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C. Díaz-Guerra, J. Piqueras, J. A. García, A. Remón, Christine Opagiste. Cathodoluminescence and photoluminescence studies of sintered BaCuO2. Journal of Luminescence, Elsevier, 1997, 71 (4), pp.299-304. <10.1016/S0022-2313(97)00096-3>. <hal-00566906>

Journal of Luminescence 71 (1997) 299-304

Cathodoluminescence and photoluminescence studies of sintered $BaCuO_2$

C. Diaz-Guerra[a], J. Piqueras[a], J.A. Garcia[b], A. Remon[b], C. Opagiste[c]

a *Departamento de Fisica de Materiales, Facultad de Ciencias Fisicas, Universidad Complutense, E-28040 Madrid, Spain*
b *Departamento de Fisica Aplicada II, Facultad de Ciencias, Universidad del Pais Vasco, Lejona (Vizcaya), Spain*
c *Laboratoire Structure de la Matière. Université de Savoie, B.P. 240, 9 Rue de l'Arc-en-Ciel, F-74942 Annecy le Vieux Cedex, France*

Abstract
The capability of luminescence techniques to characterize $BaCuO_2$ and in particular to detect the presence of this compound as impurity phase in high-T, superconductors (HTSC) has been investigated. Cathodoluminescence (CL) in the scanning electron microscope and photoluminescence (PL) have shown that the luminescence emission of $BaCuO_2$ can be separated from those of Y-, Bi- and Tl-based HTSC. The main luminescence bands and their decay times in $BaCuO_2$ are described.

Keywords: Cathodoluminescence; Scanning electron microscopy; Time-resolved photoluminescence

1. introduction

In the study of physical and structural properties of high temperature superconductors (HTSC) ceramics, the presence of impurity phases is an important factor to be considered in the analysis of experimental results. Impurity phases are often related to precursors, and information is available on their nature and content in the matrix. In other cases however, unknown phases appear during treatments received by the samples which cause partial decomposition of the superconductors.

One of the phases which can appear as a result of decomposition of different HTSC systems is $BaCuO_2$ whose physical properties have not been often reported. In particular, $BaCuO_2$ is known to show luminescence properties [l] which makes luminescence techniques potentially useful for the detection of this compound in HTSC ceramics.

On the other hand, several luminescence bands are related to structural features of HTSC [2-4], and the knowledge of the luminescent behaviour of impurity phases appears necessary to separate the luminescence response of matrix and impurities. In the present work photoluminescence (PL) and cathodoluminescence (CL) in the scanning electron microscope (SEM) are used to investigate the luminescence of sintered $BaCuO_2$.

2. Experimental method

Samples were prepared by a solid state reaction from a mixture of BaO_2 and CuO precursor powders. After pressing the stoichiometric mixture in order to obtain the $BaCuO_2$ phase, the pellets were heated in air at 980°C during 16 h. After regrinding, the same thermal treatment was applied. X-ray diffraction (XRD) investigations showed that the sample was nearly pure. Only small amounts of $Ba_2Cu_3O_6$ impurity phase could be detected.

CL investigations were performed in a Hitachi S-2500 SEM equipped with a cooling stage system (Oxford Instruments) providing a continuous temperature control from 77-300 K. Accelerating voltage was 20 kV. For panchromatic CL images acquisition the light arising from the sample was concentrated by an optical lens on a H957-08 photomultiplier (PM), directly attached to a window of the microscope. In order to record CL spectra, an optical guide was used to feed the light to the entrance slit of an Oriel 78215 computer controlled monochromator, with the PM placed at the exit slit. Monochromatic CL spatial distribution was studied in a similar way fixing the desired wavelength in the monochromator.

Steady-state PL, time-resolved spectra (TRS) and lifetime measurements were performed using a CD900 spectrometer system (Edinburgh Instruments), with a R955 PM in a Peltier cooled housing. For steady-state spectral measurements, a 450 W Xe lamp was used as an excitation source and a δ Xe flash lamp with a 2 μs pulse of 285 nm (4.35 eV) light for TRS. Lifetime measurements were performed using the multichannel scaling technique. The samples were cooled, between 10 and 270 K, in a closed cycle helium cryostat.

A liquid nitrogen cooled Ge detector was used to study the PL emission in the 800-1800 nm spectral range in which no measurable signal was observed.

3. Results and discussion

At 10 K, the maximum PL intensity is obtained by using the excitation energy of 4.35 eV (285 nm). In the corresponding emission spectrum a wide band with peaks at 2.70 eV (459 nm) and 2.54 eV (487 nm) is observed (Fig. 1). The 2.54 eV band fits to a gaussian curve whose peak position and FWHM (0.73 eV) do not change by increasing the temperature up to about 200 K. At higher temperature the band broadens and the intensity decreases. Fig. 2 shows a series of spectra at different temperatures between 10 and 270 K. Above this temperature the intensity is too low to record spectra with the experimental system used. The evolution of total PL intensity with temperature is shown in Fig. 3 and above 140 K an exponential decrease is observed.

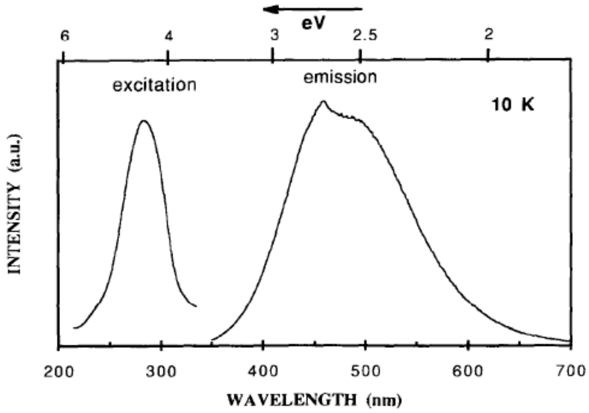

Fig. 1. PL excitation and emission spectra of $BaCuO_2$ recorded at 10 K

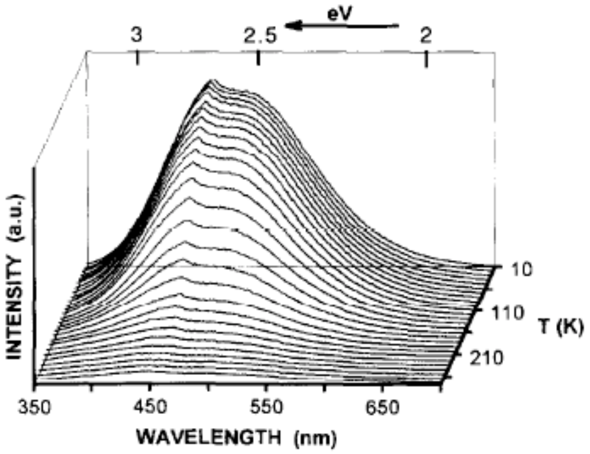

Fig. 2. $BaCu0_2$ PL spectra evolution with temperature.

The activation energy of the thermal quenching is about 50 meV Fig. 4 shows time resolved PL spectra at 10 K for different delay times. Both peaks (2.70 and 2.54 eV) present a similar evolution with increasing delay time. The intensity as a function of time can be represented by the equation:

$$I(t) = A + B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2)$$

with a fast decay component τ_1 of about 10 μs and a slow component τ_2 of about 200 μs. A represents the correction for constant background level. The adjusted values of B_1 and B_2 show that the fractional intensity,

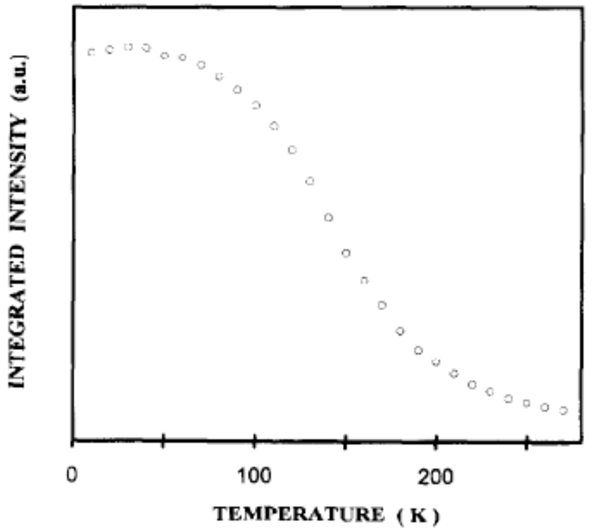

Fig. 3. Total PL intensity evolution with temperature.

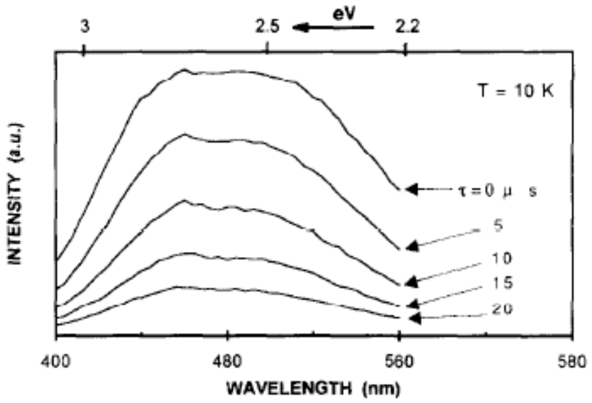

Fig. 4. Time resolved PL spectra recorded at 10 K for different delay times.

defined as $f_i = 100\ B_i\tau_i/(\sum B_i\tau_i)$, of the slow process is about 11 times lower than the fractional intensity of the fast process.

CL and emissive images of the sample show an inhomogeneous distribution of luminescence not related to specific topographic features (Fig. 5).

Fig. 6 shows a series of CL spectra, recorded at temperatures between 80 and 290 K, of an extended area of the sample including bright and dark regions. These spectra are, as the PL spectra, representative of an average emission in the sample. A broad CL band peaked at about 2.5 eV, and extending to higher energies, dominates the spectra. Another wide band centered near 3.0 eV appears as a shoulder of the main emission. The reported PL bands at about 2.55 and 2.70 eV seem to be included in the 2.5 eV peaked CL emission, while the 3.0 eV CL band is not observed in PL spectra. Such variations are often observed when luminescence spectra corresponding to different excitation techniques are compared. In particular PL under monochromatic excitation is known to be more selective, and in our sample excitation with 4.35 eV (285 nm) light favors the intense emission at about 2.70 eV. Excitation with electrons reveals, more clearly, a strong emission in the range 2.4-2.6 eV, as well as a different band at about 3.0 eV. CL spectra of selected areas show the inhomogeneity of the distribution of the different luminescent centers in the sample. In particular, strong emitting regions (as

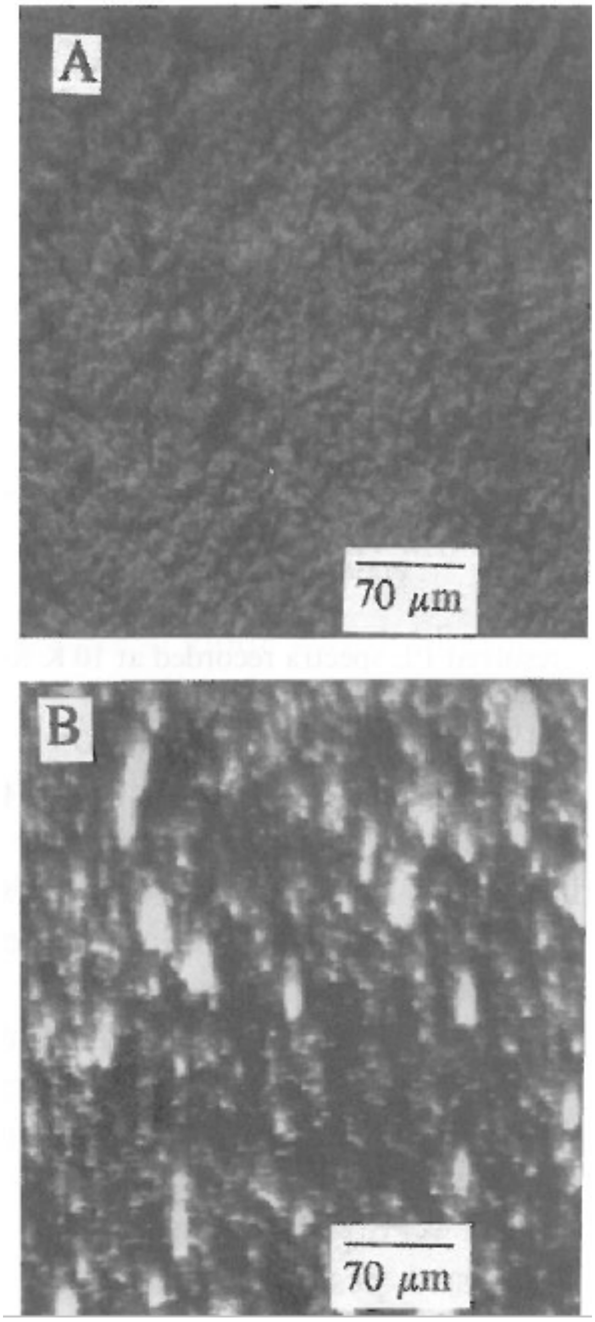

Fig. 5. Secondary electron (a) and panchromatic CL (b) mode images of an extended area of the sample.

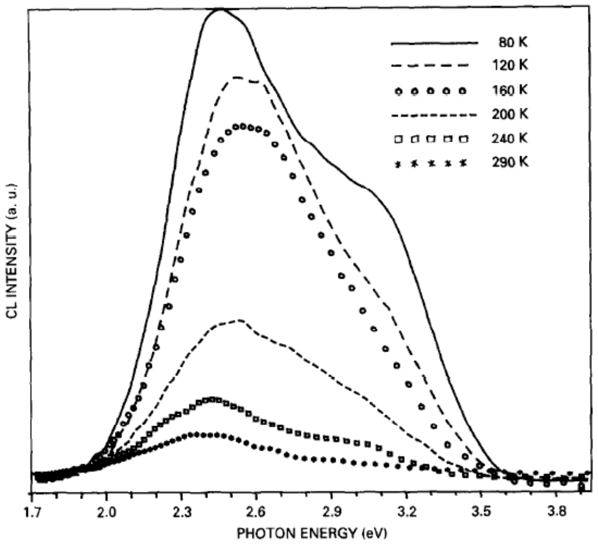

Fig. 6. Temperature dependence of the $BaCuO_2$ CL spectra.

imaged in the CL micrographs) typically show the spectrum that can be seen in Fig. 7 recorded at several temperatures. Here the low-energy band centered now at about 2.6eV dominates the emission.

In some areas of the sample, low- and high energy CL emission bands appear more clearly resolved (Fig. 8). CL monochromatic images recorded at 3.08 and 2.38 eV (Fig. 9) show that the spatial distribution of the luminescent centers is not the same, which indicates that at least two different radiative centers are involved in the emission.

The existence of luminescence emission from HTSC in the blue-green spectral range has been previously reported. In particular, CL and PL results obtained under similar experimental conditions as in this work, show that $YBa_2Cu_3O_{7-x}$ (YBCO), $Bi_2Sr_2CaCu_3O_{8+x}$, (Bi-2212) and $Tl_2Ba_2CuO_{6+x}$ (Tl-2201) exhibit luminescence bands at about 2.85 and 2.3 eV [2-8]. The latter band is related to oxygen deficiency or disorder phenomena in the oxygen sublattice, while the 2.85 eV band has been found to be also of intrinsic character and is attributed to an oxygen quasimolecule [9] or a complex involving F centers [10].

The present results show the difference of luminescence spectra of $BaCuO_2$ and the above mentioned HTSC materials. CL and PL enable to detect

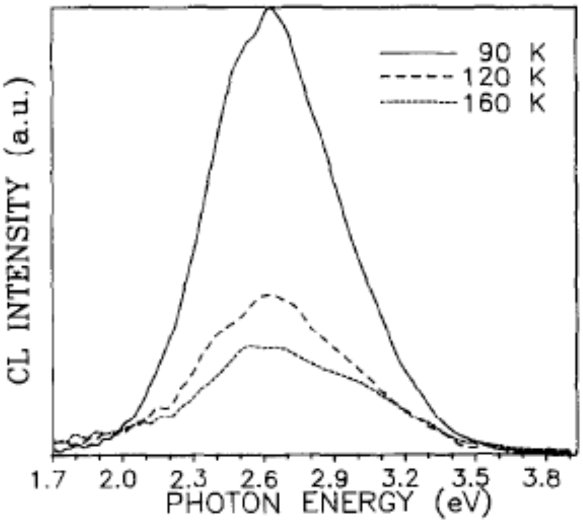

Fig. 7. CL spectra recorded at several temperatures in a bright zone of the BaCuO, sample.

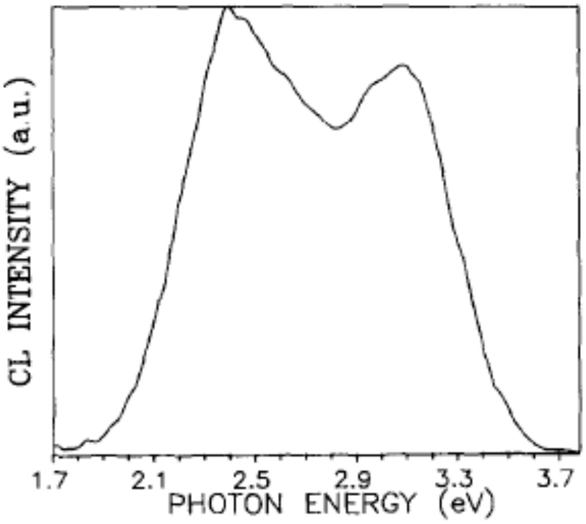

Fig. 8. CL spectrum of a small area of the $BaCuO_2$ ceramic.

$BaCuO_2$ in a HTSC matrix. CL microscopy in particular, could be used to obtain spatial distribution in $BaCuO_2$ phases. In addition to the different spectral features shown by $BaCuO_2$ and the mentioned HTSC materials, the decay times of emission are also different. Previous time-resolved spectroscopic studies have shown two components of τ with values of 34 and 87 μs for YBCO (5), and 12 and 70 μs for Bi-2212 [4].

CL or PL mechanisms in $BaCuO_2$ as well as the mechanisms causing the thermally stimulated luminescence [1] have not been described previously to our knowledge. The present data do not enable us to propose a luminescence mechanism, but makes it

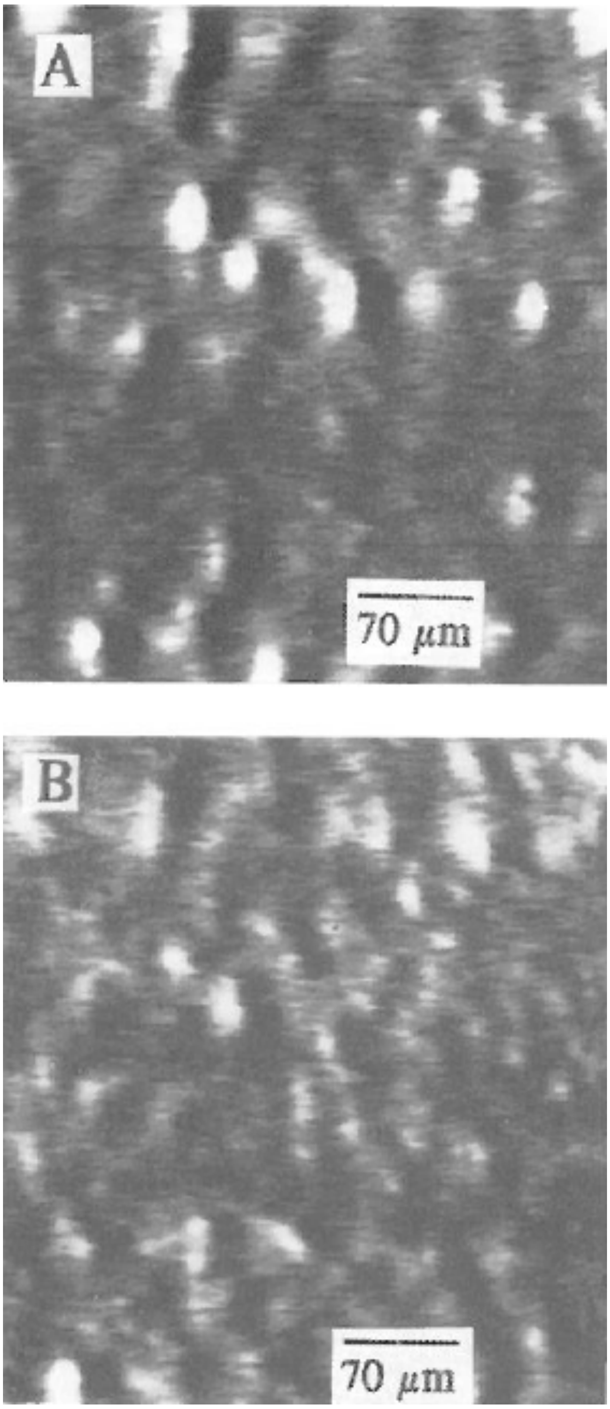

Fig. 9. Monochromatic CL micrographs of the area showed in Fig. 5. (a) 2.38 eV (521 nm) image. (b) 3.08 eV (403 nm) image.

possible to separate the luminescence of $BaCuO_2$ as impurity phase, from the HTSC luminescence. On the other hand, the comparison of the present CL results with the previously mentioned work on CL microscopy and spectroscopy of HTSC provides some comments on the $BaCuO_2$ luminescence. As CL images show, the distribution of CL intensity in $BaCuO_2$ is highly inhomogeneous. Spectral analysis has shown that in bright and dark areas of the sample two luminescence bands, whose relative weights depend on the area considered, are present. In HTSC a qualitatively similar CL intensity distribution has been observed, and a number of experiments enabled the interpretation of the CL intensity fluctuations as due to local variations in oxygen content or degree of order. Since XRD of the samples used in this work show only the presence of small amounts of $Ba_2Cu_3O_6$ impurity phase, the distribution of CL intensity would be related to structural defects and/or local changes in composition. Previous works on the crystal structure and composition of $BaCuO_2$ have shown that large deviations from the ideal composition are usual. In particular, oxygen content can vary among different samples between 1.8 and 2.5 oxygen in the formula unit [11, 12]; and local variations in a sample can take place as in the case of HTSC. Oxygen content changes and ordering effects in $BaCuO_2$ involving oxygen atoms and Cu^{2+} ions, have been reported in the past years [13, 14].

4. Conclusions

Two luminescence bands in the visible range with fast and slow decay components, centered at about 2.70 and 2.55 eV, are detected in $BaCuO_2$ by PL spectroscopy. CL spectra show two broad bands peaked near 2.5 and 3.0 eV. The first seems to include both PL emission bands, whereas the latter is not observed in PL spectra. CL microscopy has revealed that the 2.50 and 3.05 eV bands are associated with centers that show a different spatial distribution. The luminescence spectra of $BaCuO_2$ differ from spectra of several investigated HTSC. This fact enables us to use luminescence techniques to detect the presence of $BaCuO_2$ as an impurity phase in Y-, Bi- and Tl-based superconductors.

Luminescence in the $BaCuO_2$ sample investigated has an inhomogeneous distribution which could be related to local compositional and structural changes.

Acknowledgements
This work has been supported by DGICYT (Project PB93-1256) and by CICYT (Project MAT95-1184-E). C.D.G. acknowledges MEC for an FPI research grant.

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