



On the nature of slow emission at 3.8 eV in crystalline α -Al₂O_{3- δ}



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HIGHLIGHTS

- Thermo-optical treatment leads to emergence of new active centers in α -Al₂O_{3- δ} .
- The new type of centers emits as F⁺ centers around 3.8 eV, but has different parameters.
- These new centers can be destructed by irradiation and thermal or optical stimulation.
- These centers are complex and consist of interstitial Al and anion vacancy.

ARTICLE INFO

Article history:

Received 25 October 2015

Received in revised form

25 December 2015

Accepted 26 December 2015

Available online 30 December 2015

Keywords:

Anion-defective corundum

Thermo-optical treatment

Defect formation

Radioluminescence

Photoluminescence

Luminescent centers

ABSTRACT

A comparative research of thermoluminescence, X-ray luminescence, and photoluminescence in initial and thermo-optically treated and X-ray irradiated anion-defective corundum (α -Al₂O_{3- δ}) samples has been carried out. A new type of center has been identified emitting near 3.6–3.8 eV up to 800 K, excited at 5.9 eV, and having a lifetime of about 300 ms at 300 K in the excited state. This type of centers was found to be created only at thermo-optical treatment, including ultraviolet irradiation with $\lambda \approx 280$ –320 nm and simultaneous heating of α -Al₂O_{3- δ} samples to 550–670 K, and be destructed thermally at $T \geq 670$ K or when exposed to X-ray radiation or light with quantum energies of 5.9 and 3.1 eV. The center type found is assumed to have a complex structure consisting of interstitial aluminum, anion and cation vacancy, and slightly displaced regular ions in the nearest surrounding.

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1. Introduction

It is well known (Yukihara et al., 2003) that responses and kinetics of thermally and optically stimulated luminescence (TL and OSL) of crystalline anion-defective corundum (α -Al₂O_{3- δ}) and TLD-500 detectors on their basis depend on the extent of filling of not only the main dosimetric trap responsible for the TL peak at 450 K but also the deeper ones. One way of filling deep traps, particularly one of them depleted near 720 K, is ultraviolet (UV) irradiation at a temperature of 550–670 K (Surdo et al., 2013). This procedure is referred to as thermo-optical treatment (TOT).

In Solov'ev et al. (2012), it is found that TL spectra are also altered essentially in α -Al₂O_{3- δ} samples subjected to TOT. Prior to TOT, emissions of the F⁺ and F centers (anion vacancies with one

and two electrons, respectively) are registered in the spectrum with domination of the latter, whereas after TOT, UV emission with a maximum at $h\nu_{em} \approx 3.6$ –3.8 eV prevails in TL peaks at 450 and 720 K. Its spectral and luminescent parameters are similar to those of the F⁺ centers. However, such an increase of contribution of F⁺ emission to the TL response is least possible. First, when using, as in Solov'ev et al. (2012), microsecond time resolution in recording TL spectra, according to (Surdo et al., 2005), luminescence of the F centers will predominate that of F⁺ centers, as the lifetimes in an excited state are $\tau_F = 36$ ms and $\tau_{F^+} = 2.1$ ns. Second, given considerable thermal quenching of luminescence of the F⁺ centers at $T > 600$ K (Evans and Stapelbroek, 1978), it is difficult to explain its prevalence in the TL peak at 720 K. Third, several difficulties arise in the explanation of luminescence of the F⁺ centers in the TL process when both electrons and holes are released (Surdo, 2007). Both the first and second are improbable for energy reasons. In oxides with a wide energy gap, including α -Al₂O₃, the F²⁺ state (an empty anion vacancy) is energetically wasteful. Hence, the reaction $F^{2+} + \text{electron}^- \rightarrow (F^+)^* \rightarrow F^+ + h\nu$ (3.8 eV) cannot be realized. On

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the contrary, the ground state of the F^+ center is fairly close ($\sim 2.5\text{--}3$ eV) to the top of the valence band, and the reaction $F + \text{hole}^+ \rightarrow (F^+)^* \rightarrow F^+ + h\nu$ (3.8 eV) cannot be energetically balanced.

The objective of this study is therefore to conduct a systematic research on the effect of TOT on the luminescent and optical properties of $\alpha\text{-Al}_2\text{O}_3\text{-}\delta$ crystals and reveal a possible nature of UV radiation induced by TOT.

2. Experiment

The objects of the research were 5-mm-diameter and 1-mm-thick single crystals of $\alpha\text{-Al}_2\text{O}_3\text{-}\delta$ with a concentration of anion vacancies of approximately 10^{17} cm^{-3} . For controlled filling of the main and deep traps, the samples studied were annealed at 1200 K for 100 s prior to each measurement of TL and OSL curves. The TOT was done by UV irradiation from a DRT-240 mercury lamp at 670 K for 300 s.

The spectra of optical absorption, X-ray luminescence, and photoluminescence (OA, XL and PL) and PL excitement, polarization, and PL decay kinetics were measured on a Cary-60 UV–Vis spectrophotometer and Cary Eclipse Fluorescence Spectrophotometer manufactured by Agilent Technologies. XL was excited by X-ray radiation of an Eclipse tube (*Rh* anode, $U = 45$ keV). The samples were placed on a specially designed holder to improve reproducibility of the results for repeatedly relocated samples. When measuring time-resolved PL spectra and decay kinetics, the delay time (δt) relative to the excitation pulse and the duration of the registration window (Δt) were chosen based on the lifetimes of active centers.

3. Results and discussion

Fig. 1 (curves 1–3) depicts the XL spectra of the initial and TOT-exposed $\alpha\text{-Al}_2\text{O}_3\text{-}\delta$ sample before and after a 6-Gy X-ray treatment. The spectra exhibit two prominent bands with maxima near 3.0 and 3.8 eV. Moreover, a considerable change in their intensities is striking as the above procedures are performed. The initial sample XL spectrum (curve 1) displays a prominent band with a maximum at $h\nu_{em1} = 3.00$ eV and a half-width $H_1 = 0.44$ eV that is caused by luminescence of the F centers. Another XL UV band with $h\nu_{em2} = 3.79$ eV and $H_2 = 0.36$ eV is of low intensity and most probably belongs to the F^+ centers (Evans and Stapelbroek, 1978). After TOT, the F band with $h\nu_{em1} = 3.00$ eV essentially decreases in the XL spectrum, while the UV band becomes more intense, and is

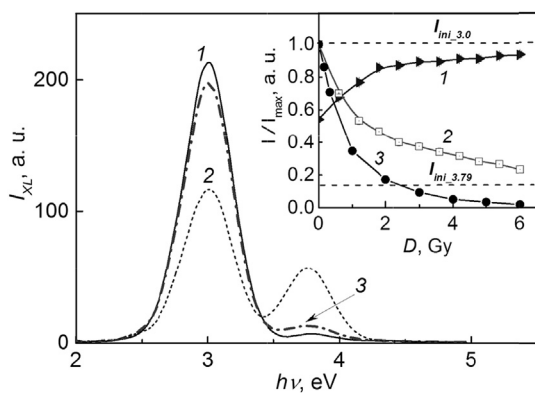


Fig. 1. XL spectra measured in an initial (1) and TOT-exposed (2, 3) $\alpha\text{-Al}_2\text{O}_3\text{-}\delta$ sample before (2) and after a 6-Gy X-ray treatment (3). The inset shows dose dependences of XL responses in the bands at 3.0 eV (1) and approximately 3.8 eV (2) and TL response in the 720-K peak (3) for the $\alpha\text{-Al}_2\text{O}_3\text{-}\delta$ sample subjected to TOT.

shifted to the low-energy region and gains in width. It is already characterized by parameters $h\nu_{em3} = 3.76$ eV and $H_3 = 0.41$ eV, different from the ones typical of the F^+ centers.

Intensities of the XL bands of the sample subjected to TOT change inversely (Fig. 1, curve 3; inset, curves 1 and 2) as the radiation dose increases. At a dose of approximately 6 Gy, they approach the $I_{ini,3.0}$ and $I_{ini,3.8}$ levels corresponding to XL responses in bands with $h\nu_{em1} = 3.0$ eV and $h\nu_{em2} = 3.8$ eV in the initial sample, respectively. Besides, the inset of Fig. 1 shows a dose dependence of TL response in the peak at 720 K (curve 3) that is induced by the TOT procedure described earlier, whose spectrum is dominated by UV emission with $h\nu_{em} = 3.6$ eV and $H = 0.61$ eV. It can be seen that, as the dose increases to 6 Gy, the aforementioned TL response decreases similarly to the XL UV band. It is also important to note that the trap responsible for the 720-K TL peak can be depleted by light with $h\nu_{ex} = 3.1$ eV.

The evidence presented above suggests that the TOT induces a new type of emission centers in anion-defective corundum, whereas high-dose irradiation destroys them. Such centers can be formed, for instance, at recharge of already known centers. However comparative OA spectrum studies carried out on initial, TOT-exposed, and additionally irradiated samples did not show any detectable changes, including absorption regions of the F and F^+ centers. Nonetheless, manifestations of new centers are still possible in photoluminescence studies. Therefore, with a view of their detection, time-integrated spectra of excitation at $h\nu_{em} = 3.75$ eV were measured on $\alpha\text{-Al}_2\text{O}_3\text{-}\delta$ samples before and after TOT (Fig. 2a). It can be seen that concentrations of F^+ centers before (curve 1) and after TOT (curve 2), assessable by the intensities of excitation bands with maxima at 4.8 and 5.4 eV, are virtually the same. This finding is in good agreement with OA data. However, together with manifestations of F^+ centers in the excitation spectrum, a new band at approximately 6.0 eV is found for the TOT-exposed sample.

Significant differences were registered in a comparative study of PL decay kinetics measured at $T = 300$ K, $\delta t = 0.1$ ms, $\Delta t = 5$ ms, $h\nu_{ex} = 5.9$ eV, and $h\nu_{em} = 3.75$ eV in the initial and TOT-exposed $\alpha\text{-Al}_2\text{O}_3\text{-}\delta$ sample (Fig. 2b, curves 1 and 2, respectively). Only the sample subjected to TOT exhibited a prominent slow component with a time constant $\tau_{new} = 300 \pm 6$ ms. The τ_{new} value considerably decreases with increasing T to reach 5 ms at $T = 350$ K. A repeated measurement of kinetics at $T = 300$ K in an $\alpha\text{-Al}_2\text{O}_3\text{-}\delta$ sample subjected to TOT showed its invariance ($\tau_{new} = 300$ ms) and insignificantly reduced initial PL intensity. In summary, the results obtained might evidence the formation of a new center upon TOT, rather than involvement in the de-excitation process of shallow traps filled, for example, by phototransfer of charge carriers from deeper traps and normally causing long afterglow with durations of unities and dozens of seconds or longer (Surdo et al., 2013).

Using data on a considerable gap between τ_{new} and $\tau_{F^+} = 2.1$ ns at $T = 300$ K (Surdo et al., 2001), time-resolved excitation spectra for the newly found UV emission with $h\nu_{em} = 3.75$ eV were investigated more selectively at $\delta t = 0.1$ ms $\gg \tau_{F^+}$ and $\Delta t = 20$ ms. This resulted in a minimized contribution of excitation bands of the F^+ centers at 4.8 and 5.4 eV and a clearly singled out excitation band of the slow UV emission (Fig. 2a, curve 3). The excitation band thus revealed has the following parameters: $h\nu_{ex} = 5.9$ eV and $H \approx 0.54$ eV. Significantly, the stated excitation band parameters of the newly found emission are close to, but not the same as the parameters for the F and F^+ centers (Surdo et al., 2001).

Therefore, comparative time-resolved measurements were carried out at $\delta t = 200$ ms and $\Delta t = 20$ ms in an initial and TOT-exposed sample (Fig. 3, curves 1 and 2, respectively) to detect

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