JOURNAL OF MATERIALS SCIENCE 30 (1995) 2765–2768

Cathodoluminescence microscopy of high T_c superconducting YBCO and BSCCO materials

P. R. FLETCHER
Department of Materials, Imperial College, Prince Consort Road, London SW7 2BP, UK
C. LEACH
Manchester Materials Science Centre, University of Manchester and UMIST, Manchester MI 7HS, UK

Spectroscopic and imaging cathodoluminescence (CL) microscopy has been used to study high T_c YBCO and BSCCO superconducting thin films and pellets in the scanning electron microscope. The effects of beam parameters, such as voltage, current, and diameter, have been investigated with a view to optimizing the CL signal intensity whilst preventing sample damage. Limiting the CL signal generation volume to within the thin film is important in eliminating any substrate contribution. Areas of strong luminescence have been observed in YBCO and BSCCO pellets as well as BSCCO thin films. At low beam energies, there is some correlation between the CL and secondary electron images. The CL spectra of the strongly luminescent spots differed from those of the poorly luminescencing superconducting phases. CL was able to identify a copper-rich impurity phase in the BSCCO material, and a barium cuprate phase in the YBCO material. It is proposed that the quality of a thin film, with respect to impurities, can be monitored using CL.

1. Introduction

Polycrystalline bulk and thin films of YBCO and BSCCO typically have low critical current densities, J_c, at liquid nitrogen temperatures. In order for these materials to be used in high-power applications ($J_c > 10^6$ A cm^{-2}), their J_c values need to be increased by up to two orders of magnitude. Cathodoluminescence (CL) microscopy is one of several analysis methods which have been applied to these materials in order to investigate the material properties that might affect T_c and J_c.

Although the CL technique is becoming increasingly accessible, as an add-on for both optical microscopes and the scanning electron microscopes (SEMs), relatively little work has been carried out to determine the homogeneity of superconductor materials using CL. It has been established, however, that, in general, impurity phases present within these bulk superconductors give rise to strong luminescence, whereas regions of superconducting stoichiometry tend to luminesce only weakly at room temperature [1–4]. Non-superconducting YBCO-related phases such as Y_2O_3, $BaCO_3$, and Y_2BaCuO_5, produce strong CL emissions [1] which are far more intense than that of the superconducting YBCO itself. However, these data were collected from single-phase materials; only the Y_2BaCuO_5 phase has so far been observed in bulk YBCO material.

Many workers have reported a feature common to CL observations of high T_c materials; the positions of strongly luminescent spots tend to correlate very poorly with the surface microstructure [3, 5–7]. However, in a previous work [4], we have correlated the bright spots with impurity phases in the microstructure, in particular to yttria and barium cuprate. The density of the spots gave an indication of the concentration of second phases and thus quality of the superconductor sample. In the case of the thallium-based superconductor, for instance, the intensity of the bright spots was measured to be 250 times that of the dark contrast regions [6]. Barkay and Azoulay [8], using BSCCO thin films and panchromatic CL, imaged superconducting paths by exploiting the BSCCO materials weak CL emission compared with the stronger emission from the MgO substrate, although the film thickness was not uniform. CL emissions from MgO have been studied elsewhere, and can be affected by defects and impurities [9, 10].

CL excitation conditions have been considered with regard to reducing sample damage. It is known that the use of high beam currents and prolonged irradiation can produce increased luminescence intensity, resulting from the creation of luminescent defect sites [5, 7, 11].

2. Experimental procedure

Bulk pellet samples of YBCO and BSCCO were fabricated. The BSCCO thin film studied (approximately 1 μm thick) was produced by sequential thermal evaporation on to a single-crystal MgO (0 0 1) substrate

0022–2461

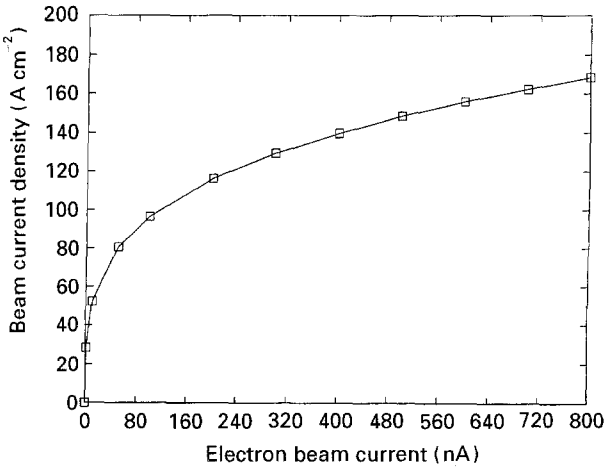

Figure 1 Relationship between the beam current and the beam current density in the SEM.

[12]. The YBCO thin film was laser ablated on to a $SrTiO_3$ substrate using standard deposition parameters.

Secondary electron and CL images were collected in a Jeol JSM 840A SEM fitted with an Oxford Instruments spectroscopic CL detector and wavelength resolved by a Bentham monochromator with a slit width of 2 mm. A photomultiplier with a wavelength response of 200–800 nm amplified the CL emissions. The beam characteristics used for luminescence excitation were calculated for the case of a tungsten filament in a microscope operating at optimum resolution [13] and are described in Fig. 1. For all the spectroscopic CL data presented here, the electron-beam accelerating voltage was 10 kV, giving an excitation depth of approximately 0.7 μm [9], thus eliminating substrate CL emissions. Such conditions allowed some correlation between panchromatic CL and secondary electron images to be made.

The spectra presented are not corrected for the system's spectral response. Energy dispersive X-ray analysis (EDX) was carried out in a Jeol JSM 35CF SEM, with a Link Systems analytical computer, at an accelerating voltage of 15 kV.

3. Results

Fig. 2a and b show CL and secondary electron images of a BSCCO pellet. At this low beam energy, some surface correlation of the emissive features is seen. Intense CL spots of the type seen in Fig. 2a are frequently observed in or around small pores in the microstructure. In analysing the thin films, the emissive contribution of the highly luminescent MgO substrate has to be considered in order to determine the overall CL response of the superconducting material. The luminescent properties of the YBCO and BSCCO bulk materials and that of the MgO itself were used to identify spurious peaks due to the "see through" MgO substrate contributions collected during CL analysis of thin films.

Fig. 3 shows a graph of beam current versus CL intensity for the BSCCO sample, collected with the SEM in spot mode. At beam currents of 600 nA and above, the CL intensity was found to increase with time suggesting that the sample was being damaged in some way by the electron beam.

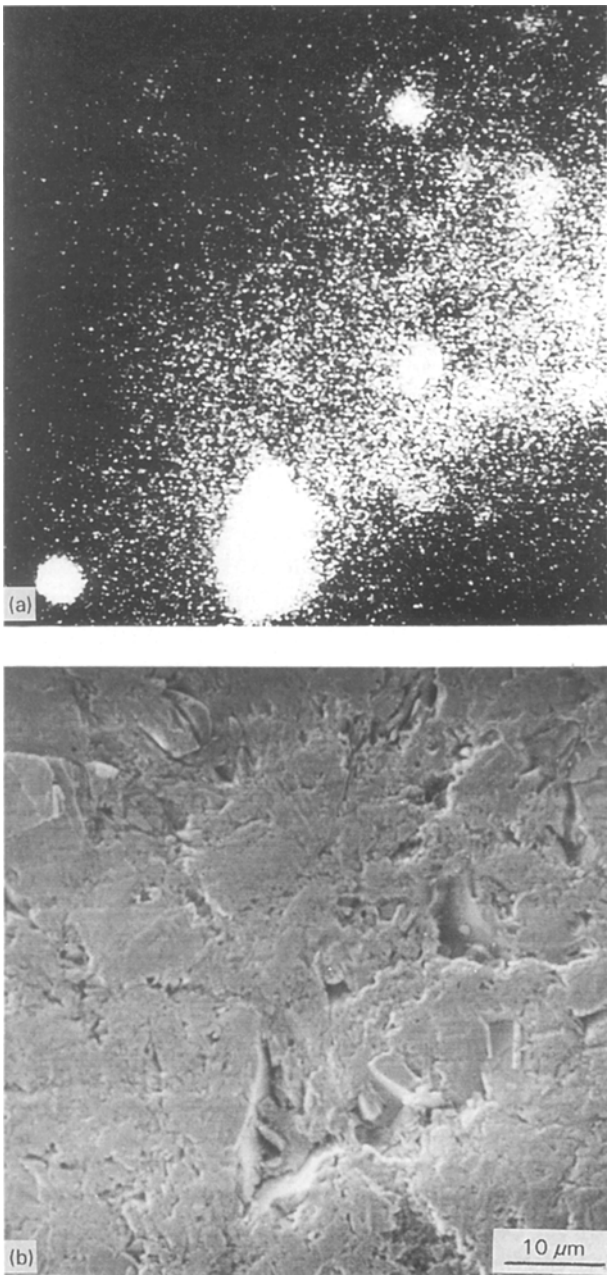

Figure 2 (a) Panchromatic CL image of BSCCO, and (b) corresponding SE image.

Different CL spectra were also collected from a thick film of BSCCO. Each of the spectra was recorded at a beam current of 300 nA, thus minimizing any sample damage. These are shown in Fig. 4a–c and indicate three distinct emissions found in the BSCCO pellet at room temperature. The spectrum in Fig. 4a was recorded from the weakly luminescent superconducting phase, whereas Fig. 4b and c were recorded from strongly luminescing spots. EDX analysis revealed the particle giving the spectrum in Fig. 4c to be copper-rich compared with the superconducting phase, indicating that the strong luminescence emission is due to the presence of an impurity.

The YBCO pellet also had strongly luminescent areas, shown in Fig. 5a, which correlated well with features in the corresponding secondary electron image, Fig. 5b. For example, CL spectra show differences between the spectra of the weakly emitting superconducting phase (Fig. 6a) and one of the strongly

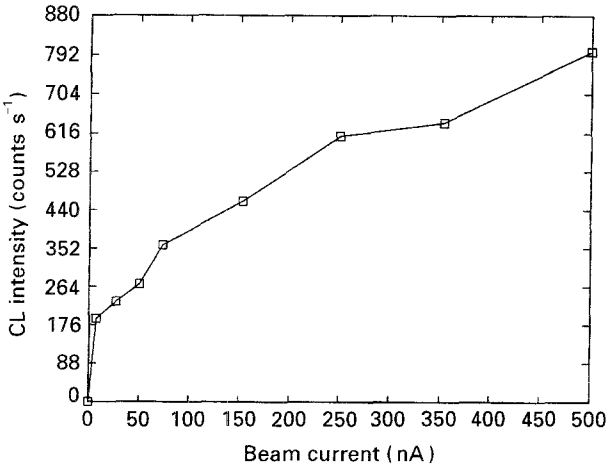

Figure 3 The luminescence intensity of a bright spot recorded in Fig. 2a as a function of beam current.

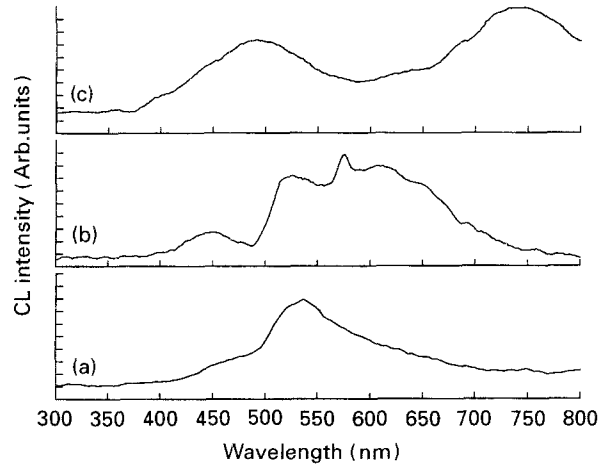

Figure 4 CL spectra from three regions of the BSCCO pellet: (a) from the weakly luminescing superconducting region; (b, c) from impurity phases.

emitting spots (Fig. 6b) indicating that it is again an impurity.

A CL spectrum of the BSCCO film is shown in Fig. 7. This is similar to the bulk material spectrum in Fig. 4a, with no extra peaks due to the substrate shining through. Thus, with the use of the correct beam conditions, a luminescence contribution from the substrate can be avoided. If higher energy beam conditions are used, peaks due to the substrate can be removed by determining the response of the substrate with respect to beam energy.

No luminescent spots were detected in the laser-ablated YBCO thin film.

4. Discussion

In the case of the samples observed here at 10 keV, good correlation between the CL and secondary images was maintained. At higher beam energies ($E_b > 20$ keV), CL features are not easily correlated with the surface microstructure of the sample as sub-surface luminescent sites, not visible in the secondary electron image, were activated due to the increased excitation volume (~ 2.3 μm depth). Poor microstructural correlation is thus caused by sub-surface light generation; channelling through the material away

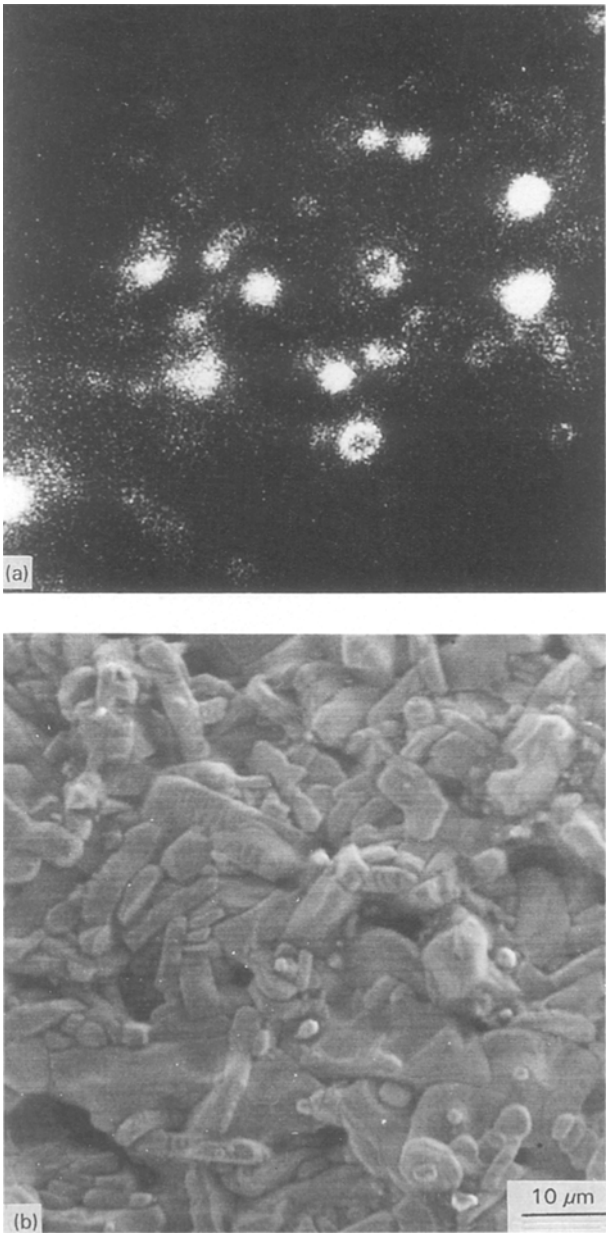

Figure 5 (a) Panchromatic CL image of YBCO, and (b) corresponding SE image.

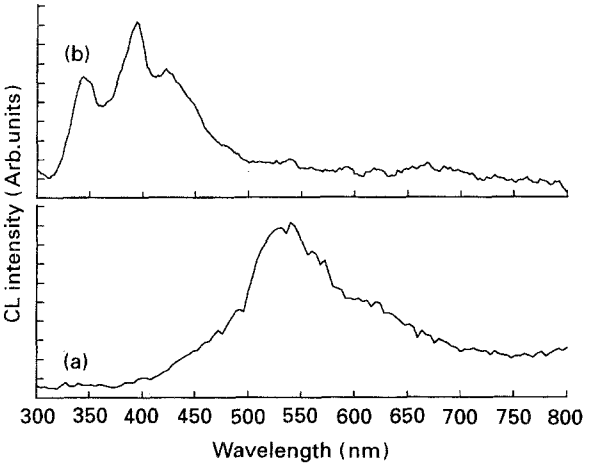

Figure 6 Spectra from two regions of the YBCO pellet: (a) from the weakly luminescent superconducting region, (b) from an impurity phase.

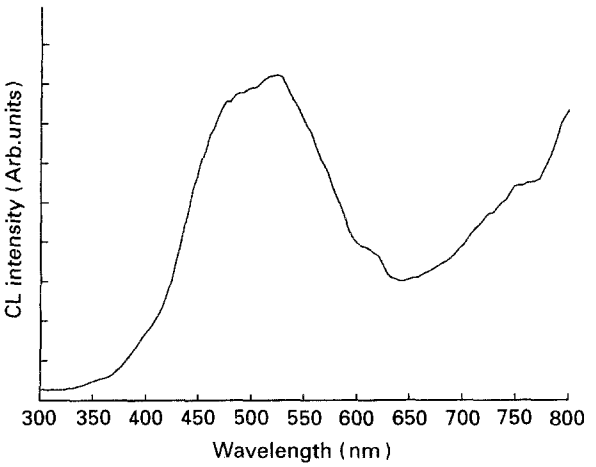

Figure 7 CL spectrum from the superconducting region of the BSCCO thin film.

from the origin by total internal reflection and subsequent emergence at light-scattering defects, e.g. pores, grain boundaries and second-phase inclusions. In a previous work [4], better correlations were obtained by polishing the surface of the material, to remove anomalies due to topographical effects.

Luminescent sites have previously been correlated directly with impurity phases within a YBCO pellet [4]. The results here confirm the presence of impurities, via CL and EDX, in both the YBCO and BSCCO samples, with their location predominately at sites of pores in the microstructure. This juxtaposition is the probable result of impurity segregation during the sintering process, or poor densification around existing second-phase particles. The impurities in both systems have characteristic CL spectra which are very different from those of their respective superconducting phases. The small size of many of the brightly luminescent particles meant that it was impossible to determine their precise composition by EDX. However, some particles were large enough to analyse qualitatively. In the case of the BSCCO system, a copper-rich phase generated emission bands at 490 and 750 nm, whilst for the case of YBCO, a band at 390 nm is generated by a barium cuprate phase [4, 8]. We can thus conclude that variations in the CL spectra clearly indicate the presence of impurities in the microstructure without the need for EDX analysis.

The beam conditions used for the collection of CL data are important. At beam current above 600 nA on a BSCCO impurity phase and on the weakly luminescent superconducting phase, the measured CL intensity was found to increase with time. In the superconducting phase, this has been tentatively attributed to damage in the oxygen sub-lattice, giving rise to an increased number of active luminescent sites [5]. However, no CL spectra have been reported in the literature for oxygen-deficient YBCO ($\delta > 0.4$), and thus no comparison could be made here to support the contention that the signal change is due to oxygen depletion.

Quantitative CL and EDX analysis of thin films with large thickness variations was not possible without knowing the local film thickness. A qualitative approach is to consider substrate CL peak intensities at different beam energies. If the MgO peak is present in the thin-film spectrum, then a simple removal of the MgO contribution can be carried out by considering this peak intensity. However, it should be noted that the luminescence contribution from the substrate can change significantly locally, due, for example, to surface defect states, cleavage slip planes, and impurities [10]. An assumption of the CL analysis which also has to be made is that the area of film under analysis is of superconducting stoichiometry because different phases will have different light-absorption characteristics. Thin films of uniform thickness when analysed by CL gave comparable spectra to those of the bulk material as seen by comparison of Figs 4a and 7.

5. Conclusion

Superconducting BSCCO and YBCO materials are weakly luminescencing in the visible range. Strongly luminescent impurity phases are clearly visible within the microstructure. Although thin-film CL analysis is hampered by the strong substrate luminescence when MgO is used, it has been shown that the use of low electron beam voltages with thin-film samples can allow the collection of light emission originally from the film alone. Imaging CL can, therefore, be used to map out the distribution of many non-superconducting phases in bulk and thin-film material.

Acknowledgements

PRF acknowledges the support of a SERC postgraduate studentship with additional CASE support from the National Physical Laboratory, Teddington, UK.

References

1. J. H. MILLER Jr, J. D. HUNN, S. L. HOLDER, A. N. DIBIANCA and C. R. BAGNELL, *Appl. Phys. Lett.* **56** (1990) 89.
2. B. J. LUFF, P. D. TOWNSEND and J. OSBORNE, *J. Phys. D Appl. Phys.* **21** (1988) 663.
3. V. N. ANDREEV, *JETP Lett.* **10** (1987) 492.
4. P. R. FLETCHER and C. LEACH, *J. Mater. Sci.* **28** (1993) 6774.
5. I. YA. FUGOL and V. N. SAMAROV, *Mod. Phys. Lett. B* **12** (1990) 803.
6. Y. FUJIWARA and S. HIRATA, in "Proceedings of the Extended Abstracts of the International Superconductivity Elect. Conference", ISEC, Tokyo, June 1989, p. 338.
7. F. DOMINGUEZ-ADAME, P. FERNANDEZ, J. PIQUERAS, P. PRIETO, C. BARRERO and M. E. GOMEZ, *J. Appl. Phys.* **71** (1992) 2778.
8. Z. BARKAY and J. AZOULAY, *Appl. Phys. Lett.* **17** (1990) 1808.
9. B. G. YACOBI and D. B. HOLT, "Cathodoluminescence microscopy of inorganic solids" (Plenum, New York, 1990).
10. P. R. FLETCHER and C. LEACH, *J. Eur. Ceram. Soc.*, submitted.
11. J. PIQUERAS, P. FERNANDEZ and J. L. VICENT, *Appl. Phys. Lett.* **57** (1990) 2722.
12. J. MULLER, PhD thesis, University of London (1993).
13. D. B. HOLT, "Quantitative scanning electron microscopy" (Academic Press, London, 1974).
14. S. DATTA and D. B. HOLT, *J. Microsc.* **118** (1980) 367.

Received 30 June
and accepted 5 September 1994