

Relaxation Processes in α -Al₂O₃ Crystals with F⁺- and F-Centers during Pulse Excitation by Electrons and Synchrotron Radiation

A.I. Surdo, V.S. Kortov*, V.A. Pustovarov*, V.Yu. Yakovlev**

Ural State Technical University, 19 Mira Str., Ekaterinburg, 620002, Russia, (343)3754594, E-mail: ais@dpt.ustu.ru

**Ural State Technical University, 19 Mira Str., Ekaterinburg, 620002, Russia*

***Tomsk Polytechnical University, 30 Lenin Ave., Tomsk, 634034, Russia*

Abstract – The ionizing radiation energy is transferred to F⁺- and F-centers in α -Al₂O₃ through two channels. One of the channels is characterized by a migration-free transport mechanism since there is not any delay between the pulse excitation and its relaxation involving short-lived F⁺-centers. More inertial processes of the energy transport to active centers and the energy dissipation in the second channel are limited by the diffusion-controlled motion of excitons. This conclusion is confirmed by temperature, density and concentration dependences of the radioluminescence kinetics of F⁺-centers.

1. Introduction

New information about the electronic structure of F⁺- and F-centers in α -Al₂O₃ [1, 2], which was obtained by methods of the time-resolved subnanosecond optical spectroscopy, stimulates formulation and solution of new tasks. They are connected primarily with the excitation of F⁺- and F-centers by radiations over wider energy and time intervals. These radiations may include pulsed electron beams (PEBs) and X-ray synchrotron radiation (SR). The effect of these factors on perspective materials, including those sensitive to radiation, is studied more and more extensively. The posed problems present both fundamental and purely applied interest. Of no small importance in this respect is the study of processes involved in the transfer of energy of these radiations in corundum, which is, on the one hand, a typical representative of the class of wide-gap oxides and, on the other hand, a material used in available and projected detectors of ionizing radiations.

This study deals with the transformation of SR and PEB energies to electron excitations (EE's), and also migration of EE's and the transport of their energy to F⁺- and F-centers directly or during relaxation.

2. Samples and Experimental Methods

The cathodoluminescence (CL) and X-ray luminescence (XL) studies were performed using five types of α -Al₂O₃ single crystals with different vacancy concentrations C_{V_a} . Since F²⁺-centers were not detected so far in equilibrium conditions in corundum, C_{V_a} was estimated considering concentrations of F- and F⁺-centers (C_F and C_{F^+}), which were calculated using optical absorption (OA)

data and Smakula's formula. The anion-deficient samples Nos. 1 and 2 (in what follows referred to as α -Al₂O_{3- δ}), which were prepared by thermochemical coloring, contained anion vacancies mostly in the form of F-centers. The concentration C_{V_a} was $\sim 0.5 \cdot 10^{17} \text{ cm}^{-3}$ and $1.4 \cdot 10^{17} \text{ cm}^{-3}$ in the samples Nos. 1 and 2 respectively. The third type (No. 3) was a thermochemically colored crystal, which was additionally exposed to fast electrons ($E_e = 16 \text{ MeV}$) at a fluence of $6 \cdot 10^{18} \text{ eL/cm}^2$. The electron irradiation caused a considerable increase in the concentration of F⁺-centers only, $C_{F^+} = 0.4 \cdot 10^{17} \text{ cm}^{-3}$, while $C_{V_a} = C_F + C_{F^+}$ was $\sim 1.8 \cdot 10^{17} \text{ cm}^{-3}$. The sample No. 4 had the maximum concentration of single vacancies ($C_{V_a} \approx 6.4 \cdot 10^{18} \text{ cm}^{-3}$). Defects were produced by reactor neutrons ($\Phi_n = 10^{17} \text{ n/cm}^2$) in the last sample. For comparison, a conditionally stoichiometric α -Al₂O₃ crystal (sample No. 5) with C_{V_a} estimated at less than 10^{16} cm^{-3} was used.

Time-resolved SR and XL spectra and the luminescence kinetics in these samples were examined in special installations at the Tomsk Polytechnic University and the Institute of Nuclear Physics (Novosibirsk) using methods described in Refs. [3, 4]. The excitation radiation had the following parameters: $E_m = 62 \text{ keV}$, $\tau_1 = 0.43 \text{ ns}$ and $f = 4 \text{ MHz}$ for SR; $E_e = 250 \text{ keV}$, $\tau_1 = 3 \div 15 \text{ ns}$, $f \leq 10 \text{ Hz}$ and $W = 1 \div 160 \text{ mJ/cm}^2$ for PEBs.

3. Results

The XL bands at 3.8 eV in the colored samples Nos. 1 and 2 had nearly equal FWHM ($H = 0.42 \pm 0.02 \text{ eV}$) at 295 K both in quasistationary and time-resolved spectra. What mattered more was that they did not differ from their counterparts for F⁺-centers. It was remarkable also that although $C_F \gg C_{F^+}$, the XL intensity of F⁺-centers was high and largely exceeded the XL intensity of F-centers in nanosecond-resolved spectra at small Δt and δt (the time window width and its delay relative to the excitation pulse respectively). Moreover, most of the light sum in the time-resolved XL spectra at $\delta t \leq 200 \text{ ns}$ and $\Delta t = 40 \text{ ns}$ was not illuminated near 3.8 eV. Analogous results were obtained in the case of the PEB excitation [5] and for the samples Nos. 3 and 4. It was concluded from these data that the excitation energy was transferred predominantly to F⁺-centers, or unstable F⁺-centers

were formed due to the redistribution of the electron density near F-centers under the action of SR and PEBs, or both processes took place concurrently. Considering earlier data [5], the second and third variants should be preferred.

In the case of the anion-defective samples (Nos. 1–4) the XL decay curves with $h\nu_{\text{rad}} = 3.8$ eV at $T = 295$ K could be described for 10–80 ns by exponential dependences with τ varying between 2.2 and 22 ns (Fig. 1, 1–4). An important fact was that while FWHM values of the observed luminescence bands were equal to those of F^+ -centers during the intracenter excitation, their kinetics obviously had a much larger inertia ($\tau > \tau_{F^+} = 2.1$ ns). Remarkably, the decay was the slowest in the sample No. 1 (curve 1) and the fastest in the sample No. 4 (curve 4). Moreover, the data in Fig. 1 suggested a correlation between C_{V_a} and τ : the decay time of the XL at 3.8 eV was the longest in crystals with the smallest concentration of F-type centers.

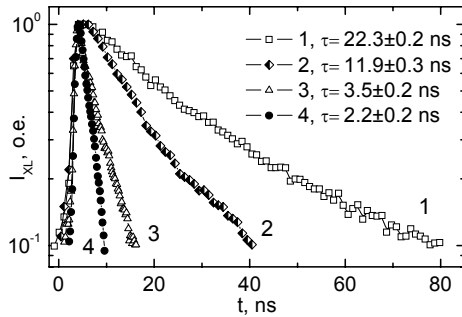


Fig. 1. XL kinetics at 3.8 eV in $\alpha\text{-Al}_2\text{O}_3$ samples No. 1 (1), No. 2 (2), No. 3 (3) and No. 4 (4) during SR excitation, $T = 295$ K

When the temperature dropped to 80 K, the XL kinetics at 3.8 eV was considerably complicated. A short component with $\tau_1 \approx 2.2$ ns, which approached τ_{F^+} , appeared in the kinetic curves of all the samples studied. The analysis of the kinetics demonstrated that the slower component τ_2 decreased from 235 ns in the sample No. 1 to 15 ns in the sample No. 4 as the concentration C_{V_a} of the crystals increased. It may be inferred therefore that the growth of the concentration of anion vacancies led to the acceleration of SR-initiated relaxation processes involving F^+ -centers. Of no small importance was the detected inconsistency between the lifetime of the excited state of an F^+ -center and the variation dynamics of the XL intensity at 3.8 eV, which also had a strong temperature dependence. These observations pointed to a high probability that localized low-energy EE's participated in the transport of the excitation energy to F^+ -centers.

Analyzing further specific features of the XL at 3.8 eV, our attention was drawn to the luminescence kinetics of F^+ -centers at $T = 80$ K in the sample No. 1,

which had the smallest concentration of anion vacancies. In addition to the largest $\tau_2 \approx 235$ ns, the kinetic curve included the buildup stage with $\Delta t_b \approx 45$ ns (Fig. 2, 1). Figure 2 also shows the decay kinetics in the luminescence band of E-type self-trapped excitons (STE's) at 3.8 eV (curve 2, for the identification see [6, 7]) in the sample No. 5. It is important that the kinetic curves of the XL at 3.8 eV have similar shapes for the samples Nos. 1 and 5. The τ_1 values differed little, while the difference of Δt_b and τ_2 was larger in these samples. Specifically, the buildup time and the slow component were larger in the sample No. 5 ($\Delta t_b \approx 65$ ns and $\tau_2 \approx 950$ ns). Also, as distinct from the CL kinetics of E-excitons [8], we observed a fast component with the constant $\tau_1 = 2.2$ ns at $T = 80$ K in the XL kinetics near 3.8 eV in the stoichiometric sample. This component approached the lifetime of the excited state of an F^+ -center.

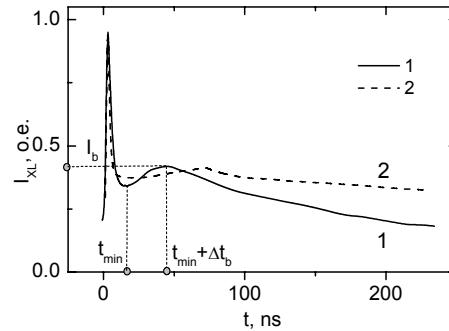


Fig. 2. XL kinetics at 3.8 eV in samples No. 1 (1) and No. 5 (2) during SR excitation, $T = 80$ K

A detailed comparative examination of time-resolved XL spectra of the samples No. 1 ($\alpha\text{-Al}_2\text{O}_{3-\delta}$) and No. 5 ($\alpha\text{-Al}_2\text{O}_3$) yielded the following results. When $\delta t = 0$ ns and $\Delta t = 40$ ns, FWHM values and positions of the maximums of the bands near 3.8 eV differed little: $h\nu_m = 3.79 \pm 0.02$ eV and $H = 0.35 \pm 0.02$ eV for the sample No. 1 and $h\nu_m = 3.80 \pm 0.02$ eV and $H = 0.35 \pm 0.02$ eV for the sample No. 5. When the delay time increased ($\delta t = n \cdot 41.2$ ns where $n = 1, 2, 3, 4, 5$), the parameters of the XL band near 3.8 eV remained unchanged in the sample No. 1 and the band at 3.80 eV widened ($H \approx 0.43$ eV) in the sample No. 5.

Nearly equal values of the fast components in the luminescence kinetics with $h\nu_{\text{rad}} = 3.8$ eV ($\tau_1 \approx 2.2$ ns) and the parameters of the XL bands with $h\nu_m = 3.8$ eV at a short delay time in the stoichiometric and anion-deficient samples might point to the formation of a large number of F^+ -like defects in these samples. It followed from the experiment that the generation rate of such defects was the largest in $\alpha\text{-Al}_2\text{O}_{3-\delta}$ and $\alpha\text{-Al}_2\text{O}_3$ immediately at the moment of the excitation SR pulse. Since stationary OA spectra did not exhibit any significant change of the concentration of F^+ -centers

in both samples after SR experiments, these defects might be thought of as metastable.

The further analysis of instantaneous spectra and the parameters of the bands near 3.8 eV, which were measured at $\delta t = n \cdot 41.2$ ns ($n=1, 2, 3, 4, 5$), demonstrated that in the stoichiometric sample No. 5 unstable F^+ -like defects transformed to E-type STE's with characteristic luminescence whose band was wider than the luminescence band of F^+ -centers ($h\nu_m = 3.81$ eV and $H = 0.43$ eV at $T = 80$ K [8]). One more proof of this transformation was the fact that over the time interval of 10–250 ns the XL kinetics at 3.8 eV (see Fig. 2, 2) was similar to the CL kinetics of E-excitons ($\tau_2 \sim 100$ –400 ns and $\Delta t_b \sim 50$ –100 ns) [6, 8]. Researchers [7, 8] also found that the CL buildup time of E-type STE's increased with decreasing temperature and correlated with the fast component of the decay time τ_{A1} (~ 20 ns) of the CL of A-type STE's ($h\nu_{rad} = 7.6$ eV): $\tau_{b,E} \approx 4\tau_{A1}$. One more result of the study [8] is important for the discussion below. It was shown that the introduction of anion vacancies suppressed the luminescence of self-trapped A- and E-excitons.

So, the spectral and kinetic data on the XL of F^+ -centers in anion-defective corundum samples and their comparison with analogous data for E-excitons are indicative of a sufficiently high probability of the exciton mechanism for excitation of the luminescence of F-type centers. The acceleration of the relaxation process shows up at $T = 300$ K as the decrease in the fast component of the decay time of the XL of F^+ -centers with growing concentration of anion vacancies to $\tau_{F^+} = 2.1$ ns, which is characteristic of the intracenter excitation, and at $T = 80$ K as the complication of the kinetics and shortening of the slow component τ_2 . Therefore, the transfer of energy by excitons may be assumed to be diffusion-controlled. The proposed hypothesis can be verified if, for example, dependences of the luminescence kinetics of F^+ -centers on the temperature and the density of the PEB excitation are comprehensively analyzed upon band-to-band excitation.

Similarly to the X-ray SR excitation, the CL kinetics at 3.8 eV with the buildup were measured at $T = 80$ K only for the thermochemically colored samples No. 1 and No. 2. The comparison of the parameters of the CL kinetics and the concentrations of anion vacancies in the samples Nos. 1 and 2 showed that the growth of C_{v_a} was followed by the decrease in τ_1 from 50 to 25 ns, Δt_b (200 ns \rightarrow 100 ns), and τ_2 (450 ns \rightarrow 160 ns). It is significant also that at $T = 80$ K the values of τ_1 , Δt_b and τ_2 were considerably different in one and the same sample No. 1 exposed to an electron beam and X-ray SR. Similarly to the case of $T = 295$ K, they were larger upon the electron excitation.

The fast component was absorbed by the grown slow component in the CL kinetics with $h\nu_{rad} = 3.8$ eV,

which was measured at $T = 80$ K in the sample No. 3. The buildup stage was not discriminated and the decay time constant τ_2 decreased still more (~ 60 ns). This observation confirmed the aforementioned tendency of τ_2 to decrease with growing C_{v_a} .

So, the appearance of the buildup stage and its shortening together with τ_2 upon the X-ray excitation relative to its duration upon the electron excitation suggest an intimate relationship of the revealed phenomena with diffusion and, probably, some other processes. For example, density effects can appear during electron and SR excitations. If the CL kinetics of, e.g., F^+ -centers does not change radically with growing W and, simultaneously, their luminescence intensity rises at the buildup stage, the excitation energy transfer to remote centers should be assumed to be a diffusion-controlled process and its mechanism should be taken as the exciton one with a high probability.

The effect of the density of the PEB excitation at $T = 80$ K on the CL kinetics of F^+ -centers in the samples Nos. 1 and 2 was analyzed next. Specifically, when W increased from 1 to 160 mJ/cm² in the sample No. 2, the CL intensity at 3.8 eV increased almost linearly on the logarithmic scale at the buildup maximum I_b , while Δt_b decreased from 100 to 50 ns and τ_2 was reduced from 120 to 65 ns. In addition, the considerable decrease in Δt_b and τ_2 began only at $W > 20$ mJ/cm². Analogous density effects were also observed in the sample No. 1. According to the theoretical estimate of the instantaneous temperature increase ΔT of the surface layer of the sample under exposure to an electron beam, even if radiation heating and the accompanying release of carriers from traps do take place, these effects can be neglected at least when $W < 30$ mJ/cm². Then at $W < 30$ mJ/cm² the form of the CL kinetics of F^+ -centers is not connected with diffusion-controlled recombinations involving thermally released electrons and/or holes. Considering this fact, the circle of possible mechanisms for the transfer of the band-to-band excitation energy to F^+ - and F-centers may be narrowed still more and limited to exciton mechanisms. Furthermore, a strong argument in favor of the exciton mechanism rather than the electron-hole mechanism is the more efficient exciton excitation of F^+ - and F-centers at $T_1 = 295$ K than at $T_2 = 10$ K [2].

More experimental evidence in support of the diffusion-controlled migration of trapped EE's was produced by temperature dependences of the CL kinetics at 3.8 eV in the thermochemically colored samples Nos. 1 and 2. Considering the density effects, they were analyzed at $W = 12$ mJ/cm². The obtained dependences exhibited the same behavior in both samples: as the temperature elevated from 80 K to 200 K, the amplitude I_b increased, while the fast (τ_1) and slow (τ_2) decay components and the buildup time Δt_b

shortened. The first distinction referred to τ_1 , Δt_b and τ_2 values, which were ~ 2 times larger in the sample No. 1 with a smaller concentration of anion vacancies. The second distinction was related to the temperature, at which the fast component of the kinetics was absorbed by the strongly grown slow component. As would be expected from the diffusion theory, this absorption occurred at a higher temperature ($T > 160$ – 170 K) in the sample No. 1 with the smallest C_{v_a} concentration than in the sample No. 2 ($T > 115$ – 120 K). Therefore, to obtain a more representative sampling of I_b , Δt_b and τ_2 values over a wide temperature interval, in what follows we shall present data for the sample No. 1. For the subsequent analysis, the kinetic curves were approximated by the equation

$$I = I_1 \cdot \exp(-t/\tau_1) + I_b \cdot \exp(t/\tau_b) \cdot \exp(-t/\tau_2) / [\exp(t/\tau_b) - 1 + a], \quad (1)$$

where I_1 and τ_1 denote the intensity and the decay time constant of the fast component; I_b , τ_b and τ_2 are the intensity, the buildup time constant and the decay time constant of the complicated slow kinetics; a is a fitting parameter, which relates the buildup stage and the fast and slow kinetics and influences little the I_b , τ_b and τ_2 values analyzed below.

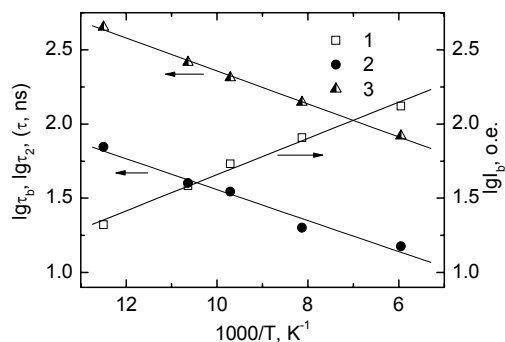


Fig. 3. Temperature dependences of the parameters of the CL kinetics of F⁺-centers in sample No. 1 at $W=2$ mJ/cm²: 1 – I_b ; 2 – τ_b ; 3 – τ_2

Figure 3 presents dependences $I_b = f(T)$ (1), $\tau_b = f(T)$ (2) and $\tau_2 = f(T)$ (3), which, as is seen, can be described in the Arrhenius coordinates by linear functions. Values of the activation energy E_a , which were calculated from $I_b = f(T)$, $\tau_b = f(T)$ and $\tau_2 = f(T)$, were nearly equal ($\sim 22 \pm 2$ meV). A similar value of E_a equal to $\sim 21 \pm 3$ meV was also obtained from the dependences $I_b = f(T)$ and $\tau_2 = f(T)$ for the sample 2. Furthermore, values of the Δt_b and τ_2 , and also the activation energy determined from $\tau_2 = f(T)$ for the sample No. 1 differed little from their counterparts, which were determined for emission from E-excitons ($E_a = 22$ meV) and A-excitons ($E_a = 31$ meV) in

stoichiometric samples [6]. It is important that at temperatures of 80–100 K a direct relationship existed between τ_b of the CL of F⁺-centers and τ_{A1} of the CL of an A-exciton. Specifically, as the temperature elevated, τ_b (see Fig. 3) and τ_{A1} [8] decreased, while the relation $\tau_b \approx k \cdot \tau_{A1}$ was maintained between these values (k being the proportionality factor). The obtained data also suggested that the k value depended on the anion vacancy concentration C_{v_a} and penetrability of the excitation radiation.

Summarizing what has been said above, it is quite reasonable to suppose that the obtained temperature dependences $I_b = f(T)$, $\tau_b = f(T)$ and $\tau_2 = f(T)$ for the CL of F⁺-centers result from the diffusion motion of self-trapped A- and E-excitons or similar excitons, transformations from the A to E type with growing T , and their subsequent localization near F⁺- and F-centers.

4. Conclusion

One of the most important results of the study is that processes of the transfer of the energy of PEBs and X-ray SR to F⁺- and F-centers and their kinetics in α -Al₂O₃ depend on the temperature, the concentration of both F⁺- and F-centers, the excitation density and radiation penetrability. Also, the analysis of the obtained results suggests that at temperatures of 80–300 K the transport of the excitation energy to F⁺- and F-centers is a diffusion-controlled process and is realized most probably by excitons. Mechanisms and models of the processes separately at low and moderate temperatures are described in more detail in Ref. [9].

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