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P Pokorny† and A Ibarra

Instituto de Investigación Básica, CIEMAT, Avenida Complutense 22, E-28040 Madrid, Spain

Abstract. The recently discovered high-intensity thermoluminescence (TL) emission in Al$_2$O$_3$ doped with Cr and Ni is analysed more deeply by measuring the effects of x-ray irradiation on the optical absorption in parallel with the TL process, together with the effect of optical bleaching. It is proposed that the high-intensity peak is due to oxygen vacancies, induced by the presence of Ni. The main recombination centre is Cr.

1. Introduction

In spite of extensive studies of the thermoluminescence (TL) of Al$_2$O$_3$ (see for example references in [1]), there have been very few studies on the effects of impurities on the TL characteristics, and most of them have mainly aimed to find, from a phenomenological point of view, a material more sensitive to ionizing radiation [2–5]. Only recently has some systematic work been done for the common Cr impurity [6]. This interest has been induced by the discovery of a very high-intensity TL process in Al$_2$O$_3$ doped with C [7]. This material has been obtained by melting under strong reducing conditions in the presence of graphite. Its high-intensity TL emission together with the high sensitivity to ionizing radiation (around 50 times higher than that of TLD100) and low effective atomic number opens the application of this material as a high-sensitivity dosemeter [7].

It has been shown that the vacancy centres (specially F and F$^+$) play an essential role in the TL glow curves of Al$_2$O$_3$, both in the case of these high-sensitivity dosemeters [7] as well as in the case of high-purity materials [1]. In fact, the main emission detected during the TL process in most cases is at 2.95 eV and has been related to recombination in F centres. The only other emission that appears in many cases is that at 1.77 eV associated with electron–hole recombination in Cr ions.

A large number of TL peaks have been detected in the different types of Al$_2$O$_3$, indicating that very different traps and recombination centres are possible in the Al$_2$O$_3$ host, but it is interesting to note that most of the peaks appear in the temperature ranges between −60 and 0 °C and 100 and 250 °C. Although other peaks are observed at other temperatures, usually they are very small. Most of the peaks in the higher-temperature range seem to be associated with the release of holes from different V centres, at least in the nominally pure samples [1, 8].

Recently [9] it has been found that the presence of Ni and Cr in the Al$_2$O$_3$ matrix induces a big change in the characteristics of the TL glow curve and, in some cases, very *high-intensity peaks are observed (more than 150 times higher than* TLD100 *for the same* x-ray dose [10]). In this work the TL glow curve of this high-emission material is analysed in parallel with optical absorption measurements to determine the defects responsible for this high emission and the role of Ni in the process.

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† On leave from Institute of Physics, Czech Academy of Science, Na Slovance 2, Praha 8, Czech Republic.

2. Experimental details

The irradiations are made at room temperature using either a ^{60}Co source at a dose rate of 7 Gy s^{-1} or a tungsten-anode Siemens Kristalloflex 2H x-ray tube at a maximum dose rate of 0.5 Gy s^{-1}. Samples were x-ray-irradiated through an aluminium plate 1 mm thick.

The TL measurements are made in the temperature range from 20 to 400 °C at a heating rate of 0.26 °C s^{-1} in a vacuum chamber described elsewhere [11]. The TL glow curves were detected and recorded by an EMI 9659QB (extended S20 cathode) photomultiplier connected to a Philips PM8222 recorder. The emission spectra were performed by means of a motor-driven Bausch and Lomb monochromator inserted between the sample and the photomultiplier, in the range 200 to 750 nm at a scan rate of 6.5 nm s^{-1}. The data have been corrected for the photomultiplier and monochromator standard response. Phosphorescence measurements are made at a constant temperature (± 0.1 °C) as a function of time, either at a fixed wavelength or total emitted light. The stabilization of the temperature takes about 1 min and introduces an error in the starting time for phosphorescence measurements that must be taken into account to make theoretical fittings.

Light emitted by the sample during x-ray irradiation (radioluminescence) can be measured by means of an optical fibre that couples the irradiation chamber and a high-resolution monochromator. The spectra obtained have been corrected by taking account of the photomultiplier and grating response.

A high-intensity (450 W) Xe lamp and a Bausch and Lomb monochromator are used for sample photostimulation at different wavelengths.

Optical absorption measurements were made with a Cary 17 spectrophotometer in the range 200–2500 nm.

Samples of $10 \times 10 \times 1$ mm^3 were prepared from Al$_2$O$_3$ single crystals grown by the Verneuil method and used for jewellery purposes. They were annealed in air at 900 °C for 10 min and then slowly cooled down to room temperature. The orientation of the crystal was unknown. Chemical analysis indicates that the main impurities are Cr (around 250 ppm) and Ni (around 10 ppm). Other impurities like Mn, Fe, V, Ti and Mg are not detected (detection limit around 10 ppm).

3. Results

The main data of the chemical analysis results are confirmed by measuring the optical absorption on the samples before irradiation. Figure 1 shows the spectrum obtained in the sample annealed up to 900 °C. It has a small band around 2.25 eV, two dominant bands at 3.1 and 4.4 eV, another small band at 5.4 eV and a sharp increase in the far-ultraviolet (UV) suggesting a peak between 6 and 7 eV. The bands at 3.1 and 4.4 eV are related to the presence of Ni^{3+} [12, 13]. The band at 2.25 eV and a part of the 3.1 eV band should be associated with the presence of Cr^{3+} [14, 15]. These assignments are consistent with the chemical analysis in relation to both the Ni and Cr. Owing to the high oscillator strength of the Ni^{3+} [12], a small concentration can be easily detected. Using the Smakula formula [16], it is possible to estimate the concentration of Ni^{3+} from the height and halfwidth of the 4.4 eV band. The result obtained is around 10^{18} cm^{-3}, in close agreement with the chemical analysis.

The band at 5.4 eV could be related with: (i) oxygen vacancies (F$^+$ centres) or (ii) Cr^{2+} centres. The first possibility is supported by taking into account that the F$^+$ centre has two characteristic absorption bands at 5.4 and 4.8 eV [1]. It is also known that sometimes
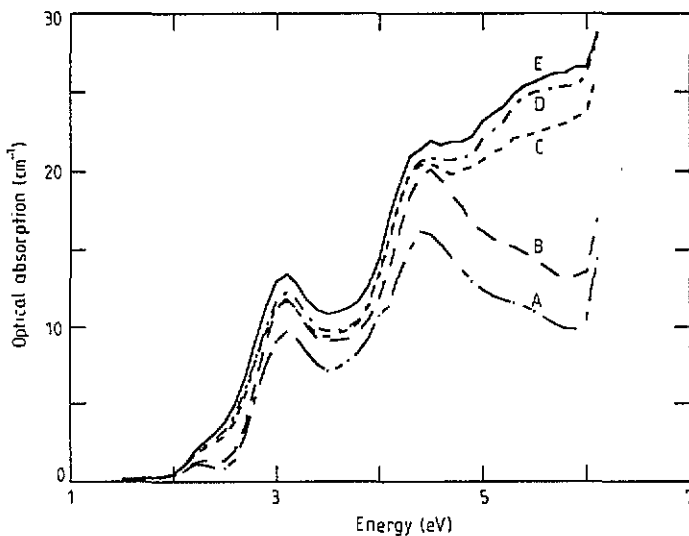
Figure 1. Room-temperature optical absorption spectra of Al_2O_3:Cr,Ni: as annealed (curve A) and x-ray irradiated up to a dose of 330 Gy (B), 900 Gy (C), 1800 Gy (D) and 5000 Gy (E).

centres associated with the presence of oxygen vacancies appear as a consequence of the growth process [1]. However, the concentration of these oxygen vacancies is rather small. Assuming an oscillator strength of 1, usual in these materials [17], and a halfwidth of 0.7, the estimated concentration of F and F^+ centres, using the same procedure as before, will be lower than 10^{17} cm^{-3}. On the other hand, the band at 5.4 eV has also been related to the presence of Cr^{2+} [1]. It is quite difficult to discriminate at this moment between the two alternatives; in fact, we will see that probably both types of centres are present in the material.

The sharp increase around 6 eV can probably be related with the very effective charge-transfer absorption bands of Cr^{3+} or Ni^{3+} (at 7.0 eV) [12].

Figure 2 shows the glow curve obtained for different doses up to 10^4 Gy. Typically the TL glow curve of this material shows a small peak at 175 °C and a dominant one at 330 °C. The main characteristic of this TL process is its high efficiency (around 150 times more photons are emitted than in TLD100 for a similar dose and around 1000 times more than in a typical nominally pure Al_2O_3 [10]). The observed dose dependence is linear up to 5×10^3 Gy and saturates for higher doses. For low doses a small shift of the peak position to higher temperatures can be observed and a higher halfwidth. This behaviour indicates that the TL process is not of first order [18].

The emission spectra have been measured at different doses and temperatures. No dose dependence has been found. Representative spectra for different temperatures are given in figure 3. The main feature consists of an intense emission around 1.78 eV with two broad sidebands at around 1.70 and 1.85 eV. The relative proportion of the band at 1.78 eV to the sidebands is a function of temperature, decreasing strongly for temperatures over 300 °C. These emissions, including their temperature dependence, have usually been related to excited Cr^{3+} [8, 14, 19].

Phosphorescence measurements are made at different temperatures to determine if there is only one process or several close superimposed peaks, and to determine the glow-curve parameters. Figure 4 shows the phosphorescence curves obtained at 277, 290 and 310 °C.
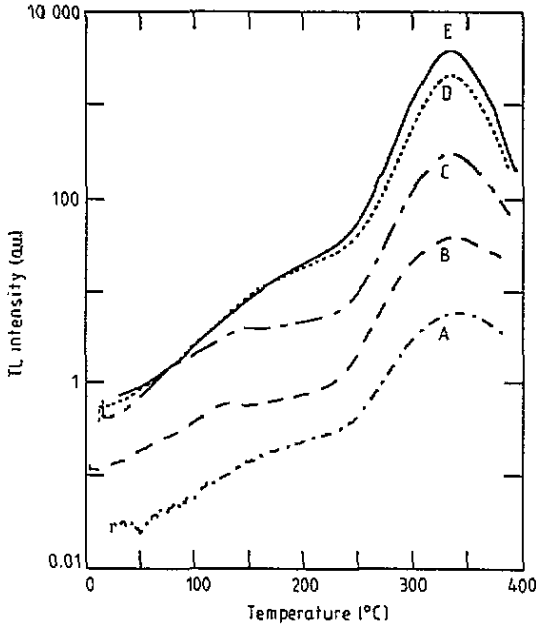
Figure 2. TL glow curve of Al_2O_3:Cr,Ni, x-ray irradiated at room temperature up to 10 Gy (curve A), 30 Gy (B), 180 Gy (C), 1400 Gy (D) and 10000 Gy (E).
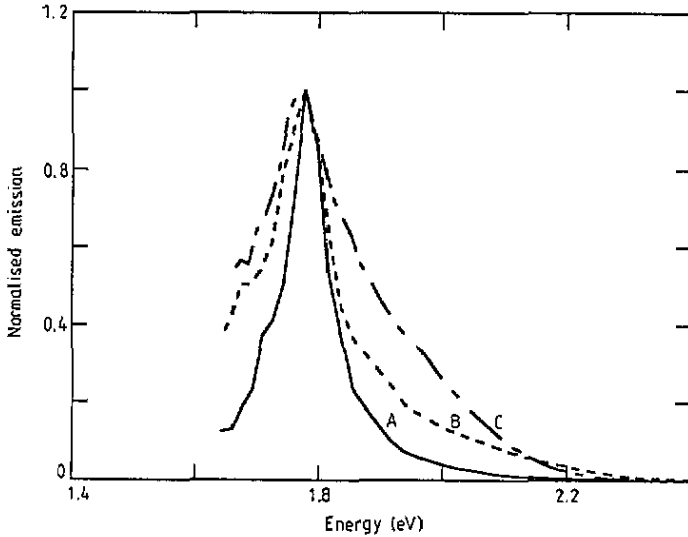

Figure 3. Emission spectra at different temperatures during the TL glow curve of Al_2O_3 doped with Cr and Ni, x-ray irradiated at room temperature: (A) 130 °C, (B) 220 °C and (C) 320 °C.

They show a typical non-exponential behaviour that will be analysed later in this work.

Information about the defects involved in the TL process can be obtained from the study of the change induced by x-ray irradiation on the optical spectra of the samples and the annealing of these effects. Figure 1 shows these changes for several x-ray doses. A
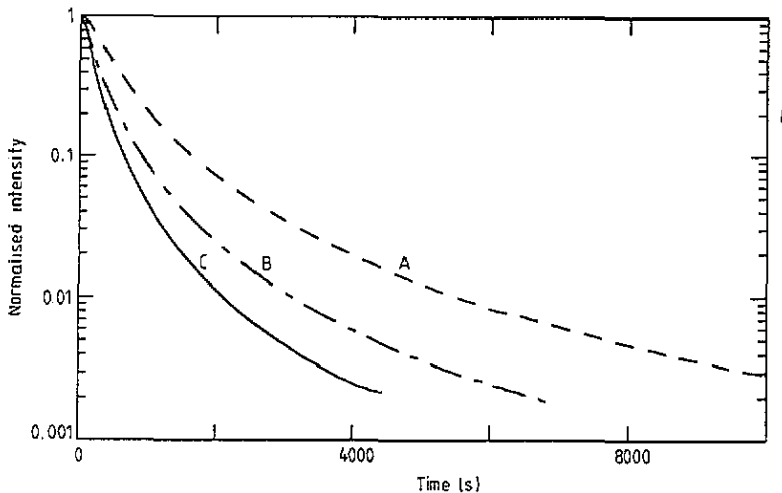
Figure 4. Phosphorescence decay at 277 °C (A), 290 °C (B) and 310 °C (C) of Al$_2$O$_3$:Cr,Ni, x-ray irradiated up to a dose of 1000 Gy.

large increase can be observed in the heights of the bands in the region of 5–6 eV and an increase of the bands at 4.1 and 2.8–3.1 eV. From the difference between the irradiated and the annealed spectra, it can be seen that the increase of the optical absorption in the 5–6 eV region is associated with the increase of bands around 6.1 eV (related to F centres [1]) and 5.4 eV (F$^+$ centres or Cr^{2+}), the increase of 4.4 and 3.1 eV bands should be associated with an increase of the Ni^{3+} concentration, whereas a new band appears around 2.8 eV and a wide structure is developed around 3.5 eV. All these effects disappear after an annealing to 900 °C. Figure 5 shows the difference between the optical spectra of an x-ray-irradiated sample annealed to different temperatures and the one obtained after an annealing to 900 °C. The results obtained indicate that most of the irradiation effects on the optical spectra decrease in a sharp step between 300 and 400 °C. Only the bands at 4.4 and 3.1 eV seem to be more temperature-resistant. This step seems to correlate with the observed TL glow curve. Figure 6 shows the normalized height of x-ray-induced absorption bands at 2.8, 4.4 and 6.1 eV as a function of the annealing temperature, compared with the observed TL glow curve.

Ultraviolet light illumination induces a TL glow curve very similar to those observed with x-ray or gamma irradiation, but with a much lower intensity, indicating that the same processes are induced independently of the excitation source used. This can be used to determine the correlations between the optical absorption bands and the observed TL processes, by the study of the spectral sensitivity of the UV-induced TL. These measurements have been made by illuminating the sample for 3 h at different wavelengths. The obtained TL area has been corrected for the lamp spectra. The measured spectral sensitivity can be observed in figure 7. It shows a large peak around 5.4 eV.

In addition, light illuminations at different wavelengths have been made in samples previously irradiated with x-ray radiation up to a dose of 300 Gy. Illumination with wavelengths at an energy higher than 6.3 eV induces an increase of the TL, whereas illumination with light of lower energies decreases the measured TL intensity. Figure 8 shows the bleaching effect induced in the observed TL by the light illumination. A very high sensitivity to 6.1, 3.4 and 2.25 eV illumination can be observed. The data of figure 8 have again been corrected for the lamp spectra.
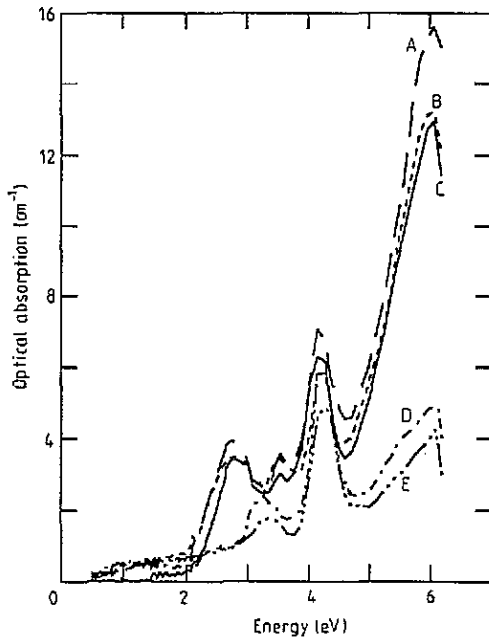
Figure 5. Difference spectra between the optical absorption spectra obtained in Al$_2$O$_3$ doped with Cr and Ni, annealed up to different temperatures after an x-ray irradiation up to 1000 Gy, and the one obtained in the sample annealed at high temperature (900 °C): (A) 25 °C, (B) 210 °C, (C) 300 °C, (D) 360 °C and (E) 400 °C.
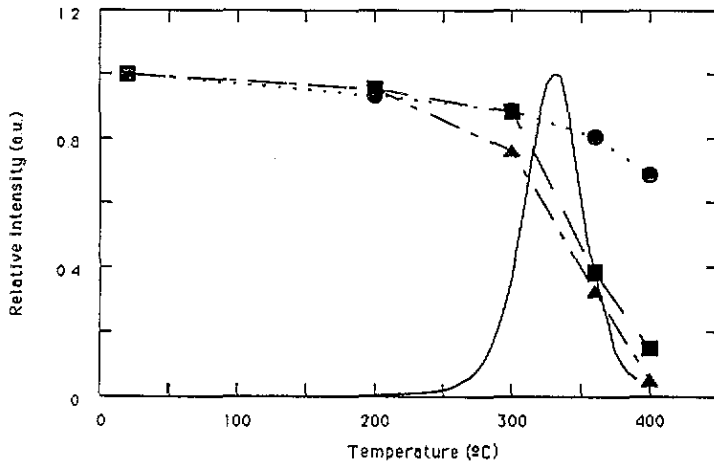

Figure 6. Normalized height of the absorption bands induced by x-ray irradiation at 6.1 eV (■), 4.4 eV (●) and 2.7 eV (▲) as a function of the annealing temperature compared with the observed TL glow curve (———).

Finally, radioluminescence measurements were made to obtain more information about the centres that play some role during the irradiation. Figure 9 shows the luminescence spectra obtained under irradiation at room temperature. The main feature of the spectrum is the structure around 1.77 eV clearly related to Cr^{3+} ions, but it is possible to observe a
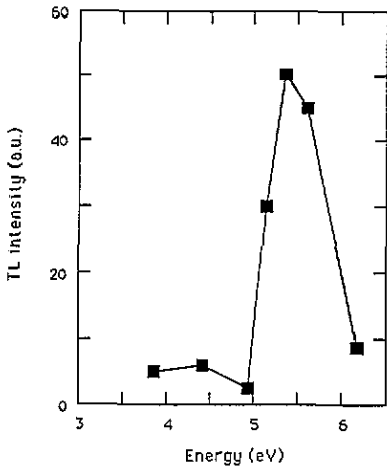
Figure 7. Normalized area of the TL glow curve obtained after UV illumination at different wavelengths.
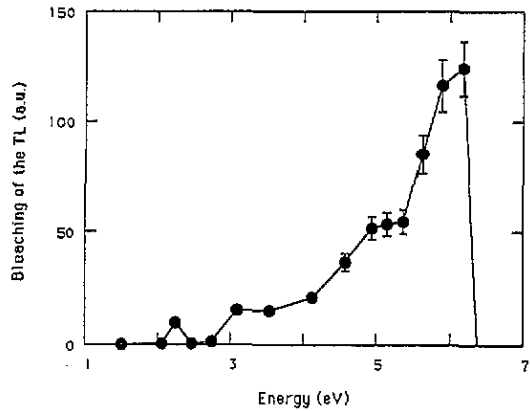

Figure 8. Normalized bleaching effect of light illumination at different wavelengths in Al$_2$O$_3$:Cr,Ni previous x-ray irradiated up to 300 Gy.

very low band around 4 eV. Luminescence bands in this region have been related to F$^+$ centres [1].
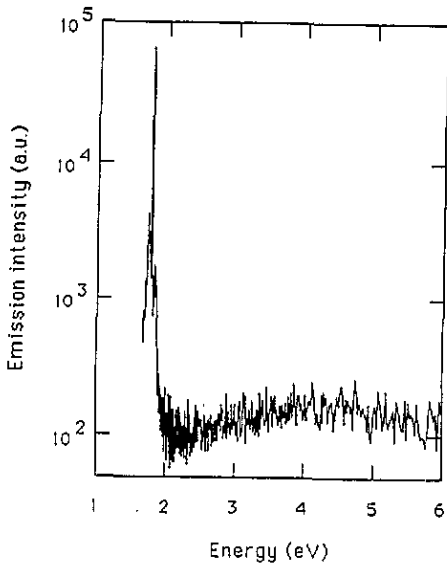

Figure 9. Radioluminescence of Al$_2$O$_3$:Cr,Ni samples at room temperature under x-ray irradiation of 0.5 Gy s^{-1}.

4. Discussion

Peaks at relatively high temperatures have been mentioned in the literature, although usually they are of small intensity and appear with others [2, 3, 6, 20, 21]. The presence of the 330 °C peak has been related to the emission of holes (from Cr^{4+} ions) [2] or electrons [3]. In

general, it has been related to the presence of Cr [2, 21] but some evidence indicates that this assignment is not conclusive. In fact, a peak at this temperature has been observed in Al_2O_3 doped with other impurities [3], and in a recent work in which the thermoluminescence of Al_2O_3 doped with Cr is studied, the presence of a high-temperature peak has not been observed [6]. Moreover, we have found that the 330 °C TL peak does not appear in samples of the same origin as the ones studied in this work, but doped with a similar concentration of Cr [9]. So, it is clear that the origin of this peak in our samples is related not only to the presence of Cr, but to the presence of Ni or some other defect. The observation of a very high TL intensity in this material makes the study of this peak and the determination of its parameters an interesting target.

The optical absorption spectra before irradiation (figure 1) show that most of the Ni impurities are in the Ni^{3+} form, but the increase of the 3.1 and 4.4 eV bands after x-ray irradiation indicates the presence of some Ni^{2+} before irradiation that changes to Ni^{3+} as a consequence of it. The presence of Ni^{2+} before irradiation requires some defects for charge compensation. It has been shown that the band at 5.4 eV can be related to Cr^{2+} or F^+ centres. Taking the previous result into account, the small band at 5.4 eV could be related to the presence of some F^+ centres. This suggestion can be supported because the number of F^+ centres estimated from the height of the band before irradiation (around 10^{17} cm^{-3}) is approximately the same as the number of Ni^{3+} centres that appear as a consequence of irradiation. The lack of the luminescence of F and F^+ centres during the TL process can be due to the perturbation of the oxygen vacancy by near impurities. This effect has been observed in similar materials [22, 23, 24]. It can also change the thermal stability of F centres. The presence of F^+ is confirmed by the very low luminescence band at 4 eV observed during irradiation. However, the presence of some Cr^{2+} before irradiation and its contribution to the 5.4 eV band cannot be completely discounted, as we will see later.

The room-temperature (RT) irradiation induces, according to the data of figure 1, the increase of Ni^{3+} concentration (bands at 3.1 and 4.4 eV), the increase of two bands at 3.5 and 2.7 eV of unknown origin and the increase of F centres (band around 6.1 eV). The band at 3.5 eV has been associated with the presence of some aluminium vacancies, which trap holes during irradiation, producing V centres [1, 8]. Most of these effects recover after heating to 400 °C simultaneously with TL emission (see figure 6); only the Ni^{3+} concentration decreases at higher temperatures. Although it is known that the x-ray irradiation induced charge changes in Cr^{3+}, and the formation of Cr^{2+} and Cr^{4+} has been proposed, we have not obtained evidence for the effect of irradiation on Cr^{3+}, but it seems that the formation of Cr^{2+} can be neglected because the increase of any band at 5.4 eV is not observed.
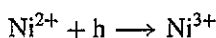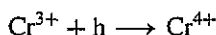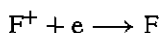
The observed emission at 1.7 eV is undoubtedly related to Cr^{3+} emission and it has been observed in almost any type of sapphire sample owing to its high emission efficiency. The emission of Cr^{3+} has been associated with electron capture in Cr^{4+}, hole capture in Cr^{2+} or even energy transfer from a near defect working as a recombination centre, and so it cannot be used to differentiate between the alternative models.

These results suggest that the electrons and holes produced during irradiation are trapped in F^+ centres, Ni^{2+} and probably aluminium vacancies and Cr^{3+} ions, producing F centres, Ni^{3+}, Cr^{4+} and V centres (together with at least one other centre responsible for the 2.7 eV band). During heating at 330 °C, electrons are released from F centres and recombine at Cr^{4+} ions, and V centres or holes are released from Cr^{4+} ions and recombine in F centres, producing in both cases Cr^{3+} emission. The recovery of the original Ni^{3+} concentration at a temperature over 400 °C indicates that the Ni ion does not play an essential role in this process and suggests that another charge-release process at higher temperatures could be observed.

The TL glow curve induced by UV illumination can be used to discriminate between the two alternatives. The observed peak at 5.4 eV in the spectrum of the intensity of the TL excited by UV light should be associated with Cr^{2+}. F^+ centres can be neglected because no band at 4.8 eV is observed in the excitation spectra, and F^+ has bands at 4.8 and 5.4 eV. The illumination of Cr^{2+} will induce Cr^{3+} and the release of one electron. This electron can be trapped at F^+ centres, producing F centres that will be the origin of the observed TL. The alternative of Cr^{4+} is incompatible with the Cr^{2+} effects.

On the other hand, the decrease of the TL intensity when the irradiated sample is illuminated with light of 6.1, 3.4 and 2.25 eV can be explained by the decrease of F concentration due to the release of electrons (6.1 eV) or by the capture of holes released from Cr^{3+} ions (3.4 and 2.25 eV bands).

Summarizing, during x-ray irradiation the following reactions occur:

$$F^+ + e \longrightarrow F$$

$$Cr^{3+} + h \longrightarrow Cr^{4+}$$

$$Ni^{2+} + h \longrightarrow Ni^{3+}$$

$$\text{vacancy} + h \longrightarrow \text{ V centres.}$$

During heating, reactions of the following form are observed:

$$F + \text{thermal energy}(330\,^\circ C) \longrightarrow F^+ + e$$

$$Cr^{4+} + e \longrightarrow (Cr^{3+})^* \longrightarrow Cr^{3+} + h\nu.$$
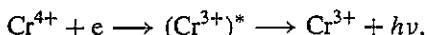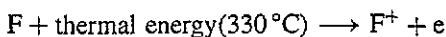
So, the charge carriers of the 330 °C peak are electrons, the traps responsible for this peak are F centres and the recombination centres are Cr^{4+} ions.

These results confirm the important effect of F centres in the TL properties of Al$_2$O$_3$ material. In agreement with the results of [3] and [7], very high-intensity TL peaks are observed when oxygen vacancies are present in the material. The different temperatures at which these peaks appear can be explained by the perturbation of the defects by impurities nearby.

The TL glow curve has been analysed using several procedures [18]. Phosphorescence measurements at different temperatures show non-exponential behaviour. They have been analysed by using two different methods, and both produce a kinetic parameter around 1.45 ± 0.1. The methods used are the representation of

$$\log(-\mathrm{d}I/\mathrm{d}t) \text{ versus } \log I$$

that gives a straight line of slope equal to the kinetic parameter, and the representation of

$$I^{(b-1)/b} \text{ versus } t$$

with different b, that produces a straight line if b is correct. From the representation of the slopes obtained using the second method as a function of $1/T$ it is possible to obtain the activation energy of the process, although large errors are possible due to uncertainty in the starting time. The estimated values are $b = 1.5$ and $E = 1.75$ eV.

5. Conclusions

This paper has studied the TL glow curve obtained in Al_2O_3 doped with Cr and Ni. It has a main peak at 330 °C of very high intensity and a linear dose dependence up to high doses. This peak seems to be related to the emission of electrons from F centres and their recombination with Cr^{4+} ions. The oxygen vacancies are induced by the presence of Ni ions.

More work is in progress to confirm further the role of Cr^{4+} ions and the F centre concentration, and the origin of the absorption bands at 3.7 and 2.7 eV.

Acknowledgments

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