber with oil-free pumping at P = 10^{-6} torr or in thin-walled quartz ampoules, which were connected to the vacuum system through a nitrogen trap. Impurities were determined on a SPRUT-001 (Russia) X-ray fluorescence analyzer. X-ray power diffraction analysis was performed on URD-63 and HZG-4 X-ray diffrac-

Characteristics of the alumina samples

Sample no.	Sample	S, m^2/g	Temperature, °C*	Phase composition as determined by X-ray diffraction
1	γ-Al$_2$O$_3$	205	630***	γ-Al$_2$O$_3$
2	Al$_2$O$_3$-700	188	700	γ-Al$_2$O$_3$
3	Al$_2$O$_3$-1000	120	1000	80% δ-Al$_2$O$_3$ and 20% γ-Al$_2$O$_3$
4	Al$_2$O$_3$-1200	4	1200	α-Al$_2$O$_3$
5	Bm (γ-AlOOH)	250**		γ-AlOOH
6	Bm-630	168	630	γ-Al$_2$O$_3$
7	Bm-830	124	830	γ-Al$_2$O$_3$
8	Bm-1000	77	1000	δ-Al$_2$O$_3$
9	γ-Al$_2$O$_3$	–	750	γ-Al$_2$O$_3$, corresponds to sample no. 1 from [11]
10	0.1%Cr/γ-Al$_2$O$_3$	–	750	γ-Al$_2$O$_3$, corresponds to sample no. 2 from [11]
11	0.1%Fe/Al$_2$O$_3$	–	750	γ-Al$_2$O$_3$, corresponds to sample no. 5 from [11]

 *Calcination time at the specified temperature is 6 h.

 ** After 3-h activation at 550°C according to the SEASOL GmbH certificate.

***Calcination temperature is specified in the legend.

tometers. Specific surface areas were measured on an ASAP-2400 (Micromeritics) instrument.

RESULTS

The luminescence spectra (Fig. 1) excited by pulsed nitrogen laser radiation at 337.1 nm that we recorded for hydrated γ-Al$_2$O$_3$ samples (S = 188 m^2/g, T_c = 700°C) in atmospheric conditions have a band with peaks within 500–630 nm. However, this band in our spectra has a more complex structure than in the spectra reported by Knozinger and Jeziorowski [2] and Breysse et al. [4]. The luminescence intensity increases by 25% as the sample temperature decreases from 20 to –160°C (570- and 625-nm bands). Temperature quenching at 300°C is as small as 20%.

For intermediate phases of the γ-…δ-…θ-Al$_2$O$_3$ series, we found a luminescence band peaking at 770 nm about 100 nm wide, which is intrinsic exclusively to intermediate phases and unobserved in undoped α-Al$_2$O$_3$ and initial γ-AlOOH samples.

The 770-nm luminescence peak intensity increases about 2.5-fold with decreasing temperature from 20 to –160°C; with increasing temperature to 300°C, this luminescence peak experiences practically complete temperature quenching.

Luminescence of OH$_s$ Groups at 500–650 nm

Upon in vacuo calcination of Al$_2$O$_3$ samples below ~300–350°C (for T ~ 300°C, the OH$_s$ surface concentration n_{OH} is about 7 nm^{-2}, or ~50% of the monolayer [12]), the overall luminescence intensity at 500–650 nm is three to four times higher than in the spectra of samples calcined in atmospheric conditions. Dehydroxylation at higher temperatures decreases the lumi-

nescence intensity (Fig. 1, curve 2). It is likely that luminescence enhancement is due to the cessation of quenching of OH$_s$ luminescence in the presence of physisorbed water.

Figure 2 illustrates variations in relative intensities of luminescence peaks within 500–650 nm for sample 3 (δ-Al$_2$O$_3$, S = 120 m^2/g, T_c = 1000°C), which was dehydroxylated in vacuo at T_c = 300°C for 4 h, in response to consecutive hydroxylation for 0.3 and 20 h in atmospheric conditions. The spectra are normalized to the
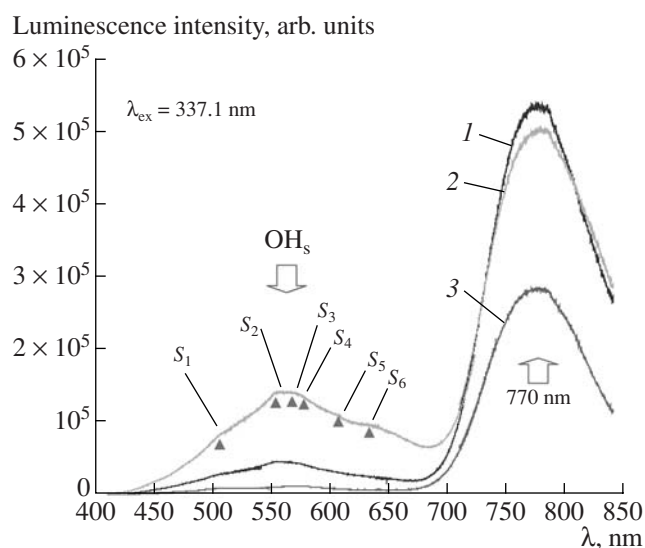

Fig. 1. Survey luminescence spectra of (1) the initial hydrated γ-Al$_2$O$_3$ sample (sample 2, S = 188 m^2/g, T_c = 700°C) and (2, 3) samples dehydroxylated in vacuo for 4 h at (2) 350 and (3) 630°C. The spectra were recorded at 20°C. Excitation: pulsed nitrogen laser radiation at 337.1 nm.
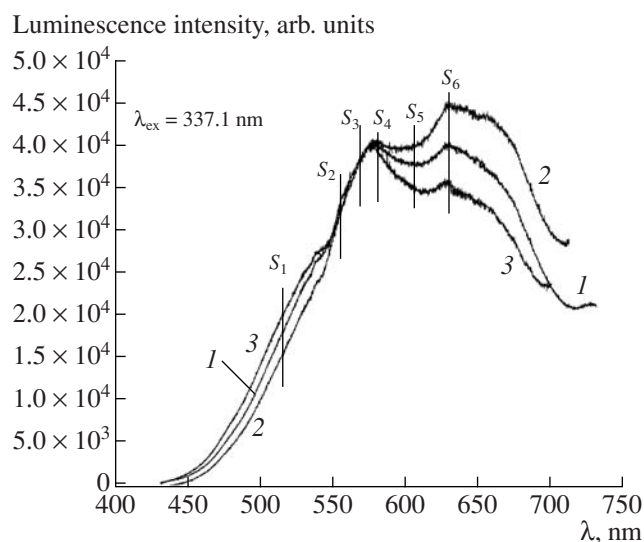
Fig. 2. Luminescence spectra of OH_s groups in the range 500–650 nm for (*1*) a δ-Al_2O_3 sample (sample 3, Condea, $T_c = 1000°C$), which was dehydroxylated in vacuo for 4 h at $T_c = 300°C$ and then in atmospheric conditions for (*2*) 0.3 and (*3*) 20 h. The spectra are normalized to the peak intensity at 570 nm and recorded at 20°C. Excitation: pulsed nitrogen laser radiation at 337.1 nm.

Fig. 3. Luminescence spectra of OH_s groups in the range 500–650 nm for (*1*–*3*) a γ-Al_2O_3 sample (sample 2, Condea, $T_c = 700°C$), which was dehydroxylated in vacuo for 4 h at (*1*) 150, (*2*) 500, and (*3*) 630°C, and for (*4*) a δ-Al_2O_3 sample (sample 3, $T_c = 1000°C$), which was also dehydroxylated in vacuo for 4 h at 770°C. Spectra *1* and *2* are normalized to the peak intensity at 570 nm and recorded at 20°C. All spectra are excited by pulsed nitrogen laser radiation at 337.1 nm.

570-nm peak intensity. They show that hydroxylation changes the intensity ratio between peaks at 500–515 and 633 nm without changing the band envelope.

The luminescence intensity decays about 30-fold upon the surface dehydroxylation of Al_2O_3 in vacuo below 800°C (Fig. 3), which correlates with the temperature dependence of the surface hydroxide group concentration [12]. Subsequent one-day surface hydration in atmospheric conditions recovers the initial luminescence level. Not only does dehydroxylation and subsequent partial hydroxylation give rise to a relative change of the structure of luminescence bands at 500–515 and 633 nm, but also lines appear at 553, 567, and 577 nm; in the initially hydroxylated sample, these lines are unresolved. This implies that the luminescence band at 500–650 nm assigned to hydroxide groups, actually, consists of several lines (S_1–S_6) at 500–515, 553, 567, 577, 607, and 633 nm, respectively, which can be assigned to various types of OH_s surface groups.

Luminescence at 770 nm

The luminescence band at 770 nm (Fig. 1), about 100 nm wide, was observed in the spectra excited at 337.1 nm for all samples of the γ-…δ-…θ-Al_2O_3 series, except for undoped α-Al_2O_3 samples and untreated γ-$AlOOH$. This luminescence band does not experience quenching because of adsorbate water. However, this band is sensitive to the degree of surface hydroxylation. Therefore, before recording spectra in atmospheric
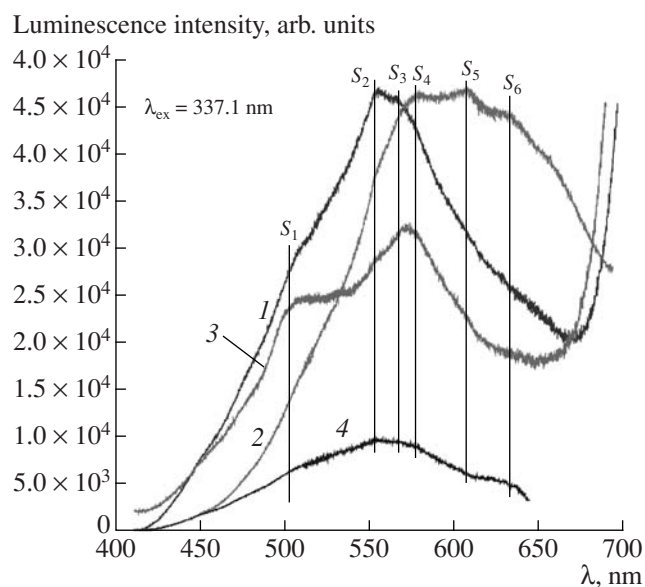
conditions, we hydrated samples in air for 4 h at 100°C and then stored them in identical conditions.

To elucidate the influence of temperature on the phase composition and specific surface area, we calcined the precursor γ-$AlOOH$ sample for 6 h in air at 150–1200°C in 150-K steps. The table lists selected characteristics of intermediate samples. Luminescence spectra were recorded in atmospheric conditions at 20°C.

The appearance of luminescence (Fig. 4) coincides with the onset of γ-Al_2O_3 formation, and its intensity peaks at $T_c = 500$–630°C, which correlates with the maximal surface area of the sample. A further increase in the calcination temperature to 1000°C for sample 3 gives rise to a twofold to threefold decrease in luminescence intensity, which correlates with a decrease in the specific surface area. For sample 4 with the pure α-Al_2O_3 phase ($S = 4$ m^2/g, $T_c = 1200°C$), the aforementioned luminescence band was not observed.

The sensitivity resource of spectral measurements implies that the nonappearance of luminescence in α-Al_2O_3 is due to the phase composition of the sample and not to the calcination temperature or a decrease in the specific surface area upon the phase transition to the α phase. This was verified for several Al_2O_3 samples with different phase-transition temperatures to the α phase.
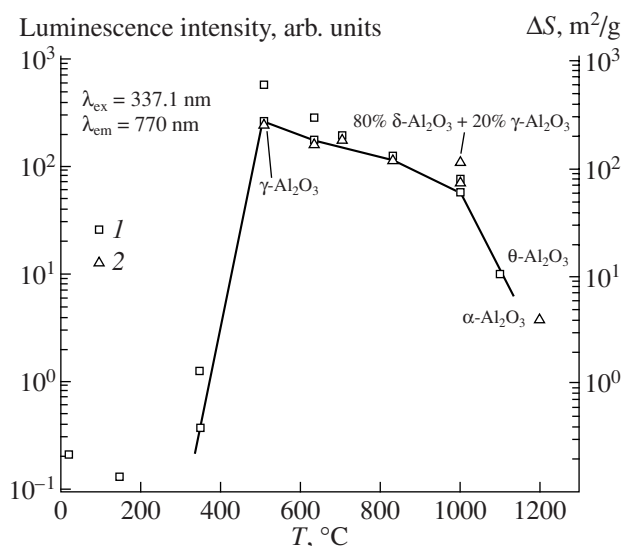
Fig. 4. (*1*) Luminescence intensity at 770 nm vs. calcination temperature in atmospheric conditions for the initial γ-Al$_2$O$_3$ sample (Bm). (*2*) Specific surface area and phase composition vs. calcination temperature. The spectra are recorded at 20°C. Excitation: pulsed nitrogen laser radiation at 337.1 nm.

Fig. 5. (*1*) Luminescence intensity at 770 nm vs. in vacuo dehydroxylation temperature for a δ-Al$_2$O$_3$ sample ($S = 117$ m^2/g, $T_c = 1000$°C). (*2*) OH$_s$ group concentration vs. temperature [12].

The second set of measurements was intended to reveal the influence of the degree of surface hydroxylation on 770-nm luminescence.

To dehydrate and eliminate organics from the surface, samples were calcined in air at 500°C for 6 h. Sample 2 (γ-Al$_2$O$_3$) was dehydroxylated in vacuo for 4 h at 150–630°C in 150-K steps. The luminescence spectra displayed in Fig. 5 were recorded at room temperature. To avoid variations in phase composition during in vacuo calcination, we took sample 3 (δ-Al$_2$O$_3$; $S = 120$ m^2/g; $T_c = 1000$°C) as the precursor for 800°C.

The observed luminescence intensity is affected by the concentration of surface hydroxide groups. Calcination in vacuo at 800°C for 4 h decreases the luminescence intensity about 100-fold relative to the initially hydroxylated sample. Subsequent one-day surface hydration in atmospheric conditions recovers the initial luminescence level. A similar effect is provided by 4-h hydration at 100°C in atmospheric conditions.

To determine the possible influence of Fe^{3+} and Cr^{3+} trace bulk impurities on 770-nm luminescence, we recorded spectra in atmospheric conditions for a γ-Al$_2$O$_3$ sample that contained 0.01 wt % Cr and 0.05 wt % Fe (sample 9, $T_c = 750$°C) and doped samples that contained 0.1% Cr/γ-Al$_2$O$_3$ and 0.1% Fe/γ-Al$_2$O$_3$ (samples 10 and 11, respectively; $T_c = 750$°C). The 770-nm luminescence intensity relative to the initial sample increased twofold for the 0.1% Fe/γ-Al$_2$O$_3$ sample and decreased 2.5-fold for the 0.1% Cr/γ-Al$_2$O$_3$ sample.

The luminescence decay kinetics for the 770-nm band in sample 2 (γ-Al$_2$O$_3$, 700°C) at 20°C within the time interval from 50 μs to 10 ms was fitted to the biexponential function $I = I_{01} e^{-t/\tau_1} + I_{0.2} e^{-t/\tau_2}$ with times $\tau_1 = 5 \times 10^{-4}$ s and $\tau_2 = 2.71 \times 10^{-3}$ s.

DISCUSSION

In choosing the 337.1-nm nitrogen laser wavelength for excitation, we were guided by the following: on the one hand, this wavelength falls within the absorption band of OH$_s$ groups at 300–350 nm for Al$_2$O$_3$ [4] and ThO$_2$ [9] and, on the other, it is insufficient for the excitation of luminescence associated with point defects of Al$_2$O$_3$ at 200–250 nm. Excitation outside the absorption bands of Cr^{3+} impurity ions also made it possible to resolve from the wide luminescence band characteristic of Cr^{3+}–Al$_2$O$_3$ whose short-wave boundary is at 680 nm.

In the models [12–15] describing the surface properties of various intermediate Al$_2$O$_3$ phases and interpreting the observed IR adsorption spectra of OH$_s$ surface groups in the range from 3650 to 3810 cm^{-1}, seven well-resolved lines are assigned to two types of OH$_s$ groups (terminal and bridging groups). The highest frequencies (3800–3745 cm^{-1}) refer to three types of terminal groups denoted as OH^4–OH^6 according to [14]. Low-frequency bands (3730–3650 cm^{-1}) refer to bridg-

ing OH groups linked to two or three variously coordinated aluminum cations. The spectra of Al_2O_3 samples of various phase compositions are characterized by approximately identical sets of OH_s groups, which differ in relative luminescence intensities. A characteristic feature of γ-Al_2O_3 is the high intensities of the lines corresponding to OH^{66} groups (3733 cm^{-1}) and OH^{64} groups (3693 cm^{-1}) [14–16].

The initial dehydroxylation stage below 400°C (Fig. 2) involves the recombination of two neighboring OH_s groups, one being more acidic (terminal $OH^6 > OH^5 > OH^4$) and the other more basic (bridging $OH^{653} > OH^{663} > OH^{553} > OH^{553}$...) [14]. At higher dehydroxylation temperatures, some types of OH_s groups that are less abundant at the initial dehydroxylation stage can appear as a result of the recombination of discrete OH_s groups.

Proceeding from the spectra in Figs. 2 and 3, the longest wavelength line S_6 at 633–650 nm can be assigned to the luminescence of OH^6 terminal groups and the line S_4 at 577 nm to OH^4 terminal groups.

The luminescence bands at 500–515, 553, 567, and 607 nm can arise both from bridging groups, which are linked with two or three aluminum cations, and from emission transitions from excited levels whose wavefunctions are combinations of the functions of variously coordinated surface groups OH_s.

The more rigorous assignment of S_1–S_6 lines to particular types of OH_s surface groups for Al_2O_3 is beyond the scope of this work. This requires tandem use of FTIR and laser-induced luminescence spectroscopy and, possibly, quantum-chemical calculations.

Luminescence at 770 nm differs from that at 500–650 nm in its temperature dependence and the absence of quenching upon water adsorption in an atmospheric setting. However, both luminescence bands are due to OH_s groups on the Al_2O_3 surface. The results of measurements illustrated by Figs. 4 and 5 show that the luminescence intensity of these centers depends both on the specific surface area and OH_s group concentration and on the crystal structure. γ-AlOOH and α-Al_2O_3 do not luminesce at 770-nm; their aluminum ions have an octahedral coordination. On the other hand, cationic and anionic vacancies are characteristic precisely of intermediate Al_2O_3 phases, including θ-Al_2O_3.

It is noteworthy that, because the temperature at which the luminophore concentration and total OH_s concentration decrease at equal rates is on the order of 500°C (Fig. 5), the OH_s fraction responsible for 770-nm luminescence is likely not high and does not exceed 5–10%.

Presumably, the observed luminescence centers are sensitized by OH_s groups coordinated in a certain mode, and the observed radiation transitions occur from excited levels of the activator associated with Al_2O_3 structure defects characteristic of tetrahedral Al^{3+} ions.

Such defects can likewise be generated by tetrahedrally coordinated impurity Fe^{3+} ions. According to Pott and McNicol [17], a band at 765 nm with a decay time of 9 ms at room temperature is characteristic of Fe^{3+} phosphorescence in γ-Al_2O_3. Enhancement of phosphorescence with increasing Fe^{3+} percentage is observed for percentages below 0.01 wt %; quenching is observed for percentages above 0.1 wt %. Apparently, the 330-nm band in the excited spectrum of highly disperse Fe^{3+}/γ-Al_2O_3 (Pott and McNicol [18] assigned it to Fe^{3+} charge-transfer transition) can arise from OH_s groups. If so, our revealed dependence of 770-nm luminescence on the degree of surface hydroxylation in the intermediate phases of the γ-…δ-…θ-Al_2O_3 series would appear only when excitation occurs in the spectral region we use. If the spectrum is excited in the region of intrinsic absorption bands of tetrahedral Fe^{3+} ions in Al_2O_3 at higher wavelengths than 380 nm, the observed intracenter phosphorescence should not depend on the degree of surface hydroxylation.

Gorelik et al. [19] described the luminescence band at 770 nm excited by 337.1-nm pulsed nitrogen laser radiation in nanocrystalline Al_2O_3 samples in atmospheric conditions but assigned this band to Cr^{3+} luminescence in Al_2O_3, which is at variance with our data.

Breysse et al. [4] mentioned, for η-Al_2O_3 samples, a luminescence band at 760 nm with an excitement peak at 310 nm with the luminescence intensity strongly decaying at high dehydroxylation temperatures, but they neither reported spectra nor interpreted the structure of luminescence centers. We have not found other works that describe the 770-nm luminescence band or the scheme of its excitation via OH_s surface groups.

Efficient quenchers for the above-described 770-nm luminescence band, which is associated with OH_s surface groups of Al_2O_3, are likely immobilized mononuclear and polynuclear complexes of transition or precious metals that can be stabilized in place of OH_s groups or at surface defects in the immediate vicinity of these groups.

CONCLUSIONS

We have studied the laser-induced luminescence of surface hydroxide groups excited by pulsed laser radiation at 337.1 nm for undoped Al_2O_3 of various phase compositions. We have demonstrated that the luminescence band at 500–630 nm described by Knozinger and Jeziorowski [2] and assigned by them to terminal hydroxide groups actually consists of S_1–S_6 lines with the main peaks at 500–515, 553, 567, 577, 607, and 633 nm, which can be assigned to various types of OH_s surface groups.

We have found that the luminescence band at 770 nm is characteristic of intermediate phases of the γ-…δ-…θ-Al_2O_3 series containing trace levels of bulk

Fe^{3+} impurities. With 337.1-nm excitation, this band depends on the degree of Al_2O_3 hydroxylation.

The most important thing with our discovered effect is that it demonstrates the utility of luminescence spectra for microstructural studies of the surface properties of transition Al_2O_3 phases even in atmospheric conditions.

ACKNOWLEDGMENTS

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