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Extrinsic Defects in UV-irradiated MgO Single Crystal Detected by Thermoluminescence

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Abstract: MgO single crystal sample previously irradiated with ultraviolet light (UV) 4.8 eV has been studied using thermoluminescence (TL) technique in the temperature range 170-500°K, in this study, we were mainly interested in the extrinsic defects (impurities), these impurities are localised in four distinct regions, Cr^{3+} is assigned to the first region 680-760 nm, in the second region 465-500 nm we find Ni^{2+}, Fe^{3+} is localised in the third region 310-375 nm and lastly the Ca^{2+} and K^{+} have been found to emit in the 180-260 nm region.

Key words: Thermoluminescence, MgO, extrinsic defects, UV irradiation, deconvolution

INTRODUCTION

In oxide materials, defects often presents and are responsible for specific optical and electrical proprieties. These defects play a significant role in the radiative emission.

The luminescence can be used as an indicator of the presence of different intrinsic and extrinsic defects in insulator or semiconductor material. The intrinsic defects in MgO were the subject of our first study (Kadri *et al*., 2005).

The motivation for the present research was to determine the extrinsic (impurities) type defects Cr, Ni, Fe, Ca and K present in our sample MgO single crystal. The measurements were carried out using thermoluminescence (TL) and absorbance techniques. The deconvolution method has been used in the determination with precision the emission bands related to these defects.

MATERIALS AND METHODS

In the literature review of different irradiation and MgO studies aiming to determine extrinsic defects (impurities) such as Cr, Ni, Fe, K and Ca contained in our sample we find the following:

Concerning the chromium impurity, Jiménez *et al.* (1985) found that the large red emission band at 730 nm (1.7 eV) lies in the region which characterizes the Cr^{3+}, this emission is due to the capture of holes released from traps, in his quality assessment of MgO substrate materials, Flecher and Leach (1995) found the presence of several peaks in the red region between 696 and 740 nm, which is also confirmed widely in the documentation that substitional Cr^{3+} ions are responsible for the red peaks. Kawaguchi (2001) also attributes the 730 nm band to the Cr^{3+} impurity, Chao (1971) reported a red band which peaks at about 700 nm with vibrational sidebands lines in thermo luminescence spectrum of MgO and assigned the band to Cr^{3+} impurity, Kantorovich *et al.* (2001) considers that substitutional Cr^{3+} in MgO occupies a Mg site, at small concentration, most chromium ions are in octahedral (cubic) symmetry sites without neighboring vacancies and are mostly responsible for a broad 2.00 eV absorption band and a sharp 1.776 eV (700 nm) peak (the R- line), Karner *et al.* (2001) in their neutron-irradiated MgO single crystals study, found two kinds of luminescence bands one of which belongs to the red region and is apparently due to Cr^{3+} in sites with different symmetry, the R-line is situated at 1.776 eV.

Concerning the Nickel impurity, observable peaks in the visible region have been revealed for four distinct excitation (emissions) 476, 481, 486 and 490 nm in Flecher and Leach (1995), these results correlate very well with the TL data of Ralph and Townsend (1970) for substitutional Ni^{2+} ions.

As far as the iron impurity is concerned there is some controversy about its role, some suggest that the red emission band is ascribed to it as well as chromium Ziniker *et al.* (1972) and Clement and Hodgson (1984), other authors attribute Fe^{3+} emission to the ultra violet region Jiménez *et al.* (1995), a small band of 340 nm (3.65 eV) in the 320-380 nm region occurs and is possibly

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related to Fe^{3+} emission due to hole capture by Fe^{2+} ions. Acceptor impurities such as Li, Na, K from group I are known to give rise to rather deep traps for holes and the luminescence bands due to their presence are observed at energies less than 6 eV (greater than 207 nm), the monovalent substitutional impurity K^+ belongs to acceptors and are rather find on surface because of their relatively big size Molnar (2000), emitting in the ultra violet region. Also if it is assumed that the 6.9 eV (180 nm) band is due to Ca^{2+} impurities, we must admit that at concentrations as small as several ppm practically all excitons decay at Ca^{2+} ions, a situation not very likely to take place, Rachko and Valbis (1979).

Thermoluminscence and absorption measurements were carried out at University of Science and Technology of Oran (Algeria), Electronic Microscopy and Material Science Laboratory (2006). The sample analysed in this work is a single crystal MgO polished from Soekawa chemicals Japan. The dimensions of the sample are $10\times10\times1$ mm^3. It is known that the MgO crystal have the NaCl structure with a cubic-face-centred (cfc) Bravais lattice with a cubic lattice constant of 4.21 Å. A micro probe analysis of this crystal showed an impurity content of Cr, Ni, Fe, Ca and K in small quantities. Firstly the sample was irradiated by an UV Hg source lamp (4.8 eV for 10 min in air) at low temperature -100°C (170°K).

Secondly the crystal was thermally heated in a furnace to a temperature between 170 and 500°K. Thermoluminescence (TL) emission is detected through a Spectrograph CP 200 Jobin Yvon connected to a CCD 3000 (coupled charge device) cooled to 150°K, with wavelength bands of 250-1200 nm for grating 133 g mm^{-1} and 180-1000 nm for grating 200 g mm^{-1}.

The TL spectrum were recorded and analysed with Spectramax software, by means of the Fourier self-deconvolution method which synthetically narrows the effective trace bandwidth features, this aids identifying the principal bands, it can also be useful for more accurate determination of the number of peaks in a trace region, the band positions and areas.

RESULTS AND DISCUSSION

The TL curves recorded from -100°C (170°K) to room temperature showed that the spectral intensity decreases, whereas in the second heating that is from room temperature up to 230°C (500°K) we noticed that the spectral intensity increases up to a maximum limit at 110°C (380°K) then start decreasing with increasing temperature (Kadri *et al*., 2005).

In TL experimental analysis of extrinsic defects (impurities: Cr, Ni, Fe, K and Ca) in MgO single crystal and by considering the different irradiation techniques mentioned in the previous literature review, we considered a single spectrum at -40°C (233°K) as shown in Fig. 1 to be deconvoluted (Fig. 2), three emission bands appears 694, 715 and 737 nm, where the 715 nm (1.73 eV) is the dominant peak and is attributed to Cr^{3+} its TL- intensity spectra is represented in Fig. 3 where it can be seen that intensity behaves differently with regards to temperature varying from -100°C to ambient and from ambient to 230°C, whereas the two other emissions are assumed vibrational side bands.

A close look at the 280-500 nm region where the Ni and Fe impurities are located according to the literature, only weak intensity signals were found what made impurity identification rather difficult, deconvolution method applied to the spectrum band maximum temperature of 110°C (Fig. 4) has been used to determine the emission bands.

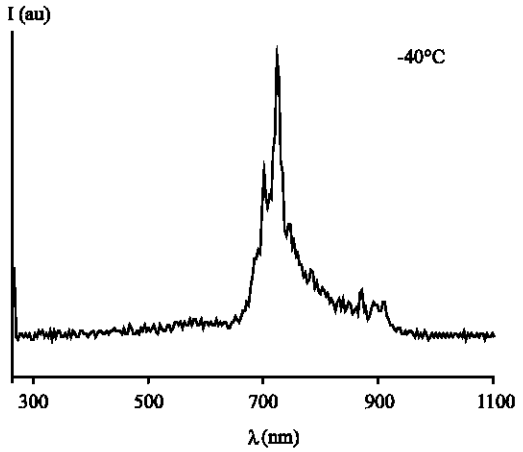

Fig. 1: Spectrum recorded at -40°C (233°K) (grating 133g mm^{-1})

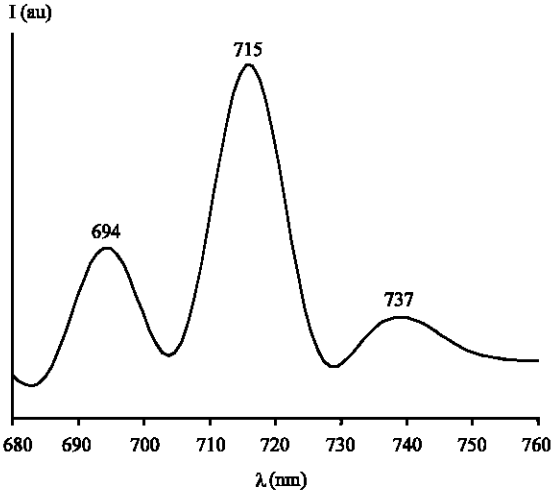

Fig.2: Sub-region 670-770 nm deconvolution of the spectrum (Fig. 1)

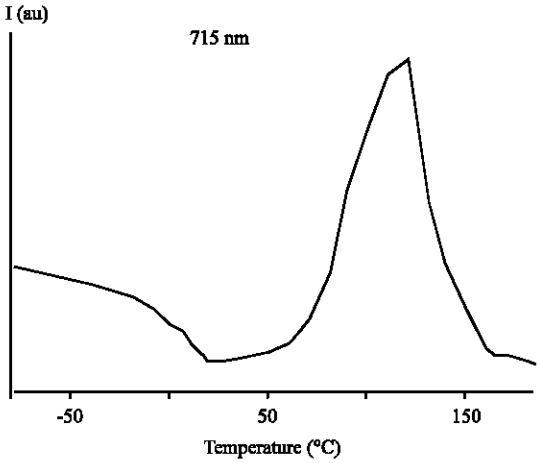

Fig. 3: TL-intensity curve versus temperature of the 715 nm band (Cr)

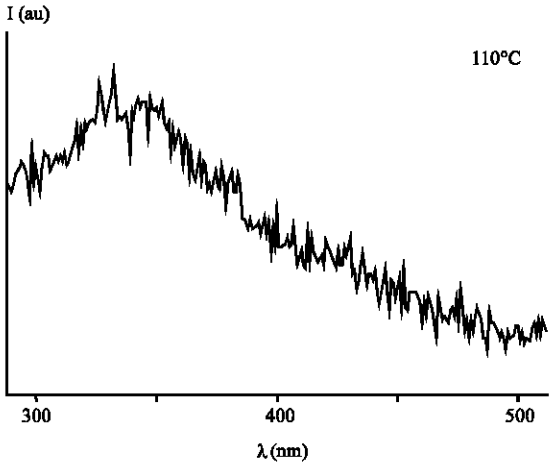

Fig. 4: Spectrum recorded at 110°C (380°K), region of interest (280-500 nm) (grating 133 g mm^{-1})

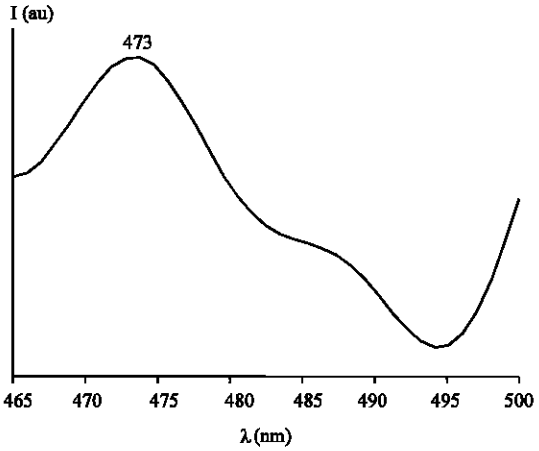

Fig. 5: Sub-region 465-500 nm deconvolution of the spectrum (Fig. 4)

Two sub-regions has been identified 465-500 nm (Fig. 5) and 310-375 nm (Fig. 6) responsible of Ni and Fe emissions, respectively.

In the first sub-region we recorded a dominant emission at 473 nm (2.62 eV) which was two assigned to Ni^{2+}, its TL-intensity spectra is shown in Fig. 7, in the second deconvolution region two emissions were recorded 330 and 350 nm, the most probable emission according to what was already achieved in previously mentioned works in the literature corresponding to Fe^{3+} is the 330 nm (3.75 eV) band, its TL-intensity spectra is shown in Fig. 8.

A second recorded spectrum at a maximum temperature of 110°C with a grating of 200 g mm^{-1} was chosen to have a closer look at the 180-260 nm region (Fig. 9), again and by the mean of the deconvolution method we found four peaks 190, 210, 233 and 243 nm

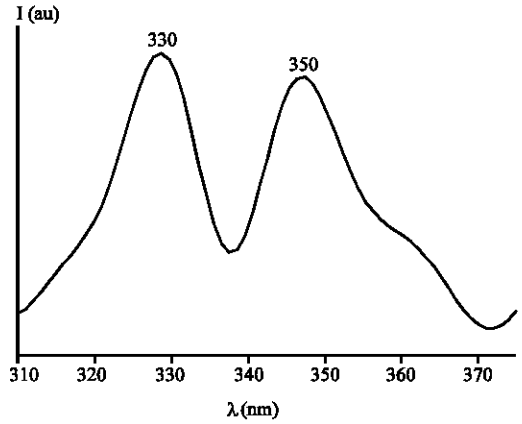

Fig. 6: Sub-region 310-375 nm deconvolution of the spectrum (Fig. 4)

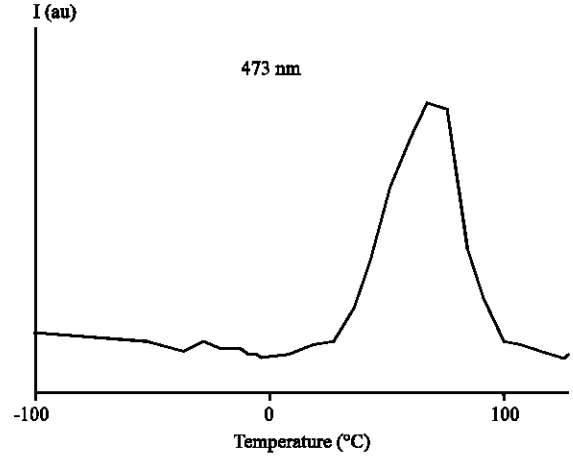

Fig. 7: TL-intensity spectra versus temperature of the 473 nm band (Ni)

(Fig. 10), the 190 nm (6.52 eV) emission band is attributed to Ca^{2+} not to excitons since that the energy is less than 6.9 eV as was proposed by Rachko and Valbis (1979), for the TL-intensity (Fig. 11), the other three emissions are localised in the energy region less than 6 eV (greater than 207 nm) where the luminescence bands of K^+ are likely to occur.

It can easily noticed that results obtained in the present work agree to a very high extent with results obtained elsewhere (see literature review) and come also to confirm some other undertaken works, even though the analysis techniques might be different.

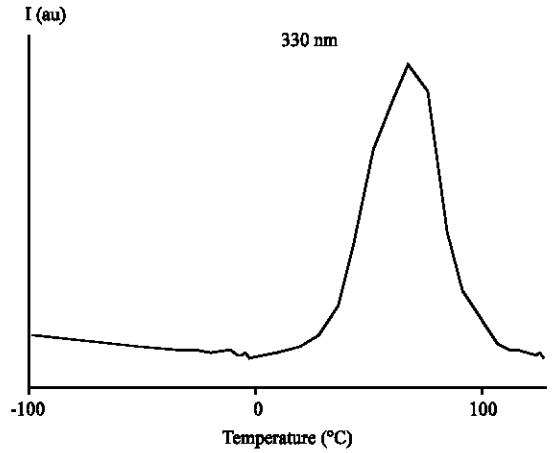

Fig. 8: TL-intensity spectra versus temperature of the 330 nm band (Fe)

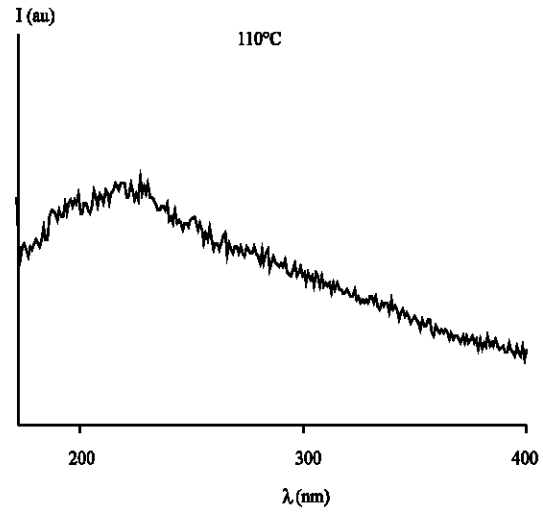

Fig. 9: Spectrum recorded at 110°C (380°K), region of interest (170-400 nm) (grating 200 g mm^{-1})

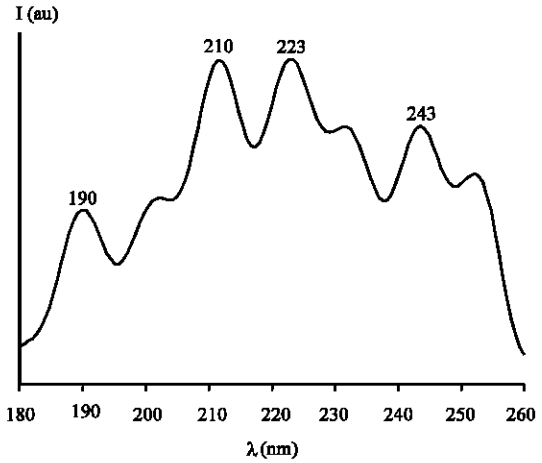

Fig. 10: Sub-region 180-260 nm deconvolution of the spectrum (Fig. 9)

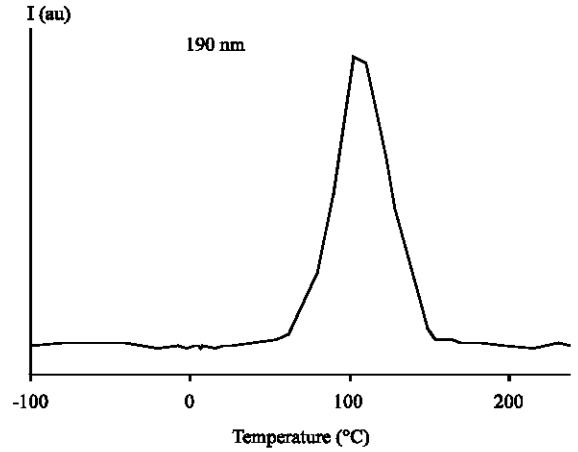

Fig. 11: TL-intensity curve versus temperature of the 190 nm band (Ca)

CONCLUSIONS

In this study the thermoluminescence (TL) combined with absorbance and deconvolution method has been used to determine the extrinsic defects of MgO single crystal previously irradiated by UV (4.8 eV), the analysis of results indicates emission bands for Cr^{3+} at 715 nm, Ni^{2+} at 473 nm, Fe^{3+} at 330 nm, Ca^{3+}at 190 nm and for K^+ three emission bands are localised 210, 223 and 243 nm one of which is attributed to this impurity. Important results for the evolution of the characteristics and properties of magnesium oxide were presented. These experimental results are in agreement with the prediction of the standard insulator MgO. The deconvolution method has enabled us to determine a certain number of identified and non identified emission bands regardless of the intensity of the recorded spectra. We intend, in near future work to

undergo much deeper investigations in order to attribute these non identified emissions to defects which may be contained in the sample.

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