Eur. Phys. J. B **12**, 35–38 (1999)

THE EUROPEAN
PHYSICAL JOURNAL B

EDP Sciences

Luminescence property studies of α-Al$_2$O$_3$ by means of nanosecond time-resolved VUV spectroscopy

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Received 20 October 1998 and Received in final form 20 January 1999

Abstract. The luminescence spectra of corundum monocrystals grown by different methods are investigated by means of a time-resolved spectroscopy method at temperatures 90 K and 300 K. The existence of fast and slow emission in the VUV luminescence spectra of irradiated and nonirradiated crystals was observed. We observed luminescence bands with a maximum at 326 nm produced by F$^+$ centers. A new type of fast luminescence at the band of 270 nm was found. This is known as cross-luminescence and is connected with the recombination of valence band electrons with the holes in the low ground band. It was shown that the band of 410 nm isn't due to to anionic centers (F-centers), but is determined by the short lifetime center of emission (F$^-$-centers).

PACS. 61.72. y Defects and impurities in crystals; microstructure – 61.72.Ji Point defects (vacancies, interstitials, color centers, etc.) and defect clusters – 61.80. x Physical radiation effects, radiation damage

1 Introduction

The luminescence investigations of materials have advanced recently due to the demands in new rapid radiation-stable crystals, for example corundum crystal α-Al$_2$O$_3$. Analysis of investigations [1,2] revealed that up to now there is no consensus about the optimal crystal type for luminophors, laser active media and so on. It is clear now, that for every concrete application one should look for its own optimal scintillator. In particular, in some detectors it is necessary to use the rapid scintillator emission in the VUV spectra region.

Radiation induced defects in α-Al$_2$O$_3$ have been intensively studied by many investigators [2,3] lately. The defects (colour centers) were obtained by electron, neutron or ion beam bombardment. With electron irradiation the defects are predominantly isolated, while with neutron bombardment the defects may aggregate, and with ion implantation dense cascades of defects are obtained [4].

As soon as the possibility of using synchrotron radiation (SR) had appeared, the spectral range of investigations grew wider. The new methodological possibilities for VUV spectroscopy connected with using impulse time SR structure also appeared [5].

Although there has been definite success in the investigations of optical properties of corundum monocrystals the physics responsible for spectral properties, quantum output remain poorly investigated.

So, the main goal of this work is investigating light centers in corundum monocrystals, possessing fast UV and VUV luminescence under the SR excitation.

2 Experimental

The measurements of spectral characteristics of corundum crystals were carried out on the optical beam line of the S-60 electron accelerator (E-680 MeV). Another optical channel for luminescence characterisation measurements by means of the high in SR has the following values: $I \sim 2\text{–}3\times10^{14}\,\mathrm{ph\,sm^{-2}\,s^{-1}}$, $E \sim 1\,\mathrm{keV}$. The working range of the monochromator, is $\lambda \sim 120\text{–}520$ nm. It is possible to measure both integrals (in time), and time-resolved emission spectra at temperatures 300 and 90 K [5,6]. The technique of time-resolved spectroscopy under pulsed SR excitation was used for the selection of the fast and slow components of the emission.

The nominally pure stoichiometric α-Al$_2$O$_3$, were grown by different methods: the horizontal-oriented crystallisation method- HOC; vertical – oriented crystallisation method – GOI (State Optical Institute) and Czochralski, Verneuil.

The crystals were irradiated by 50 MeV electrons and 2 MeV neutrons temperatures 10 ℃ and 100 ℃ respectively.

The irradiation was performed at GANIL with Pb ions of 3.5 MeV/amu energy at equilibrium charge state, corresponding to an electronic stopping power of 42 keV/nm [4].

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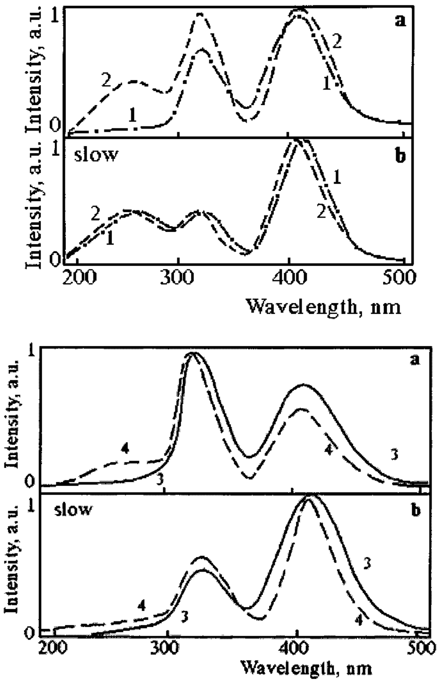

Fig. 1. (a) Luminescence emission of HOC: 1) unirradiated at 300 K; 2) the same at 90 K; 3) irradiated with dose 6×10^{17} e/cm^2 at 300 K; 4) irradiated with dose 6×10^{17} e/cm^2 at 90 K. (b) "Slow" component spectra of HOC: 1) unirradiated at 300 K; 2) the same at 90 K; 3) irradiated with dose 6×10^{17} e/cm^2 at 300 K; 4) irradiated with dose 6×10^{17} e/cm^2 at 90 K.

3 Experimental results and discussion

After irradiation, anion (F^-, F^+-centers), cation (V-centers) and interstitial ions are formed. Besides, at irradiation there occurs an inelastic interaction, which changes the charge states of pre-irradiation structure defects [7].

The luminescence spectrum (LS) in the quasi-stationary excitation region at 300 K (Fig. 1a) consists of two degenerate bands with maxima at 326 nm and 410 nm. At 90 K (curve 4) one can see the new band with a maximum at 270 nm. After electron irradiation the intensity of the 410 nm band decreases and that of the 326 nm increases. A strong decrease of intensity of the 270 nm band which relates to formation of F^+-center with a maximum at 255 nm during the absorption is observed.

The kinetics of luminescence decay showed that there are two time-resolved components in the LS (Fig. 1b). The duration of the "fast" component (326 nm) with half-width of 0.4 eV and 0.34 eV at 300 K and 90 K respectively is $\sim$ 5 ns. The characteristics of this band are not changed after irradiation.

In the regime of "slow" component excitation (when the intensity of SR pulse is minimal with pulse interval of $\sim$ 10 ns), the intense Gaussian shaped band at 410 nm and weak band at 326 nm (Fig. 1b) are measured at $\tau \sim 30$ ns. At 90 K in the LS one can see also the band at 270 nm, but the 410 nm band becomes narrower.

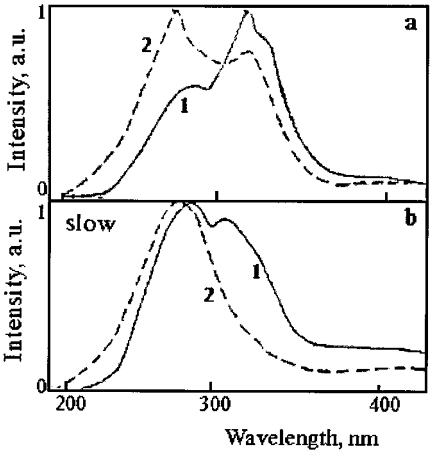

Fig. 2. Luminescence emission of GOI: 1) unirradiated at 300 K; 2) the same at 90 K. (b) "Slow" component spectra of GOI: 1) unirradiated at 300 K; 2) the same at 90 K.

After irradiation, in the spectrum of the "slow" component at 300 K one can see the band at 415 nm with half-width of 0.42 eV and weak band at 326 nm which is, however, twice as intense as that in irradiated crystals. The band at 270 nm is not revealed at 90 K (Fig. 1b, curve 4). At the irradiation dose of 5×15^{15} e/cm^2 this band has high intensity at 90 K.

In the LS of GOI (Fig. 2a) stationary regime of luminescence excitation there is a weak 410 nm band (326 nm and 270 nm bands are not resolved at 300 K). The intensity of the 270 nm band sharply increases and shifts to the long wavelength side (Fig. 2a, curve 2).

The GOI's "fast" component has one intensive band at 326 nm with half-widths of 0.46 eV and 0.43 eV, at 300 K and 90 K respectively.

Figure 2b presents the spectrum of the "slow" component. The intensity of the 270 nm band sharply increases and shifts to 283 nm. The band at 326 nm shifts to 314 nm due to strong overlapping of the 270 nm and 326 nm bands. In the spectrum of the "slow" component there is an intense wide band with maximum at 280 nm.

In the crystals irradiated by Pb^{208} ions one can observe the band with its maximum at 329 nm and in the spectrum of the "slow" component – the bands at 410 nm and 270 nm in irradiated corundum are observed for the first time in this work (Figs. 3a and 3b). The band at 270 nm can be explained by the cross-luminescence type transition of electrons from a high valent zone to the place of hole in the core band [5]. This transition energy gap is of the order of the forbidden zone ($\sim$ 9.5 eV). The "fast" component can be stipulated by F^+-centers (325 nm). In the irradiated crystals, where F^+-centers are not present, the band 326 nm was attributed to E-luminescence [8], although neither width nor lifetime (280 ns) at 90 K correspond to the E-luminescence. It is supposed that the band at 326 nm is stipulated by F^+-centers ($\tau \sim$ 5–6 ns) [2]. Figures 4a and 4b presents the spectrum of excitation of Verneuil's crystals. The above mentioned maxima

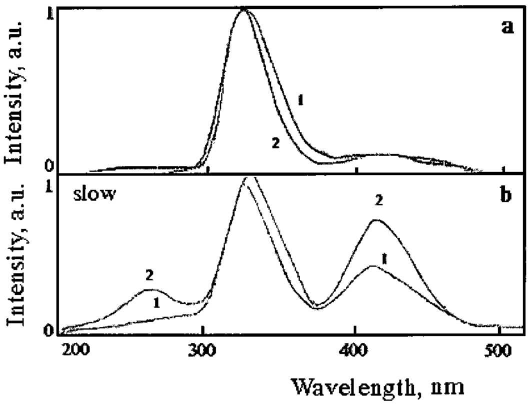

Fig. 3. Luminescence emission of Czochralski: 1) irradiated with dose 1.2×10^{12} Pb/cm^2 at 300 K; 2) irradiated with dose 1.2×10^{12} Pb/cm^2 at 90 K. (b) "Slow" component spectra of Czochralski: 1) irradiated with dose 1.2×10^{12} Pb/cm^2 at 300 K; 2) irradiated with dose 1.2×10^{12} Pb/cm^2 at 90 K.

at 270 nm and 410 nm are observed in all regimes of measurement.

We think that observation of the band 410 nm is a consequence of the value of the oscillator's force, which for an F$^-$-center is ~ 3. Because of such a value, the band is observed at 410 nm.

Maxima at 165–170 nm (7.2–7.5 eV) are observed in excitation spectrum in all crystals (unirradiated, irradiated) and have an exciton nature. The relatively large intensity emission bands can be explained by assuming that electron-hole pairs formed by SR are bound in excitations of a Frenkel-type. At 90 K the intensity of the emission bands is higher than at 300 K.

The nature of the 410 nm band formation has not yet been found, but it does not relate to F-centers (410 nm) since its lifetime is ~ 36 ms. However, from the 410 nm band behaviour, it can be certainly stated that it is determined by the anionic center of emission. Based on the data taken from reference and the results of our experiments, it can be concluded that the 410 nm band is determined by the short lifetime center of emission - F$^-$-center with the lifetime of several ~ ns.

It was shown [9–11] that the ground term of an F-center is located in corundum in the crystal forbidden band, 4.8 eV higher than the valence band border. It was shown also that the higher term is located below the conduction band by 1 eV. The F$^-$-center observation verifies that it can be formed either under high-energy particle irradiation or under ion beams (SR quants, etc.) irradiation. The F$^-$-center formation process will take place as a result of free charge formation, in particular the electron, and their capture by F^{2+}-centers by the reaction F^{2+} + 3e → F$^-$ [12]. However, the nature of F$^-$-terms is not established definitively and requires additional investigations.

The investigations performed in this work were supported by grant A-102 of the International Science-Technical Center.

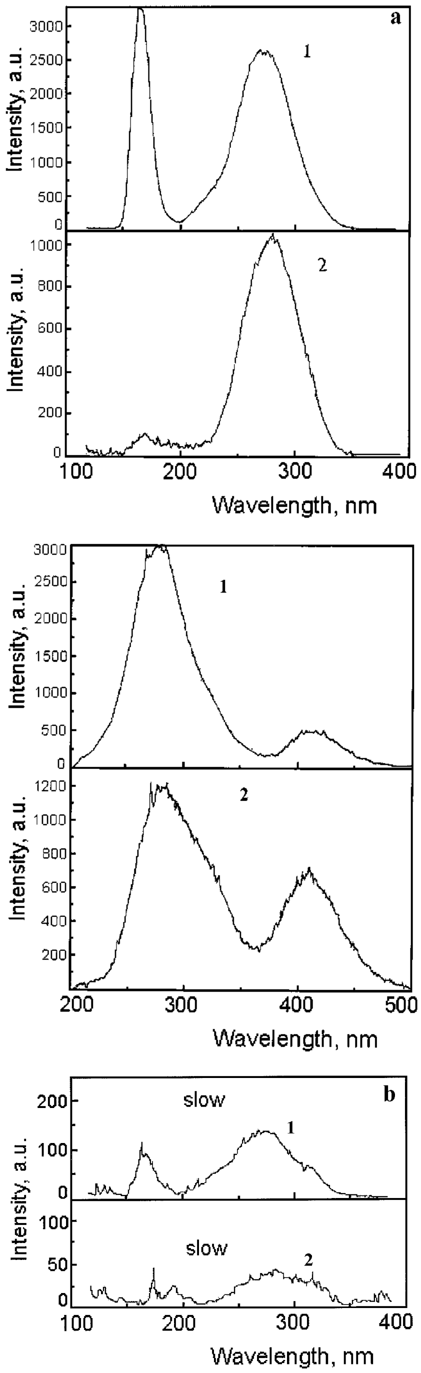

Fig. 4. (a) Luminescence emission of Verneuil: 1) unirradiated at 90 K; 2) the same at 300 K; (b) "Slow" component spectra of Verneuil: 1) unirradiated at 90 K; 2) the same at 300 K.

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