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SEM cathodoluminescence studies of heat-treated MgO crystals

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Résumé. — La luminescence des monocristaux de MgO a été étudiée avec un microscope électronique à balayage (SEM) équipé d'un système pour la détection de cathodoluminescence spectroscopique (CL).

Le spectre CL corrigé du MgO se compose d'une grande bande bleue avec un pic à 460 nm et une large émission ou dominée par un pic à 722 nm. En recuisant les échantillons dans l'air, le monoxyde de carbone à l'hydrogène change le spectre d'une façon considérable. L'oxydation coupe la bande bleue en plusieurs pics et plateaux et enfin supprime complètement le pic causé par défaut, mais ne produit pas d'effet sur la position ou la forme de l'émission rouge. En contradiction, recuit hydrogène, elle produit un aiguisement de la large bande rouge en six pics, pendant que la bande rouge n'est pas affectée. Un effet vraisemblable est noté pour le traitement en monoxyde de carbone, sauf que de très longs recuits suppriment totalement les pics rouges et les remplacent par une large bande nouvelle à 645 nm.

Abstract. — The luminescence of MgO single crystals has been investigated using a scanning electron microscope (SEM) with a detection system for spectroscopic cathodoluminescence (CL) studies.

The corrected CL spectrum of MgO consists of a large blue band with a maximum at 460 nm and a broad red emission with a dominant 722 nm peak. Annealing treatments in air, carbon monoxide or hydrogen change the spectra considerably. Oxidation divides the blue band into a number of peaks and shoulders and finally eliminates the deformation-induced peak entirely but has no effect on the shape or position of the red emission. In contrast, heating in hydrogen produces a sharpening of the broad red luminescence into six peaks, whilst the blue band remains unaffected. A similar effect was observed for carbon monoxide treatment except that very long annealing times completely eliminated the red peaks and replaced them by a new broad band at 645 nm.

1. Introduction. — Our earlier observations [1] showed that deformed MgO has a corrected cathodoluminescence (CL) spectrum containing two broad bands which are well separated in wavelength (~ 300 nm apart). Monochromatic CL SEM micrographs taken at the blue 466 nm (2.66 eV) peak of the first band showed that the emission was localized at the slip planes. The red emission is a composite of overlapping bands with a prominent 770 nm (1.61 eV) peak and remains unaffected by crystal deformation. Monochromatic (one wavelength) micrographs taken at the red wavelength still show a homogeneous emission distribution after deformation.

The origin of the blue band has been the subject of a recent investigation by Chen *et al.* [2] who interpreted their results as showing that negative ion vacancies are generated in the slip bands during deformation and these then act as recombination centres for the observed photoluminescence (PL). Subsequently, Llopis *et al.* [3] confirmed by means of SEM panchromatic (all wavelengths) CL studies that the blue emission could only be seen at the slip bands. In MgO the presence of negative-ion vacancies

after deformation is certain from the observation of F^+ colour centres (oxygen-ion vacancies occupied by single electrons) [4, 5]. However, Velednitskaya *et al.* [6] believe that the blue CL *rosette* pattern around indentations is due to interstitial defects but Newton and Sibley [7] argue that vacancy loops, which have been observed in damaged MgO, would probably annihilate any interstitial clusters formed. Pennycook *et al.* [8] produced evidence indicating that much of the CL around an indentation can be associated with dislocations. Sibley *et al.* [4] reported that the blue thermoluminescence (TL) in γ -irradiated MgO was due to Fe^{3+} impurity ions but Ziniker *et al.* [9] found no blue TL emission in either relatively pure or iron doped MgO and Newton and Sibley [7] later demonstrated that the blue TL was associated with deformation accidentally introduced during sample preparation.

The red luminescence band is believed to be an impurity effect due to either chromium or iron [10, 11]. The valence states of metal impurities in MgO can be altered by annealing at elevated temperatures or by ionizing radiation as reviewed by Henderson and Wertz [12]. In the case of iron, Davidge [13] showed that annealing in an oxidizing atmosphere (oxygen or air) yields Fe^{3+} , the naturally occurring form, whilst

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in a reducing atmosphere (carbon monoxide) Fe^{2+} states are obtained. In hydrogen annealing the Fe^{3+} is reduced to metallic Fe. Therefore it appeared likely to be instructive to study the cathodoluminescence of MgO crystals subjected to various heat treatments.

2. Experimental procedure. — All cathodoluminescence (CL) data was taken using a JEOL JSM-35 scanning electron microscope (SEM) fitted with a specially developed spectroscopic light detection system [14]. This employs a semi-ellipsoidal mirror and light guide to collect the CL and feed it to a grating monochromator, placed outside the microscope, for spectral analysis. The wavelength range 240 to 900 nm was monitored using a cooled EMI 9558 QA photomultiplier with an extended S20 response. The signal was then passed to a photon counting circuit and stored in a multi-channel scaler for further computer processing. It could also be video displayed on the SEM screen to produce panchromatic (all wavelengths) or monochromatic (single wavelength) CL micrographs. Since the response of the system varies considerably with wavelength a calibration and correction procedure was applied to obtain emission spectra in photons emitted per second per resolution interval *versus* wavelength or photon energy. Further details of the system and the method of calibration can be found in Steyn *et al.* [14].

The magnesium oxide crystals used in these experiments were all obtained from the Norton Research Corporation. Independent spectrochemical analysis at Imperial College and at the International Tin Research Institute showed that the samples contain 200–250 ppm of iron as the only major impurity with 5–10 ppm of Si, Ti, Al, Ca, Zr, Mn and Ni. For the SEM, specimens were cut and polished in hot orthophosphoric acid into small rectangular blocks and coated with a transparent conducting film to eliminate charging effects.

The spectral resolution throughout this work was 5 nm and the SEM beam voltage was 35 kV. All spectra were taken at room temperature.

3. Results and analysis. — The purpose of this work is to study the way in which annealing in different gaseous environments can alter the CL in MgO crystals. Typical starting material always exhibits a blue and an unresolved multiple red band as shown by the bottom curves (zero hour) in figures 1 and 2 respectively. Figure 1 summarizes the effect of annealing in an oxidizing atmosphere for different lengths of time at a temperature of 1 500 K. Considerable spectral changes occur in the wavelength region 300 to 620 nm. Prolonged oxidation splits the blue CL emission into a well defined intense band at 490 nm (2.53 eV) with a second much smaller peak at 420 nm (2.95 eV) and a shoulder at ~ 370 nm (3.35 eV). This double peaked spectrum appears to

Fig. 1. — A series of CL emission spectra for the blue and near U.V. region taken after annealing in air at 1 500 K for different time periods. The spectra have been shifted vertically to avoid confusion. Oxidation alters only this blue luminescence band.

be similar to that observed from undeformed MgO [1]. The results suggest that the blue luminescence is a composite of several bands probably arising from a number of different defect configurations.

The shape and position of the red band between 620 and 820 nm remains unaffected by oxidation but annealing at 1 700 K in hydrogen or carbon monoxide causes many of the hitherto overlapping bands to alter in prominence as shown in figures 2 and 3 respectively. Continuous heating in H_2 (Fig. 2) produces a sharpening of the red luminescence into six clearly defined bands with peaks at ~ 680 nm (1.82 eV), 689 nm (1.79 eV), 700 nm (1.77 eV), ~ 715 nm (1.73 eV), 722 nm (1.72 eV) and ~ 746 nm (1.66 eV), whereas initially the only prominent band was at 722 nm with subsidiary peaks at about 688 nm (1.80 eV), 760 nm (1.76 eV) and 746 nm.

Figure 2 also exhibits variations in relative intensity between the different peaks with increasing annealing time. Although the SEM conditions were nominally the same each time, the absolute intensities within any family of curves in figures 1, 2 and 3 are subject to some instrumental variation as well as variation from place to place over the sample.

Figure 3 illustrates the changes in CL after annealing samples in carbon monoxide. It can be seen that except for the appearance of a new shoulder at

Fig. 2. — A series of CL emission spectra taken after annealing in hydrogen at 1700 K for varying lengths of time. Reduction changes the appearance of these red emission bands but leaves the blue band unaffected.

~ 638 nm (1.94 eV) there are many spectral similarities between a 5 hour CO and a 20 hour H_2 treatment. With further reduction in CO this shoulder becomes a wide band of high photon emission with a maximum at 645 nm (1.92 eV) whilst the series of emission bands around 680 to 750 nm which had earlier dominated this region disappear. Reducing atmospheres (CO or H_2) have no effect on the intense blue luminescence.

All spectra presented in figures 1, 2 and 3 have been corrected for instrumental losses throughout the detection range of the system. Failure to apply a spectral correction can lead to erroneous deductions as outlined in earlier publications [15, 16].

There is evidence to suggest that the red emission in MgO arises from iron impurities in several charge states. For instance, we have observed that the red CL bands become more intense and better defined with an increase in the concentration of Fe which was the only major impurity in these samples [17]. The annealing results also seem to support this view since oxidation increases the fraction of Fe^{3+} , the normal state of iron, and so has no effect on the red luminescence. On the other hand, in a reducing atmo-

Fig. 3. — A series of CL emission spectra taken after annealing in carbon monoxide at 1700 K for different lengths of time. These series of red bands seen in figure 2 disappear with prolonged reduction in CO, but this results in a new band with a peak at 645 nm. The blue luminescence band was again unaffected.

sphere, Fe^{3+} ions are converted to Fe^{2+} , thereby causing a number of spectral changes in the 620 to 820 nm region as shown in figures 2 and 3. The origins of the 645 nm (Fig. 3) and the 490 nm (Fig. 1) peaks which appear after carbon monoxide and oxygen treatment respectively are still unknown. However, a low temperature X-ray-excited luminescence peak at 2.5 eV (496 nm) has tentatively been ascribed to Ni impurity [10] but apparently this peak has not been seen at room temperature.

The 460 nm blue peak is emitted from slip planes [1, 2, 3]. It is virtually eliminated by oxidizing annealing. This behaviour would be difficult to explain on a dislocation recombination mechanism. Interstitials are also unlikely. Suppression by oxidation thus suggests that oxygen vacancies are involved in the luminescence centres as originally suggested by Chen *et al.* [2].

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DISCUSSION

Comment. — Dr. J. CASTAING.

Is your observation on point defect creation by dislocation motion in agreement with that of Rozhanskii *et al.* [1] who used ion implantation to check their conclusion ?

[1] ROZHANSKII, V. M., VELEDNITSKAYA, M. A., SCHREIBER, J. and KRASNOPEVTSEV, V. V., *Sov. Phys. Solid State* **19** (1977) 1159-1160.

Name. — D. B. HOLT.

Author's reply : Unfortunately Rozhanskii *et al.* give no indication whether their spectra are corrected for detector response and they ignore the complex,

multi-peaked shapes of both the red and blue emissions. The first omission makes critical comparison of our spectra, which differ in detail, impossible, and the second invalidates their interpretations. For example they say that Mg-implantation and indentation change the spectra in the same way but the only similarity is that both result in the maximum height of the blue emission being greater than that of the red. However, their spectra show that Mg-implantation results in a much narrower band peaking at a different wavelength than either of the bands in the emission from the indented material. This cannot therefore be accepted as evidence that an interstitial mechanism is responsible for the emission from indented material.

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