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# Correlation between Fe, Cr, and the broad red emission band in $\gamma$-ray-irradiated MgO

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Absorption and luminescence spectra for MgO have been obtained during $\gamma$-ray irradiation and subsequent thermal annealing. The growth and annealing of the $Fe^{3+}$ band is attributed to the existence of various electron-trapping centers. A clear correlation is observed between Fe and Cr, with $Cr^{3+}$ acting as an electron trap during irradiation. In addition, the results indicate that the broad-band emission at 700 nm is most likely due to $Fe^{2+}$, arising from reactions of the type $Fe^{3+}+e^-$ and $V+Fe^{1+}$.

## I. INTRODUCTION

From the large amount of data which now exists for x- and $\gamma$-ray-irradiated MgO, it has become quite clear that significant electronic charge-transfer processes occur both during irradiation and on subsequent thermal annealing. This is evidenced especially by the observed valence changes of the ever present impurities, and by the growth and annealing of $V$-type centers.[1-3] The observable effects of a number of defect centers which participate in the charge-transfer processes have been positively identified, and, in particular, the $Fe^{3+}$ absorption band at 290 nm,[4,5] the $V$-type—center bands between about 500 and 600 nm,[1,5,6] and the $Cr^{3+}$ emission lines at 700 and 720 nm,$^{-1}$ are well documented. However, to date the inter-relation between the different defect centers remains to a large extent an open question, as does also the nature of the broad emission bands at around 400 and 700 nm observed in both radioluminescence (RL) and thermoluminescence (TL). The difficulty arises from the large and varied impurity content of MgO, and hence is to be expected when one is attempting to correlate data not only from different samples but also from different experiments in which a wide range of experimental conditions exists. Clearly these limitations are of paramount importance when one is dealing with different processes which may be competing in the release and trapping of charge both during irradiation and thermal annealing.

To minimize these problems the results presented here have been obtained for a single sample observed *in situ* both during and following irradiation. The results are concerned almost exclusively with Fe and Cr, and show an important inter-relation between these impurities, $Cr^{3+}$ being observed as an electron-trapping center. In addition, the results strongly suggest that the broad 700-nm emission band is due to $Fe^{2+}$.

## II. EXPERIMENTAL PROCEDURE

The experimental setup consists of a sample chamber mounted in the beam line of a HVEC 2-MeV Van de Graaff accelerator, together with a spectrophotometer system which permits in-beam measurements of both optical-absorption and light-emission spectra. The sample mount contains a heating element which permits the sample to be heated in vacuum ($\lesssim 2\times10^{-6}$ Torr) linearly from 10 °C to 650 °C. In this way once the sample is mounted it may be heated, cooled, and observed optically both during, and following irradiation without further handling. Sample irradiation can be done directly with electrons of up to 2 MeV, or with bremsstrahlung $\gamma$ rays produced by stopping the electron beam in a gold target.

A single MgO crystal ($5\times5\times1$ mm$^3$) from W. C. Spicer (99.99% purity; see Table I for impurity analysis), was heated to 600 °C and then allowed to cool slowly. Following this initial treatment, the sample was repeatedly irradiated at 20 °C and 120 °C with bremsstrahlung $\gamma$ rays at $3.5\times10^4$ rad h$^{-1}$ for 7 h. During irradiation, absorption spectra from 224 to 700 nm were recorded; the RL was too weak to be monochromatically observed. Following each irradiation the sample was heated to 600 °C at 10 °C min$^{-1}$. During these thermal annealings observations were made in four different ways: absorption spectra and total light emission between scans, continuous TL glow peaks, wavelength-resolved TL spectra between 250 and 800 nm (10 °C per scan), and wavelength-resolved TL spectra between 644 and 794 nm (4 °C per scan). Owing to red emission from the sample oven, optical-absorption spectra could only be recorded up to about 300 °C. In addition, a final irradiation was made and the sample removed. Photostimulation spectra for the $Cr^{3+}$ emission were obtained for the irradiated and then annealed sample in a Jobin-Yvon JY3 spectrofluorometer. A further sam-

TABLE I. Sample impurity content in ppm ($w$).

| Impurity | Al | Ca | Cr | Fe | Mn | Na | Ni | Ti | V |
|---|---|---|---|---|---|---|---|---|---|
| Sample 1 | 160 | 180 | 90 | 160 | 10 | 440 | 30 | 10 | 5 |
| Sample 2 | 190 | 195 | 20 | 260 | 10 | 370 | 36 | 10 | 5 |

ple cleaved from the same crystal block was irradiated directly with 250-keV electrons ($\sim 10^5$ rad h$^{-1}$) to observe RL spectra between 20 °C and 200 °C. Finally, both samples were chemically analyzed. Computer fitting has been used to treat both the optical-absorption spectra and the light-emission spectra.

## III. RESULTS

The inset of Fig. 1 shows the absorption spectrum for the main sample as cleaved and following heating to 600 °C, indicating an increase in the 290-nm Fe$^{3+}$ absorption band. A very similar effect was observed for the second sample. This may be due to the different cooling rate in the annealed sample relative to that of the crystal formed in the production melt.[7] For all the results the absorption spectrum obtained following the 600 °C annealing was taken as the zero spectrum. Following irradiation, heating to 600 °C was found to anneal the observed induced defects, reproducing the zero spectrum. With this treatment the results were reproducible upon reirradiation.

During irradiation at 20 °C the most important change is a monotonic increase in the Fe$^{3+}$ absorption band at 290 nm (Fig. 1). Upon heating immediately following irradiation, the Fe$^{3+}$ band is observed to anneal in several steps (Fig. 1), at about 80 °C, 170 °C, and at least one more step (unobserved) between 300 °C and 600 °C, by which temperature annealing is complete. Differential analysis ($\Delta\mathrm{Fe}^{3+}/\Delta T$) of the 80 °C annealing stage shows a composite nature consisting of two annealing steps, a main step centered at 80 °C and a secondary step between about 90° and 120 °C. Irradiation at 120 °C produces a similar smaller monotonic increase in the Fe$^{3+}$ band, and subsequent annealing follows the 20 °C case (without the 80 °C annealing stage); see Fig. 1. In addition, a broad region between about 500 and 600 nm is observed to grow during the 20 °C irradiation, consistent with several unresolved bands. Absorption bands in this region are known to correspond to different types of $V$ centers.[1,5,6,8] Upon heating, the bands are observed to anneal essentially in a single step between 40° and 70 °C, a slight difference being observed depending on the wavelength. In Fig. 1 this behavior is shown for 540 nm (corresponding to the region of $V^0$, $V^-$, and $V_{\mathrm{Al}}$) and 570 nm ($V_{\mathrm{OH}}$). $V^0$ and $V_{\mathrm{OH}}$ annealing together with a TL glow peak have been observed to occur between about 50 °C and 60 °C,[9] in complete agreement with these observations.

The light emission observed during the optical-absorption thermal annealing shows two separate peaks at about 80 °C and 170 °C, coinciding with the Fe$^{3+}$ annealing (Fig. 1). In order to obtain better temperature resolution as well as wavelength-resolved TL spectra, this light emission has also been observed during annealing as TL glow peaks (total emission), wavelength-resolved spectra from 250 to 800 nm, and wavelength-resolved spectra from 644 to 794 nm; to observe the main TL emission at about 700 nm, see Figs. 2 and 3. The TL glow peaks (Fig. 2) indicate that the light emission observed at about 80 °C is composed of three unresolved peaks at approximately 55 °C, 82 °C, and 105 °C (a similar composition has been observed by Ziniker *et al.*[10] with three unresolved peaks at about 72 °C, 90 °C, and 102 °C). The monochromatic TL scans show that all the TL peaks (55 °C, 82 °C, 105 °C, and 170 °C) are composed predominantly of a broad emission band at about 700 nm. The 82 °C peak (between about 65 °C and 90 °C) is observed together with the characteristic Cr$^{3+}$ lines at 700 and 720 nm; see Fig. 3. These lines are not observed outside this temperature range although the intensity of the 700-nm broadband is still high. In ad-

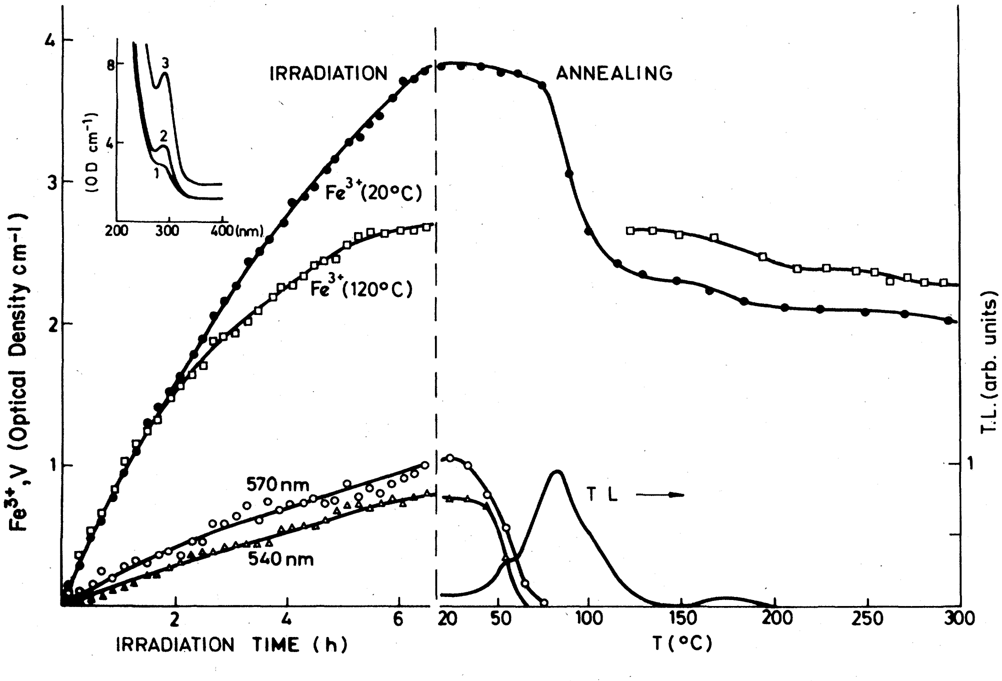

FIG. 1. Growth and annealing of the Fe$^{3+}$ and $V$-type centers, together with the TL emission. The inset shows the Fe$^{3+}$ band in the (1) as-cleaved sample (2), the sample heated to 600 °C, and (3) the irradiated sample.

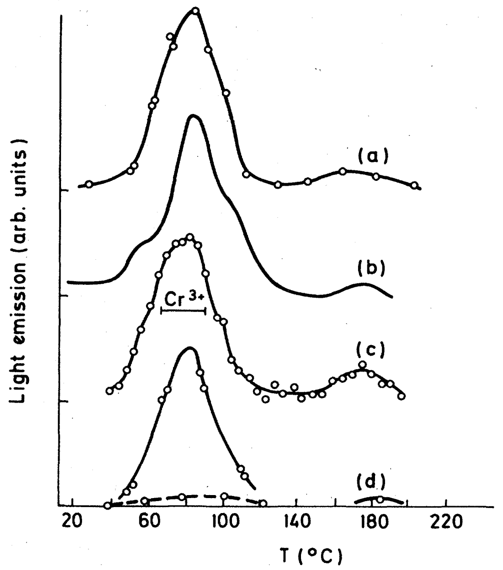

FIG. 2. TL spectra: (a) Between absorption-spectra annealing scans. (b) Full TL glow peaks. (c) 700-nm broadband intensity obtained from fast scans. The temperature range of $Cr^{3+}$ emission is indicated. (d) 700-nm (solid line) and 400-nm (dashed line) intensities obtained from slow scans.

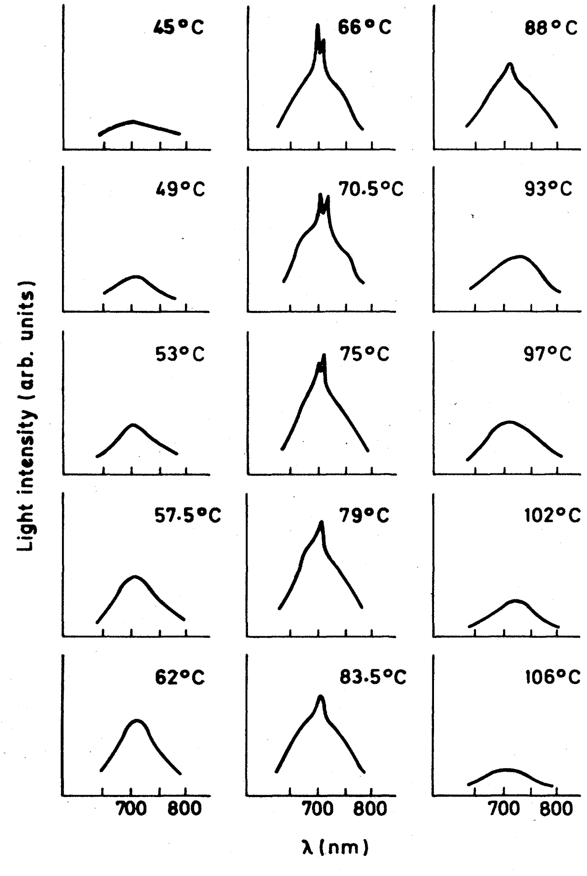

FIG. 3. Spectra observed (fast scans) during the main TL emission. The temperatures correspond to midscan (700 nm).

dition, a weak emission band near 400 nm is observed between 40 °C and 120 °C (Fig. 2). Photostimulation results obtained by excitation at 455 nm (maximum of one of the $Cr^{3+}$ excitation bands[11]) and by observing the $Cr^{3+}$-line emissions indicate that upon irradiation about 40% of the $Cr^{3+}$ is suppressed.

In order to obtain more information about the observed light emissions, a second sample was irradiated directly with 250-keV electrons and the RL spectrum measured. These supplementary results may be summarized as follows. Two emission bands are observed at about 376 and 700 nm, both with structure. The 700-nm emission increases during irradiation and consists of the characteristic $Cr^{3+}$ lines together with an underlying band. Upon increasing the temperature from 20 °C to 200 °C the $Cr^{3+}$ lines are observed with continually decreasing resolution, and, in particular, in the range 50° to 100 °C the resolution is comparable with that observed in the TL measurements and shows that the failure to observe $Cr^{3+}$ lines above 90 °C in TL is not merely a temperature effect. Finally, the results of the chemical analysis for the two samples are given in Table I.

## IV. DISCUSSION

### A. Cr-Fe relation

The observed form of the $Fe^{3+}$-band growth during irradiation at 20 °C and 120 °C, and band annealing in distinct steps, is consistent with a reversible process in which $Fe^{3+}$ is formed upon irradiation due to the excitation of $Fe^{2+}$ and subsequent electron capture at different types of traps; thermal release of these trapped electrons and recapture at $Fe^{3+}$ leads to the observed structured annealing. That electrons rather than holes are involved is evident from the existence of several $Fe^{3+}$ annealing stages; hole release upon annealing would lead to a single stage. The growth of the $Fe^{3+}$ band upon irradiation at 120 °C is as would be expected if the electron traps responsible for the 80 °C stage were unstable. An analogous structure exists in the alkali halides in which a correlation between the *F*-center growth and annealing has been observed due to the existence of several distinct interstitial traps.[12] Abramishvili *et al.*[13] have also observed $Fe^{3+}$ in MgO anneal in various stages following irradiation, in agreement with our observations.

The 700-nm TL peaks at 82 °C, 105 °C, and 170 °C correlate perfectly with the observed $Fe^{3+}$ annealing steps not only in position but also in width and intensity (see Table II). Moreover, the 82 °C peak which correlates with the main $Fe^{3+}$ annealing step is observed with the $Cr^{3+}$-line structure (Figs. 1 and 3). This observed correlation is consistent with an interaction between Fe and Cr during annealing of the form

$$Fe^{3+}+Cr^{2+}\rightarrow Fe^{2+}+Cr^{3} .$$

The component structure of the $Fe^{3+}$ band growth as evidenced by the difference observed between the 20 °C and 120 °C irradiations implies that the reverse reaction, $Fe^{2+}+Cr^{3+}\rightarrow Fe^{3+}+Cr^{2+}$, occurs during irradiation, with $Cr^{3+}$ acting as an electron trap. The number of

TABLE II. Number of $Fe^{3+}$ and $V$-type centers annealed and $Cr^{3+}$ formed together with the 700-nm broadband intensity for each annealing step. The light intensity has been normalized to 10 for the 82 °C step.

| $T$ (°C) | 55 | 82 | 105 | 170 |
|---|---|---|---|---|
| $Fe^{3+}$ ($10^{17}$ cm$^{-3}$) | | 10±2 | 2.3±0.6 | 1.5±0.3 |
| $Cr^{3+}$ ($10^{17}$ cm$^{-3}$) | | 12±3 | | |
| $V$ ($10^{17}$ cm$^{-3}$) | ~1 | | | |
| 700 nm (a.u.) | 1.1±0.1 | 10 | 2.7±0.3 | 1.7±0.3 |

$Fe^{3+}$ ions involved in the 80 °C step has been calculated using published oscillator-strength values for the $Fe^{3+}$ 290-nm band[14] and agrees well with the number of $Cr^{3+}$ ions involved in this step as calculated from the photostimulation results and the chemical analysis (see Table II).

A relationship between Cr and Fe has been previously suggested[13,15,16] based on EPR observations; however, a precise correlation was not observed. $Cr^{3+}$ has been reported to have a large electron-capture cross section,[15,17] and, furthermore, has been observed to recover upon annealing in a single narrow step at about 70 °C.[8] All these results are consistent with our findings.

The Cr-Fe reaction does not account for all the observed $Fe^{3+}$ annealing steps; clearly, other electron-trapping centers must be involved. Possible candidates are $Mn^{3+}$, $V^{3+}$, $Ti^{4+}$ and $Co^{2+}$, and even $Fe^{2+}$, a small proportion of which is known to change to $Fe^{1+}$ on irradiation.

### B. Nature of the broad emission band at 700 nm

In general, red emission in MgO has been almost exclusively associated with Cr, in many cases without actually observing the $Cr^{3+}$ lines or only performing a single monochromator scan at a glow-peak maximum.[1,2,10] However, doubts about absorption-band and emission assignment in MgO have been expressed,[18] and, in particular, regarding the nature of the broad, red emission band at 700 nm.[10,17,19] TL measurements in MgO with different Cr content indicate that the line and broadband emissions are of a different nature.[17] Our TL measurements support this view. Both Mn (Ref. 17) and Fe (Refs. 10 and 19) have been suggested to be responsible for the broad red emission. Our results are consistent with $Fe^{3+}+e^{-}\rightarrow Fe^{2+}+h\nu$ giving rise to the red-band emission, which is observed in all the $Fe^{3+}$ annealing steps. The correlation between the $Fe^{3+}$ annealing steps and the 700-nm band-emission intensity is given in Table II.

### C. $V$-center annealing

$Fe^{3+}$ annealing does not account for all the TL emission observed. In these experiments there was little $V$-center production ($\leq 10^{17}$cm$^{-3}$). Both the thermal treatment (slow cooling from 600 °C) and the impurity content (in particular, Cr, Mn, and Ti) are known to reduce $V$-center production.[5] However, the annealing of the $V$ centers observed correlates with the 55 °C TL emission (Fig. 1). This light emission consists of a broadband at 700 nm identical to that observed with the $Fe^{3+}$ annealing stages, and would suggest a reaction of the form $V+Fe^{1+}\rightarrow Fe^{2+}+h\nu$. In this case the intensity of the 700-nm emission band and the number of $V$ centers annealed should be in the same ratio as the 700 nm intensity-$Fe^{3+}$ step. This is indeed the case, as may be seen in Table II. A reaction between $Fe^{1+}$ and $V$ centers has been tentatively suggested to explain $Fe^{1+}$ annealing observed to occur somewhere between 20 °C and 100 °C.[20,21]

## V. CONCLUSIONS

The results presented here indicate a clear correlation between Cr and Fe both during irradiation and upon annealing, in which $Cr^{3+}$ acts as an electron trap. This relationship observed despite the occurrence of numerous trapping and release processes would suggest that Cr and Fe exist in close positions within the crystal lattice. The observations support other findings that the red emission around 700 nm is not entirely due to $Cr^{3+}$, and point to $Fe^{2+}$ as the most likely source. $V$-type—center annealing has been observed to lead to the 700-nm band emission and is most probably associated with an $Fe^{1+}$-to-$Fe^{2+}$ change.

It is clear that within a relatively narrow temperature range numerous processes are involved in the annealing of irradiated MgO. The relative importance of these processes will strongly depend on the impurity content and treatment of the samples used. For example, cases in which the iron content is significantly lower, but with important $V$-center formation, could lead to a dominant TL process associated with $V$-center annealing. With these considerations in mind it is not surprising that so many different and apparently conflicting conclusions have been reached. Neither pulsed-annealing nor TL measurements without continuous monochromatic scanning are adequate methods to study these processes.

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