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

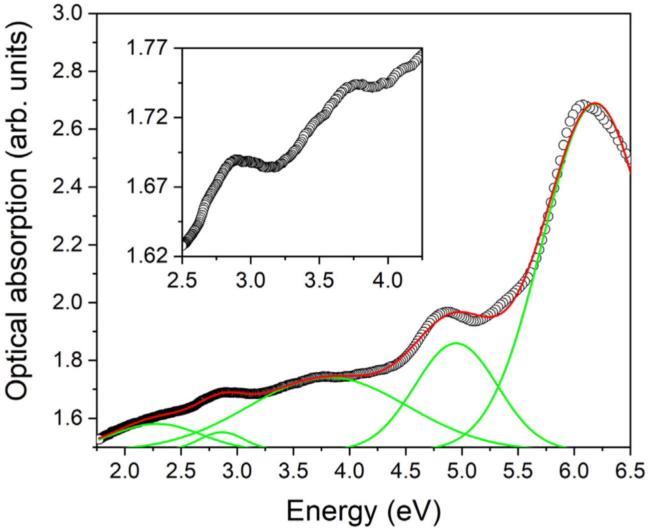

Fig. 1. Optical absorption of a α-Al$_2$O$_3$:C, Mg single crystal (open circles) together with the results of Gaussian (green lines) spectral deconvolution and best fit (red line). The inset highlights the absorption bands between 2.5 and 4.25 eV. (For interpretation of the references to color in this 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$_2$O$_3$ and Al$_2$O$_3$: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.

Table 1
Absorption/excitation and emission bands of F-type defects in Al$_2$O$_3$ [6] and Al$_2$O$_3$: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)

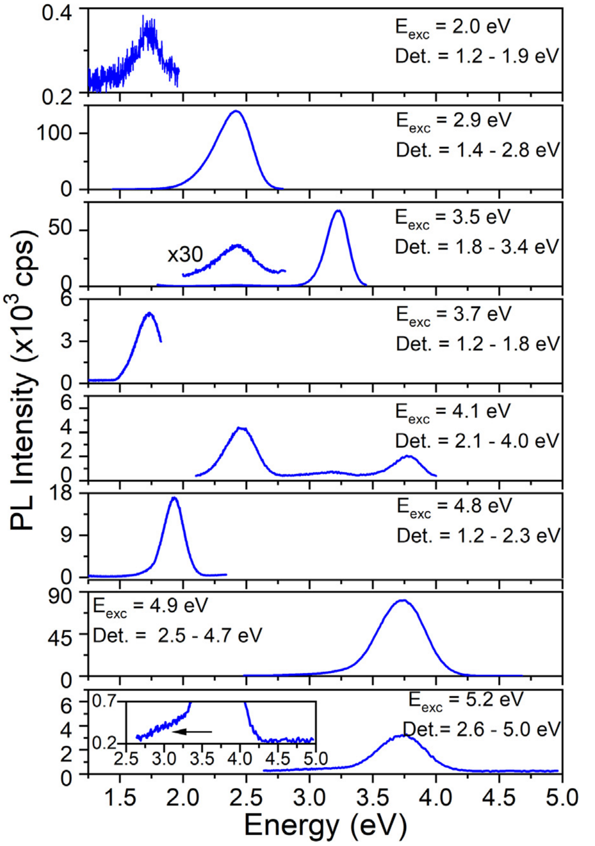

Fig. 2. Photoluminescence spectra of a α-Al$_2$O$_3$:C, Mg single crystal obtained under different excitation energies. The detection range of each measurement is indicated.

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 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$_2$O$_3$:C,Mg,where electron traps have been studied in detail, has been the subject of extensive investigation [8–13], but the

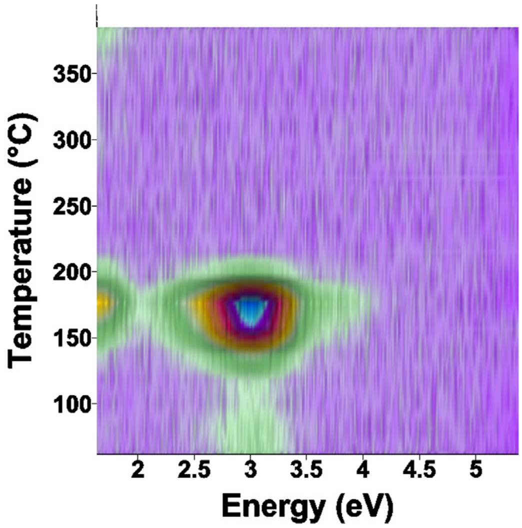

Fig. 3. TL emission of a α-Al_2O_3:C, Mg single crystal as a function of temperature and photon energy.

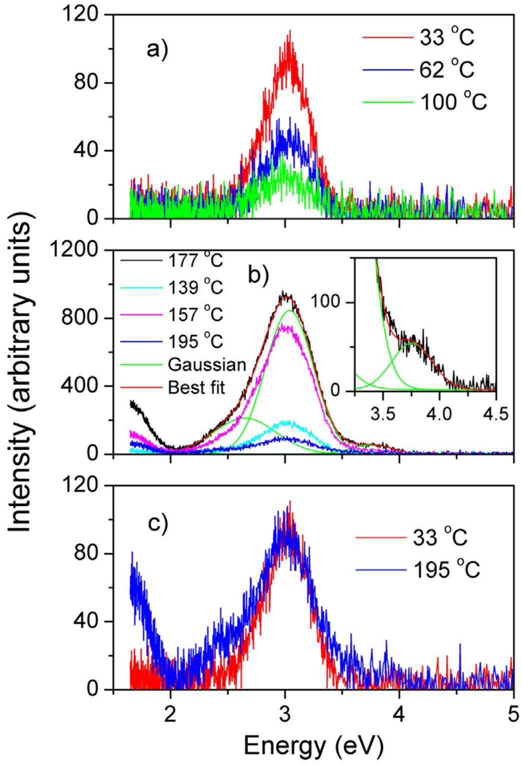

Fig. 4. a) Selected TL spectra within 33 and 100 °C; b) selected TL spectra between 177 and 195 °C, together with Gaussian fitting of TL spectra obtained at 177 °C. The inset highlights the contribution of a weak band within about 3.5–4.0 eV; c) comparison between TL spectra obtained at 33 and 195 °C. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

role of luminescent defects as recombination centers in the TL process has not received the same attention. In order to elucidate the contribution of the different luminescence centers to each of the glow peaks that compose the complex TL glow curve of α-Al_2O_3:C,Mg, TL measurements were done. These results are presented in Figs. 3 and 4.

Fig. 3 presents the TL response as a function of the temperature and emission energy where several emission bands can be seen. Around RT, the only emission band centered at about 3.0 eV was assigned to unperturbed F centers [6]. This band was also observed at higher temperatures, within about 130–210 °C, together with other emission bands. The band emitting within 3.5–4 eV was assigned to F^+(Mg) and F^+ centers. Another emission band increased in intensity for energies progressively lower than 2.0 eV but could only be partially detected because of limitations of the sensitivity range of the CCD detector. This band was assigned to $F_2{}^+$(2Mg) centers whose emission is centered at 1.65 eV [7]. The weaker emission between about 2.0 and 3.0 eV was assigned to $F_2{}^{2+}$(2Mg) and unperturbed F_2 centers. The emission above 350 °C at energies below 2 eV was ascribed to the blackbody radiation of the system.

Fig. 4a presents selected TL emission spectra at temperatures from RT to 100 °C. The spectra were composed of a single band centered at about 3.0 eV and ascribed to unperturbed F centers. Fig. 4b presents selected TL emission spectra at higher temperatures, within 177 and 195 °C. These spectra presented four emission bands at about 3.8 eV (cf. inset; F^+ and F^+(Mg) centers), 3.0 eV (unperturbed F centers), and 2.6 eV, in addition to some emission below 2.0 eV ($F_2{}^+$(2Mg) centers). The presence of these bands could be visually identified in the spectra but were more clearly indicated by means of Gaussian fitting (green lines) of the spectrum obtained at 177 °C and corresponding best fit (red line). The determination of the peak position of the 2.6 eV band had a higher degree of uncertainty since this band is a small shoulder superimposed to the dominant emission at 3.0 eV. The 2.6 eV band was tentatively assigned to $F_2{}^{2+}$(2Mg) and unperturbed F_2 centers known to emit at 2.4 and 2.5 eV, respectively [7]. Fig. 4c compares the TL spectra obtained at 33 and 195 °C. While these spectra presented nearly the same peak intensity, it was noted that the 33 °C TL glow peak was composed by a single emission band at 3.0 eV. On the other hand, the 195 °C spectrum presented additional emissions around 2.5 eV ($F_2{}^{2+}$(2Mg) and unperturbed F_2 centers), below 2 eV ($F_2{}^+$(2Mg) centers), and possibly around 3.9 eV (F^+ and F^+(Mg) centers). These results demonstrated that these centers contribute as recombination centers at high temperatures only. Previously, Akselrod [8] and Rodriguez *et al.* [9] reported on TL spectroscopy measurements of α-Al_2O_3:C,Mg in similar spectral and thermal ranges. However, both groups reported TL emission only between about 150 and 200 °C, with Akselrod reporting two emissions centered at 330 nm (3.76 eV) and 420 nm (2.95 eV), and Rodriguez *et al.* emissions at 325 nm (3.82 eV), 415 nm (2.99 eV), 520 nm (2.38 eV) and 750 nm (1.65 eV). Interestingly, none of these works detected emission associated with the glow peak obtained about RT that is being spectrally analyzed for the first time in this work.

RL measurements were executed as a function of temperature to gain insight into the thermal quenching of the defect-based luminescence centers as shown in Fig. 5 (black lines). Also shown are the Gaussian fittings used to extract the area and peak position of each band. Fittings were restricted to the 2.0–4.5 eV spectral region. High confidence fittings were obtained up to 200 °C (coefficient of determination $R^2 \sim 0.997$–0.999). While the confidence of the fittings decreased for higher temperatures, fittings were still reliable to be representative of the overall behavior of the RL spectra (lowest $R^2 = 0.976$ for the spectrum at 400 °C). At RT, the spectrum was dominated by a band centered at 3.05 eV together with two bands centered at about 2.5 and 3.8 eV, in addition to an incomplete band centered below 2 eV. The band at 2.5 eV was assigned to $F_2{}^{2+}$(2Mg) and unperturbed F_2 centers, the band at 3.05 eV to unperturbed F centers, and the band at 3.8 eV to unperturbed F^+ and F^+(Mg) centers [6,7]. The incomplete band below 2 eV was tentatively assigned to $F_2{}^+$(2Mg) centers that are known to emit at 1.65 eV [7]. Its intensity saturated the detector below about 1.7 eV hindering any further analysis. The intensity of all bands increased up to 50 °C (100 °C for the 3.05 eV band) and decreased for higher temperatures. However, thermal quenching occurred at a different rate for each band. The 3.05 eV band dominated the spectra up to 200 °C and the 2.5 eV band dominated the spectra for higher temperatures.

The emission intensity, i.e., the area of each band obtained from the

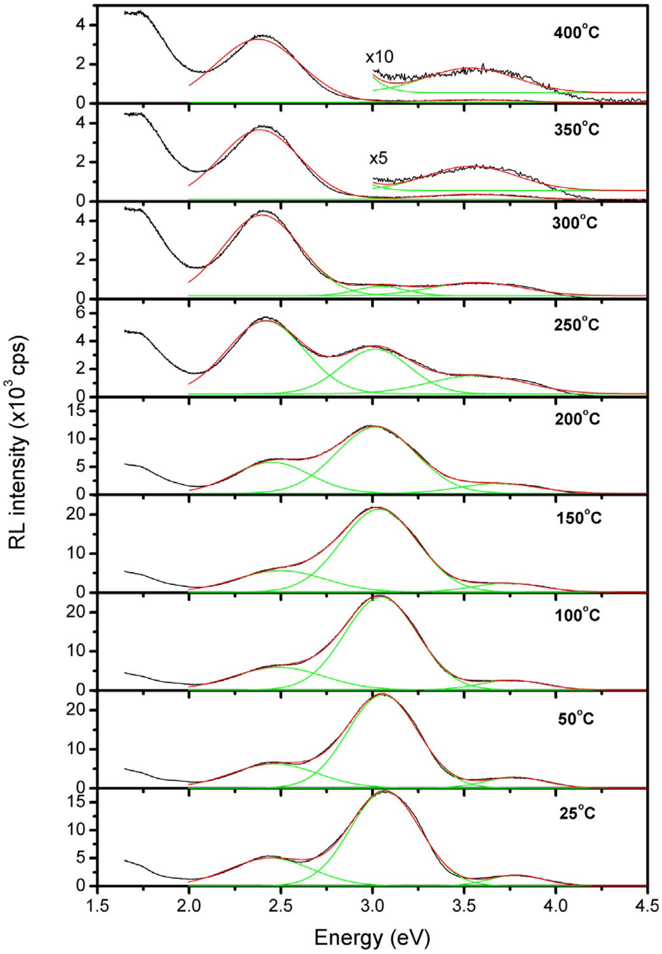

Fig. 5. RL spectra together with 3-band Gaussian fitting (green lines) and best fit (red line) obtained at different temperatures. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

best fitting procedure, as a function of the temperature is shown in Fig. 6a. All bands showed a decrease in intensity for temperatures above about 100–150 °C that was ascribed to thermal quenching. Moreover, the peak position of these bands was also monitored as a function of the temperature (Fig. 6b). Overall, the bands presented a trend to shift to lower energies for higher temperatures, with the 3.8 eV band presenting the strongest decrease reaching ~3.5 eV at 400 °C. This trend can be explained by the structural thermal expansion known to occur for Al_2O_3 single crystals at higher temperatures [14]. Also, the decrease of the binding energy of the electron(s) in the potential well originated by the oxygen vacancy(ies) is expected to play a role in this trend. In the alkali halides, the relationship between the lattice parameter and the absorption energy of the electron in color centers, including color center aggregates, has been well-established in what is commonly referred to as the 'Mollwo-Ivey' relation [15,16]. In the case of oxides, while there is some experimental evidence that a similar type of relation may hold [17], it has been suggested that it is the average oxygen spacing that controls the behavior of electron energy in color centers, including in Al_2O_3 [18].

It is interesting to compare the results presented in Figs. 4a and 5. Up to about 100 °C, TL emission was relatively weak and exclusively at 3.05 eV. For higher temperatures, up to slightly above 200 °C, TL emission was dominated by the 3.0 eV band but with contribution of other bands, including at 3.8, 2.5 and below 2 eV. Finally, no TL emission was observed slightly above 200 °C. RL results as a function of temperature showed that up to about 200 °C the band at 3.05 eV dominated the spectra and that it was essentially thermally quenched at 300 °C. Meanwhile, already at 250 °C, the 2.4 eV band dominated the RL spectra concomitant to the fact that no more TL emission was observed. Based on these results, while other defects also contributed to the TL signal, it was concluded that unperturbed F centers were the most important recombination centers of the TL process.

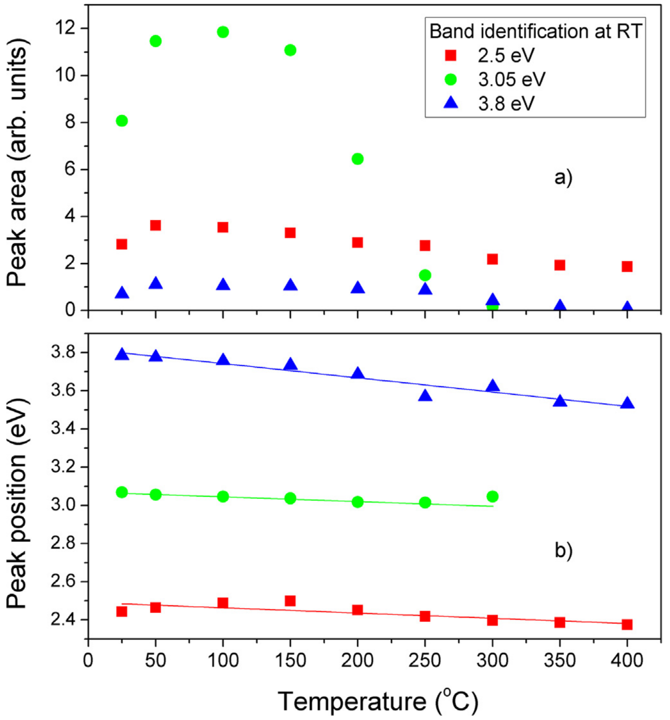

Fig. 6. a) Area of Gaussian bands, and b) peak position obtained from the fitting of the RL spectra obtained as a function of temperature. The lines are guides to the eye, only.

4. Conclusions

In this work, the luminescent properties of a α-Al_2O_3:C,Mg crystal was investigated at high temperatures, up to 400 °C. The use of complementary techniques revealed the presence of several F-type defects, namely: unperturbed F, F^+, and F_2 centers, and Mg-perturbed F^+(Mg), F_2^+(Mg), F_2^+(2Mg), and F_2^{2+}(2Mg) centers. TL spectroscopy measurements revealed a complex behavior. Different types of defects acted as luminescence recombination centers at different temperatures. In particular, this work showed for the first time that unperturbed F centers are the sole TL recombination centers close to RT. Fading of TL signal above about 200 °C corresponds to the thermal quenching of unperturbed F centers.

Acknowledgments

This material is based upon work supported by the National Science Foundation under Grant No. 1653016. N.M. Trindade acknowledges financial support from the Brazilian agency São Paulo Research Foundation (FAPESP), grant #2017/11663-1. The authors are grateful to Dr. M.S. Akselrod with Landauer, Inc., Crystal Growth Division, Stillwater, OK, for the α-Al_2O_3:C,Mg crystal.

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