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# Intrinsic Defects in UV-irradiated MgO Single Crystal Detected by Thermoluminescence

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**Abstract:** The Thermoluminescence (TL) properties of an MgO single crystal sample were studied from 170 to 500°K after UV-irradiation (4.8 eV for 10 min). The aim of this study was to determine the MgO intrinsic defects centers and in particular the F, $F^+$, $F_2$ and $F_{cat}$ centers, these defects are localized in the 270-570 nm region, their TL signal was characterized by four emission bands detected at wavelengths 540, 380, 350 and 290 nm, respectively.

**Key words:** Thermoluminescence, MgO, intrinsic defects F, $F^+$, UV irradiation, deconvolution

## INTRODUCTION

Nominally pure α-$Al_2O_3$ and MgO single crystals are excellent electrical insulators. At room temperature their electrical conductivities are respectively on the order of $10^{-18}$ and $10^{-20}$ $\Omega^{-1}$ $cm^{-1}$[1]. In addition to many applications, MgO single crystals have a promising application as a substrate for thin film production and in particular for superconducting thin film fabrication[2]. Defects in the MgO single crystals, such as anion or cation vacancies and the processes involving these defects (their formation, migration, localization, clustering, trapping, thermal release of charge carriers, luminescence, etc.) have been largely investigated in the literature[3]. These defects play a significant role in the radiative emission. Luminescence can be used as an indicator of the presence of lattice defects in insulator or semiconductor material.

The search for the F and $F^+$ centers in MgO, that is, the oxygen ion vacancies containing two and one electron, respectively, has a long history[4,5]. The $F_2$ centers are defined as oxygen divacancies[6] while the $F_{cat}$ centers correspond to $F^+$ center adjacent to divalent cation $Ca^{2+}$ impurity[7].

The aim of this study was to determine the intrinsic defects (F, $F^+$, $F_2$ and $F_{cat}$ centers). The measurements was carried out using Thermoluminescence (TL) and absorbance techniques. The deconvolution method have been used in the determination of the emission bands related to these defects.

## MATERIALS AND METHODS

Kappers *et al.*[4] measured a 392 nm (3.16 eV) peak at 298°K which at 77 °K is 385 nm (3.22 eV). These results agree well with values obtained by Chen *et al.*[8] who identified this luminescence as due to the $F^+$ centers. A second peak was observed at 516 nm (2.4 eV) and attributed to the F' centers. In MgO material both the $F^+$ center and F center have their primary optical-absorption transition near 5 eV[9]. Excitation at this energy produces, in general, two luminescence bands, one at 3.22 eV and the other at 2.3 eV[9-11]. INDO calculations[12-14] of optical properties of $F^+$ and F centers in MgO have been compared with the experimental measurements (Table 1 and 2).

Kawaguchi[15] assigned the weak emission band around 400-500 nm to F type centers. In Photoluminescence (PL), Rosenblatt *et al.*[16] reported the 390 and 530 nm bands in time-resolved spectra of MgO different defect densities and attributed the bands to $F^+$ and F center. Bulk F and $F^+$ centers in MgO give rise to an intense absorption band at around 5 eV. Kappers *et al.*[4] also found that due to $F^+$ and F centers, the band is actually the convolution of two distinct absorption bands at 4.96 and 5.03 eV. Under neutron irradiation other bands at 3.5, 2.1 and 1.2 eV have been observed and associated to the presence of aggregates of F centers[9,17]. In the optical absorption used to characterize the defects, Caceres *et al.*[6] attributed the absorption at 252 nm (4.92 eV) to $F^+$ and the absorption at

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Table 1: Calculated absorption and luminescence energies in MgO and $\alpha$-$Al_2O_3$

| | MgO | | $Al_2O_3$ | |
|---|---|---|---|---|
| Materials | $F^+$ (eV) | F (eV) | $F^+$ (eV) | F (eV) |
| Absorption | 4.97 | 4.98 | 5.2<br>5.5<br>5.8 | 5.9 |
| Luminescence | 3.60 | 2.61 (singlet)<br>2.72 (triplet) | 4.0 | 2.8 |

Table 2: Experimental measurements of optical properties for single vacancy centers in oxides (A: Absorption, L: Luminescence)

| | F center (eV) | | $F^+$ center (eV) | |
|---|---|---|---|---|
| Materials | A | L | A | L |
| MgO | 5 | 2.3 | 4.9 | 3.1 |
| $Al_2O_3$ | 6 | 3.0 | 6.3<br>5.4<br>4.8 | 3.8 |

Table 3: Experimental measurements of optical properties for dimer centers in oxides (A: Absorption, L: Luminescence)

| | $F_2$ (eV) | | $F_2^+$ (eV) | | $F_2^{2+}$ (eV) | |
|---|---|---|---|---|---|---|
| | A | L | A | L | A | L |
| MgO | 3.63 | 3.31 | | 2.61 | 3.82 | 2.81 |
| $Al_2O_3$ | 4.10 | 2.40 | 3.5 | 3.26 | 2.70 | 2.22 |

355 nm (3.49 eV) and 975 nm (1.27 eV) to the dimer centers $F_2$ (oxygen divacancies). Kotomin *et al.*[14] reported, as shown in the Table 3, experimental measurements of optical properties (luminescence and absorption) for dimer center in oxides.

In their TL analysis of $\alpha$-$Al_2O_3$ material, the electron trapped by an anion vacancy in the neighborhood of $Ca^{2+}$ impurities constitutes the $F_{cat}$ center corresponding to $F^+$ center adjacent to a divalent cation[7], where, the emission band is 285 nm[18].

In view of the above considerations, we can infer that emission from F, $F^+$, $F_2$ and $F_{cat}$ centers is in the 270-570 nm range.

Thermoluminescence and absorption measurements were carried out at the University of Science and Technology, Electronic Microscopy and Material Science Laboratory (2005). A single polished crystal MgO from Soekawa chemicals Japan is analyzed. It is well known that MgO crystals have the NaCl structure with a cubic-face-centered (cfc) Bravais lattice, the cubic lattice constant being 4.21Å. The crystals used has an area of 10 $mm^2$ and is 1 mm thick. A micro-probe analysis of this crystal showed an impurity content of K, Ca, Cr, Fe and Ni in small quantities. The thermoluminescence technique used is based on the thermal effects of MgO previously irradiated at a temperature of -100°C (170°K) by UV light (4.8 eV for 10 min) from a Hg lamp. The UV radiation populates various traps in the band gap. The MgO sample is then heated from 170 to 500°K. Thermoluminescence (TL) emission was measured using the Spectrograph CP200 Jobin Yvon connected to a CCD3000 (coupled charge device) cooled at 150°K. The analyzed wavelength range was 250-1200 nm with a 133 g $mm^{-1}$ grating. The TL spectrum were recorded and treated with Spectramax software, by means of Fourier self-deconvolution method which synthetically narrows the effective trace bandwidth features. This allows the identification the principal bands and it can also be useful for very accurate determination of the number of peaks, band positions and areas in a trace region.

## RESULTS AND DISCUSSION

In experimental procedure, the TL spectra recorded from -100°C (170°K) up to room temperature showed that the spectral intensity decreases, whereas in the second heating step, that is from room temperature up to 230°C(500°K). The intensity increases to a maximum peak at 110°C then start decreasing with increasing temperature (Fig. 1).

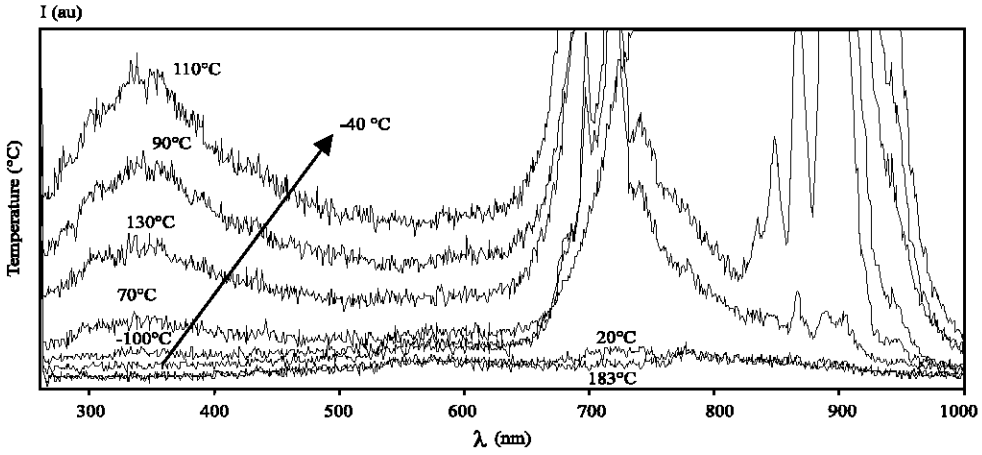


Fig. 1: TL measured spectra I = f ($\lambda$) for various temperatures (region of interest: 270-570 nm)

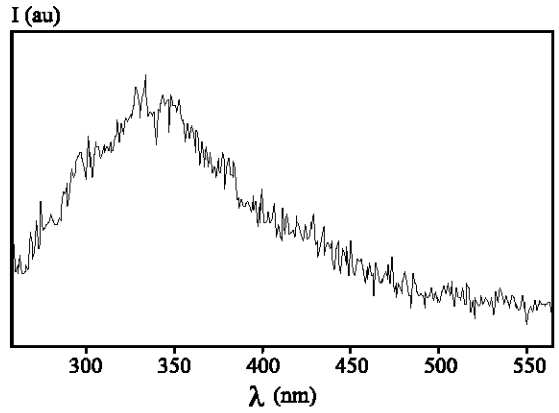


Fig. 2: Spectrum recorded at 110°C (380°K), region of interest (270-570 nm)

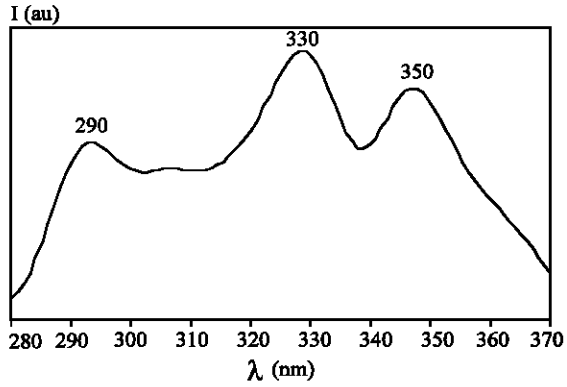


Fig. 3: Sub-region 270-360 nm deconvolution

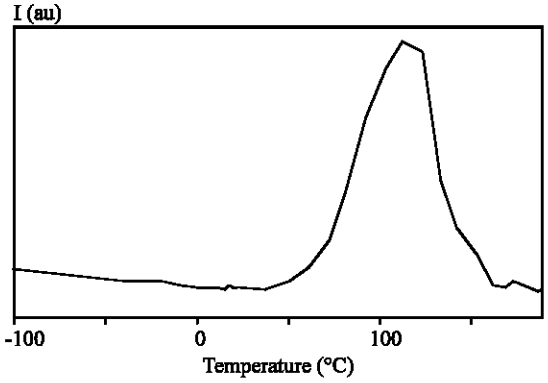


Fig. 4: TL-intensity curve versus temperature of the 290 nm band ($F_{cat}$)

Identifying the F, $F^+$, F and $F_{cat}$ centers in the 270-570 nm region, where emission bands are located, is rather difficult because of weak signal intensity. This is overcome by the use of deconvolution. In order to do this, we start by considering the largest signal, namely the 110°C spectrum (Fig. 2).

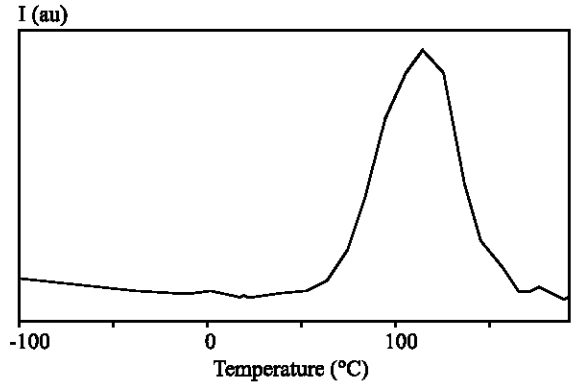


Fig. 5: TL-intensity curve versus temperature of the 350 nm band ($F_2$)

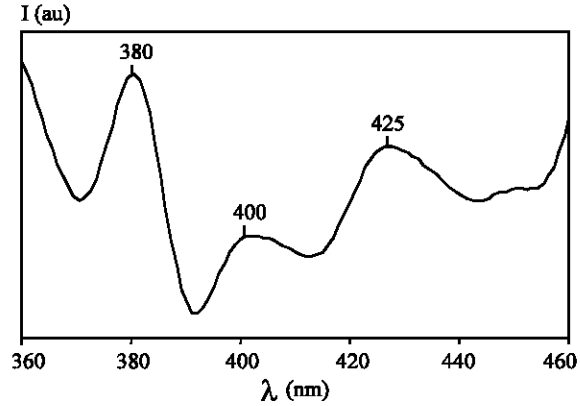


Fig. 6: Sub-region 360-460 nm deconvolution of the spectrum of Fig. 2

The deconvoluted region (270-570 nm) has been divided into three sub-regions (270-360 nm), (360-460 nm) and (460-570 nm) for more accuracy control. In the first sub-region emission bands 290, 330 and 350 nm can be seen Fig. 3. The 290 nm (4.27 eV) emission band is assigned to $F_{cat}$ center together with the $F_2$ center at 350 nm (3.54 eV), their corresponding TL-intensity curves are represented in Fig. 4 and 5, respectively.

In the second sub-region the emission bands recorded are 380, 400 and 425 nm (Fig. 6), the 380 nm (3.26 eV) emission band is probably due to the $F^+$center, its TL-intensity curve is represented in Fig. 7. In the last sub-region, however, the recorded emission bands are, 475, 510 and 540 nm (Fig. 8), the emission band recorded at 540 nm (2.3 eV) is attributed to the F center its TL curve is represented in Fig. 9.

The mechanism of F centers TL emission is closely linked to the release of the excited centers F and $F^+$, the excited states F*, $(F^+)$* is obtained when an electron is

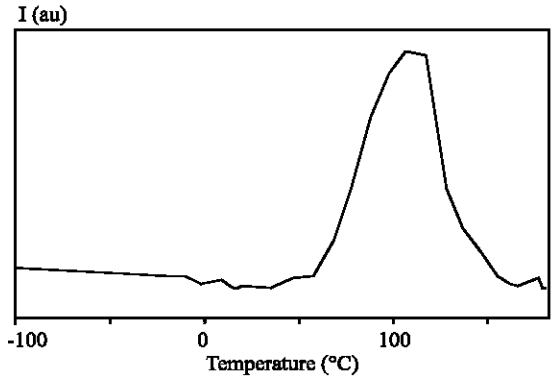


Fig. 7: TL-intensity curve versus temperature of the 380 nm band ($F^+$)

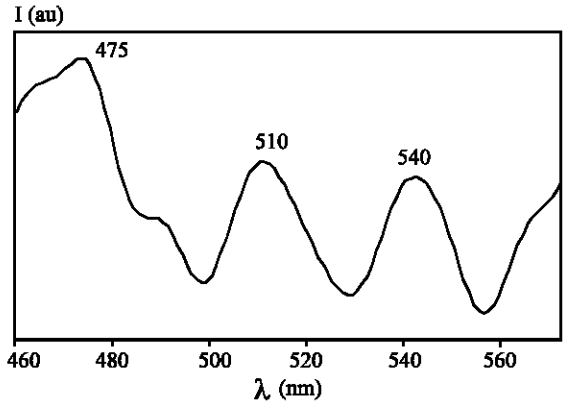


Fig. 8: Sub-region 460-570 nm deconvolution of spectrum of Fig. 2

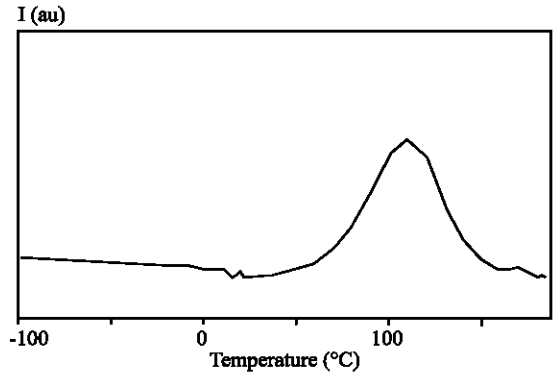


Fig. 9: TL-intensity curve versus temperature of the 540 nm band (F)

captured or when a hole is released by a trap, as illustrated below:

$F^+ + e^- \rightarrow (F)^* \rightarrow F + h\upsilon$ (540 nm)
$F + e^+ \rightarrow (F^+)^* \rightarrow F^+ + h\upsilon$ (380 nm)
$F^{2+} + e^- \rightarrow (F^+)^* \rightarrow F^+ + h\upsilon$ (380 nm)
Where, $F^{2+}$ is a non occupied oxygen vacancy.

In this TL experimental analysis of intrinsic defects in MgO single crystal (by considering the different irradiation techniques mentioned in the previous literature review), it can easily be noticed that results obtained in agree to a very high extent with results obtained elsewhere and come also to confirm some other undertaken studies.

## CONCLUSIONS

In this study the Thermoluminescence (TL) combined with absorbance and deconvolution method is used to characterize the intrinsic defects of MgO single crystal UV irradiated (4.8 eV), the analysis of results strongly indicates emission bands for F center at 540 nm, $F^+$ center at 380 nm, $F_2$ center at 350 nm and for the $F_{cat}$ an emission band at 290 nm.

The deconvolution method has enabled us to determine a certain number of identified emission bands. In near future studies, we intend to solve for the unidentified bands and attribute these bands to intrinsic and/or extrinsic defects.

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