

# Impurity effects on the thermoluminescence of Al<sub>2</sub>O<sub>3</sub>

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The thermoluminescence of several Al<sub>2</sub>O<sub>3</sub> samples doped with different impurities (mainly Cr and Ni) is studied. The main characteristics (emission spectra, dose dependence, peak parameters) of the observed thermoluminescence glow curve are determined. A very high peak is found at 335 °C for some concentrations of Ni. The possible use of this material for dosimetry applications is discussed.

## INTRODUCTION

The thermoluminescence (TL) of Al<sub>2</sub>O<sub>3</sub> has been widely studied during the last 30 years. It has been proposed as a UV and an ionizing radiation dosimeter. A considerable number of peaks has been found, although the traps responsible for them are clearly identified in only a few cases. Large differences, even in pure samples of different origin (Ref. 1 and references cited therein), are observed in the TL spectra.

It is known that X-ray or gamma irradiation does not induce displacement damage in Al<sub>2</sub>O<sub>3</sub>, so the observed TL response is related to charge transfer processes.<sup>2</sup> Recently it was discovered that oxygen deficient Al<sub>2</sub>O<sub>3</sub> doped with Cr shows very interesting dosimeter properties, together with a sensitivity to gamma irradiation several times higher than LiF:Mg, Ti (TLD-100) detectors. This behavior seems to be related to oxygen vacancies.<sup>3</sup> Other workers<sup>4,5</sup> found an increase in sensitivity to ionizing irradiation with the presence of Ti, Mo, and Si impurities. However, systematic studies of the impurity effects on the TL characteristics of Al<sub>2</sub>O<sub>3</sub> have been started only recently, even for the better known Cr doped Al<sub>2</sub>O<sub>3</sub> system.<sup>6</sup>

In this article, the optical absorption and the TL response of Al<sub>2</sub>O<sub>3</sub>, both pure and doped with different impurities (Ni, Cr), are analyzed in the search for new systems with higher sensitivities.

## EXPERIMENT

Irradiations were made at room temperature (RT) using a tungsten anode Siemens Kristalloflex 2H x-ray tube at a dose rate of 0.5 Gy s<sup>-1</sup>. Samples were x-ray irradiated through a 1-mm-thick aluminum plate.

The thermoluminescence measurements were made from RT to 400 °C at a heating rate of 0.26 °C s<sup>-1</sup> in a vacuum chamber described elsewhere.<sup>7</sup> 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 measured by means of a motor-driven Bausch and Lomb monochromator inserted between the sample and the photomultiplier; measurement was in the range 200–750 nm at

a scan speed of 6.5 nm s<sup>-1</sup>. The TL glow curve and spectral data have been corrected for the photomultiplier and monochromator efficiency.

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

Samples of 10×10×1 mm<sup>3</sup> were prepared from different Al<sub>2</sub>O<sub>3</sub> single crystals growth by the Verneuil method used for jewelry purposes. They were annealed in air at 900 °C for 10 min and then slowly cooled down to room temperature. The samples were of four types, a nominally pure grade (type 1), a Cr doped one (type 2), and two different grades doped with Ni and Cr (types 3 and 4). Table I shows the concentration of the impurities in these samples as obtained by wet chemical analysis. Other impurities, like Fe, Mn, V, Ti, and Mg, are below the detection limit (around 10 ppm). The orientation of the samples was unknown.

## RESULTS

The chemical analysis results are in agreement with the optical absorption measured on the as-received samples. The optical absorption measurements are shown in Fig. 1. Type 1 samples [Fig. 1(a)] show two very small peaked bands at 3.45 and 5.4 eV and a steady increase in the deep UV. This spectrum is very similar to those observed in other nominally pure samples,<sup>1,8–10</sup> and the observed bands have been associated with residual impurities. Type 2 [Fig. 1(b)] shows several peaked bands at 2.25, 3.1, and 5.4 eV, a small band at 4.8 eV, and a sharp increase in the UV. This increase and the bands at 2.25 and 3.1 eV are undoubtedly associated with the presence of Cr<sup>3+</sup> (see Refs. 4 and 9).

Types 3 and 4 show very similar spectra [Figs. 1(c) and 1(d)] but with different intensities. They have a small band around 2.25 eV, two dominant bands at 3.1 and 4.4 eV, and a band again at 5.4 eV with a sharp increase in the UV. The bands at 3.1 and 4.4 eV are related to the presence of Ni<sup>3+</sup> (Refs. 9 and 11), in agreement with the chemical analysis results. The concentration of Ni is around a factor of two times higher in type 3 than in type 4, and the same relationship can be found for bands at 3.1 and 4.4 eV. Due to the high oscillator strength of the Ni<sup>3+</sup> (Ref. 9), a small concentration can be easily detected. The band at 2.25 eV and a part of it at 3.1 eV should be associated with the presence of Cr<sup>3+</sup>. These assignments are again consistent

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TABLE I. Impurity content (in ppm) of the samples used.

Impurity	Sample type			
	1	2	3	4
Cr	<22	>400	50	250
Ni	<10	<10	22	12

with the chemical analysis (type 4 has a higher Cr concentration and the 2.25 eV band is higher than for type 3). The UV increase may be related to the presence of both  $Ni^{3+}$  and  $Cr^{3+}$  (Ref. 9).

Some information about the mechanisms involved in the TL process can be obtained from the study of the changes induced by x-ray irradiation on the optical absorption spectra of the samples. Figure 1 also shows these changes for the sample types studied in this work. The largest change is observed for type 4 [Fig. 1(d)], which shows a notable increase in the heights of the bands in the region of 5–6 eV and an increase in the bands at 4.4 and 3.1 eV, indicating an increase of the  $Ni^{3+}$  concentration, together with a new band around 2.8 eV. Type 3 shows similar changes [Fig. 1(c)] after x-ray irradiation, but their absolute values are much smaller. In contrast, type 1 shows very small peaks at 1.8 and 3.2 eV, [Fig. 1(a)] together with a wide structure centered at 4 eV. The 4 eV structure has usually been associated with the presence of  $V$  centers.<sup>10</sup> Finally, type 2 shows an increase of the optical spectra around 4 to 5 eV [Fig. 1(b)], similar to the  $V$  band in the previous sample, and a decrease of the 2.25 and 3.1 bands due to a change of the  $Cr^{3+}$  concentration. All these effects disappear after annealing up to 900 °C.

TL glow curves have been obtained for the four sample types irradiated to 20 kGy (see Fig. 2). Type 1 samples shows two main peaks at 120 and 175 °C and a secondary peak at 290 °C. Type 2 shows light emission over a very wide temperature range with small peaks around 175, 275, and 360 °C. Both samples have their maximum intensities at much lower temperatures than those of types 3 and 4.

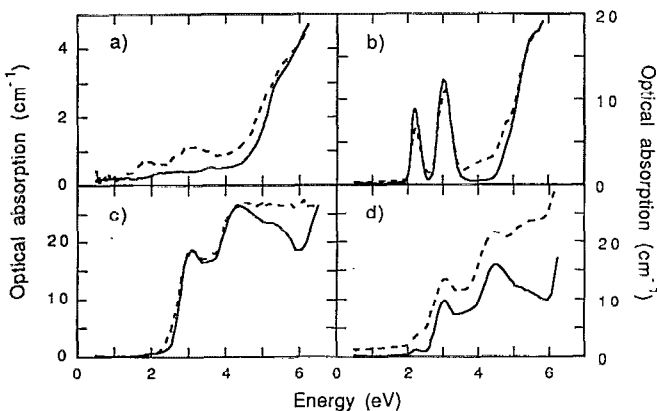


FIG. 1. Room temperature optical absorption spectra of sample (a) type 1, (b) type 2, (c) type 3, and (d) type 4 before (—) and after (---) x-ray irradiation up to 20 kGy.

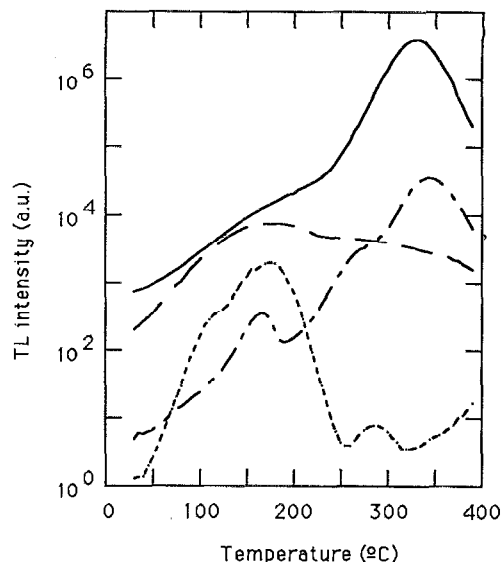


FIG. 2. TL glow curve after a room temperature x-ray irradiation (20 kGy) of sample type 1 (---), type 2 (—), type 3 (—), and type 4 (—).

The samples with higher Ni concentration (type 3) have small peaks at 175 and 275 °C and a dominant peak at 350 °C, whereas the one with a higher Cr concentration (type 4) shows a similar peak structure (small peaks at 175 and 275 °C and a dominant one at 335 °C) with a much higher intensity. Type 4 samples show TL intensities 100 times higher than type 3, 500 times higher than type 2 samples, and 1000 times higher than type 1. It should be noted that the TL intensities of Fig. 3 and all the others in this work have been corrected by the photomultiplier response, taking into account the emission spectra. That means that the intensity axis is directly proportional to the number of emitted photons.

The emission spectra have been measured at different temperatures. For each sample type, all peaks demonstrate the same emission. Representative spectra for each sample type can be found in Fig. 3. All the samples show an intensive emission around 1.78 eV with two broad side bands

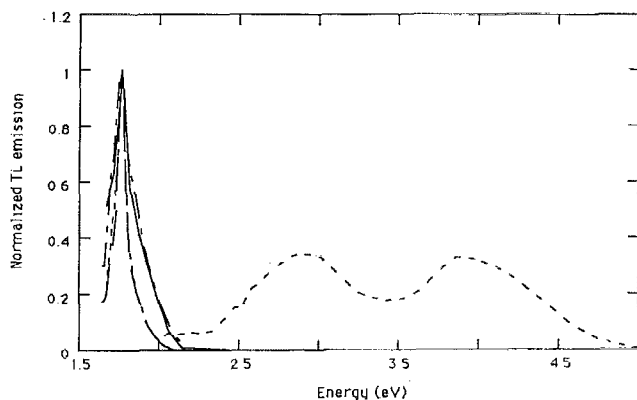


FIG. 3. Normalized emission spectra of sample type 1 (---) at 175, type 2 (---) at 175, type 3 (—) at 330, and type 4 (—) at 330 °C.

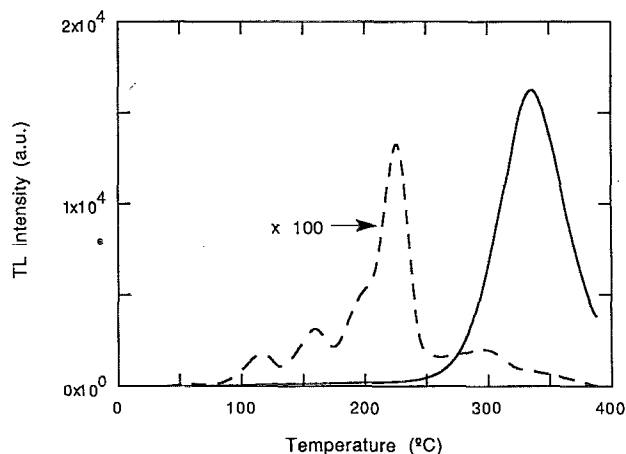


FIG. 4. TL glow curve after a room temperature x-ray irradiation up to a dose around 330 Gy of sample type 4 (—) and a TLD-100 dosimeter (---).

at 1.72 and 1.84 eV. This emission broadens with temperature, the reason being because the 1.75 eV band for sample types 3 and 4 (taken at around 330 °C) is broader than the same emission of sample types 1 and 2 (taken at 175 °C). This emission is generally associated with excited  $\text{Cr}^{3+}$  (Refs. 4 and 10). This assignment is consistent with the known presence of  $\text{Cr}^{3+}$  in these samples, as observed by optical absorption. This is the only emission in crystal types 2, 3, and 4, but in crystal type 1 two emission bands around 2.9 and 4 eV are also observed. These have been previously observed in pure  $\text{Al}_2\text{O}_3$  crystals<sup>1,6</sup> and have been attributed to recombination processes in  $\text{F}$  and  $\text{F}^+$  centers.

The high intensity of the TL glow curve for sample type 4 suggests its possible use as a dosimeter material. To check this possibility the TL glow curve has been compared, at several doses, to that obtained from a TLD-100 dosimeter. It was found that the total number of photons emitted by sample type 4 is 150 times more intense. Figure 4 shows the results obtained for a dose of about 330 Gy.

Figure 5 shows the x-ray dose dependence of the TL peak height for sample types 1, 3, and 4. Type 1 saturates at low dose, typical of nominally pure materials,<sup>10</sup> whereas types 3 and 4 do not show saturation up to a dose of over 5000 Gy. For lower doses they show a sublinear dependence over at least three orders of magnitude. This dose dependence is very similar to that found in other "dosimetric" aluminum oxide crystals<sup>1,12</sup> and has a very high saturation level compared to the behavior of pure grades. A small shift of the peak position has been found as well as a higher half-width for low doses in type 4. This behavior is not observed in any of the other materials. Figure 6 shows the peak position and the half-width as a function of the dose for sample types 3 and 4.

## DISCUSSION

As mentioned earlier, the 2.25 and 3.1 eV optical absorption bands observed in sample types 2, 3, and 4 are due to the presence of  $\text{Cr}^{3+}$ , whereas the bands at 3.1 and 4.4

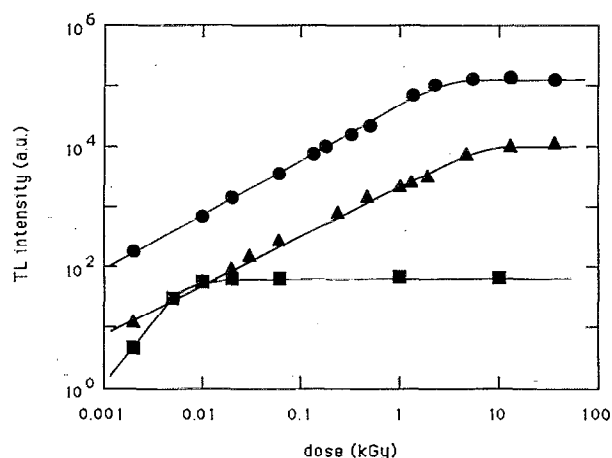


FIG. 5. Dose dependence of the 175 °C TL peak height for sample type 1 (■), type 3 (▲), and type 4 (●).

eV in sample types 3 and 4 are related to  $\text{Ni}^{3+}$ . In addition to these bands, in the optical absorption spectra a band at 5.4 eV has been observed in all the samples analyzed, although with very different relative intensity. This band could be related to oxygen vacancies ( $\text{F}^+$  center) or  $\text{Cr}^{2+}$  centers. The first possibility is supported by the presence of a small absorption band at 4.8 eV for type 2 (the  $\text{F}^+$  centers has two characteristic absorption bands at 4.8 and 5.4 eV<sup>1</sup>) and the emission of light at 4 eV (also a characteristic of  $\text{F}^+$  centers<sup>1</sup>) during the TL of type 1. Sometimes centers associated with the presence of oxygen vacancies appear as a consequence of the growth process. However, the concentration of these oxygen vacancies is small. Assuming an oscillator strength of 1, usual in these

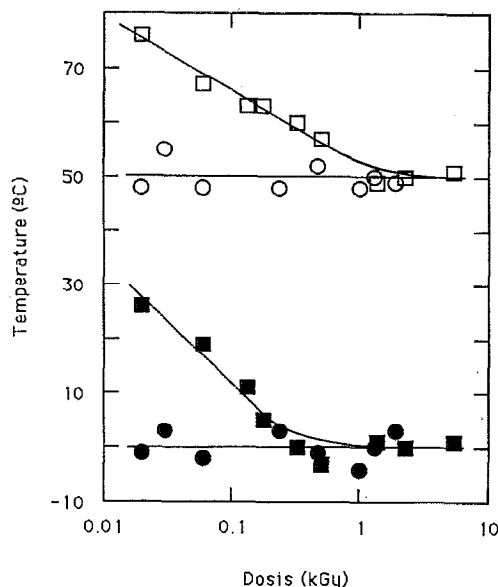


FIG. 6. Dose dependence of the half width (open symbols) and shift of the temperature at the 330 °C TL peak maximum (full symbol) for sample types 3 (○) and type 4 (□).

materials,<sup>13</sup> and a half width of 0.7 eV, the estimated concentration of F type centers, using the Smakula formula,<sup>14</sup> will be around  $10^{16}$ – $10^{17}$  cm<sup>-3</sup> for the different sample types. The band at 5.4 eV has been also attributed to the presence of Cr<sup>2+</sup> (Ref. 1). However, the data available makes it difficult to discriminate between these alternatives.

The TL results obtained for the type 1 samples (nominally pure crystal) are in close agreement, both in peak positions and emission bands, to those observed in other pure samples and previously published<sup>10</sup> where all the observed peaks are related to the release of holes from V-type centers.

The TL of sample type 2 shows a unique feature as light emission occurs over the whole temperature range from 100 to 250 °C, without isolated peaks. This behavior has been previously observed.<sup>6</sup> It is not clearly understood but seems to be related to Cr<sup>3+</sup> concentration. For low concentration isolated sharp peaks are measured, but these broaden and shift with increasing Cr<sup>3+</sup> concentration and a very low continuous TL is observed over the whole temperature range.

The role of Cr<sup>3+</sup> in sample type 2 is clearly confirmed by the optical absorption measurements by which it is possible to observe a clear decrease of Cr<sup>3+</sup> concentration after irradiation [Fig. 1(b)]. During the whole annealing process, emission associated with Cr<sup>3+</sup> is clearly visible (Fig. 3). The decrease of Cr<sup>3+</sup> after x-ray irradiation can be caused by the formation of Cr<sup>2+</sup> or Cr<sup>4+</sup>. The formation of Cr<sup>4+</sup> seems more probable because the absorption band at 5.4 eV (associated with Cr<sup>2+</sup>)<sup>1</sup> does not increase. Hence, the x-ray irradiation of sample type 2 induces an increase of Cr<sup>4+</sup> concentration by releasing one electron from the Cr<sup>3+</sup> ions. This process is reversed during heating up to 400 °C by the recombination of an electron to the hole located at the Cr<sup>4+</sup> site or by the release of the hole by the Cr<sup>4+</sup> and its recombination at another site. Both processes can be accompanied by light emission associated with Cr<sup>3+</sup>.

The TL glow curves found for sample types 3 and 4, in spite of their different intensities, show a similar shape to a main high temperature peak (330–350 °C). In the literature there are very few references to high temperature peaks and usually it is not the dominant feature of the spectra.<sup>4–6,15</sup> Kvapil *et al.*<sup>5</sup> observed a peak at 320 °C associated with the release of holes from the Cr<sup>4+</sup> ions in samples of Al<sub>2</sub>O<sub>3</sub> doped with Cr and its growth under reducing conditions, whereas Kalfky *et al.*<sup>16</sup> found a thermostimulated current (TSC) peak at 315 °C related to the release of electrons from some undetermined centers. The observation of very high TL intensity for sample type 4 makes the study of this peak and the determination of its parameters an interesting subject.

The optical absorption spectra before irradiation [Figs. 1(c) and 1(d)] indicate that most of the Ni impurities in sample types 3 and 4 are in the Ni<sup>3+</sup> form. The increase in the 3.1 and 4.4 eV bands as a result of x-ray irradiation [Fig. 1(d)] suggests that some Ni<sup>2+</sup> should be present. The observed increase at 5 to 6 eV can be associated with an increase in the concentration of F centers. This fact, to-

TABLE II. Activation energy and kinetics order obtained for sample types 3 and 4, using different fitting procedures.

Fitting method	Sample type 3		Sample type 4	
	<i>b</i>	<i>E</i>	<i>b</i>	<i>E</i>
Initial slope		1.8±0.2		1.7±0.1
Peak shape	1.1±0.1	1.8±0.05	1.6±0.1	1.9±0.1
Whole curve	1.1±0.1	1.7±0.1	1.6±0.1	1.8±0.1
Curve fitting	1.0±0.1	1.9±0.1	1.7±0.1	1.85±0.1

gether with the previously mentioned increase of Ni<sup>3+</sup> concentration, gives added support to the suggested presence of F<sup>+</sup> centers in all the samples studied.

The similarities between the TL glow curve shape (Fig. 2), emission spectra (Fig. 3), and dose dependence (Fig. 5) of sample types 3 and 4, together with the similar optical absorption spectra and their response to x-ray irradiation, suggest that the observed high temperature peaks are associated with the same process, in spite of the slightly different temperature in the maximum and in the kinetics parameter (this will be discussed later). The observed differences could be related to changes in the relative concentration of the defects involved.

Taking into account that this peak is not observed here in sample type 2, nor is it reported in other papers in which samples doped with Cr are analyzed,<sup>6</sup> it is clear that the origin of this peak is not only related to Cr, but that the presence of Ni or some other center associated with it is necessary since the observed emission at 1.78 eV is undoubtedly related to Cr<sup>3+</sup> emission.

The 335 °C peak of sample type 4 appears at higher temperatures and is wider for small irradiation doses (Fig. 6). This behavior is typical of charge release processes with a kinetics order parameter different from first order.<sup>17</sup> This effect is not observed for sample types 1 and 3. An estimation of the kinetic parameter for the different peaks can be obtained from the shape of the peak, using the procedure developed by Chen,<sup>17</sup> who computed the geometrical factor  $\mu_g$  ( $\mu_g = \delta/\omega$ , where  $\delta = T_2 - T_m$ ,  $\omega = T_2 - T_1$ , and  $T_m$  is the temperature of the maximum and  $T_1$ ,  $T_2$  are the low and high temperatures at which the intensity is half of the maximum).  $\mu_g$  has been calculated for the high temperature peak of sample types 3 and 4 at different doses. The results were 0.43 and 0.50, respectively, and do not depend on dose. The kinetics order factor *b* can be estimated from the geometrical factor  $\mu_g$ , using a relationship between them.<sup>17</sup> The results are  $1.1 \pm 0.1$  and  $1.7 \pm 0.1$  for sample types 3 and 4. Using these numbers, it is possible also to calculate the activation energy *E*. The values obtained can be found in Table II, together with those obtained using other fitting procedures like the initial slope [by which *E* is obtained from the slope of the representation of  $\ln(I)$  vs  $1/kT$ ], the whole curve analysis [by which *E* and *b* are estimated from the slope of the straight line obtained from the representation of  $\ln(I/n^b)$  vs  $1/kT$  if *b* is correct],<sup>17</sup> and the curve fitting to an analytical expression (by which a procedure<sup>18</sup> has been used with the analytical expression for the peak shape modified to a more general one). In

general, it has been found that the activation energy is the same about  $1.8 \pm 0.2$  eV for sample types 3 and 4, whereas the kinetic order is different and is around 1.1 and 1.6, respectively.

## CONCLUSIONS

In this work the TL glow curve of several nominally pure and doped  $\text{Al}_2\text{O}_3$  samples has been studied. It has been found that the addition of Ni to samples doped with Cr induces a completely different TL glow curve, with a main peak at 330–350 °C, together with the presence of  $\text{F}^+$  centers that are, in some way, involved in the charge release process. The intensity of this peak can be very high for some concentrations of Ni and Cr, suggesting its possible use as a radiation sensitive material. Sample type 4 shows a photon emission 150 times higher than by TLD-100 dosimeters for the same irradiation dose. More work is necessary to optimize the Ni and Cr concentration and to determine the charge carrier responsible for the observed TL process and the trapping and recombination centers involved in the light emission.

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