Journal of Luminescence 186 (2017) 189–193

Contents lists available at ScienceDirect

Journal of Luminescence

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

Spectrally resolved thermally stimulated luminescence of irradiated anion-defective alumina single crystals

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ARTICLE INFO

Article history:
Received 19 December 2016
Received in revised form
27 January 2017
Accepted 8 February 2017
Available online 9 February 2017

Keywords:
Alumina
Luminescence
Emission spectra
Aggregate defects

ABSTRACT

Thermally stimulated luminescence (TSL) spectra in the 313–580 K temperature range have been studied in anion-defective alumina crystals (named in literature as Al_2O_3:C) exposed to different irradiation doses. The TSL curve features two peaks with the maxima at $T_{m1}=437$ K and $T_{m2}=565$ K. The TSL spectrum of the first peak contains the emission of F centers and the R line of Cr^{3+} impurity ions. The absence of the emission of F^+ centers indicates that electron traps are responsible for the first dosimetric TSL peak. The TSL spectrum of the second peak features emission bands of F, F^+ centers, R line as well as a wide band centered at 550 nm and associated with the formation of aggregate centers (F_2 and F_2^{2+}) under irradiation. Possible excitation mechanisms of the TSL emission bands that involve both electron and hole traps related to anion vacancies and impurities are discussed.

1. Introduction

Due to the numerous technological, mineralogical and catalytic importance of corundum (α-Al_2O_3), its electronic structure, optical properties and radiation defects have been the subject of considerable experimental and theoretical studies (see, e.g., [1–10] and references therein). Among various applications of α-Al_2O_3 in the form of single crystals and ceramics, particular attention has been given to anion-defective crystals of α-Al_2O_3 (with high content of as-grown/prepared oxygen vacancies) due to their promising usage as highly sensitive luminescent detectors of ionizing radiation [11–15]. Highly sensitive TLD-500 detectors based on anion-defective alumina (named in literature as Al_2O_3:C single crystals) have been extensively studied and successfully used in dosimetry for over two decades. However, the nature of dosimetric traps responsible for the main thermally stimulated luminescence (TSL) peak at 440-450 K as well as for optically stimulated luminescence (OSL) is still unclear. There are debatable opinions on the luminescence mechanisms in the dosimetric peak of the detectors studied.

At present, a hypothesis that the main dosimetric TSL peak is a superposition of several peaks is widely accepted [16–20]. The shape and temperature position of the peak varies from sample to sample. The samples with a narrow (a half-width of 30-40 K) and a wide (a half-width over 50 K) dosimetric TSL peak at the heating rate of 2 K/s can be singled out [16]. In some samples, the peak broadens and its temperature position shifts toward high temperature, while sometimes the TSL curve has even two distinct sub peaks [17]. The fact that the main dosimetric peak in anion-defective alumina crystals is non-elementary confirms that there are several traps responsible for its emergence. Several attempts to experimentally separate and theoretically verify the elementary components of the dosimetric TSL peak and the related active traps have been performed. For example, a possibility of decomposition of the TSL peak into three components using the T_m–T_{stop} method has been shown [21]. The presence of some elementary constituents in the structure of the main TSL peak has been demonstrated in [22], where the authors studied the samples with different shapes of the dosimetric peak. A good agreement between the TSL curves measured experimentally and calculated in the model involving three active traps and one recombination center has been obtained.

An important contribution to a better understanding of the underlying TSL processes was made by the studies, which showed differences in the nature of the traps responsible for a low-temperature or a high-temperature part of the dosimetric peak of anion-defective alumina crystals. The low-temperature part has been associated with electron traps based on the changes in the concentration of F^+ centers during the annealing of the main TSL peak [17]. In a number of papers, the hole nature of the traps active in the high-temperature part of the dosimetric peak is

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http://dx.doi.org/10.1016/j.jlumin.2017.02.023

revealed. Such hypothesis has been made earlier based on the analysis of temperature-induced changes in the spectral structure of the main TSL peak [23]. Similar inferences were made at the study of the sensitization effect of the samples demonstrating narrow and wide peaks when deep traps are filled [24]. The differences found in dose response of thermally stimulated phototransfer OSL of the samples with different half-width of the dosimetric peak confirmed the electron nature of its low-temperature part and hole nature of the high-temperature part of TSL that obeys a non-the-first-order kinetics [25]. According to the suggested model a narrow dosimetric peak is associated with a monoenergetic electron trap, while a wide peak manifests the presence of both low-temperature electron and high-temperature hole traps with similar activation energies [24]. The fact that the traps of different energy depth contribute to the formation of the main TSL peak has been experimentally proved by the activation energy varying within the peak [16,26].

One can hypothesize that the traps of different nature and energy depth, which are active in the temperature range of the dosimetric peak, affect the TSL spectrum of alumina crystals. However, there have been very few works devoted to the study of the emission spectra in the main and higher-temperature TSL peaks. It is only known that the TSL spectrum of the main peak can feature three bands. The emission band of F centers (two electrons in the field of an oxygen vacancy) peaked at 410 nm is a dominating one, while the weaker bands at 330 and 693 nm are associated with F^+ centers and Cr^{3+} impurity ions, respectively [27]. However, the interconnection between TSL spectra and complex structures of the traps responsible for the reported TSL peak has not been discussed. The current paper presents the results of the experimental study of TSL spectra in the 313–580 K temperature range in anion-defective alumina crystals after their exposure to various doses of X-ray and γ-radiation. Based on these studies, the nature of traps responsible for several TSL peaks in this temperature region is discussed below.

2. Samples and methods

Standard TLD-500 detectors made of anion-defective alumina single crystals were studied. The samples with a certain amount of oxygen vacancies formed via thermochemical coloration were in the form of discs 5 mm in diameter and 1 mm thick. The concentration of F centers, which was calculated from the measurements of optical absorption by using Smakula formula, was about $1.3 \cdot 10^{17}$ cm^{-3}.

The TSL studies of irradiated samples were performed in a Janis VPF-800 cryostat. An X-ray tube (W anode, 40 kV, 10 mA) was used for sample irradiation at room temperature, providing a dose rate approximately 20 $Gy/s/cm^2$. Some specimens were irradiated with a ^{60}Co source of γ-radiation. TSL curves were recorded using a Hamamatsu H8259 photon counting head in the temperature interval of 295-650 K at a heating rate of 10 K/min, controlled with a LakeShore 335 temperature controller. If necessary, a neutral glass filter NS-13 (Russia) was placed in front of H8259 to reduce the integral intensity. The TSL spectrum was repeatedly measured for 60 s using an ARC SpectraPro 300i grating monochromator equipped with a CCD detector with a spectral sensitivity in the range of 190–1100 nm. Considering the given heating rate, each emission spectrum was measured within a temperature interval of 10 K. This allowed us to measure several spectra in the temperature range of each TSL peak. The experiment was fully controlled using the Lab-View based software.

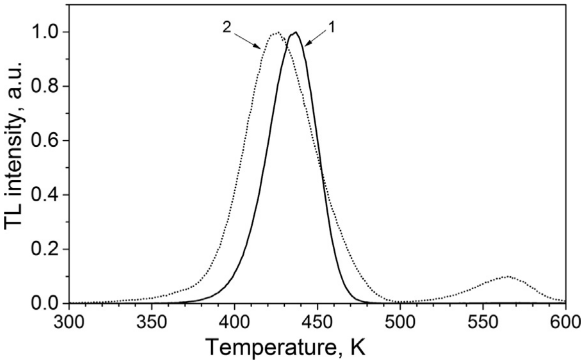

Fig. 1. Normalized TSL curves of anion-defective alumina single crystals X-irradiated with a dose of 0.08 kGy (1) and 2 kGy (2).

3. Results and discussion

3.1. TSL glow curves

Fig. 1 shows normalized TSL curves recorded from two anion-defective alumina samples exposed, respectively, to 0.24 and 6 kGy doses of X-ray radiation. In the case low radiation dose of 0.24 kGy, only one TSL peak at 437 K is registered, which is further referred to as the main dosimetric peak. Its half-width (FWHM) is 34 K, and according to the accepted classification, it is a narrow one. It is noteworthy that the main TSL peak is slightly shifted to the region of lower temperatures with respect to its position at 440–460 K known from earlier publications [11,15]. This is due to a substantially lower heating rate of 10 K/min used in the present research to facilitate the spectra recording, compared to the heating rate of 2 K/s used in standard dosimetric measurements. At high exposure dose, a high-temperature TSL peak at 565 K emerges, its intensity rising with exposure dose. It is known that an isolated main TSL peak is registered in the samples exposed to low radiation doses [11]. High-temperature TSL peaks in the range of 500–850 K appear after high-dose irradiation, when the luminescence yield of the main peak is saturated and charge carriers undergo efficient trapping by deep traps in alumina [15].

The parameters of the main TSL peak change with the rise of exposure dose. Table 1 shows the results on the temperature position of the peak T_{max}, its FWHM and Δ_1/Δ_2 ratio, where Δ_1 and Δ_2 are related to the half-widths of the low-temperature and high-temperature regions of the TSL peak, respectively, taken from T_{max}. It can be seen that when the dose increases, T_{max} shifts to lower temperatures, as it is typical of the TSL processes described by the second order kinetics [28]. At the same time, FWHM of the main TSL peak increases mainly due to the broadening of its high-temperature part. The broadening of the TSL peak with an increasing dose could be related to the formation of radiation-induced defects serving as additional luminescence centers. It would be natural to suggest that such defects are also responsible for the neighboring TSL peak at 565 K, the intensity rise of which starts just after the end of the main peak. According to Table 1, the most remarkable changes in the parameters of the dosimetric TSL peak

Table 1
Changes in the parameters of the main TSL peak with the rise of X-ray irradiation dose in anion-defective alumina crystals.

Exposure dose, kGy	T_m, K	FWHM, K	Δ_1/Δ_2
0.08	437	34	1.27
0.4	431	44	0.97
2	426	49	0.89
10	424	48	0.90