Homogeneity assessment of $YBa_2Cu_3O_{7-x}$ single crystals by cathodoluminescence microscopy

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Cathodoluminescence (CL) of $YBa_2Cu_3O_{7-x}$ single crystals has been investigated in the scanning electron microscope. Some regions of the crystals, generally related to steps or other growth features, show enhanced CL intensity. Spectra show the presence of two emission bands centered at about 2.85 and 2.3–2.4 eV, respectively. In the regions of higher CL intensity, the 2.3 eV band, which has been attributed to defects in the oxygen sublattice, shows a higher relative intensity. © *1996 American Institute of Physics.* [S0021-8979(96)00314-3]

I. INTRODUCTION

Luminescence of high-temperature superconductors (HTSC) has been investigated often in past years. Besides luminescence emission related to impurity phases or residual precursors, the existence of intrinsic luminescence emission related to electronic processes in superconductors materials is a well-established effect. Ginder *et al.*[1] in photoexcitation experiments in La_2CuO_4 reported on luminescence at about 2 eV and confirmed the existence of long-lived stable electronics defect states. Cooke *et al.*[2] studied the thermally stimulated luminescence (TSL) in different superconductors and suggested the presence of F-type defects as one possible reason to explain the observed emission. Cathodoluminescence (CL) in $YBa_2Cu_3O_{7-x}$ ceramics has been described by several authors[3–6] as visible emission with bands in the blue-green spectral range. More recently, CL in the scanning electron microscope (SEM) has been used to characterize HTSC ceramics. Miller *et al.*[7] observed that insulating phases in $YBa_2Cu_3O_{7-x}$ emit higher CL signals than nominally metallic phases, and other CL microscopy works indicated the relationship between certain luminescence features and oxygen-depleted zones in $YBa_2Cu_3O_{7-x}$.[8–11] In particular a 2.3 eV emission band was related to centers involving oxygen vacancies. A band at the same energy has been reported in CL microscopy studies of $Tl_2Ba_2CuO_{6+x}$ (Ref. 12) and $Bi_2Sr_2CaCu_2O_x$ (Ref. 13) ceramics. Another intrinsic luminescence band centered at about 2.85 eV has been investigated by different authors by CL and photoluminescence (PL) in Bi- and Y-based superconductors. Fugol *et al.*[14] attribute the 2.85 eV emission to electron transitions due to a charge transfer process involving an F center and a negative molecular oxygen ion, and Stankevitch *et al.*[15] consider the possibility of an oxygen quasimolecule as the center responsible of the 2.85 eV luminescence that they observed in $YBa_2Cu_3O_{7-x}$ and $Bi_2Sr_2CaCu_2O_{8+x}$ single crystals. Although the different reports show the similarity of luminescence spectra of ceramic samples and single crystals, the information obtained by CL microscopy refers mainly to ceramics samples. The results on ceramics suggest that the application of the CL technique to single-crystal characterization would be useful to study homogeneity of the samples at micron level in relation to oxygen content and/or oxygen-related defects or other luminescent centers. In the present work, CL in the SEM is used to study such homogeneity questions in the case of $YBa_2Cu_3O_{7-x}$ single crystals.

II. EXPERIMENTAL METHOD

The samples (Superconix, Inc., U.S.A.) were platelets of about $2\times2\times0.1$ mm^3 in size, grown from a slowly cooled melt of precursors. The critical temperature T_c was 85 K as determined by magnetic measurements based in the Meissner effect. Vickers diamond pyramid indentations, made with an Akasi MVK-E3 microhardness system, were used to introduce local plastic deformations in one of the samples. Applied load was 100 g.

The observations were performed in a Hitachi S-2500 SEM. The samples were studied in the emissive and CL modes at an accelerating voltage of 20 kV and currents lower than 10 nA. Temperature was fixed at 80 K. In order to get the CL images the light arising from the crystal was concentrated by an optical lens on a photomultiplier attached to a window of the microscope. An Oriel 78215 computer controlled monochromator was used to record the CL spectra.

III. RESULTS AND DISCUSSION

SEM images in the secondary electron mode reveal the existence of regions with different topographic features. Some areas of the crystal have a flat surface crossed by steps or terraces [Fig. 1(a)]. Adjacent to this area a more complex relief like the growth platelets shown in Fig. 2(a) can be observed. Some regions of the sample show the growth ledge structure imaged in Fig. 3(a). CL images show an inhomogeneous distribution of luminescence in the crystal, mainly related to some of the features observed in the topography images as Figs. 1(b), 2(b), and 3(b) show. In spite of this correlation, observations under different orientations of the crystal relative to the detector have shown that CL contrast is not a topographic effect. This is confirmed by the CL spectra recorded at different regions of the crystal in order to study the origin of the luminescence distribution. Figure 4(a) shows the spectrum in a large flat area free of steps or other bright features. Spectra recorded in bright regions, as the steps shown in Fig. 1, depend on the area considered but all show a broadening of the luminescence band due to a higher

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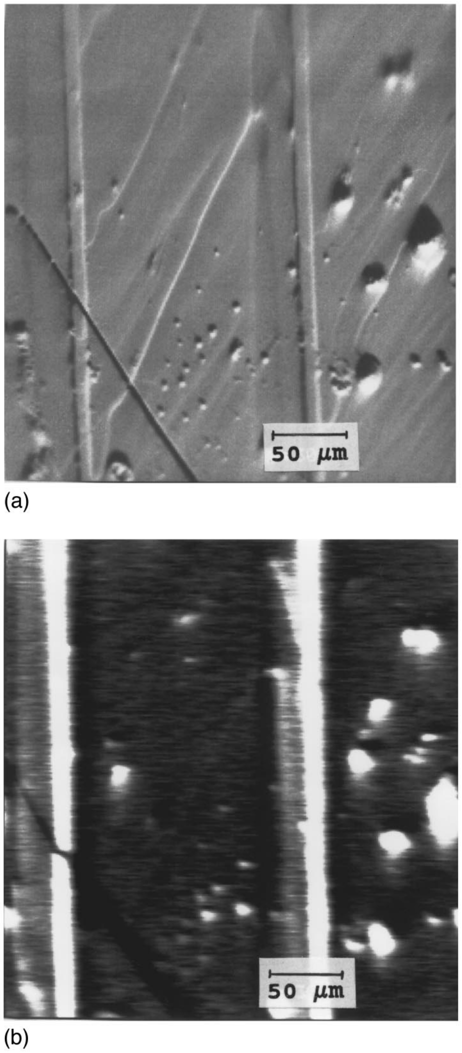

FIG. 1. Step structure on the surface of one crystal: (a) secondary electron image; (b) panchromatic CL image.

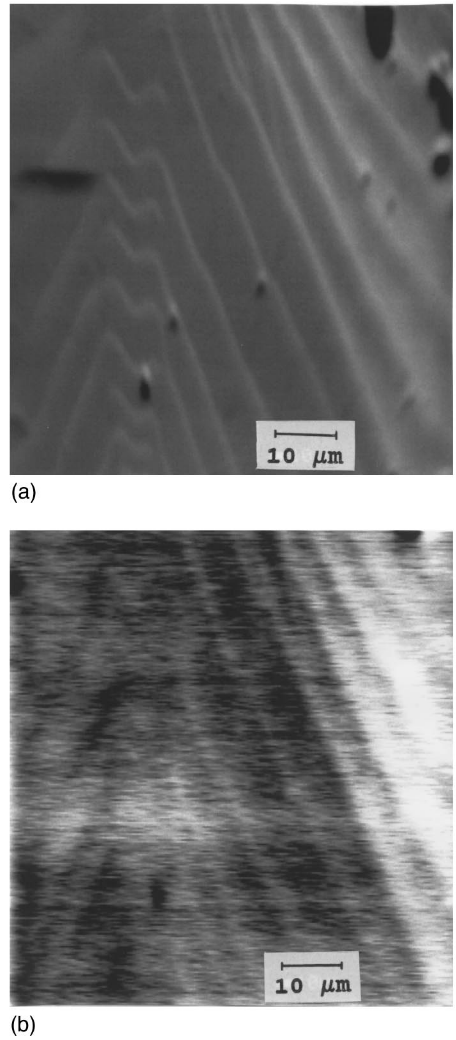

FIG. 2. Surface growth platelets imaged in the (a) emissive and (b) CL modes.

relative intensity in the 2.2–2.4 eV spectral region compared with the emission at about 2.8–2.9 eV. In some cases two bands appear resolved in the blue-green spectral range [Fig. 4(b)]. Figure 5 shows secondary electron and CL images of an area damaged by the diamond indentor. The indentation figure is distorted due to the curvature of the surface of the as-received sample. The mechanical treatment causes the local increase of CL emission as well as spectral changes. A well-resolved band peaked at about 2.3 eV appears in the spectrum recorded from the deformed area (Fig. 6).

The appearance of the broad luminescence band in the spectrum of Fig. 4(a), representative of the macroscopic crystal, agrees with previous spectra of single crystals recorded by nonspatial resolved photoluminescence, e.g., Refs. 14 and 15. In our case the spectrum extents to lower energies showing significative intensity up to 2 eV instead of the 2.5 eV energy which appears as an approximate limit in Ref. 15. The CL spectrum of this work includes a component at about 2.3 eV, resolved in the spectra of localized areas. The appearance of the 2.3 eV is either an effect of a different crystal defect structure, as compared with crystals of Refs. 14 and 15, or is due to a different excitation in CL and PL experiments. It is known that often CL and PL spectra of a given sample show different features due to the more selective excitation in the PL technique. The band dominating the spectrum of Fig. 4(a) is a complex band whose main components are the often reported emissions at 2.85 and 2.3 eV related to processes in the oxygen sublattice.

The use of CL microscopy reveals the existence of structural inhomogeneities in the crystal which influence its electronic properties. Spectra show that regions with enhanced intensity present a higher relative emission in the green (about 2.3–2.4 eV) range [Fig. 4(b)]. These regions often correspond to growth steps or other topographic features. In particular, some of the step distributions and growth morphologies observed here are similar to those previously described and discussed in other works.[16,17] In Ref. 16, groups of steps (as in Fig. 1) with different spacings between individual steps were suggested to be originated from dislocations or dislocations groups with different characteristics. In Ref. 17 parallel growth ledges or growth platelets were observed, which have some similarity to the structures appearing in some regions of the crystals investigated in this work (Figs. 2 and 3). The main CL contrast is observed in the steps and ledges or in some of the straight features clearly imaged in the secondary electron images. Spectra of these

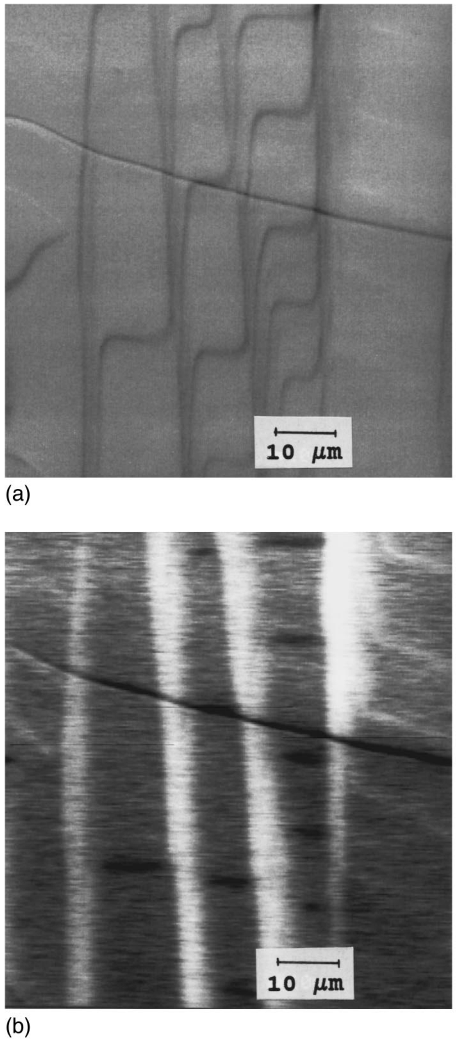

FIG. 3. Growth ledge structure in one of the samples: (a) secondary electron image; (b) CL image.

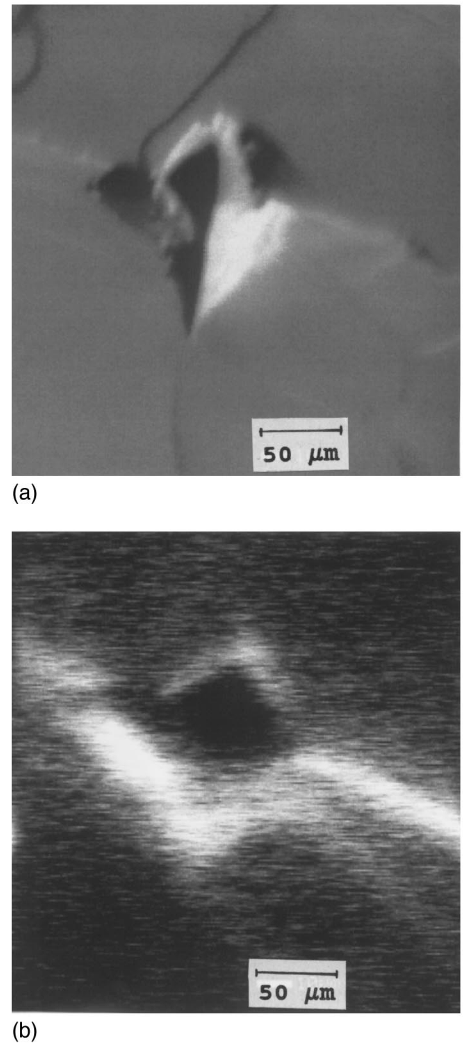

FIG. 5. (a) Secondary electron and (b) CL images of an indented area.

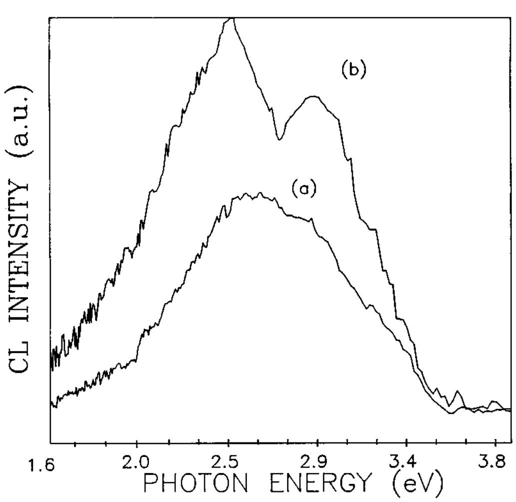

FIG. 4. CL spectra recorded (a) at a flat area of one crystal and (b) at a growth step.

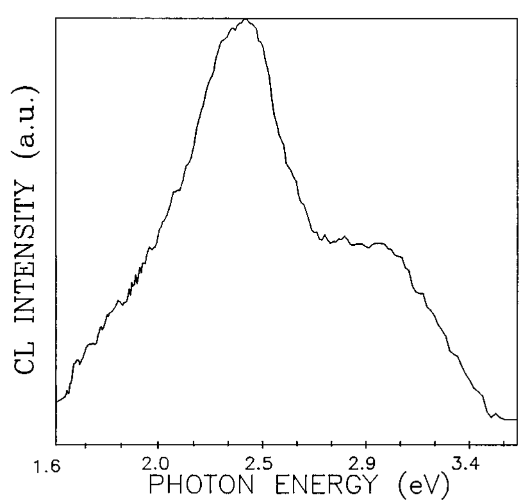

FIG. 6. CL spectrum from the region deformed by an indentation.

regions show that centers related to the 2.3 eV emission accumulate at the steps or other interfaces during the growth process. These centers have been proposed to involve oxygen vacancies as described in Sec. I.

The CL image and spectrum of an indentation [Figs. 5(b) and 6] reveal the defect generation in the deformed area. The increase of the 2.3 eV band indicates that some of the deformation-induced defects are the oxygen vacancy related defects detected at the growth features as well as in $YBa_2Cu_3O_{7-x}$ ceramics after annealing or electron irradiation treatments.[10–12] Oxygen vacancy generation and the related luminescent effects, caused by indentation or other deformation treatment, have been often described in the case of some ionic crystals, mainly MgO, e.g., Ref. 18.

IV. CONCLUSION

CL microscopy shows the existence of inhomogeneities of the defect structure in $YBa_2Cu_3O_{7-x}$ single crystals grown from a slowly cooled melt of precursors. Defects related to oxygen deficiency appear concentrated at growth steps and other interfaces in the crystals. Local deformation of the samples causes the generation of the same kind of defects, as CL microscopy and spectroscopy reveal.

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