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Detection of Oxygen-Depleted Zones in $YBa_2Cu_3O_{7-x}$ by Luminescence

By

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Previous cathodoluminescence (CL) works in the scanning electron microscope (SEM) [1 to 3] indicated that oxygen-depleted zones of $YBa_2Cu_3O_{7-x}$ emit a higher luminescence signal than oxygen-rich regions. The luminescence increase observed during electron irradiation in the microscope is attributed to the electron induced oxygen loss. The evolution of CL intensity and spectra under the electron beam of a microscope have been described [2]. Besides electron irradiation, laser irradiation or thermal treatments can produce oxygen loss and consequently induce similar luminescence changes due to the appearance of a semiconducting phase. In particular Shen et al. [4] used a focused laser beam to produce the out-diffusion of oxygen from $YBa_2Cu_3O_{7-x}$ films in vacuum. In the present work CL from $YBa_2Cu_3O_{7-x}$ bulk samples after vacuum annealing or after laser irradiation is compared in order to study the effect of oxygen loss on the luminescence emission. The same set of samples has been also investigated by photoluminescence (PL) so that the effect of the excitation conditions on the luminescence spectra could be studied.

The samples used were cut from sintered $YBa_2Cu_3O_{7-x}$ disks with nominal T_c value of 93 K. Some samples were annealed in a vacuum of 10^{-2} Torr at temperatures between 100 and 500 °C. Other samples were irradiated at 10^{-2} Torr with a multi-wavelength Ar-ion laser. Photoluminescence between 90 and 300 K was measured in the range 350 to 850 nm with a Jobin-Yvon JY3D spectrofluorimeter. The experimental arrangement used for CL measurements in the scanning electron microscope has been previously described [2, 5].

The untreated samples do not show PL emission at room temperature. Only at 90 K a very weak luminescence in the 400 to 500 nm region was detected. Due to the low emission no spectra of these samples were recorded. The first luminescence changes are observed at 90 K after annealing the samples at 200 °C. This treatment causes an emission increase in the mentioned spectral region with a peak at about 440 to 450 nm. After annealing at 400 °C the spectrum of Fig. 1 is obtained with a band centered at 540 nm. No further changes were observed in the sample annealed at 500 °C. The effect of laser irradiation on the photoluminescence is similar to that of the annealing treatments. Short irradition times produce PL spectra similar to those obtained after 200 °C annealing and longer irradiation produces the spectrum of Fig. 1 (400 °C annealing).

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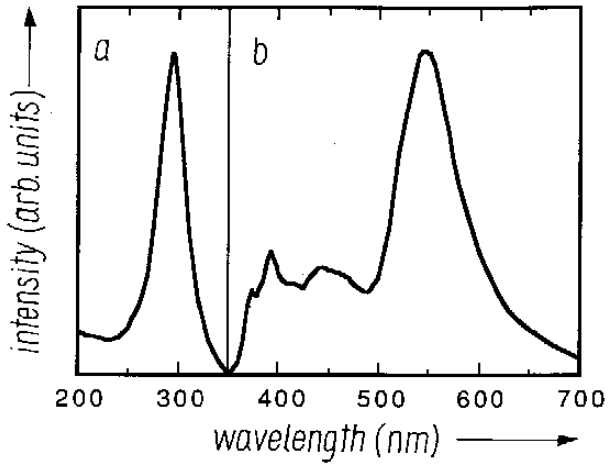

Fig. 1. PL spectra of a sample annealed at 400 °C; a) excitation spectrum of the 540 nm band; b) emission spectrum of a sample excited with 295 nm

As described in [3] and other previous works [6, 7] the CL from $YBa_2Cu_3O_{7-x}$ increases under electron bombardment. The shape of spectra can in general be described by the appearance of emission in the 400 to 600 nm region with peaks close to 450 nm and in the range 450 to 600 nm. This agrees with the PL bands at 450 and 540 nm of Fig. 1.

The effect of laser irradiation and thermal treatments is readily observed in the CL mode of the electron microscope. The laser irradiated sample shows a rough surface and a high CL emission in the irradiated area. Fig. 2a shows the room temperature CL spectrum of this sample and Fig. 2b shows the CL spectrum of the sample annealed at 400 °C. Both treatments produce the appearance of CL emission with a broad band in the 450 to 600 nm range. Short irradiation times or low (200 °C) annealing temperatures cause also a resolved CL band at about 440 nm. With longer treatments the increase of the 540 nm band masks the 440 nm emission. The peak of the 540 nm band shifts to longer wavelengths at lower temperatures, appearing at about 580 nm at 100 K.

The present results show that laser irradiation and vacuum annealing induce similar luminescence properties in $YBa_2Cu_3O_{7-x}$. Although the observed luminescence is related

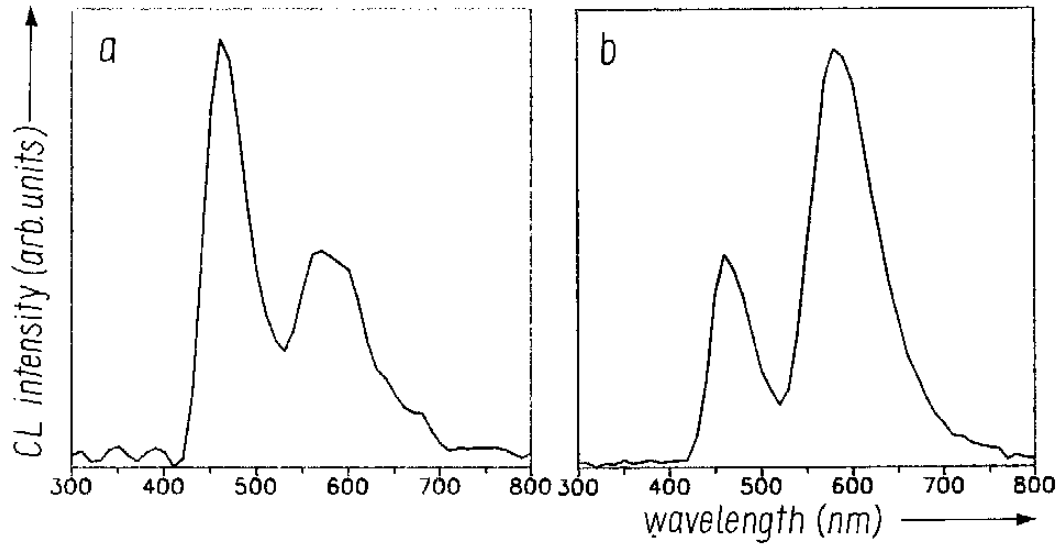

Fig. 2. Room temperature CL spectrum of a) a laser irradiated sample and b) a sample annealed at 400 °C

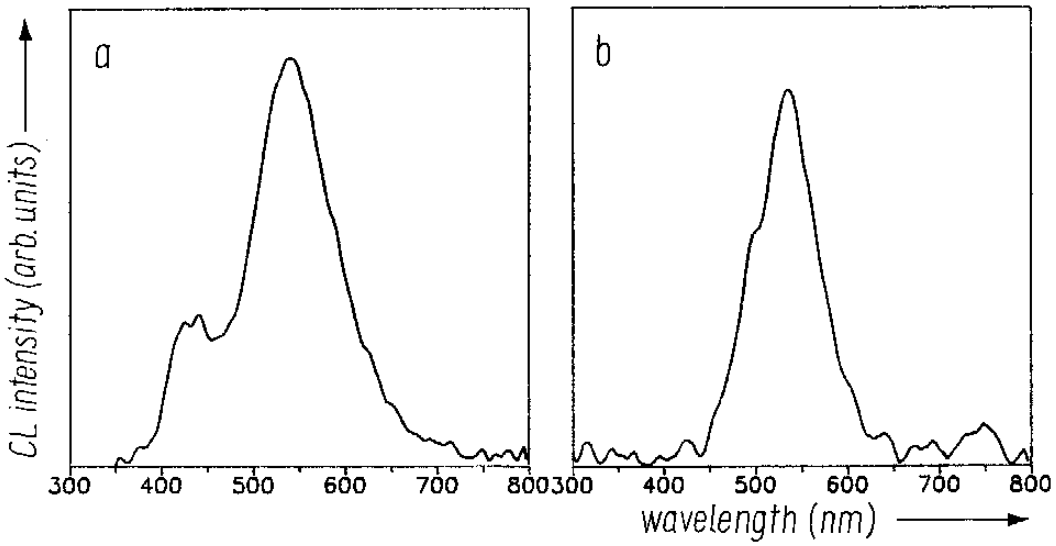

Fig. 3. CL spectra at 110 K of a laser irradiated sample; a) focused electron beam; b) defocused electron beam

to the oxygen-depleted zones resulting from the treatments, the emission bands cannot be associated to specific defects e.g. oxygen vacancies in the material. In principle the luminescence can be due to any local phase transition, for instance reordering or appearance of new phases, taking place as a consequence of changes in oxygen content. However, the fact that oxygen depleted zones induce specific luminescence features enables to detect the presence of such regions and to observe them in CL images in the scanning electron microscope. The complex luminescence spectra indicate the presence of different recombination centers. In particular the different behavior of CL bands centered at 450 and 580 nm, respectively, in a laser irradiated sample is shown in Fig. 3. With the microscope electron beam focused on the sample the spectrum of Fig. 3a is recorded, while with a defocused beam the 580 nm band becomes prominent as Fig. 3b shows. The fact that the 580 nm CL band increases when the beam is defocused can be explained by a low concentration of the centers responsible for the emission as discussed in [8].

In conclusion, different treatments producing oxygen deficiency in YBCO cause the appearance of a luminescence band at 540 nm detected by PL and CL techniques. Although from the present results it is not possible to know the nature of the centers responsible for the 540 nm band, our work points out that these centers are related to oxygen-depleted zones. Further work, aimed to get information on the nature of the center causing the 540 nm band, using samples of different compositions, is under way.

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