Journal of Luminescence 204 (2018) 598–602

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Thermoluminescence and radioluminescence of α-Al_2O_3:C,Mg at high temperatures

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ARTICLE INFO

Keywords:
α-Al_2O_3:C,Mg
FNTD
Radioluminescence
Defect
High temperature
Thermoluminescence spectroscopy

ABSTRACT

A α-Al_2O_3:C,Mg single crystal was investigated by means of optical absorption and photoluminescence measurements aimed at the identification of defects involved in the luminescence process. It was also investigated by thermoluminescence (TL) measurements as a function of the spectral emission in the 1.7–5.0 eV range. Radioluminescence measurements under X-ray excitation as a function of the temperature, from room temperature up to 400 °C were executed. These measurements revealed the presence of F, F-type, F-aggregate, and Mg-perturbed F-type and F-aggregate centers, and their thermal quenching behavior. Further, the role of these defects as recombination centers in the TL process was revealed.

1. Introduction

The fluorescence nuclear track detector (FNTD) developed by Laundaer, Inc., is based on the monocrystalline alpha-phase aluminum oxide doped with carbon and magnesium (α-Al_2O_3:C,Mg). High concentrations of defect aggregates related to oxygen vacancies are also present in these crystals. This material was first proposed for ionizing radiation detection and measurement in the early 2000s with the filing of two patents [1,2] and publications in the following years [3,4]. This detector is unique in its capability to track individual particle trajectories in combination with non-destructive laser scanning confocal fluorescence microscopy. The passage of energetic particles leads to the ionization of the crystal and the subsequent production of color centers through the capture of electrons at oxygen vacancies. The localized fluorescence of the color centers is stimulated by a focused laser beam and 3D imaging can be obtained by changing the focal depth of the laser after the scanning of the plane at a given depth. Images of planes 10 μm apart have been reported [5]. This novel FNTD is being investigated as a replacement of CR-39 PNTD (plastic nuclear track detector) for neutron and charged heavy particles dosimetry since α-Al_2O_3:C,Mg is reusable and does not require chemical processing before readout [4]. In this work, radioluminescence (RL) and thermoluminescence (TL) measurements were executed over a broad range of temperatures, from room temperature (RT) up to 400 °C. The goal of this work is to gain insight into the thermal stability and luminescence quenching of the luminescence centers in α-Al_2O_3:C,Mg and their role as recombination centers in the thermoluminescent process.

2. Experimental procedures

A Czochralski-grown one-side polished α-Al_2O_3:C,Mg $8 \times 4 \times 0.5\ mm^3$ rectangular parallelepiped single crystal fabricated by Landauer, Inc., Crystal Growth Division, Stillwater, OK, USA, was used in this work.

Optical absorption measurements were carried out in the range from 1.8 to 6.5 eV, using a Shimadzu 3600 series UV–Vis spectrophotometer.

Photoluminescence emission (PL) spectra were obtained using a Horiba Jobin Yvon Fluorolog 3 spectrofluorometer equipped with double monochrometers for both excitation and detection, and a 450 W xenon lamp as the excitation source. All measurements were carried out in ambient conditions and with a detection spectral resolution of 1 nm.

RL and TL spectroscopy measurements were executed using a customer-designed Freiberg Instruments Lexsyg Research spectrofluorometer equipped with a Varian Medical Systems VF-50 J X-ray tube with a tungsten target coupled with an ionization chamber for dose monitoring and operated at 40 kV and 1 mA. The light emitted by the sample was collected by a lens and converged into an optical fiber connected to an Andor Technology Shamrock 163 spectrograph coupled to an Andor Technology DU920P-BU Newton CCD camera. Results were not corrected for the spectral sensitivity of the system. RL measurements were executed under continuous X-ray irradiation from RT

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https://doi.org/10.1016/j.jlumin.2018.08.018
Received 23 March 2018; Received in revised form 1 August 2018; Accepted 1 August 2018
Available online 06 August 2018

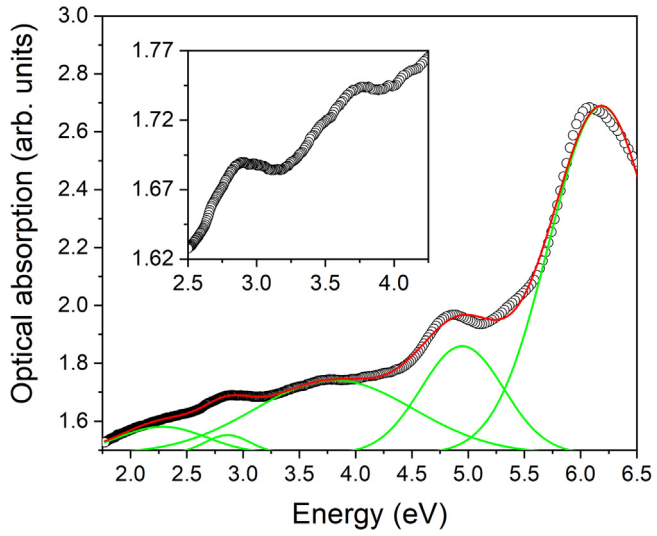

Fig. 1. Optical absorption of a α-Al_2O_3:C, Mg single crystal (open circles) together with the results of Gaussian (green lines) spectral deconvolution and best fit (red line). The inset highlights the absorption bands between 2.5 and 4.25 eV. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

up to 400 °C at a heating rate of 1 °C/s. At every 25 °C, the sample was held at a fixed temperature for 5 s to guarantee thermal equilibrium during which time period RL spectra were collected at 1 s integration time. Spectral fitting was based on Gaussian bands without any parameter restraint, after background subtraction. For the TL measurements, samples were preheated from RT up to 400 °C at a heating rate of 5 °C/s, held at 400 °C for 60 s, cooled to RT, and X-ray irradiated for 10 s. This procedure was used to empty all traps previous to each TL measurement. TL spectroscopy measurements were executed immediately after X-ray irradiation without any exposure of the sample to ambient light, from RT to 400 °C at 1 °C/s heating rate. Measurements as a function of the spectral emission in the 1.7–5.0 eV range were carried out every 20 s with an integration time of 1 s and a 19 s fixed delay before the next measurement.

3. Results and discussion

A typical optical absorption spectrum (open circles) in the ultraviolet-visible spectral range is shown in Fig. 1, together with the results of spectral analysis (Gaussian bands (green curves) and best fit (red line)). The spectrum is dominated by an intense band centered at 6.1 eV assigned to unperturbed F centers [6] together with other broad bands centered at about 4.9, 3.8, and 2.9 eV. The presence of a background due to scattering from the non-polished surface can also be seen. Many absorption and excitation bands have been reported for a variety of defects in Al_2O_3 and Al_2O_3:C,Mg [6,7]. The spectral proximity of these bands to one another limited the identification of the defects present in the sample. Table 1 summarizes the position of the absorption/excitation bands of defects in these materials. Based on these previous works, the band centered at 4.9 eV was assigned to F^+(Mg) and F_2^+(2Mg) centers, the band centered at 3.8 eV to F_2^+(2Mg) and possibly to F_2^+(Mg) and unperturbed F_2 centers, and the band at about 2.9 eV was assigned to F_2^{2+}(2Mg) [7]. The broad absorption around 2.1 eV was tentatively assigned to F_2^+(2Mg) [7]. The presence of unperturbed F^+ centers was suggested by the absorption around 4.8 and 5.4 eV [6]. Best fitting of the spectrum by means of Gaussian bands confirmed the presence of bands at 6.1, 4.9, 3.8, 2.9, and 2.2 eV.

In order to further investigate the presence of color centers, photoluminescence measurements were carried out at specific excitation energies, according to data reported in [7] (cf. Table 1). These

Table 1
Absorption/excitation and emission bands of F-type defects in Al_2O_3 [6] and Al_2O_3:C,Mg [7]. See text for the respective experimental values observed in this work.

Absorption/Excitation (eV)	Emission (eV)	Defect
6.0	3.0	F
5.4, 4.8	3.8	F^+
5.17, 4.86	3.82	F^+ (Mg)
4.1, 3.5, 2.75	2.48	F_2
3.54	3.22	F_2^+ (Mg)
4.77, 3.7, 2.0	1.65	F_2^+ (2Mg)
2.85	2.43	F_2^{2+} (2Mg)

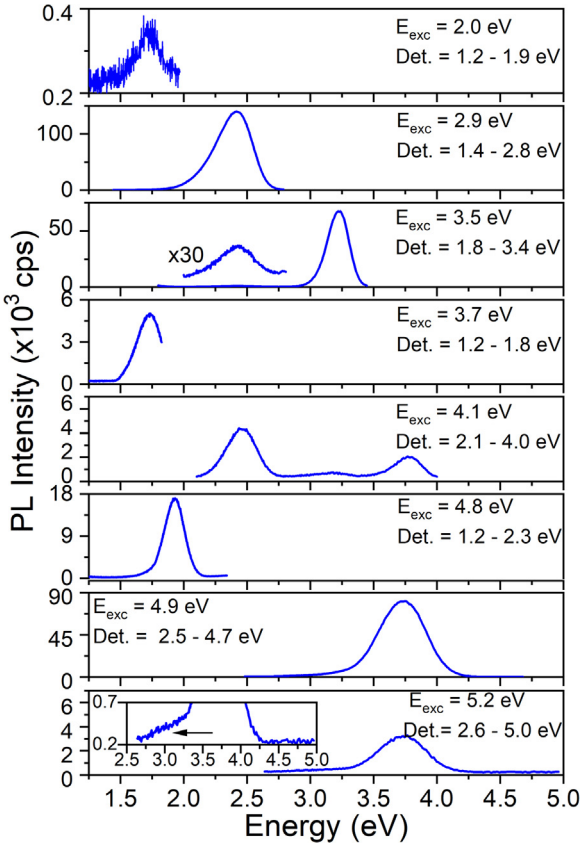

Fig. 2. Photoluminescence spectra of a α-Al_2O_3:C, Mg single crystal obtained under different excitation energies. The detection range of each measurement is indicated.

measurements revealed a number of emission bands, as shown in Fig. 2. Under excitation at 2.0 and 3.7 eV, an emission band centered at about 1.7 eV was observed confirming the presence of F_2^+(2Mg) centers. Under 4.8 eV excitation, emission at about 1.9 eV was tentatively assigned to the same defect. Under 2.9 eV excitation, emission centered at 2.4 eV showed the presence of F_2^{2+}(2Mg) and unperturbed F_2 centers. Under 3.5 eV excitation, emission at 3.2 eV was observed and assigned to F_2^+(Mg) centers and at 2.4 eV to F_2^{2+}(2Mg) and unperturbed F_2 centers. Under 4.9 eV excitation, emission at about 3.7 eV revealed F^+(Mg) and unperturbed F^+ centers. Under 5.2 eV excitation simultaneous emissions at about 3.7 and 3.2 eV were observed revealing F^+(Mg) and unperturbed F^+ centers, and F_2^+(Mg) centers, respectively. Finally, under 4.1 eV excitation, simultaneous emissions at 2.4, 3.2, and 3.8 eV were observed and assigned to the respective centers referred to above.

The TL of α-Al_2O_3:C,Mg,where electron traps have been studied in detail, has been the subject of extensive investigation [8–13], but the