

Luminescence from $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films in the scanning electron microscope

F. Domínguez-Adame, P. Fernández, and J. Piqueras

Departamento de Física de Materiales, Facultad de Fisicas, Universidad Complutense, 28040 Madrid, Spain

P. Prieto, C. Barrero, and M. E. Gómez

Departamento de Física, Universidad del Valle, A. A. 25360, Cali, Colombia

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Visible and near infrared cathodoluminescence of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films is investigated in the scanning electron microscope. In particular, possible analogies in the cathodoluminescence of both systems have been analyzed. The spectra show only minor and slightly defined common features. Low-temperature observations show the capability of the cathodoluminescence technique to detect fine structural transitions. Some transformations induced by the electron beam are described.

INTRODUCTION

Luminescence techniques have been used sometimes to detect different phases or electronic levels in high-temperature superconductors. In particular, cathodoluminescence (CL) in the scanning electron microscope (SEM) provides information about the distribution of semiconducting and metallic phases, and enables to study locally the phase changes caused by treatments applied to the superconductor.¹⁻³ Previous CL works with the electron microscope refer mainly to bulk sintered samples of Y-Ba-Cu-O (Refs. 1 and 3) and thin films of Bi-Sr-Ca-Cu-O.² In Ref. 3, CL spectra and their evolution under electron-beam irradiation were reported while in Refs. 1 and 2 only panchromatic CL emission was investigated. In the present work thin films of Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O and thick samples of Bi-Sr-Ca-Cu-O have been studied by means of CL in the SEM. CL spectra of the different samples have been obtained in order to determine the main spectral features of the Bi-Sr-Ca-Cu-O luminescence and to compare the emission of both materials. The latter point arises from the fact that different high- T_c superconductors show similar optical features, as deduced from reflectance measurements, associated with specific local structures, as Cu-O planes, in the material.⁴

EXPERIMENTAL METHOD

The samples used in this work were $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Bi}_2(\text{Pb})\text{Sr}_2\text{CaCu}_2\text{O}_x$ films of about 2 μm thickness, grown by sputtering at high (2-4 mbar) oxygen pressures on $\text{SrTiO}_3(100)$ and $\text{MgO}(100)$, respectively. Thick films about 70 μm of the Bi-Sr-Ca-Cu-O (BSCCO) system, grown on $\text{MgO}(100)$ by a melting quenching annealing (MQA) method were also investigated. The MQA films consist of a dominant 2212 phase but the 2223 phase is also present. The films showed a T_c onset about 90 K. In order to separate the possible effect of the substrate on the luminescence measurements, CL spectra of sintered samples of both materials were also obtained. The samples were observed in the emissive and CL modes in a Hitachi S-2500 or in a Cambridge S4-10 scanning electron microscope at

accelerating voltages up to 30 keV. The experimental setup for CL measurements has been described in Ref. 3.

RESULTS AND DISCUSSION

Figure 1 shows a CL spectrum of the 1.5- μm -thick Bi-Sr-Ca-Cu-O film obtained with a beam energy of 25 keV. The shape of the spectra depends somewhat on the sample region observed and on the excitation conditions—focused or defocused—of the electron beam. For this reason the red band of the spectrum is not always readily observed. The blue band appears sometimes peaked at wavelengths longer than that shown in Fig. 1. This is probably due to the complex character of the blue emission with different relative contribution of the 490-nm component. The blue band centered between 405 and 450 nm is observed even with accelerating voltages as low as 5 keV which allows to rule out a contribution of the substrate to this emission. Although the emission is not homogeneous in the sample it appears difficult to correlate CL images to the emissive mode ones.

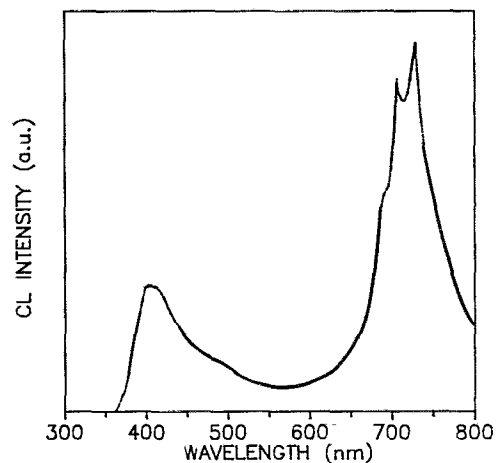
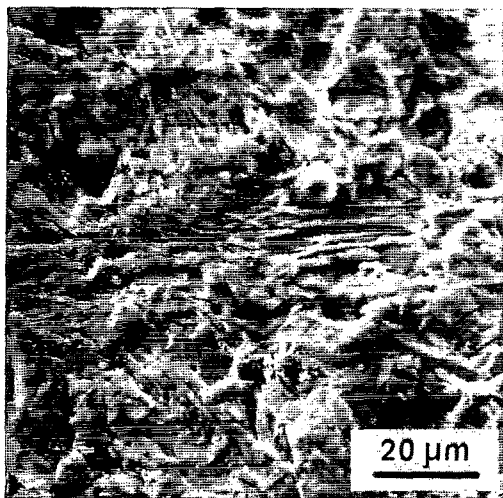
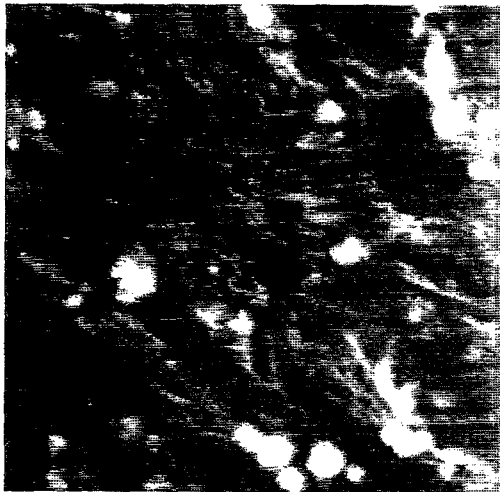


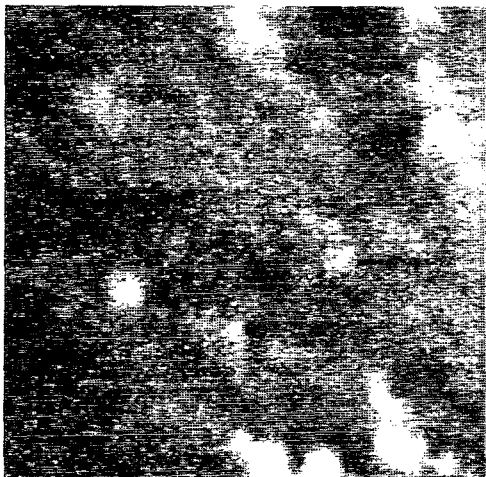
FIG. 1. CL spectrum obtained from a 1.5- μm -thick $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ film, at an accelerating voltage of 25 keV.



(a)



(b)



(c)

FIG. 2. Images obtained from a 70- μm -thick Bi-Sr-Ca-Cu-O film at an accelerating voltage of 25 keV: (a) emissive mode; (b) panchromatic CL mode; (c) CL mode with a 400-nm optical filter.

Figure 2(a) shows an electron emissive mode image of the sample grown by MQA (70- μm thickness) and Figs. 2(b) and 2(c), respectively, show the panchromatic CL image and the image corresponding to the emission selected with a 400-nm optical filter, of the same area of the sample. The CL spectra of this sample are similar to those shown in Fig. 1 although, as mentioned above, the appearance of the red band is controlled by the excitation conditions. In order to investigate spectral variations in different regions of the sample, spectra were recorded with the beam fixed on one of the bright spots of Fig. 2(b) and on the dark background, respectively. Both spectra are shown in Fig. 3. In the bright spots there is high 410-nm emission while in the dark background a broad CL band extending up to about 550 nm is observed. Sintered samples show similar spectra to those obtained in the films. All samples were stable under the electron beam unless 30-keV beam energy and high beam currents were used. In such cases changes in the sample surface and increase of the CL emission are detected.

The evolution of the CL signal by decreasing the sample temperature is associated to contrast changes as those shown in Fig. 4. Most of the bright spots observed in the CL image at 230 K [Fig. 4(b)] do not appear at 85–90 K [Fig. 4(c)]. The temperature dependence of CL intensity and contrast shows that the superconducting transition does not determine the observed variations, which would be mainly due to structural changes above T_c . Previous measurements of internal friction, thermal analysis and specific heat^{5,6} indicate that superconducting Bi-Sr-Ca-Cu-O ceramics undergo fine structural changes below room temperature. Some of such transitions can be related to the here observed luminescence changes.

Figure 5 shows the CL infrared spectrum of the MQA sample. The IR emission is not homogeneously distributed. Some regions of sizes ranging between 10 and 50 μm show

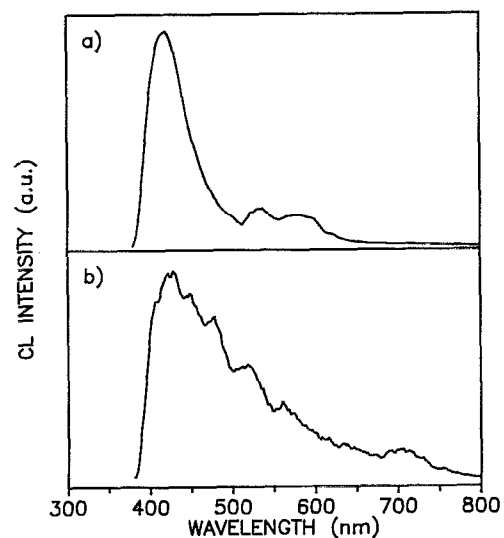
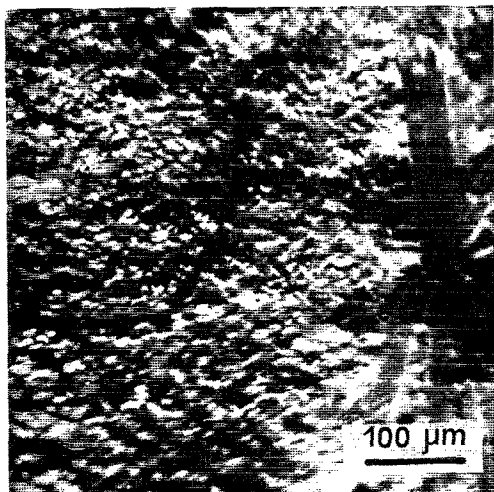
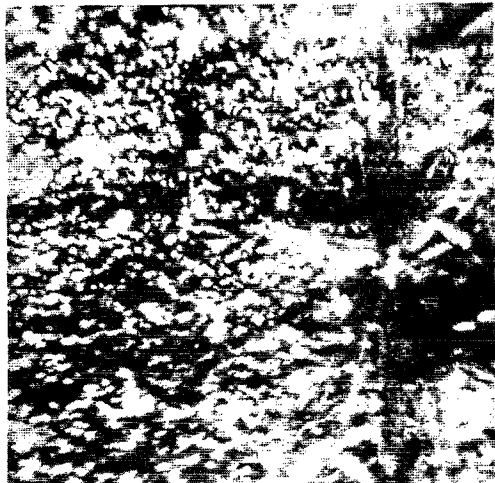


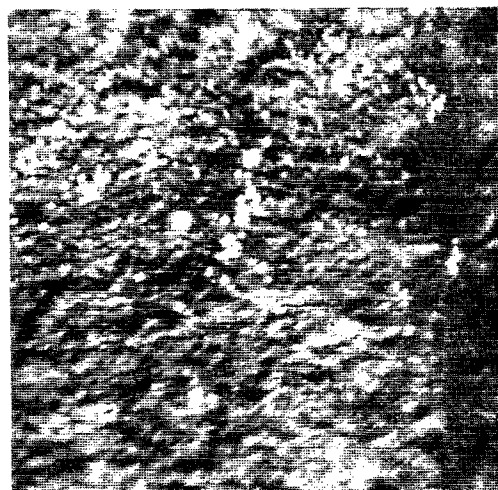
FIG. 3. CL Spectra from a 70- μm -thick Bi-Sr-Ca-Cu-O film at an accelerating voltage of 25 keV recorded (a) with the beam fixed on one of the bright spots of Fig. 2(b) and (b) on the dark background.



(a)



(b)



(c)

FIG. 4. Images obtained from a 70- μm -thick Bi-Sr-Ca-Cu-O film at an accelerating voltage of 25 keV, (a) emissive mode and panchromatic CL mode (b) 230 K and (c) 85 K.

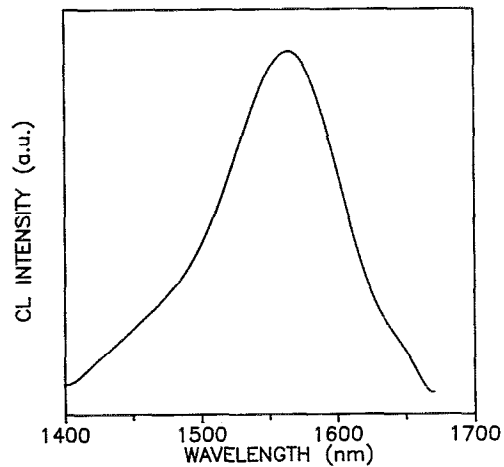


FIG. 5. Infrared spectrum from the 70- μm -thick Bi-Sr-Ca-Cu-O film at an accelerating voltage of 30 keV.

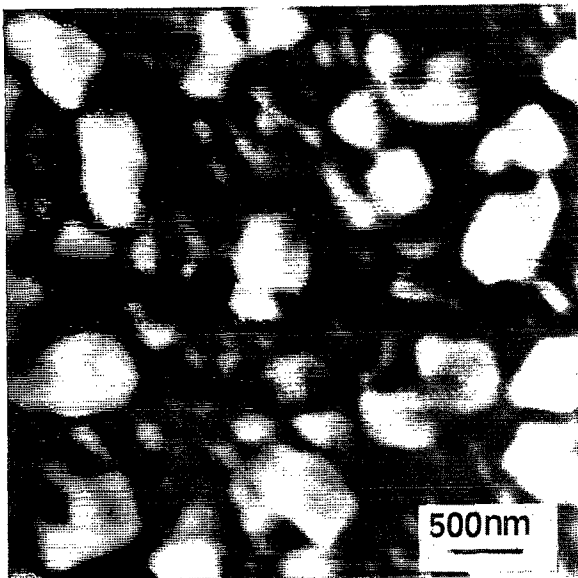
a higher emission with a directly observable slow decay. Such slow decay is also observed in regions of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ samples.

Figure 6(a) shows the secondary-electron image of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ film with a particle distribution on the surface. The presence of a high density of particles or islands in sputtered Y-Ba-Cu-O films has been previously reported⁷ and associated to the precipitation of CuO. The CL emission is higher in the islands as Fig. 6(b) shows. A possible contribution from the substrate has made difficult the spectral analysis of the CL from the film. An intense CL band peaked at about 400 nm corresponds probably to the SrTiO_3 because in this spectral region the CL emission of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ is relatively weak.³ The CL spectra from the particles are similar to that of the matrix but show a lower contribution of the mentioned blue band. However, the position of the CL peaks does not allow to determine the chemical composition of the particles.

On the other hand, as previously reported for the case of sintered $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$,³ the electron beam can cause changes detectable in the emissive mode of the SEM as well as in the CL image. Figure 7 shows an image corresponding to changes induced by different scans on the sample. The controlled use of this effect can, for instance, produce a thin strip of semiconducting phase separating two regions of metallic phase or in general be applied in superconductor heterostructures problems. The above described islands do not seem to be an obstacle for the electron-beam-induced transformations, as Fig. 7 shows.

The CL from $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ is also temperature dependent as Fig. 8 shows. As in the case of the BSCCO samples, the superconducting transition does not determine the observed CL changes. Instead, the CL increase by decreasing temperature should be related to the CL changes of the semiconducting phases of the system.

The present results show that $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$, as other high-temperature superconductors, presents a complex luminescence spectrum. The main CL peak appears at about 400 nm and overlaps with another band in the region 550–



(a)



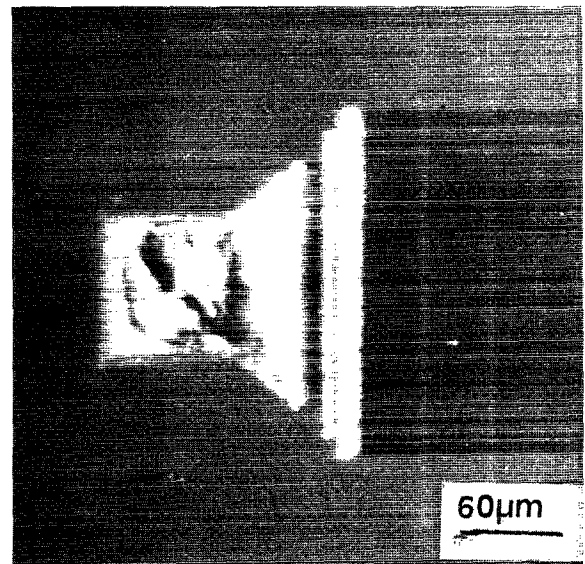
(b)

FIG. 6. Images from the surface particle distribution obtained from the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ film, (a) emissive mode; (b) panchromatic CL mode.

650 nm. The fact that the main phase is the 2212, indicates that the latter band, observed only in localized bright regions, is related to a minority phase, either 2223 or an insulating phase produced during film growth. As mentioned above, absorption and reflectance measurements of several authors have demonstrated the existence of similar optical features which could be related to Cu-O planes in different superconductors. Comparison of CL spectra from $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Bi}_2\text{Sr}_2\text{sCaCu}_2\text{O}_x$ does not reveal clear analogies that, however, cannot be ruled out. In fact, if $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ samples irradiated in the SEM are considered, some features between 490 and 590 nm are common to both systems. The same uncertainty applies to the infrared region. In both systems a broad CL band at about 1600 nm appears, as the present work and Ref. 3 show, but the



(a)



(b)

FIG. 7. Images showing the changes induced by the electron beam on the Y-Ba-Cu-O film, (a) emissive mode; (b) panchromatic CL mode.

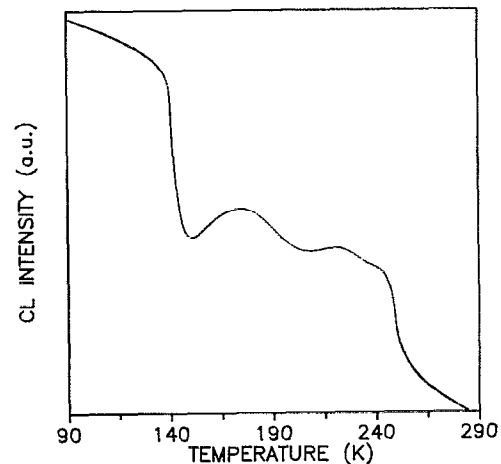


FIG. 8. Temperature dependence of CL intensity from an $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ film.

exact position of the peaks do not confirm the possibility that the infrared bands have a similar origin.

Regarding the electron-beam-induced luminescence increase, as that shown in Fig. 7 for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, it has been previously discussed³ in terms of oxygen loss during irradiation. Here the effect is described for thin films and its potential use to locally modify the superconducting properties is pointed out. The BSCCO samples are much more stable under electron beam but as is here for the first time described, CL increase is also observed in this system when high currents (about 10^{-6} A) and 30 keV beam energy are used.

CONCLUSIONS

In conclusion CL imaging as well as visible and near infrared CL spectra allows to differentiate phases in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ thin films in the electron microscope and to detect temperature and electron-beam-induced changes. The electron beam can be used to modify locally the film properties. Decreasing temperature below room temperature causes CL intensity variations related to structural changes above T_c . Comparison of CL spectra of both systems investigated does not clearly reveal

common features contrary to that found in studies of other optical properties of these materials and which have been related to Cu-O planes.

ACKNOWLEDGMENTS

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