JOURNAL OF MATERIALS SCIENCE 28 (1993) 6774–6778

Impurity phase recognition in YBCO high T_c superconductors by cathodoluminescence spectroscopy

P. R. FLETCHER, C. LEACH
Department of Materials, Imperial College, London, SW7 2BP, UK

Cathodoluminescence (CL) microscopy of $YBa_2Cu_3O_{7-x}$ using scanning electron microscopy (SEM) and light microscopy revealed the presence of impurity grains with a strong CL contrast. The impurities, present within internal pores of the material, were characterized by wavelength-resolved CL spectroscopy and by energy dispersive X-ray (EDX) analysis. Consideration of electron-beam conditions in the SEM resulted in a full correlation of microstructural features between the CL and electron emissive modes. Yellow CL emissions were generated from yttria-rich phases, and blue emissions were generated from copper-rich-barium-cuprate phases. EDX also demonstrated the presence of silicon within the pores. It is suggested that a glassy silicate phase is present, which may wet the impurity-phase grains. In identifying and characterizing these impurities, the CL technique proved to be a powerful tool in the determination of the quality of the pellet sample and hence its suitability as a target material for the laser-ablation deposition of thin films.

1. Introduction

Low critical current densities, $J_c < 10^5$ A cm^{-2} at liquid-nitrogen temperature (77 K) prevent the use of YBCO bulk material and wires in high-power applications; only "high quality" thin films are able to attain the necessary J_c of greater than 10^6 A cm^{-2}. In the laser-ablation process, the quality of the ablated films depends upon the quality of the target [1], which is itself a pellet of superconducting stoichiometry. Such materials would normally be prepared by a chemical route or, crudely, by a mix of oxides and carbonates in the appropriate proportions which would then be calcined and sintered. Processing routes like these in multi-element materials generally give rise to microstructural and compositional heterogeneities in the form of second phases and other impurities. The CL technique combined with EDX analysis can provide information about microstructural heterogeneities in the target material that can affect the thin-film quality.

The origins of quantitative CL analysis lie in the electronic-structure characterization of semiconducting materials. More recently, its use has diversified to other materials [2], including high-T_c superconductors, with the aim of enhancing the understanding of their microstructures. Light emission, via electron-beam irradiation, occurs by electron–hole pair recombination between quantum states in the energy-band structure. The nature of the electron–hole pair recombination is described more concisely by intrinsic, extrinsic, direct, indirect, and intra-band transitions [2, 3]. In wide-band-gap materials, additional states need to be generated within the band to support transitions in the visible range. Alternatively, luminescence can be generated by states internal to an ion. These self-luminescent centres, typically transition metals, should give characteristic spectral responses which are only slightly modified by the ligand field [2].

Recent literature in this field has noted the presence of strong CL contrast resulting from non-superconducting phases within YBCO 123 material superconductors. In one case [4], a luminescent impurity grain was resolved using CL on a YBCO pellet. Several researchers have imaged CL emission from the semiconducting $YBa_2Cu_3O_{7-x}$ ($x > 0.5$) phase [4–6] whilst the superconducting regions have been weakly luminescent. Induced luminescence by means of electron-beam irradiation has also been connected with the semiconducting, oxygen-deficient, 123 phase [7, 8]. CL analysis of the starting materials for YBCO pellet fabrication – Y_2O_3, $BaCO_3$ and CuO – showed significant light emissions from the Y_2O_3 and the $BaCO_3$ but not from the CuO [4–6]. Their luminescence intensity was found to be a function of stoichiometry [5, 6, 9].

At room temperature, high-T_c materials display luminescent spots. Previous studies have indicated that these have no correlation with features in the secondary-electron images [7, 10] of the materials surface. Fujiwara *et al.* [10] found that for the TlBaCaCuO system, the intensity of such a spot was 250 times that of the surrounding superconducting material. They also noted that the spectral response was different. For the YBCO and BSCCO materials, such information about the relative intensity of the CL emissive areas has not been presented. Compositional

0022–2461

mapping via EDX of these areas in the microstructure was not made. Miller *et al.* [5] discussed the importance of the beam current and its effect on CL resolution together with CL imaging.

In this contribution we will demonstrate how spectroscopic CL can be used to identify non-superconducting phases within a YBCO pellet.

2. Experimental procedure

A bulk-pellet sample of YBCO was fabricated by a conventional solid-state reaction route to produce a 123 superconducting phase material. The pellet contained grains 10–20 μm in size. The surface of the pellet was mechanically polished in order to optimize the specimen geometry for CL analysis. An ultrasonic bath was used to remove any polishing debris. The polishing compounds were checked for any CL emission; none was found.

Panchromatic CL images of the sample were recorded in colour using a Technosyn cold cathode luminescence stage, model 8200MK11, fitted to a light microscope. This was operated at 15 kV and at a load current of 200 μA illuminating approximately 1 cm^2 of the sample surface.

Collection of the CL emissions was carried out using an Oxford Instruments CL detector, and the wavelength was resolved by a Bentham monochromator with a slit width of 2 mm. A schematic of the overall system is shown in Fig. 1. Higher-order diffraction peaks were eliminated by the use of two optical filters at 400 and 700 nm. A photomultiplier with a useful wavelength range of 400 to 800 nm amplified any emissions. The spectra presented are fully corrected for the system's wavelength response. The secondary-electron and CL images were generated in a Jeol JSM 840A scanning electron microscope, operating at 10 kV with a 15 nA beam current in spot mode, for the CL-wavelength-resolved spectra collection. The penetration depth was calculated to be about 0.6 μm, which was smaller than the grain size. This offered the opportunity to correlate luminescent centres with surface features, if possible. For each analysis, the CL collection mirror was optimally focused.

EDX analysis was carried out in a Jeol 733 superProbe scanning electron microscope at an accelerating voltage of 15 kV and a beam current of 2 nA, with an Oxford Instruments AN10000 computer.

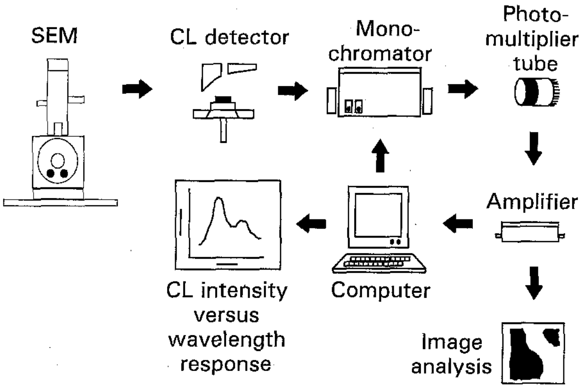

Figure 1 The CL light-collection system.

3. Results

Direct CL emission via the CL-optical-stage unit is shown in Fig. 2. The colour version of Fig. 2 illustrates four distinct types of wavelength response. These are randomly distributed at points about the surface of the pellet. Fig. 3a and b are secondary-electron and CL images, respectively, of some of the luminescent spots in Fig. 2. It can be seen that strong luminescence is observed at some, but not all, of the pores in the material. No strong CL emissions were seen to come from the polished surface. Spectroscopic analysis of the four CL emissions presented in Fig. 4 correlates well with the original colour visual representation that has been reproduced in monochrome in Fig. 2. Analysis of several emissions of the same colour showed that their wavelength response was similar. All the spectra contained broad bands rather than resolved peaks because of phonon interactions. Thus no detailed information concerning the electronic transitions giving rise to CL were obtainable. There was no change in the luminescence intensity over time, indicating there is no beam irradiation damage [3]. Fig. 5 shows SEM images showing, in detail, that in many cases the CL emissions can be attributed to grains within the pores. Because of the size of some pores, the origin of the luminescence could not be determined. Scattering of photons arises at the pore edges, as shown in Fig. 5b; this is related to the roughness of the small particles. EDX analysis of the luminescent grains is shown in Table I, for each of the four colours of excitation. The EDX system calculated the amount of oxygen by stoichiometry, and the data was corrected for any signal contribution from the surrounding YBCO matrix.

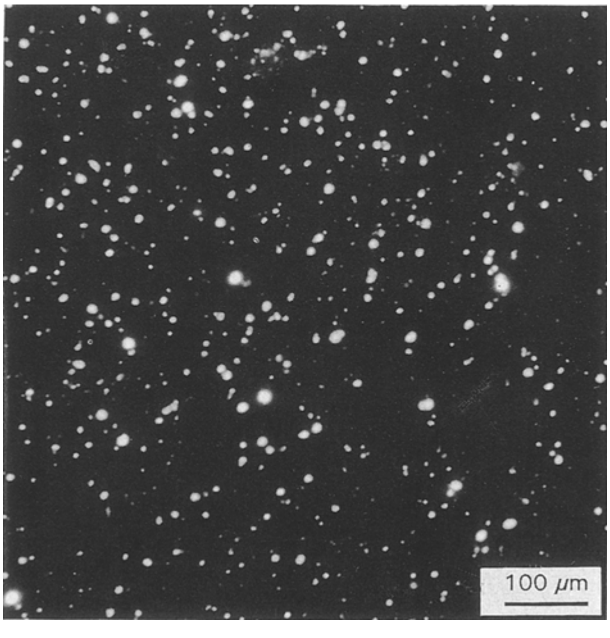

Figure 2 Panchromatic CL emission from the polished surface of a YBCO pellet.

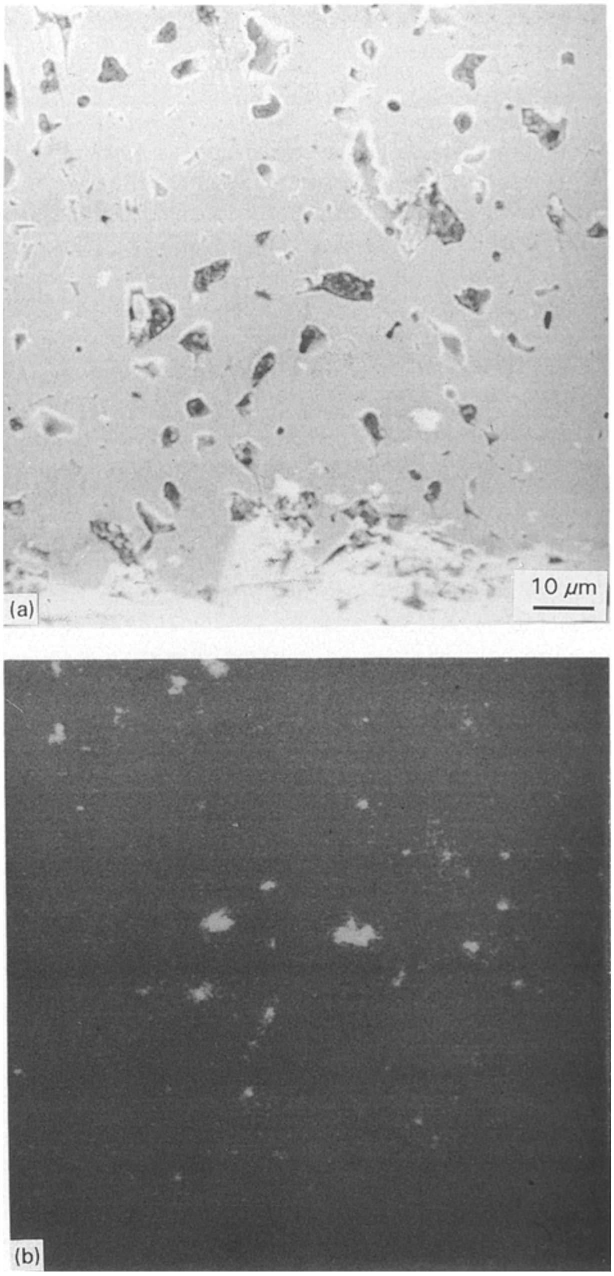

Figure 3 Micrographs of an area in Fig. 2: (a) secondary-electron image and (b) SEM CL.

4. Discussion

Phases within the YBCO pellet displayed several distinct CL emissions in the visible range. In many cases, it was possible to identify small micrometre-sized grains present at the pore surfaces (Fig. 5) that produced the luminescence. Thus, the luminescent spots could be correlated to identifiable regions in the microstructure. Other researchers, using larger electron-beam accelerating voltages and rough surface samples, were not able to determine the origin of the light spots [7, 8]. The luminescent excitations from the impurities were always at least two orders of magnitude brighter than those of the surrounding superconducting material which was found to be weakly luminescent. This is in agreement with the findings of other researchers [5–8, 10]. Variation of the electron-beam current and accelerating voltage gave no change in the density of the active sites present. Because of the low beam accelerating voltage used, subsurface pores containing luminescent grains were not excited, resulting in no direct observation of spurious luminescent spots. However, in some cases, light generated in this way and totally internally reflected might escape at pores.

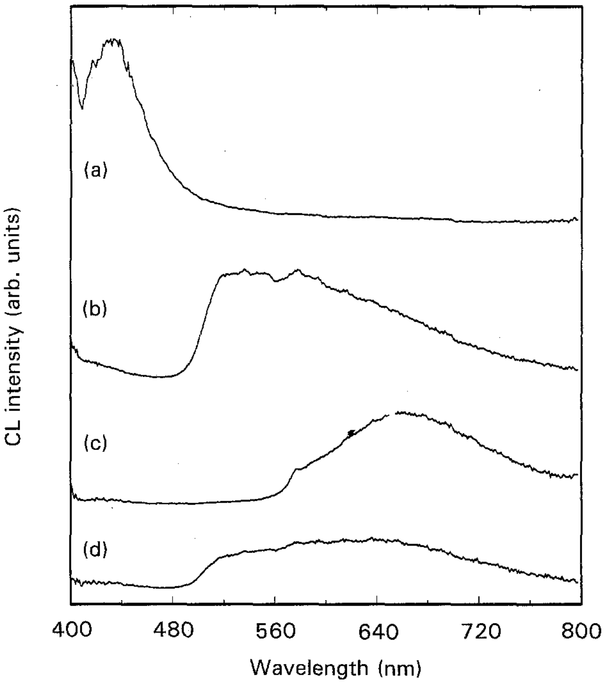

Figure 4 Corrected CL spectra from the four types of luminescence excitation: (a) the blue, (b) the green, (c) the red, and (d) the yellow excitation.

TABLE I EDX compositions for the four CL emissions

CL emission wavelength range (nm)	EDX corrected data	
	Elements	Ratio
Blue 420–460	Y, O	2:3
Green 500–600	Y, Ba, Cu, O	–
Red 620–720	Y, Ba, Cu, O	–
Yellow 500–700	Ba, Cu, O	1:3:4

Pressing powder and sintering it to produce a pellet often results in impurities or residual, unreacted, components in the microstructure which segregate to the grain boundaries or to internal/external pore surfaces [11]. The CL detected in this study was generated from pores and not from the grain boundaries. This does not rule out impurity segregation at the grain boundaries, but indicates that the impurities need to be in sufficient quantity in order for observation by the CL technique. Then, their CL excitations are distinguishable above the noise level.

The four CL emissions observed are characterized by the four wavelength-resolved spectra, in Fig. 4, and by the EDX data in Table I. Each of the four distinct excitations were unique in both their energy-band structure and their composition. The energy-band structures for each of the luminescent excitations fell in specific regions of the visible range. However, because of phonon interactions causing band broadening at room temperature [3], the exact energy of the

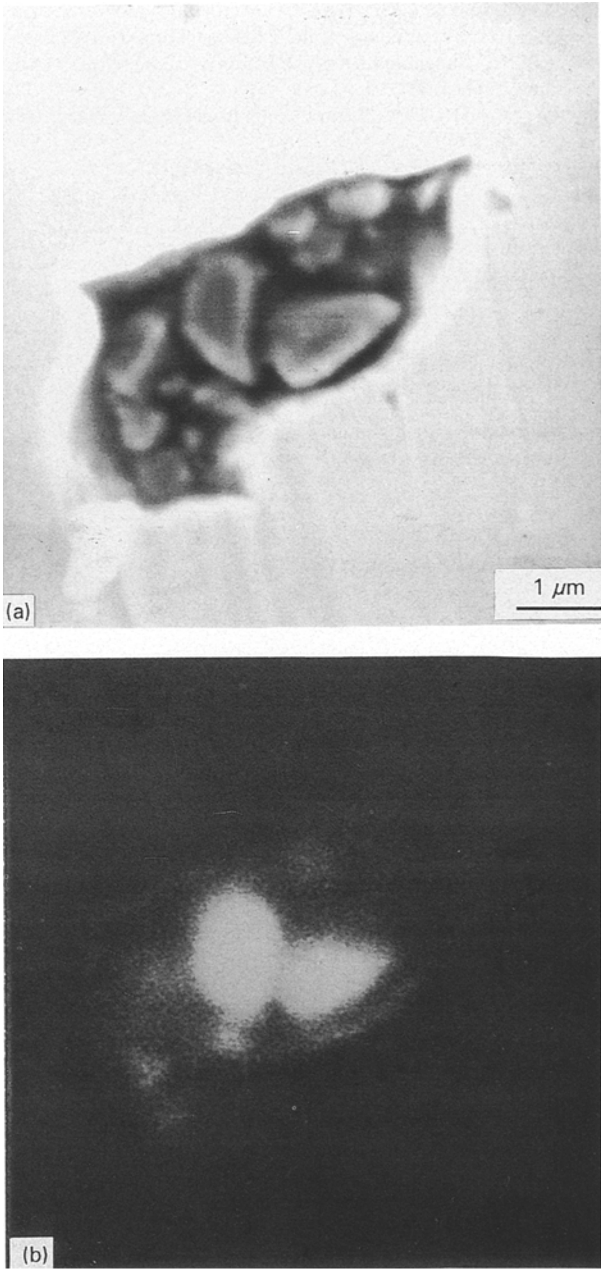

Figure 5 SEM micrographs showing small luminescent grains: (a) the secondary-electron image, and (b) the panchromatic CL image.

transitions and hence of the electronic band structures could not be calculated. Increases in luminescence intensity can be achieved by using higher beam currents or higher beam accelerating voltages but changes in the excitation response can occur as a result of beam irradiation damage [3]. The authors are currently collecting further data at liquid-helium temperatures; such temperature conditions increase the luminescent efficiency and narrow the bandwidths of the emissions, improving the overall resolution. This highlights the importance of carefully selecting the electron-beam conditions. In these cases, the intensity may increase or decrease indicating an alteration in the number of active luminescent sites produced by the electron–hole pairs across the local electronic band structure.

From the EDX data (Table I) it can be seen that yellow emissions were the result of Y_2O_3 phases [12] and the blue emissions were the result of barium-cuprate phases rich in copper. However, because of the small grain size, only the major elements present for the red and green emissions could be determined. The yellow and blue emissions did have repeatable results when different areas were analysed. However, in wide-band-gap materials, CL is mainly generated at self-excitation centres, such as transition or rare-earth impurity atoms, and changes in the trace-element concentration of the luminescent phases may change their spectra significantly. Thus, while internal self consistency was maintained in this study, there may be differences between the spectra presented here and those presented elsewhere for, say, yttria, because different starting materials are used.

Silicon, an impurity element either from the initial powders or introduced during processing, was also present in varying concentrations at the pore surfaces, most likely in the form of a glassy silicate phase, as is commonly seen in sintered ceramics.

Quantitative EDX analysis of the grains was made difficult because of their position within the pores which resulted in poor X-ray collection. Correction factors were calculated and used in order to eliminate spurious X-rays that were generated from the YBCO matrix at the pore surfaces.

The presence of these impurities in the target material has been recognized as affecting the quality of thin ablated films. Loss of epitaxy and unwanted impurity phases may therefore be generated in such films, compromising their superconducting properties.

5. Conclusion

The CL technique, as used in this work, has demonstrated its effectiveness in the characterization of luminescent regions in the microstructure of a YBCO superconducting pellet. Direct correlation between CL and secondary-electron emissive modes has enabled wavelength-resolved CL spectra and compositional information, via EDX, to be determined. This then renders the CL technique a powerful tool for quality control, in the assessment of impurity phases within a superconducting pellet material. The target quality, and ultimately the film quality, can quickly be assessed, and problems in laser-ablated film production may be reduced leading to improved film quality.

Acknowledgements

The authors acknowledge the support of a SERC postgraduate studentship with additional CASE support from the National Physical Laboratory, Teddington, UK.

References

1. D. S. MISRA and S. B. PALMER, *Physica C* **176** (1991) 43.
2. D. B. HOLT, *Scanning Microscopy* **1** (1992) 1.
3. B. G. YACOBI and D. B. HOLT, "Cathodoluminescence microscopy of inorganic solids" (Plenum, New York, 1990).
4. Z. BARKAY, G. DEUTSCHER, E. GRUNBAUM and B. DWIR *Appl. Phys. Lett.* **61** (1992) 3050.

5. J. H. MILLER Jr, J. D. HUNN, S. L. HOLDER, A. N. DIBIANCA and C. R. BAGNELL, *Appl. Phys. Lett.* **56** (1990) 89.
6. J. H. MILLER Jr, *Physica B* **165–66** (1990) 1695.
7. F. DOMINGUEZ-ADAME, P. FERNANDEZ, J. PIQUERAS, P. PRIETO, C. BARRERO and M. E. GOMEZ, *J. Appl. Phys.* **71** (1992) 2778.
8. J. PIQUERAS, P. FERNANDEZ and J. L. VICENT, *Appl. Phys. Lett.* **57** (1990) 2722.
9. B. J. LUFF, P. D. TOWNSEND and J. OSBORNE, *J. Phys. D-Appl. Phys.* **21** (1988) 663.
10. Y. FUJIWARA, S. HIRATA, M. IYORI and T. KOBAYASHI, in Proceedings of the Extended Abstracts 1989 International Superconductivity Electronics Conference, Tokyo, June 1989, p. 338.
11. W. D. KINGERY "Introduction to ceramics" (Wiley, New York, 1976).
12. V. N. ANDREEV, *JETP Lett.* **47** (1988) 618.

Received 31 March 1993
and accepted 24 May 1993