

Comparative study of the luminescence of $\text{Al}_2\text{O}_3\text{:C}$ and Al_2O_3 crystals under synchrotron radiation excitation

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Abstract

The work is related to studying the luminescence of F and F^+ centers and excitons localized around F-like centers in Al_2O_3 host based on the results of the comparative investigation of the luminescent properties of Al_2O_3 and $\text{Al}_2\text{O}_3\text{:C}$ crystals under excitation by synchrotron radiation in the 3.7-15 eV range.

Keywords: Al_2O_3 and $\text{Al}_2\text{O}_3\text{:C}$ crystals, luminescence, oxygen vacancy, F and F^+ centers, excitons

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1. Introduction

The $\text{Al}_2\text{O}_3\text{:C}$ crystals and ceramics still attract now attention due to the wide their application as dosimetric thermoluminescent and optically stimulated luminescent materials for personal and environmental dosimetry [1]. For this reason the optical and luminescent properties of $\text{Al}_2\text{O}_3\text{:C}$ were intensively studied in the last two decades using the traditional spectroscopic methods [2-4].

The luminescent properties of undoped and Ti doped Al_2O_3 crystals have been also investigated under high-energy VUV excitation [5-9]. At the same time, up to now we cannot find in the literature any results related to the VUV luminescent spectroscopy of $\text{Al}_2\text{O}_3\text{:C}$ crystals or ceramics. This stimulate us to more comprehensive comparative analysis of the luminescent properties of $\text{Al}_2\text{O}_3\text{:C}$ crystal in comparison with the properties of undoped Al_2O_3 counterpart.

2. Samples and experimental technique

The undoped Al_2O_3 crystal was grown in IISB, Erlangen, Germany in vacuum by the Czochralski method [10]. The properties of undoped Al_2O_3 crystal were also compared with the properties of $\text{Al}_2\text{O}_3\text{:C}$ crystal produced in Landauer Inc, USA [1].

Investigations of the time resolved luminescence of Al_2O_3 and $\text{Al}_2\text{O}_3\text{:C}$ crystals were performed in the framework of II-2005-105 and II-20090087 projects at the Superlumi experimental station at HASYLAB, DESY under excitation by pulsed (130 ps) synchrotron radiation (SR) with an energy of 3.7-25 eV at 10 and 300 K. The emission and excitation spectra were measured both in the time integrated regime in the limits of SR pulse with a repetition time of 192 ns and a duration of 130 ps [11]. The emission spectra were recorded with monochromator-spectrograph Spectra-Pro-308i (Acton Research Corporation) equipped with a liquid nitrogen cooled CCD camera (Princeton Instrument Inc.). The spectral resolution of the monochromator with 300 lines/mm grating was

about of 0.5 nm. Excitation spectra were recorded with the resolution of primary monochromator of about 0.3 nm by using a Hamamatsu R6358 P photomultiplier as a recording device. The excitation spectra were corrected for the spectral dependence of transmittance of Al-grating and intensity of SR beam; the emission spectra were not corrected. Using SR excitation, the decay kinetics of the luminescence was measured in the 1.2–192 ns time range.

3. Experimental results and discussion

The luminescence spectra of $\text{Al}_2\text{O}_3\text{:C}$ and Al_2O_3 crystals under excitation by SR with different energies are shown in Fig.1.

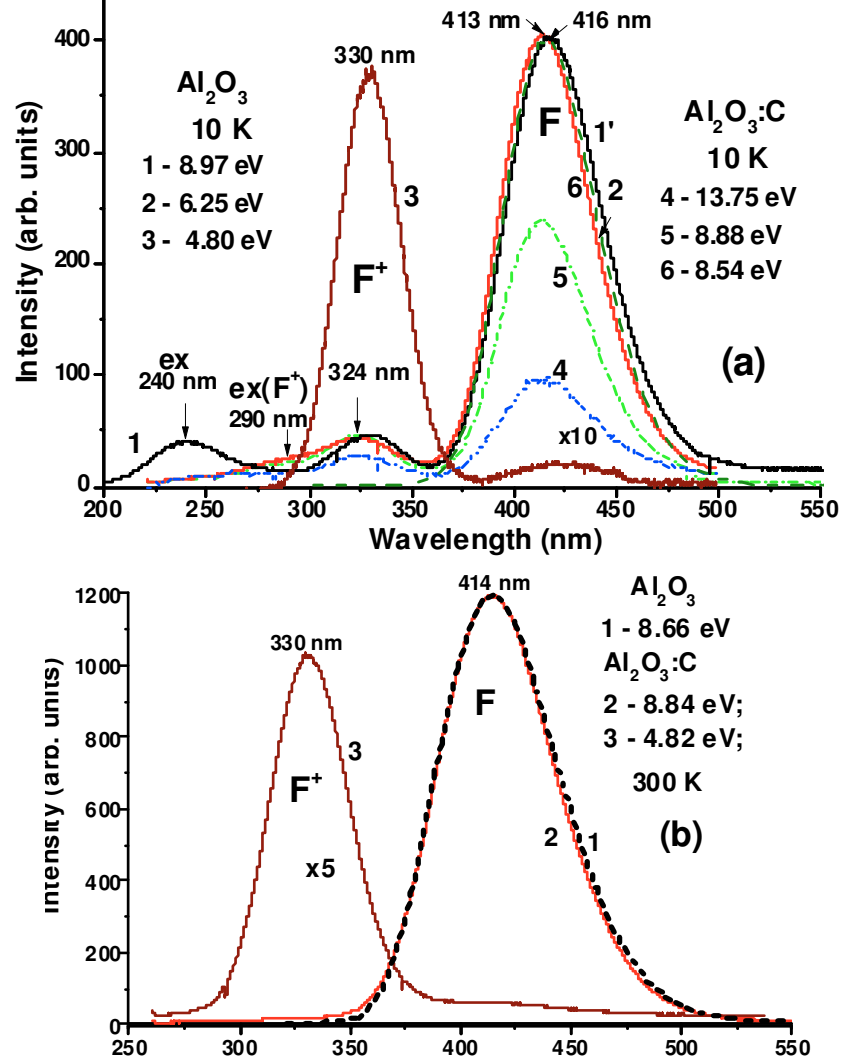


Fig.1. Luminescence spectra of Al_2O_3 and $\text{Al}_2\text{O}_3\text{:C}$ crystals at 10 K (a) and 300 K (b) under excitation by SR with energies indicated in the legend of the figure in the range of interband transitions (13.75 eV), in exciton range (8.54–8.97 eV) and maxima of excitation bands of F centers (6.25 eV) and F^+ centers (4.80–4.82 eV).

The emission spectrum of undoped Al_2O_3 crystal at 10 K under excitation by SR in the exciton range with an energy of 8.97 eV (Fig.1a, curve 1) presents the superposition of the luminescence of F^+ and F centers in the bands peaked at 330 and 416 nm, respectively [2–4], and band peaked at 240 nm related to the exciton luminescence. The emission band at 240 nm (5.16 eV) is strongly shifted in the low-energy side with respect to the band at 7.6 eV of a self trapped exciton (STE) luminescence [5, 8, 9] and can be assigned to the emission of excitons localized *around* of the defects [9] or some trace impurities [12, 13] in Al_2O_3 host. Usually the energy structure of such localized excitons is similar to that of a STE in oxides [15]. Moreover, the localized excitons and

STE states can be separated by an energy barrier at low temperatures when the energy transfer from the STE to localized state is low-effective.

The luminescence of F and F⁺ centers dominates in the emission spectra of undoped Al₂O₃ crystal (Fig.1a, curves 2 and 3, respectively) under excitation in the maxima of corresponding excitation bands of these centers at 6.35 and 4.8 eV (Fig.2b, curves 3 and 5).

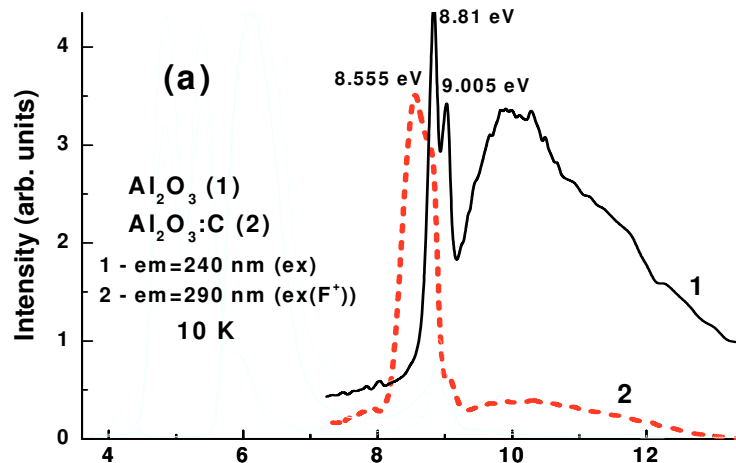
The emission spectrum of Al₂O₃:C crystal at 10 K under excitation by SR in the range of the interband transitions (13.6 eV) and the exciton range (8.88 eV) (Fig.1a, curves 4 and 5 respectively) presents superposition of the luminescence of F⁺ and F centers in the bands peaked at 324 and 413 nm, respectively, as well as the band peaked at 290 nm, related to the luminescence of excitons localized around oxygen vacancies [6, 7, 9]. The detailed comparison of the emission spectra of Al₂O₃ and Al₂O₃:C crystals at 10 K (Fig.1a) shows, that **(i)** the maxima of the emission band of F⁺ and F centers in Al₂O₃:C crystals are notably (about 5 nm) shifted in comparison with the positions of these band in Al₂O₃ crystals; **(ii)** the excitons emission of Al₂O₃ crystals in the 240 nm band is suppressed when the intensity of the emission of excitons localized around oxygen vacancies in the 290 nm bands increases.

In the RT range, the luminescence of F centers in the bands peaked at 414 nm dominates in the emission spectra of Al₂O₃ and Al₂O₃:C crystals under excitation by SR in the exciton range (8.66 and 8.84 eV, respectively) (Fig.1b, curve 1 and 2). As can see from Fig.1b, the emission bands of F centers in Al₂O₃ and Al₂O₃:C practically coincide in the RT range. At the same time, the luminescence of F⁺ centers in the band peaked at 330 nm prevails in the emission spectrum of Al₂O₃ crystal (Fig.1b, curve 3) under excitation at 4.82 eV in the maximum of the corresponding band (Fig.2, curve 5).

The luminescence of F⁺ centers in Al₂O₃ crystal in the band peaked at 325 nm at 10 K is excited in the characteristic three bands peaked at 4.84, 5.31 and 5.87 eV (Fig.2b, curve 3), related to the 1A → 2A, 2B and 3P transitions of this center, respectively [6, 7, 14]. The excitation spectrum of the F⁺ center luminescence in Al₂O₃:C crystal in the 330 nm band shows, on the whole, the same structure as in Al₂O₃ crystal but demonstrates another distribution of the intensity of the 4.84 and 5.32 eV excitation bands (Fig.2b curve 4). The observed change of the intensity of these bands in Al₂O₃:C crystals in comparison with ones for Al₂O₃ crystal can be caused by the influence of the strong excitation bands of F centers partly overlapped with the 5.37 eV excitation band of F⁺ centers.

The excitation spectrum of the F-center luminescence in Al₂O₃ crystal consists of the dominating band peaked at 6.21 eV and the band in the exciton range peaked at 8.905 eV, corresponding to the energy of creation of excitons bound with F-centers (Fig.2c, curve 5). The main excitation band of the F center luminescence in Al₂O₃:C crystal is widely elongated in the high-energy side (Fig.2c, curve 6), most probably, due to very large concentration of these centers.

The excitation spectrum of the exciton emission in the 240 nm band in Al₂O₃ crystal (Fig.2a, curve 1) shows sharp two-component peak with maxima at 8.81 and 9.005 eV. We suppose that the last band can be related to excitation of the intrinsic exciton emission of Al₂O₃ host [5, 9],



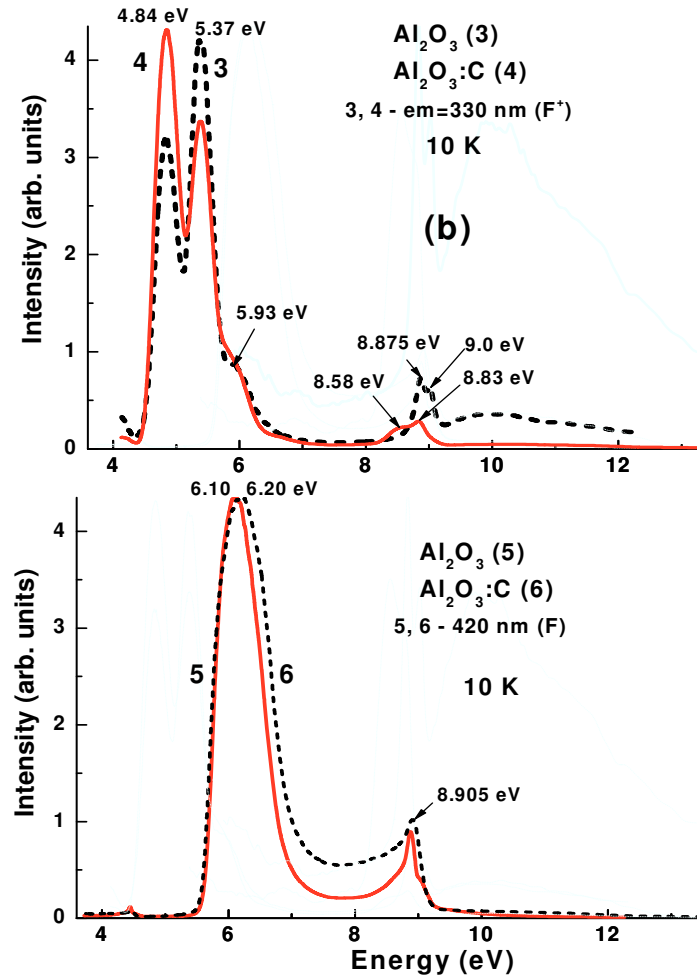


Fig.2. Excitation spectra of exciton (1, 2), F^+ (3, 4) and F (5, 6) centers luminescence in Al_2O_3 (1, 3, 5) and $Al_2O_3:C$ (2, 4, 6) crystals at 10 K. The registration wavelength is indicated in the legend of the figure.

most probably, the long-wavelength component of self-trapped exciton (STE) emission. The band peaked at 8.81 eV can correspond to the energy of creation of excitons localized around some defects, for instance, doubly charged oxygen vacancies (F center).

The excitation spectrum of the exciton luminescence in the $Al_2O_3:C$ crystal in the 290 nm band at 10 K (Fig.2a, curve 2) significantly differs from that in Al_2O_3 crystal for the 240 nm band (Fig.2a, curve 1) and consists of other two intensive bands in the exciton range peaked at 8.58 and 8.83 eV. The structure of this spectrum, which is closer to that of the excitation spectrum of the F^+ center luminescence in $Al_2O_3:C$ crystal in the same range (Fig.2b, curve 2), supports the conclusion that the emission in the 290 nm band is the luminescence of excitons localized around F^+ centers.

This conclusion is also strongly supported by the decay kinetics of the exciton luminescence of Al_2O_3 and $Al_2O_3:C$ crystals at 10 K (Fig.3). As can see from Fig.3, the decay kinetics of the exciton luminescence in the 290 nm band in $Al_2O_3:C$ crystal (Fig.3, curve 4) substantially differs from the decay kinetics of the exciton luminescence of Al_2O_3 crystal in the 240 nm band (Fig.3, curve 3) and is very close to the decay kinetic of the F^+ center luminescence in both crystals (Fig.3, curves 1 and 2). Namely, in $Al_2O_3:C$ crystal, the decay time of the main component of the exciton emission in the 280 nm band (2.6 ns) is very close to the decay times of the F^+ center luminescence (2.0 ns). Somewhat lower decay time of the F^+ emission in $Al_2O_3:C$ crystal in comparison with undoped Al_2O_3 sample (2.3 ns) can be caused by concentration quenching of the luminescence due to very large concentration of F^+ centers in this crystal.

The decay kinetics of the exciton luminescence of Al_2O_3 crystal in the 240 nm band (Fig.3, curve 3) shows similar form for the STE emission or emission of excitons localized around defects and impurities in oxides with different structures [15, 16]. The shape of the decay curve is

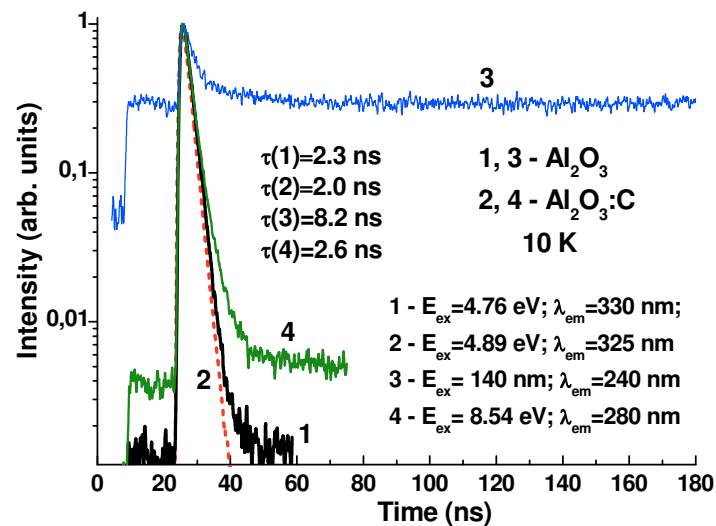


Fig.3. Decay kinetics of F^+ center luminescence at 325-330 nm (1, 2) and exciton luminescence at 240 nm (3) and 280 nm (4) in Al_2O_3 (1, 3) and $Al_2O_3:C$ (2, 4) crystals at 10 K

typical for radiative transitions from the triplet relaxed excited state and can be approximated by the fast component with a decay time of 8.2 ns and slow component with a decay time in the several hundreds μs range which cannot be well evaluated due to the narrow (~ 192 ns) time interval for observation of the luminescence between two pulses of SR. For the same reason we cannot even estimate the decay time of the F center luminescence in Al_2O_3 and $Al_2O_3:C$ crystals in the ms range.

4. Conclusion

We have shown that the luminescent properties of $Al_2O_3:C$ crystals are close to the properties of undoped Al_2O_3 analogues, grown by the Czochralski method. The luminescence of $Al_2O_3:C$ crystals is caused by the dominant emission of F-centers in the band peaked at 413 nm and emission of F^+ centers in the band peaked 324 nm. The decay time of the F^+ center luminescence in Al_2O_3 and $Al_2O_3:C$ crystals at 9 K is equal to 2.3 and 2.0 ns, respectively.

We have shown that due to carbon doping of Al_2O_3 crystal and strong increasing the concentration of oxygen vacancies and related with them F and F^+ centers, the excitons-related emission in the 240 nm band in Al_2O_3 crystal vanishes and transforms into the luminescence of excitons localized around F^+ centers in the band peaked at 290 nm with the decay time of the main component of emission of 2.6 ns. The electronic structure of F and F^+ centers and excitons localized around F^+ centers in Al_2O_3 host can be determined more exactly from the comparison of the excitation spectra both Al_2O_3 and $Al_2O_3:C$ crystals. Namely, we have estimated the energies of creation of exciton bound with the mentioned centers which are equal to 8.905, 8.8 and 8.55 eV, respectively.

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