of Electrical Engineers, London, 1986), p. 13.1.

[9]N. M. Haegel, K. Leo, S. Gisdakis, W. W. Rühle, and A. Winnacker (unpublished).

[10]According to Shockley–Read–Hall statistics we obtain in the limit of high excitation density ($n \gg n_i, N_T$) as recombination rate U:

$$U = (\sigma_n \sigma_p)/(\sigma_n + \sigma_p) v_{th} n N_T,$$

where v_{th} is the thermal velocity and σ_n, σ_p are the capture cross sections

for electrons and holes, respectively.

[11]D. Bimberg, J. Christen, A. Werner, M. Kunst, G. Weimann, and W. Schlapp, Appl. Phys. Lett. **49**, 76 (1986).

[12]J. Windscheif, H. Ennen, U. Kaufmann, J. Schneider, and T. Kimura, Appl. Phys. A **30**, 47 (1983).

[13]B. V. Shanabrook, P. B. Klein, E. M. Swiggard, and S. G. Bishop, J. Appl. Phys. **54**, 336 (1986).

[14]G. M. Martin, Appl. Phys. Lett. **39**, 747 (1981).

Influence of Bi and Mn on the green luminescence of ZnO ceramics

J. A. García and A. Remón

Departamento de Física del Estado Sólido, Facultad de Ciencias, Universidad del País Vasco, Lejona, Vizcaya, Spain

J. Piqueras

Departamento de Física de la Materia Condensada, Facultad de Ciencias Físicas, Universidad Complutense, 28040 Madrid, Spain

The effect of the addition of Bi and Mn on the photoluminescence from ZnO ceramics has been investigated. The effect of the presence of impurities on the green luminescence band can be compared to the effect of oxidizing treatments. A narrow green band has been observed in Mn-doped samples.

Sintered ZnO ceramics containing suited metal oxides are known to show the varistor effect, which can be explained[1] by mechanisms involving the grain boundaries and the associated defect concentration gradient in their proximity. Certain treatments, such as the application of mechanical stresses or heating, can cause the degradation of the current-voltage characteristics of the varistor, but the original situation tends to be restored by annealing in oxidizing ambients.[2] The distribution of vacancies and impurities as well as their behavior during annealing treatments appears then as one of the factors that determine the electrical properties of ZnO ceramics.

One experimental approach that has been widely used to study defects and impurities in ZnO is the luminescence. There are several visible and infrared emission bands that are related to the presence of impurities, as reviewed in Ref. 3. The influence of bismuth and manganese, usually present in varistor ceramics, on the visible and near-infrared luminescence of ZnO has been less investigated. In the present work the luminescent behavior in the visible range of ZnO ceramics doped with bismuth and manganese has been studied.

The ceramic samples used in this work were produced by pressing either pure ZnO powder or ZnO powder containing bismuth or manganese oxides and sintering in air for 1 h at 1200 °C. The doped samples contained 0.2 mol % Bi or 0.5 mol % Mn.
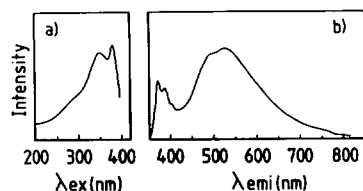
Photoluminescence emission of the samples was measured in the range 350–830 nm by using a Jobin–Ybon JY-3D spectrofluorometer with a R-928 photomultiplier. Excitation spectra of the main emission bands were also recorded. The samples were then accumulatively annealed in air from 300 to 1100 °C in 200 °C steps. The annealing time was 45 min, and the samples were slowly cooled to room temperature. The effect of each of the annealing treatments on the excitation and emission photoluminescence spectra was measured.

Excitation with light of wavelength in the range 260–390 nm produces in the undoped samples the broad green emission band peaked at about 530 nm, which has often been reported. A shoulder at about 495–500 nm is also observed. Figure 1 shows emission and excitation spectra. In the Bi-doped samples excitation with wavelengths below 370 nm produces the emission band at 530 nm. When excitation wavelengths above 370 nm are used, the emission band appears either at 530 or 645 nm, depending, apparently, on the sample region illuminated. Figure 2(a) shows the excitation spectra of the 530- and 645-nm bands in a sample region that shows higher 645-nm emission. The emission spectra are shown in Fig. 2(b). In the Mn-doped samples quenching of

FIG. 1. Photoluminescence spectra of pure ZnO. (a) Excitation spectrum of 530-nm luminescence. (b) Emission excited at 345 nm.
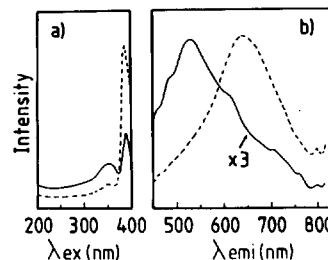

FIG. 2. Photoluminescence from Bi-doped ZnO. (a) Excitation spectra of 530-nm (solid line) and 645-nm (broken line) luminescence. (b) Emission excited at 350 nm (solid line) and 385 nm (broken line).
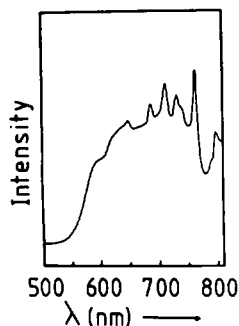
FIG. 3. Photoluminescence spectrum of Mn-doped ZnO excited at 280 nm.

FIG. 5. Photoluminescence spectra of Mn-doped ZnO after annealing at 900 °C. (a) Excitation spectrum of 530-nm luminescence. (b) Emission excited at 210 nm.

the green emission is observed in the whole excitation range. Figure 3 shows a representative spectrum of these samples.

Annealing the undoped samples above 700 °C in air causes a decrease of the 350-nm excitation peak. The annealings do not change the shape of the emission spectrum of Fig. 1, which shows the 530-nm peak throughout the thermal treatment.

The first significative changes in the spectra of doped samples are observed after the 900 °C annealing. In the bismuth-doped samples the 385–390 nm excitation peak of the 645-nm emission decreases. By exciting with 390 nm, two emission bands at 540 and 645 nm are observed, as Fig. 4 shows. Annealing at 900 °C has caused the relative decrease of the 645-nm emission band of Fig. 2. Further annealing at 1100 °C causes the disappearance of the 645-nm emission. The spectrum of the sample annealed at 1100 °C shows the green band peaked at 530 nm, which is excited with light of wavelengths in the range 280–400 nm. Annealing the manganese-doped sample at 900 °C induces the appearance of an intense emission band at 530 nm whose excitation spectrum is shown in Fig. 5(a). Figure 5(b) shows the emission spectrum obtained by exciting with a 210-nm wavelength. The green band of Fig. 5(b) was not observed before annealing.

Several authors have investigated the influence of the addition of metallic oxides on the point-defect equilibrium concentration in ZnO ceramics. The introduction of metallic atoms in the lattice during the sintering process causes changes in the equilibrium conditions of the defects. In the cases of cobalt and manganese, calculations[1,4–7] show that both dopants act in a similar way to an oxidizing atmosphere by causing the increase of the concentration of zinc vacancies and the decrease of the concentration of oxygen vacancies. The resulting concentrations of vacancies at the grain boundaries are related[4] to the varistor effect in ZnO. On the other hand, experimental results[7] indicate that bismuth has, as colbalt and manganese, an oxidizing effect. It is then to be expected that bismuth and manganese influence the green luminescence band of ZnO, which is known to be affected by oxidizing and reducing treatments. As reviewed by Riehl,[8]
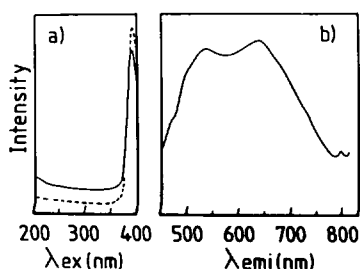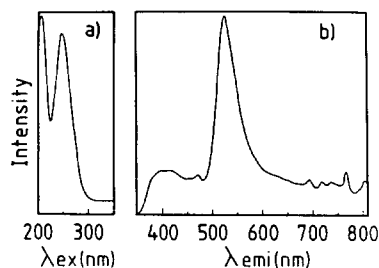

FIG. 4. Photoluminescence spectra of Bi-doped samples after annealing at 900 °C. (a) Excitation spectra of 530-nm (solid line) and 645-nm (broken line) luminescence. (b) Emission excited at 390 nm.

experiments show that a certain reduction of ZnO is necessary to obtain the green luminescence, while the luminescence disappears completely if the ZnO is fired at high temperatures in oxygen. As Figs. 2 and 3 show, the impurities used in this work influence the luminescence spectra of undoped ZnO (Fig. 1) by causing a relative decrease of the 530-nm green band, which agrees with the mentioned oxidizing effect of the impurities. In addition, Mn produces new features in the long wavelength part of the luminescence spectrum. The appearance of the luminiscence peak at 645 nm in the Bi-doped sample is partly due to the quenching of the green luminescence and the consequent relative increase of the yellow-orange luminescence band of ZnO. Although the luminescence may be directly due to the new phases that are know to be formed at grain intersections of the Bi-doped ZnO, such a possibility has not been confirmed by previous[7] cathodoluminescence observations of this kind of sample in the scanning electron microscope.

As mentioned above, the enchancement of the green emission in both kinds of doped samples is observed only after annealing at 900 °C. Although the recovery of the 530-nm band at this temperature is probably influenced by changes in the intrinsic defect concentration, the role of impurities has to be taken into account. Since at about 900 °C several impurities begin to move freely in ZnO,[9] we suggest that impurities can readjust to form centers that either do not quench the green emission or are involved in the green emission. The latter seems to be the case with the Mn-doped samples, which show, after annealing at 900 °C, a green band [Fig. 5(b)] that differs from the well-known broad band centered at 530 nm. The excitation spectra have shown that the excitation peaks of the green bands of Fig. 5(b) and of the undoped samples are different. On the other hand, the half-width of the green band in Fig. 5(b) is about 40 nm, 4 times lower than the half-width of the green band in the undoped samples. It appears that in the band of Fig. 5(b) manganese is involved.

The authors thank Dr. J. Llopis and P. Fernández for discussions.

[1] R. Einzinger, Appl. Surf. Sci. 3, 390 (1979).
[2] E. Sonder, M. M. Austin, and D. L. Kinser, J. Appl. Phys. 54, 3566 (1983).
[3] H. J. Schulz, in Current Topics in Materials Science, edited by E. Kaldis (North-Holland, Amsterdam, 1981), Vol. 7, p. 241.
[4] R. Einzinger, Ph. D. thesis, University of Munich, 1982.
[5] U. Schwing, Ph. D. thesis, University of Karlsruhe, 1984.
[6] U. Schwing and B. Hoffman, J. Appl. Phys. 57, 5372 (1985).
[7] D. Köhler, Diplomarbeit, University of Diusburg, 1985.
[8] N. Riehl, J. Lumin. 24/25, 335 (1981).
[9] E. Sonder, R. A. Zuhr, and J. R. Martinelli, Mater. Res. Soc. Symp. Proc. 60, 385 (1986).