Study of structural changes in $YBa_2Cu_3O_{7-x}$ by cathodoluminescence in the scanning electron microscope

J. Piqueras and P. Fernández
Departamento de Fisica de Materiales, Facultad de Fisicas, Universidad Complutense, 28040 Madrid, Spain

J. L. Vicent
Departamento de Fisica de Materiales, Facultad de Fisicas, Universidad Complutense, 28040 Madrid, Spain and Instituto de Ciencia de Materiales, C. S. I. C., Serrano 144, 28006 Madrid, Spain

(Received 21 June 1990; accepted for publication 21 September 1990)

Changes in the visible and infrared cathodoluminescence (CL) spectra of $YBa_2Cu_3O_{7-x}$ are detected during irradiation in the scanning electron microscope. Results indicate the influence of oxygen content on the appearance of a CL band at 450–600 nm. In irradiated samples an infrared band at 1600–1700 nm has been observed.

In recent years luminescence techniques have been used sometimes to characterize high T_c superconductors. Such techniques enable the study of the defect structure as well as the detection of different phases in the sample. Fujiwara and Kobayashi[1] observed infrared photoluminescence emission in Er-Ba-Cu-O and Nd-Ba-Cu-O systems which they tentatively assign to electronic transitions in Er and Nd ions, as well as thermally stimulated luminescence (TSL) in Gd-Ba-Cu-O systems in the range 400–600 nm. TSL measurements in Gd-Ba-Cu-O systems have been also reported by Cooke *et al.*[2] and were related to defects or transitions in the rare-earth ions. In addition, cathodoluminescence (CL) methods[3–5] have been used to study $YBa_2Cu_3O_7$ samples. In Ref. 5, CL in the scanning electron microscope (SEM) has been used to distinguish semiconducting from metallic phases in high T_c superconductors.

In the present work $YBa_2Cu_3O_7$ ceramics are investigated by means of CL in the SEM. In particular the observation conditions and the evolution of the CL spectra under the electron beam have been studied.

The samples used in this work were obtained as usual and were polished by acting directly with the border of a diamond-covered cuttoff wheel, which leads to a free-contamination surface.[6]

The samples were observed in the emissive and CL modes in a Hitachi S-2500 scanning electron microscope at accelerating voltages between 20 and 30 keV. A lens was used to focus the light onto a photomultiplier attached to a window of the microscope, in order to obtain panchromatic CL images. A light guide feeding the light into an Oriel 78215 computer-controlled monochromator was used to record spectra. In cases of low signals, spectra representing the average of a high number of measurements were readily obtained. The spectra were corrected to include the system spectral response. Monochromatic images were obtained by using optical filters or by selecting a wide slit in the monochromator. The photomultiplier used covered the range 380–850 nm. Measurements were also carried out in the infrared range 0.8–1.8 μm by using a North Coast EO-817 germanium detector.

Figure 1 shows the CL spectrum of a $YBa_2Cu_3O_{7-x}(x \sim 0.1)$ sample at the beginning of the observation. The emission is very low and almost no contrast is observed in the CL image. During the observation, CL intensity gradually increases and the spectrum changes. Figure 2 shows the spectrum of an irradiated region. The intensity values in Fig. 2 have been scaled but the increase in CL intensity is apparent in Figs. 3 and 4. The emission increase is due to the appearance of a complex CL band with several peaks in the range 400–600 nm. Figure 3 shows a CL image with bright irradiated areas. Figure 3 also shows, in the emissive mode image, a damaged surface in the irradiated region.

CL intensity increases more rapidly for higher beam current or beam energy. A threshold current able to induce CL changes has not been measured but with currents in or above the range 10^{-7}–10^{-8} A the evolution of CL can be clearly observed. Figure 4(a) shows a typical curve of CL intensity as a function of time when beam currents of 10^{-7}–10^{-8} A are used. A sharp emission increase after several minutes is observed. When the beam current is high the CL intensity quickly saturates, as illustrated in Fig. 4(b). Measurements of the CL intensity as a function of time for several wavelengths show that the increase of the integrated CL intensity is due to the emission increase in the spectral range 400–600 nm while the intensity in the red region (600–700 nm) remains constant. This fact is also concluded from the corresponding CL monochromatic images.

Unirradiated samples show a very low infrared emission with several broad peaks in the range 800–1300 nm. After irradiation an intense composite band with peaks in

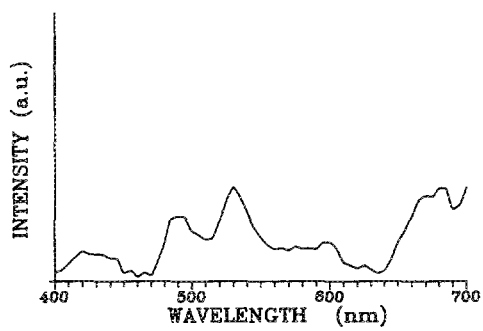

FIG. 1. CL spectrum from an unirradiated area.

 0003-6951/90/512722-03$02.00

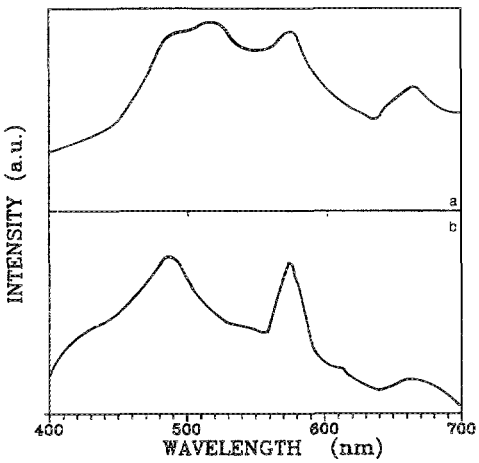

FIG. 2. CL spectrum from (a) a slightly irradiated area and (b) a severely irradiated area. Both spectra are not at the same scale. Intensities of peaks in (b) are higher than in (a).

the 1600–1700 nm region appears. Figure 5 shows the infrared spectrum from an irradiated area.

As stated above, CL emission of $YBa_2Cu_3O_7$ samples in the blue-green region has been previously reported. Andreev *et al.*[3] observe CL bands at 400 and 640 nm which increase under electron bombardment. They assume that dielectric yttrium oxide crystals are involved in the emission. Luff *et al.*[4] found bands at 450 or 500–550 nm, depending on the samples used and observed some changes produced by electron irradiation. In Ref. 5 it was found that the total CL emission from oxygen-depleted $YBa_2Cu_3O_{7-x}(x > 0.5)$ is consistently higher than that emitted by oxygen-annealed $YBa_2Cu_3O_{7-x}(x \sim 0)$. The role of oxygen in the luminescence emission of high T_c superconductors has also been pointed out in Ref. 2. In particular the authors in Ref. 2 suggest by analogy to simpler oxide systems the possibility that luminescence peaks in 450 and 660 nm are related to F and F^+ centers.

On the other hand, the change in oxygen content in $YBa_2Cu_3O_{7-x}$ is known to produce metal to semiconducting transitions, the metallic phase corresponding to small x values. Cannelli *et al.*[7] attribute the metal to semiconductor-like transitions they observed under vacuum annealing to the removal of oxygen atoms from the Cu-O basal planes which are thought to supply the carriers for the electrical conduction.

Taking into account the results described in Refs. 5 and 7 it is suggested that in the present observations, changes in the oxygen content could potentially be involved. Since oxygen-depleted regions show a higher CL emission[5] the increase of CL during electron irradiation may be due to a loss of oxygen atoms. In that case the emission in the region 450–600 nm would be associated with the presence of oxygen vacancy defects. The suggestion of Ref. 2 that pre-existing vacancies are transformed into F or F^+ centers during electron irradiation appears then less likely. In particular the curve of Fig. 4, with a sharp discontinuity, does not indicate a continuous transformation of vacancies into F-type centers. The discontinuity would rather suggest a local phase transition taking

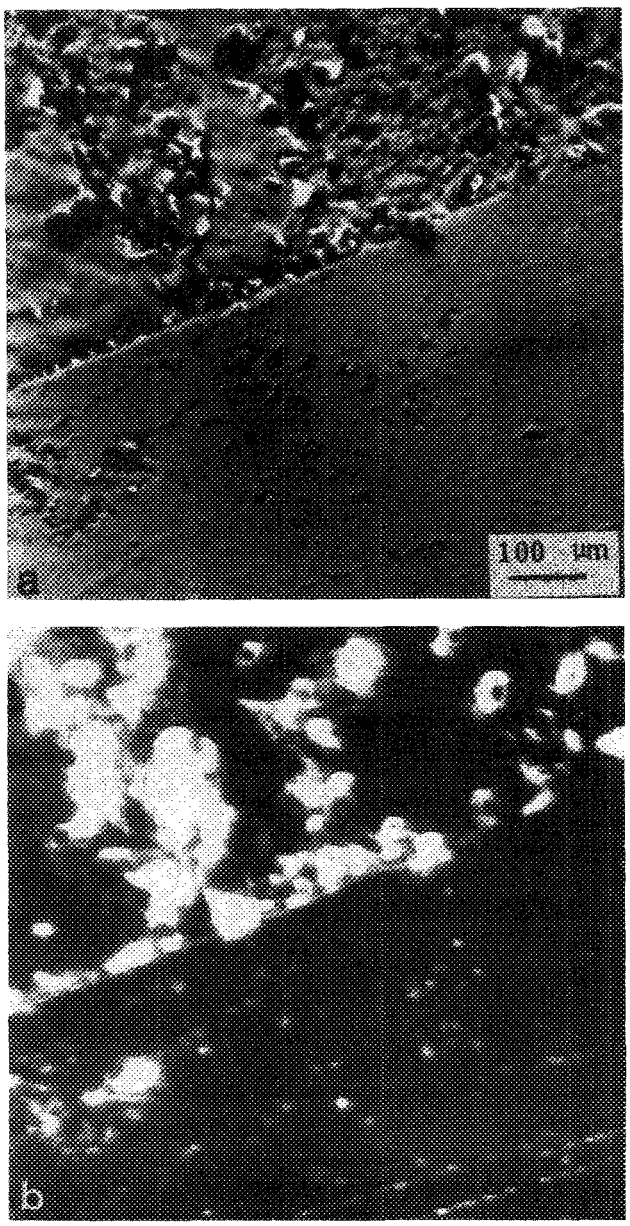

FIG. 3. SEM images from an irradiated area: (a) emissive mode; (b) CL mode.

place as a consequence of changes in oxygen content, similar to that reported in Ref. 7. On the other hand, the strong surface damage observed in the irradiated samples could imply some oxygen loss. The suggested influence of oxygen content on the appearance of the 450–600 nm CL band does not exclude the possibility that rare-earth ions are also involved in the emission.

While previous results indicate the relation between visible luminescence and oxygen content, no similar results relative to the infrared emission are available. Although changes in stoichiometry could be related to the appearance of the 1600 nm band, other possible origins of this band cannot be ruled out. As mentioned above, infrared photoluminescence bands have been observed[1] in other high T_c superconductors and assigned to electronic transitions in ions. On the other hand, Cannelli *et al.*[7] have found

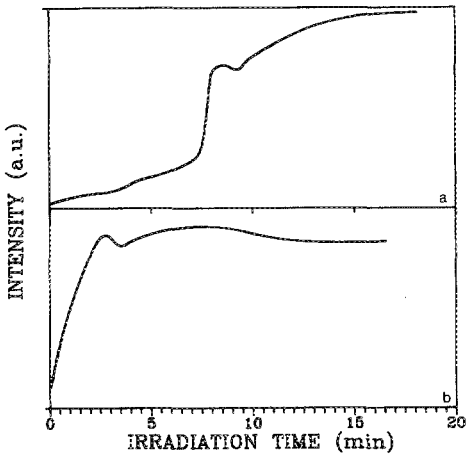

FIG. 4. Evolution of CL intensity with irradiation time (a) lower beam current (10^{-7}–10^{-8} A) and (b) higher beam current (above 10^{-7} A).

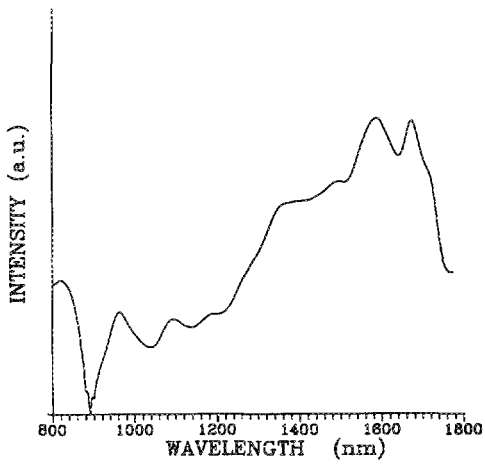

FIG. 5. Infrared CL spectrum from an irradiated area.

that the temperature dependence of resistivity of $YBa_2Cu_3O_{7-x}$ after the metal to semiconductor transition follows the exponential law of classical semiconductors with an energy gap of 0.77 eV. It is interesting to point out that this energy corresponds closely to the energy of the infrared band at about 1600–1700 nm (0.73–0.77 eV) observed in the present work.

The present results indicate that a broad CL band is related to oxygen-depleted zones of $YBa_2Cu_3O_{7-x}$. This implies that CL can be used, not only to identify impurities in this material, but also to detect different phases related to the oxygen content. The electron beam of the SEM can produce drastic changes in $YBa_2Cu_3O_7$ as revealed by visible and infrared luminescence. This means that, in principle, controlled local transitions can be induced and on the other hand, that care has to be taken when the SEM is used to study some properties or structural features of high T_c superconductors.

This work was partially supported by CICYT (Projects PB86-0151 and MAT 88-0250-CO2-02). The infrared equipment was donated by Alexander von Humboldt Stiftung.

[1] Y. Fujiwara and T. Kobayashi, IEEE Trans. Mag. **25**, 2563 (1989).
[2] D. W. Cooke, H. Rempp, Z. Fisk, J. L. Smith, and M. S. Jahan, Phys. Rev. B **36**, 2287 (1987).
[3] V. N. Andreev, B. P. Zakharchenya, S. E. Nikitin, F. A. Chudnovskii, E. B. Shadim, and E. M. Ster, JETP Lett. **46**, 492 (1987).
[4] B. J. Luff, P. D. Townsend, and J. Osborne, J. Phys. **21**, 663 (1988).
[5] J. H. Miller Jr., J. D. Hunn, S. L. Holder, and A. N. DiBianca, Appl. Phys. Lett. **56**, 89 (1990).
[6] J. Colino, J. L. Sacedón, L. del Olmo, and J. L. Vicent, J. Vac. Sci. Technol. A. (to be published).
[7] G. Cannelli, R. Cantelli, F. Cordero, and M. Ferretti, Solid State Commun. **68**, 323 (1988).