

Fast Relaxation Processes in Irradiated Anion-Defective Wide-Gap Oxides

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Abstract – Pulsed cathodoluminescence and time-resolved photoluminescence spectra were measured when anion-defective oxides of aluminum, silicon and germanium were excited by synchrotron radiation pulses at temperatures of 10 to 300 K. Single crystals and samples of low-dimensionality structures, including glass, a nanopowder and a nanoceramic, were studied. New or transformed bands, which corresponded to fast luminescence components, were present in the spectra of the nanosized oxides. F_s -centers, which are analogs of F-centers induced by oxygen vacancies, were responsible for these bands in samples with a developed internal surface.

1. Introduction

The analysis of fast processes of excitation and relaxation in irradiated wide-gap dielectric and semiconductor materials progressively gains in importance since it provides information for the theory and practical applications. These studies were spurred by the use of femto- and picosecond lasers for excitation and the new "pump and probe" technique.

Examples of fast processes and the corresponding time intervals are inelastic electron-electron scattering (10^{-14} - 10^{-13} s) and thermalization of excited charge carriers (10^{-13} - 10^{-12}). The subsequent capture of charge carriers on traps or self-trapping is characterized by the time of (10^{-12} - 10^{-10}) s. Most radiative transitions take place in the nanosecond range. For example, the $F2p \rightarrow Ba5p$ transition in BaF_2 , which determines cross luminescence, lasts for 4.1 ns; the $5d \rightarrow 4f$ transition in the activator ion of the $BaF_2:Ce^{3+}$ luminophor lasts for 18 ns; and the exciton luminescence in ZnO has the decay time of up to 0.4 ns. The microsecond-long lifetime corresponds to forbidden transitions, while the millisecond range is characteristic of the transport-limited phosphorescence [1, 2].

These data suggest that fast relaxations determine scintillation, luminescence and optical properties of materials and control their ability to store and transform the excitation energy. These processes also influence the radiation resistance of dielectrics, their optical breakdown strength upon exposure to laser pulses, and other significant properties.

In this paper we report and discuss results of the time-resolved luminescence spectroscopy study into fast radiative relaxations in Al_2O_3 , SiO_2 and GeO_2 , which are widely used in modern technologies. The

task was to ascertain if these processes differ in monocrystalline, amorphous and nanosized structures of the oxides at hand.

2. Samples and Experimental Technique

The subjects of study were monocrystalline α - Al_2O_3 samples 1 mm in diameter and nanosized powders of aluminum oxide, which were synthesized by electric explosion of aluminum wires. Part of the powder was used for preparation of Al_2O_3 ceramic samples by magnetic pulsed compaction [3]. The average size of the ceramic grains was 17 nm.

Samples of the KV quartz glass of diameter 10 mm and 1 mm thick having the optical-quality surface were studied too. The nanostructured porous ceramic was prepared by thermal decomposition of polysilazane ($H_xC_yN_2Si$) at $T = 600$ °C for 48 hours in air [4]. The samples contained pores 50 to 500 nm in size. Nanoceramic samples of GeO_2 with grains 100-120 nm in size were synthesized by sintering of a nanopowder of crystalline germanium oxide in the hexagonal modification.

Time-resolved cathodoluminescence spectra of nanostructured samples were measured using a GIN-600 pulsed electron accelerator after excitation with an electron beam (0.25 MeV, 0.02-0.5 J/cm², 10 ns). A measuring circuit, which included a MDR-3 monochromator, a FEU-97 photomultiplier and a C8-12 storage oscilloscope, was used to measure spectra over the energy interval of 1.0 to 6.0 eV at temperatures of 80 and 300 K. The spectrum of the fast component of the luminescence was measured at the moment the electron pulse ended. The contribution from slow stages of the emission decay was determined from the integral intensity of the luminescence.

The photoluminescence (PL) was measured during selective excitation by synchrotron radiation in a SUPERLUM experimental setup at the HASYLAB laboratory (Hamburg). Time-resolved PL spectra were measured in the spectral region of 2-6 eV, while time-resolved PL excitation spectra were recorded in the spectral region of 4-35 eV. The PL decay kinetics was measured using the subnanosecond time resolution. The luminescence was recorded by means of a 0.3 m ARC Spectra Pro-300i monochromator and an R6358P photomultiplier in the photon counting regime. The time-resolved spectra were measured in two time windows Δt_1 (fast) and Δt_2 (slow) delayed for δt_1 and δt_2 relative to the excitation pulse start point re-

spectively. The time regime of the measurements was chosen considering results of the preliminary analysis of the luminescence kinetic parameters.

The PL excitation spectra were normalized to the equal number of photons hitting the sample. The sample was mounted in the holder of a blow-through helium cryostat. The measurements were made at temperatures of 8-9 K and 300 K. The cryostat vacuum was $2 \cdot 10^{-10}$ Torr or better, ensuring cleanness of the sample surface at low temperatures.

3. Results and Discussion

Anion-defective single crystals of α - Al_2O_3 are widely used as ionizing radiation dosimeters that show good outlooks. When these crystals experience the stationary X-ray excitation, their luminescence spectra contain several bands whose characteristic decay time τ changes between several nanoseconds and tens of milliseconds (Fig. 1).

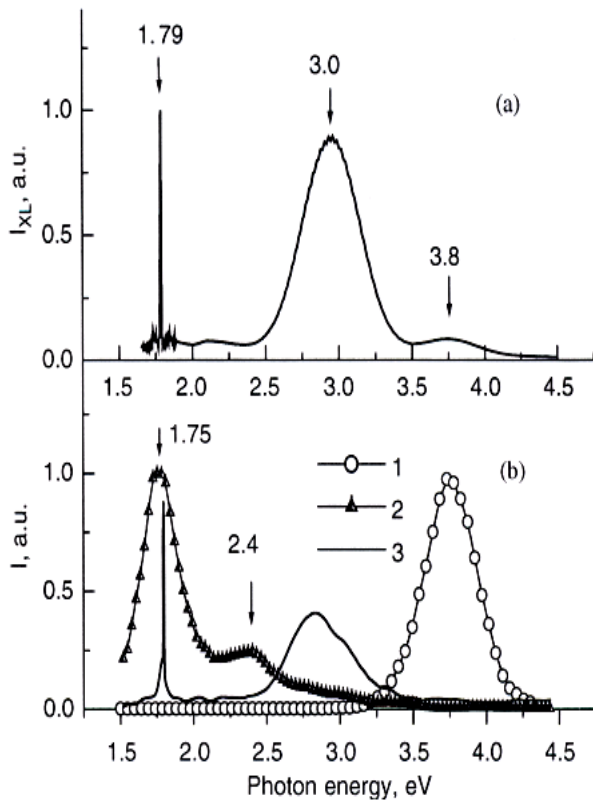


Fig. 1. (a) XL stationary spectrum and (b) time-resolved XL (1) and PCL (2, 3) spectra obtained for anion-deficient α - Al_2O_3 at $T = 295$ K (1 – $\delta t_1 = 4$ ns, $\Delta t_1 = 10$ ns; 2 – $\delta t_2 = 5$ μ s, $\Delta t_2 = 1.3$ μ s; 3 – $\delta t_3 = 2$ ms, $\Delta t_3 = 40$ μ s) [5]

The main luminescence centers are F- and F^+ -centers, which are induced by oxygen vacancies with two and one trapped electrons. In this case, $\tau_{\text{F}^+} = 2$ ns and $\tau_{\text{F}} = 34$ ms. The pulsed ($\tau_p = 0.43$ ns) cathodoluminescence (PCL) spectra include bands of impurity

centers Cr^{3+} (1.79 eV; $\tau = 4$ ms) and Tl^{3+} (1.75 eV; $\tau = 3.5$ μ s), and also those of interstitial atoms Al_i^+ (2.4 eV; $\tau = 56$ μ s) [5].

The PCL spectra of the nanopowders and the nanoceramic (Fig. 2) are characterized by a wide band.

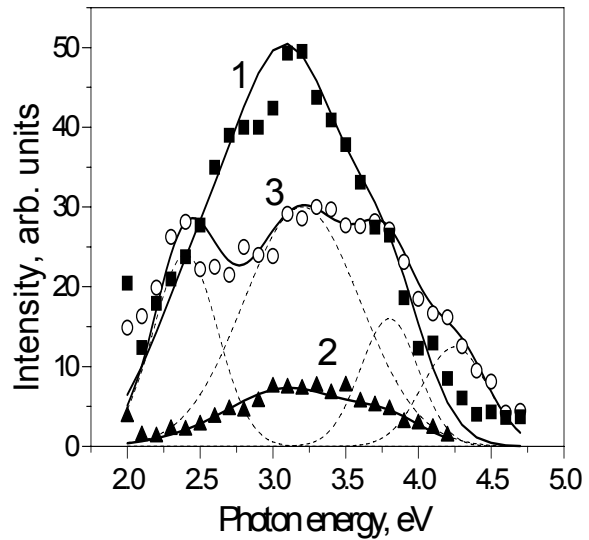


Fig. 2. Pulsed cathodoluminescence spectra for Al_2O_3 as measured at 300 K at the moment of an electron pulse (1, 3) and after a 100-ns delay (2): 1, 2 – nanopowders; 3 – nanoceramic

A set of narrower Gaussian bands with the maxima at 2.4, 3.2 and 3.8 eV can be discriminated in this band. Unlike the spectra of the nanopowders, the spectrum of the nanoceramic contains an additional luminescence band at 4.3 eV. The origin of the last band is unknown. It probably corresponds to a new type of aggregate centers, which are formed with the participation of nanoparticles and other crystallographic modifications of Al_2O_3 present in the nanopowders. The bands at 2.4 eV and 3.8 eV correspond to known luminescence centers (Al_i^+ and F^+). The wide band (FWHM ≈ 1 eV) with the maximum at about 3.2 eV apparently consists of two bands, namely the band at 3.0 eV (F-centers) and a new band at 3.2 eV. The new luminescence component is fast since its intensity sharply decreases if the delay of 100 ns is introduced. This fact was confirmed by measurements of the time-resolved PL at different values of the excitation energy (Fig. 3).

It follows from Fig. 3 that the 3.2-eV band is observed only in the "fast" window. The PL (3.2 eV) decay kinetics in the nanostructured powder at different excitation energies is shown in the inset in Fig. 3. The decay is described by two exponential stages with $\tau_1 = 0.5$ ns and $\tau_2 \approx 5.5$ ns. Remarkably, the time-resolved PL spectrum includes the band at

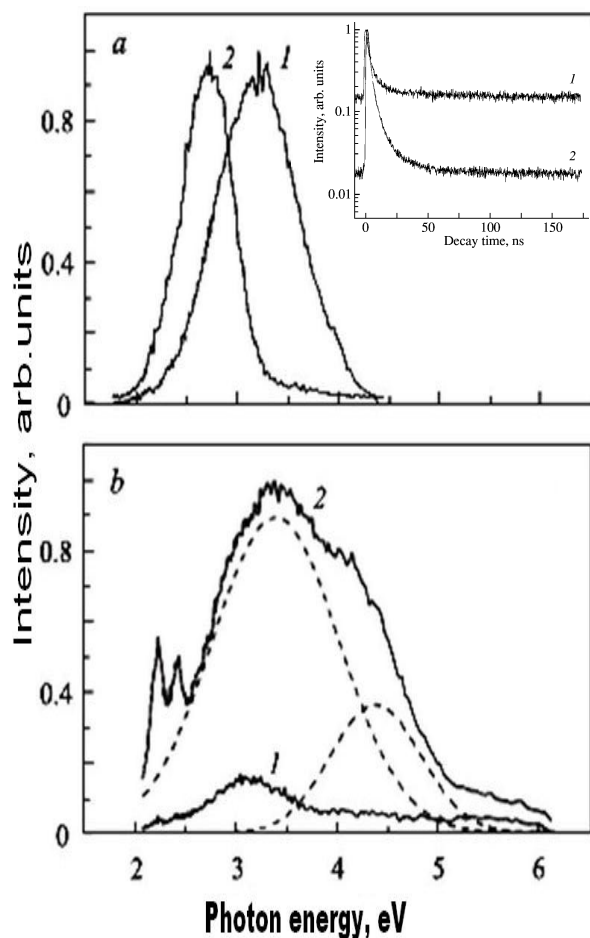


Fig. 3. Time-resolved photoluminescence spectra of Al_2O_3 nanopowders ($T = 13$ K) during excitation by photons having the energy of 6 eV (a) and 11.3 eV (b). Measurements in the "fast" (1) and "slow" (2) windows

4.3 eV after excitation by 11.3-eV photons. This band is absent in the spectra of the monocrystalline samples.

Time-resolved PL excitation spectra were measured at 3.2 eV to elucidate the origin of the fast luminescence component (Fig. 4). The excitation spectrum of the fast component comprises bands with the maximums at 5.24, 6.13 and 7.44 eV. An analogous three-band structure was observed in measured time-resolved excitation spectra of F^+ - and F-centers in single crystals of anion-defective α - Al_2O_3 [6]. The bands at 5.99, 6.1 and 8.7 eV are present. The first band corresponds to F^+ -centers and the second band is related to the intracenter transition in F-centers. The 8.7-eV line, which is located on the long-wave edge of the fundamental absorption, transforms at 13 K to a doublet with the maximums at 8.52 and 9.02 eV. This line may be related to excitons bound to F-type centers.

The band at 6.13 eV in the three-band excitation spectrum of the fast component of the PL in the nanopowders corresponds to the analogous excitation 6.1-eV band of F-centers, which cannot be responsible for the fast luminescence component. The band at

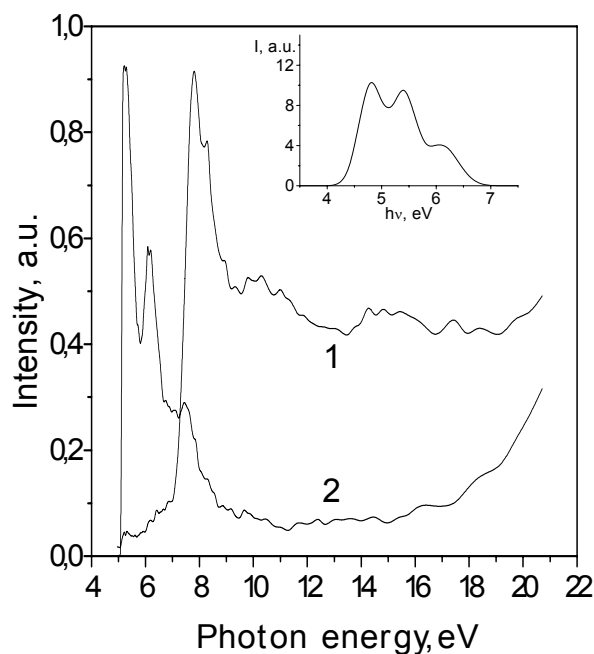


Fig. 4. Time-resolved photoluminescence excitation spectra of Al_2O_3 nanopowders ($T = 13$ K) with the slow component at 3.5 eV (1) and the fast component at 3.2 eV (2). Inset: The luminescence excitation spectrum of F^+ -centers in α - Al_2O_3 single crystals

5.24 eV in the PL excitation spectrum of the nanopowder may be correlated to the 4.8-eV band in the excitation spectrum of F^+ -centers in the single crystal. Here it may be assumed that nanostructured Al_2O_3 samples can form surface analogs of F^+ -centers (F_s^+ -centers) if one considers an important contribution of dimensional effects to properties of nanoparticles. This assumption is confirmed by the short-wave shift of the maximums in excitation bands of surface oxygen-deficient centers with respect to those of bulk centers in SiO_2 [6].

It should be noted also that the band at 7.44 eV in the PL excitation spectrum of the nanopowders, which is located near the long-wave edge of the optical absorption, may be an indication that exciton-like states bound to F-, F^+ - and F_s^+ -centers are present in the nanosized samples of aluminum oxide.

The other wide-gap oxides – SiO_2 and GeO_2 – were studied analogously. Bands with the maximums at 2.5, 3.2 and 4.1 eV are clearly seen in the PCL spectra of the quartz glasses. At the moment the electron radiation pulse ends, the luminescence is observed in the nanostructured samples in a wide spectral region of 2.0 to 4.5 eV. The spectrum analysis by resolving into Gaussian components allowed discriminating bands with the maximums at 2.3, 2.7, 3.2 and 4.1 eV. The PCL decay kinetics in the spectral region of 2.0-3.7 eV can be described by two exponents with the char-

acteristic time of about 0.05 and 0.5 μs . The measured time-resolved PL spectra exhibit an intense band with the maximum at 3.1 eV and a weaker band at 2.7 eV. These bands correspond to different types of oxygen-deficient centers (ODCs), but considerably differ from their bulk analogs by a short decay time. It was already mentioned in the foregoing that the decay time of the PCL at 2.7 and 3.1 eV in the nanostructured samples does not exceed 0.5 μs , which is much shorter than the decay time of the luminescence of bulk ODCs at 2.7 eV ($\tau = 10$ ms) and 3.1 eV ($\tau = 11$ μs) in amorphous SiO_2 [8]. One may think that in the nanostructured SiO_2 samples with a developed internal surface fast radiative relaxations at 2.7 and 3.1 eV are due to surface analogs of ODC-type defects.

A specific feature of the nanoceramic GeO_2 samples is that their PL spectra include fast luminescence bands (A_s) and (B_s), which differ by wide maximums that are shifted to the short-wave region. This situation is observed in SiO_2 with defects located on the external boundary of the samples. Considering these arguments and the absence of the bands (A_s) and (B_s) in the PL spectra of the GeO_2 single crystals, the fast luminescence centers in the nanoceramic may be referred to surface analogs of ODCs.

4. Conclusion

The study of fast relaxations in monocrystalline and low-dimensional samples of wide-gap oxides (Al_2O_3 , SiO_2 , GeO_2) revealed a general regular feature, which is characteristic of their nanostructured modifications. This feature consists in the formation of short luminescence components. In this case, either a new band

appears in the luminescence spectrum or luminescence bands of bulk centers are transformed (widen and are shifted to the short-wave region). Then it may be assumed that the excited states live much shorter in the nanostructured samples of the oxides at hand and the decrease in their lifetime is connected with dimensional effects. Fast luminescence components can appear in the anion-defective oxides because of the high concentration of F_s^+ -centers formed on the developed internal surface of the samples.

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References

- [1] R.Williams, K.Ucer, J.LoPresti, *Radiat. Measur.*, **33**, 497 (2001).
- [2] J.Wilkinson, K.Ucer, R.Williams, *Radiat. Measur.*, **38**, 501 (2004).
- [3] C.-K.Rhee, W.W.Kim, G.H.Lee, V.V.Ivanov, S.V.Zajatz, A.I.Medvedev, *J. of Metastable and Nanocrystalline Materials*, **15-16**, 401 (2003).
- [4] V.Kortov, A.Zatsepin, S.Corbunov, A.Murzakaev, *Rus. J. Solid State Physics*, **48**, № 7, 1205 (2006).
- [5] A.Surdo, V.Pustovarov, V.Kortov, A.Kishka, E.Zinin, *Nucl. Instrum. And Meth. In Phys. Research*, **A 543**, 234 (2005).
- [6] A.Surdo, V.Kortov, V.Pustovarov, *Radiat. Measur.*, **33**, 587 (2001).