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A REVIEW

Scanning Electron Microscopy Methods In The Characterization Of High Critical Temperature Superconductors

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ABSTRACT

The application of different scanning electron microscopy techniques such as cathodoluminescence, scanning electron acoustic microscopy and the secondary electron mode, to study structural and physical properties of high critical temperature superconductors is discussed. When all the mentioned techniques are considered the results show that scanning electron microscopy can provide space resolved information of different features as phase distribution, inhomogeneity in oxygen content, optical transitions, structural transitions at different temperatures or behavior in the superconducting transition. As in the case of semiconductors, scanning electron microscopy can become a powerful characterization technique for high temperature superconductors.

KEY WORDS

Cathodoluminescence, scanning electron acoustic microscopy, high critical temperature superconductors.

INTRODUCTION

Due to the different operation modes available in a SEM, this instrument can be considered in the field of materials science not only as a microscope but as a set of microcharacterization techniques. Besides the conventional emissive mode and X-ray microanalysis, other SEM-based techniques such as electron beam induced current (EBIC), cathodoluminescence (CL) or scanning electron acoustic microscopy (SEAM) provide information about physical properties of many materials. These capabilities have been widely applied to characterization of semiconductors [1]. The discovery of high temperature superconductivity in perovskite related oxides has stimulated the use of electron microscopy to investigate these materials. Conventional and high resolution transmission electron microscopy have been often used in the past years to characterize high temperature superconductors (HTSC) while reports of application of SEM refer mainly to topography observations and X-ray microanalysis. However, the variety of physical phenomena involved in HTSC indicates that other SEM based techniques are very suitable for their characterization. The phenomena are not only related to the superconducting transition but, for example, to the existence of different semiconducting and metallic phases or to fine structural changes occuring at temperatures above T_c. In the present work the application of several SEM techniques namely SEM-CL, SEAM and the emissive mode, to study physical properties of HTSC is discussed.

CATHODOLUMINISCENCE

CL in the SEM enables the study of luminescent centers and electronic properties of materials with a resolution of about 1 μm or less [2]. The light emitted as result of the interaction of the microscope electron beam with the sample is usually detected by a photomultiplier or other detector attached to a window of the microscope. Luminescence images and spectra corresponding to a selected area of the sample can be recorded. The main application of CL relates to semiconductor characterization and only recently it has been used to investigate HTSC. We discuss in this section the capability of CL in the SEM as characterization technique for HTSC.

In the past few years different luminescence techniques have been used to investigate HTSC. Cooke et al [3] have reported thermally stimulated luminescence in Gd-Ba-Cu-O systems in the visible range and related the emission to defects or transitions in rare-earth ions. Fujiwara and Kobayashi [4] observed infrared photoluminescence emission in Er-Ba-Cu-O and Nd-Ba-Cu-O systems which they tentatively assign to electronic transitions in Er and Ba ions. More detailed luminescence studies have been performed in $YBa_2Cu_3O_{7-x}$ and, to a lesser extent, in $Bi_2Sr_2CaCu_2O_x$ samples. In particular, CL in systems not attached to scanning electron microscopes has been applied to investigate $YBa_2Cu_3O_{7-x}$ [5][6][7] and some general features of the luminescence have been described. Electron excitation under different conditions was found to cause an emission in the blue-green spectral region whose temperature dependence suggests that CL is related to structural changes in the sample. On the other hand it has been observed [6] that electron beam irradiation not only produces CL but also induces some changes in the spectra. This fact indicates that care has to be taken to avoid radiation induced changes of $YBa_2Cu_3O_{7-x}$ in the SEM and that the nature of the changes should be investigated for a controlled observation of this material. Miller et al [8] studied ceramic pellets of $YBa_2Cu_3O_{7-x}$ by CL-SEM and showed the capability of the method to differentiate metallic from non-metallic phases with good spatial resolution. They found that CL microscopy can differentiate between oxygen depleted $YBa_2Cu_3O_{7-x}$ ($x>0.5$) and oxygen annealed $YBa_2Cu_3O_{7-x}$ (x_0) because of the higher CL emission of the former. Barkay et al [9] also used pan-chromatic CL-SEM to investigate thin films of the Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O systems and reported that the depth and lateral locations of the different phases can be revealed. Piqueras et al [10] applied panchromatic as well as spectral resolved CL-SEM to study $YBa_2Cu_3O_{7-x}$ (x_0.1) ceramics. In particular the suitable observation conditions and the evolution of the CL spectra under the microscope electron beam were investigated. At the beginning of the observation the light emission is found to be very low and almost no contrast is observed in the CL image. During the observation, CL intensity gradually increases and the spectrum shows that the increase is due to the appearance of CL bands in the range 450-600 nm. Taking into account the results of refs. [6] to [8] it was suggested in [10] that in the observed CL changes in the SEM the oxygen content could be involved. Since oxygen-depleted regions show a higher CL emission [8] the increase of CL during electron irradiation may be due to a loss of oxygen atoms. This observation would be consistent with the fact that change in oxygen content in $YBa_2Cu_3O_{7-x}$ is known to produce metal to semiconducting transitions, the metallic phase corresponding to small x values. Bright regions in the CL image would be associated with the presence of oxygen vacancy defects and could represent the distribution of a semiconducting phase. The irradiated regions usually show surface damage which can imply oxygen loss. Similar results have been reported in CL-SEM studies of $YBa_2Cu_3O_{7-x}$ films [11]. Fig. 1 shows an image corresponding to changes induced by scans of electron beam on a film sample. The controlled use of this effect can, for instance, produce a thin strip of material with different electrical properties than the matrix or in general be applied to superconductor heterostructures problems. In order to investigate with more

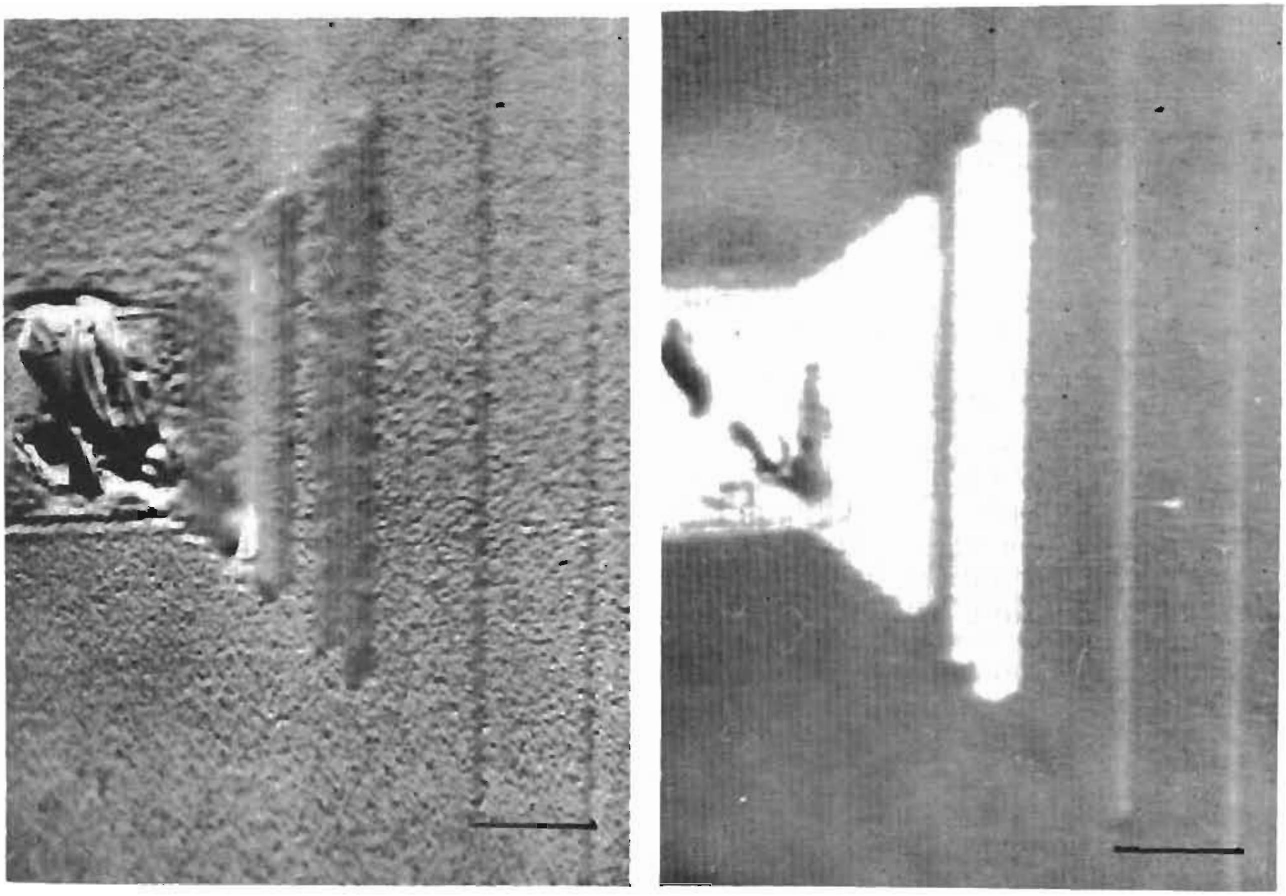

Figure 1. Images showing the changes induced by the electron beam on a $YBa_2Cu_3O_{7-x}$ film (a) emissive mode (b) CL mode. Bar = 50 μm.

detail the effect of oxygen loss on the CL emission of $YBa_2Cu_3O_{7-x}$, samples which were either heat treated in vacuum, laser irradiated or electron irradiated were studied by CL-SEM complemented by photoluminescence and micro-Raman measurements [12][13]. It was concluded that different treatments producing oxygen deficiency cause the appearance of a luminescence band centered at about 540 nm at 110K. The CL spectrum of a treated sample (Fig. 2) typically shows two bands in the blue and green spectral regions respectively. The latter is produced during the treatments but the blue band seems to be present in the starting material. This observation agrees with the photoluminescence results of Stankevich et al [14] showing the existence of an intrinsic luminescence emission of $YBa_2Cu_3O_{7-x}$ at about 430 nm. Our micro-Raman measurements [13] have shown that oxygen loss is associated to regions with intense 530 nm CL band produced by irradiation with the microscope electron beam. Although micro-Raman shows the appearance of Y_2O_3 phase in the irradiated area, comparison with CL-SEM indicates that green emission is related to oxygen loss rather than to the presence of the impurity phase. However, for the observation of the 530 nm band is necessary not only a low oxygen content but the application of a thermal or irradiation treatment to cause the oxygen loss. In samples sintered with different oxygen contents without subsequent treatments [15] only the blue emission is observed. This suggest that in the appearance of the 530 nm some ionization process related to oxygen depleted zones could be involved. Additional measurements we performed in $Bi_2Sr_2CaCu_2O_x$ show the presence of a blue band as well as a radiation induced green band. It appears possible that similar mechanisms are responsible for the luminescence in both materials. Contrast in CL images is not visible only in irradiated samples, as in Fig. 1, but also is often observed in nominally untreated samples (Fig. 3). In general the contrast would be due to the presence of phases or to composition differences, possibly oxygen content, among the different regions.

In the study of temperature dependence of CL intensity in HTSC some authors [6][7] have reported changes that could be associated with structural transitions in the material. Our CL-SEM measurements in $YBa_2Cu_3O_{7-x}$ (x_0) [15] show reproducible CL intensity steps at about 220K. This indicates the possibilty that CL-SEM measurements provide space resolved information on fine structural changes, as for instance ordering phenomena in the oxygen sublattice [6].

ELECTRON ACOUSTIC MICROSCOPY

Acoustic methods have been recently used to detect structural phase transitions at low temperatures in several HTSC (see for instance refs. [16] and [17]). In particular in [16] the photoacoustic technique is used for detection of the superconducting transition. Due to the analogies between photoacoustic and electron acoustic effects the results of [16] suggest that scanning electron acoustic microscopy (SEAM) could also be used to characterize superconductors and to study their structural transitions. A major property of SEAM as

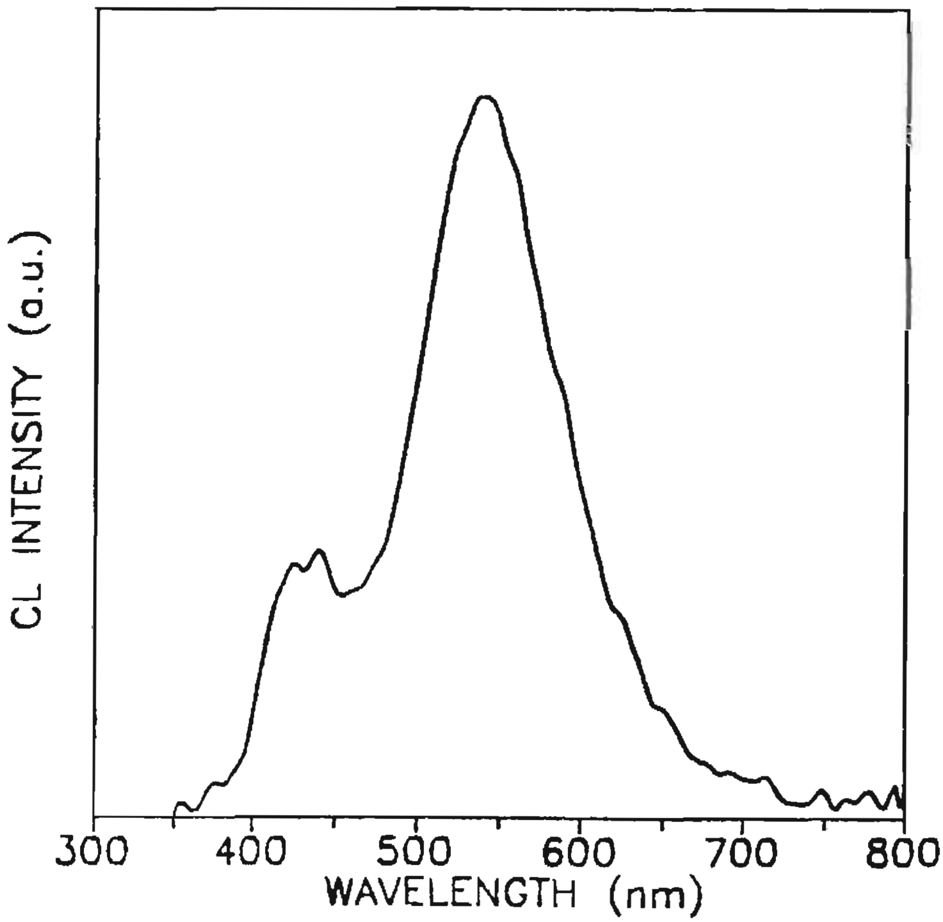

Figure 2. CL spectrum at 110K of an irradiated $YBa_2Cu_3O_{7-x}$ sample.

compared with macroscopic acoustic techniques is that the information is obtained with a space resolution of about one micron. Since SEAM is not a very extended technique we briefly describe the principle and the experimental setup. For a review see Balk in ref. [1].

SEAM is a SEM technique based on the generation of acoustic waves in a sample by the microscope electron beam. There are several physical mechanisms to explain this effect. In the thermal mechanism the periodic heating of the sample by electron beam causes thermal waves which produce elastic waves via the thermal expansion coefficient. In the particular case of semiconductors other mechanisms, related to the space charge generated by the electron beam in the sample, contribute to the generation of the elastic waves. The SEAM signal is produced by the acoustic waves, usually detected by a transducer, and is a function of different physical properties of the sample as thermal, and elastic properties. SEAM has been often applied to characterize many materials but has been only occasionally applied to HTSC [18]. Fig. 4 shows the SEAM experimental arrangement we used in the work described here. The chopping system consists of a pair of condensor plates and beam blanking electronics to create a periodic beam. A function generator produces a square-wave voltage with frequencies up to 240 kHz. The acoustic signal is detected by a piezoelectric ceramic transducer which is in contact with the bottom of the specimen. SEAM images show a contrast related to different phases or inhomogeneities in the thermoelastic properties of the sample. For instance in sintered $Bi_2Sr_2CaCu_2O_x$ the SEAM image shows dark and bright regions similar to those observed by CL (Fig. 5). Besides the visualization of these regions the most interesting possibility of SEAM is probably the detection of structural changes at different temperatures [19][20]. Fig. 6 shows the temperature dependence of SEAM intensity for a $YBa_2Cu_3O_{7-x}$ sample. The step at 130K as well as the intensity decrease of the SEAM signal above 230K correspond to the temperatures of structural changes detected by several authors in elastic moduli, specific heat or lattice constant measurements. In samples of the Bi-system the SEAM signal changes rapidly between 200K and 230K [20]. This effect can be related to the phase changes observed by several authors using different techniques in this temperature range. A systematic study to confirm the application of SEAM to detect structural changes in HTSC with high space resolution is under way.

EMISSIVE MODE

Different secondary electron emission methods in the SEM can be used for characterization of HTSC. In [21] voltage contrast was applied to inspect patterned lines of high-T_c films. Since local voltages of a sample affect the secondary electron image it is possible to visualize voltage differences on conducting lines of a circuit. In the case of HTSC the existence of normal and superconducting states above and below the critical temperature can result in two distinct voltage states. Voltages resulting from high temperature, excess current or defects can then be localized [21].

The darkening effect of secondary electron images of $YBa_2Cu_3O_{7-x}$ films during the superconducting transition have been also investigated [22]. Possible causes of the darkening are either the Meissner effect, which causes a decrease of the number of secondary electrons recorded by the detector, or a decrease of secondary electron emission [22] in the sample in the superconducting state. On the other hand the temperature dependence of the secondary electron emission can also provide information on the superconducting character of the sample. Tomashpolski et al. [23] in a study of $YBa_2Cu_3O_{7-x}$ ceramics have found that the temperature dependence of the secondary electron emission of the superconductive phase is similar to the dependence for metals while the behavior for the tetragonal and other impurity phases is markedly different.

CONCLUSIONS

A number of SEM based techiques which have been for years used to characterize

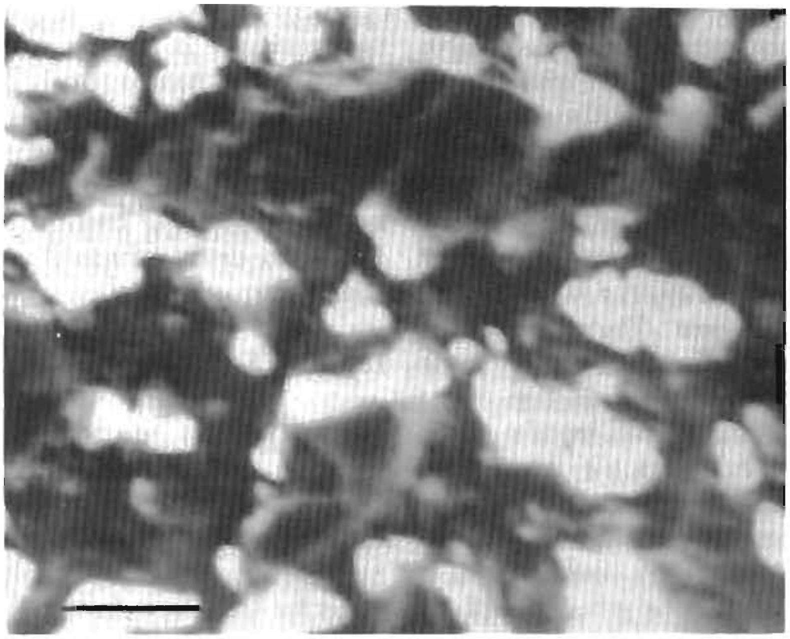

Figure 3. CL image of a sintered $Bi_2Sr_2CaCu_2O_x$ sample. Bar = 50 μm.

different electronic materials are also useful to study physical properties of high critical temperature superconductors. Due to the structural complexity and the variety of physical phenomena related to HTSC the interpretation of results obtained by SEM techniques is not always straightforward. However, it has been observed that CL-SEM, SEAM or electron emission methods can provide space resolved information of such features as phase distribution, inhomogeneity in oxygen content, optical transitions, structural transitions at different temperatures or behavior in the superconducting transition. Furthermore, other techniques, not discussed in this paper, involving electrical measurements in the sample during observation in the SEM enable the study of critical currents. Available results show that the capability of a set of SEM-based characterization methods could be further exploited after additional investigations on other HTSC systems.

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RESUMEN

En este trabajo se describe la aplicación de distintas técnicas de microscopía electrónica de barrido, como la catodoluminiscencia, la microscopía electro-acústica y el modo de emisión de electrones en el estudio de propiedades estructurales y físicas de los superconductores de alta temperatura crítica. Cada una de las técnicas mencionadas tiene sus aplicaciones específicas pero cuando se consideran todas en conjunto los resultados obtenidos hasta ahora muestran que la microscopía electrónica de barrido puede proporcionar información, con resolución espacial, de numerosas características de los superconductores como por ejemplo, distribución de fases, falta de homogeneidad en el contenido de oxígeno, transiciones ópticas, transiciones estructurales a distintas temperaturas y comportamiento en la transición superconductora. La microscopía electrónica de

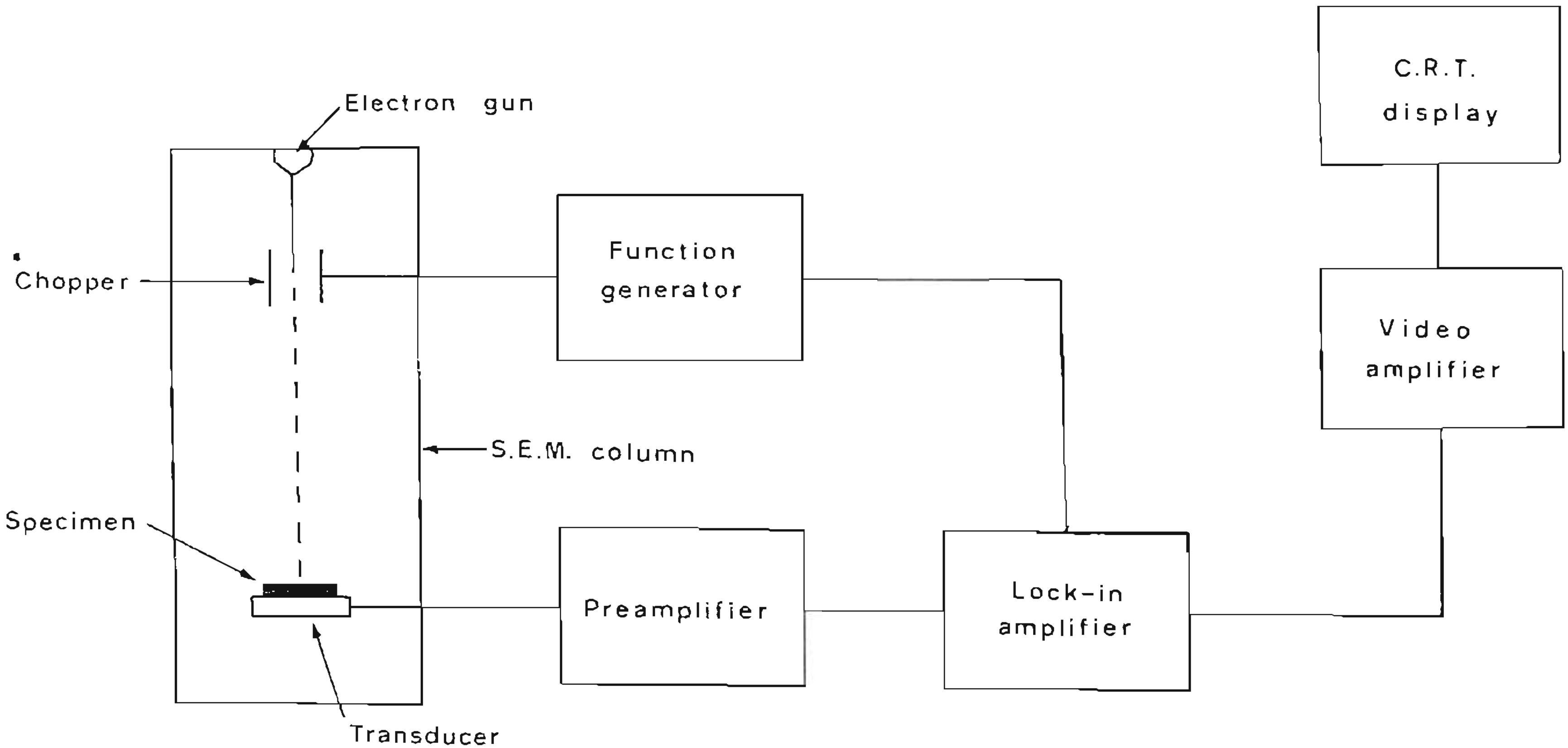

Figure 4. Experimental setup for scanning electron-acoustic microscopy (SEAM).

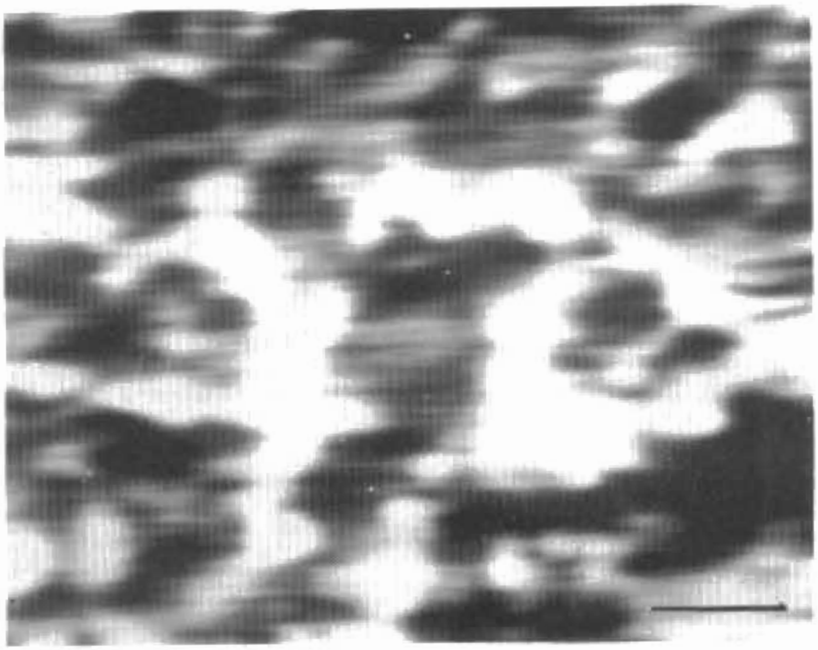

Figure 5. SEAM image of sintered $Bi_2Sr_2CaCu_2O_x$. Bar = 50 μm.

barrido puede ser una técnica importante de caracterización de superconductores de alta temperatura de manera análoga a lo que sucede en el caso de los semiconductores.

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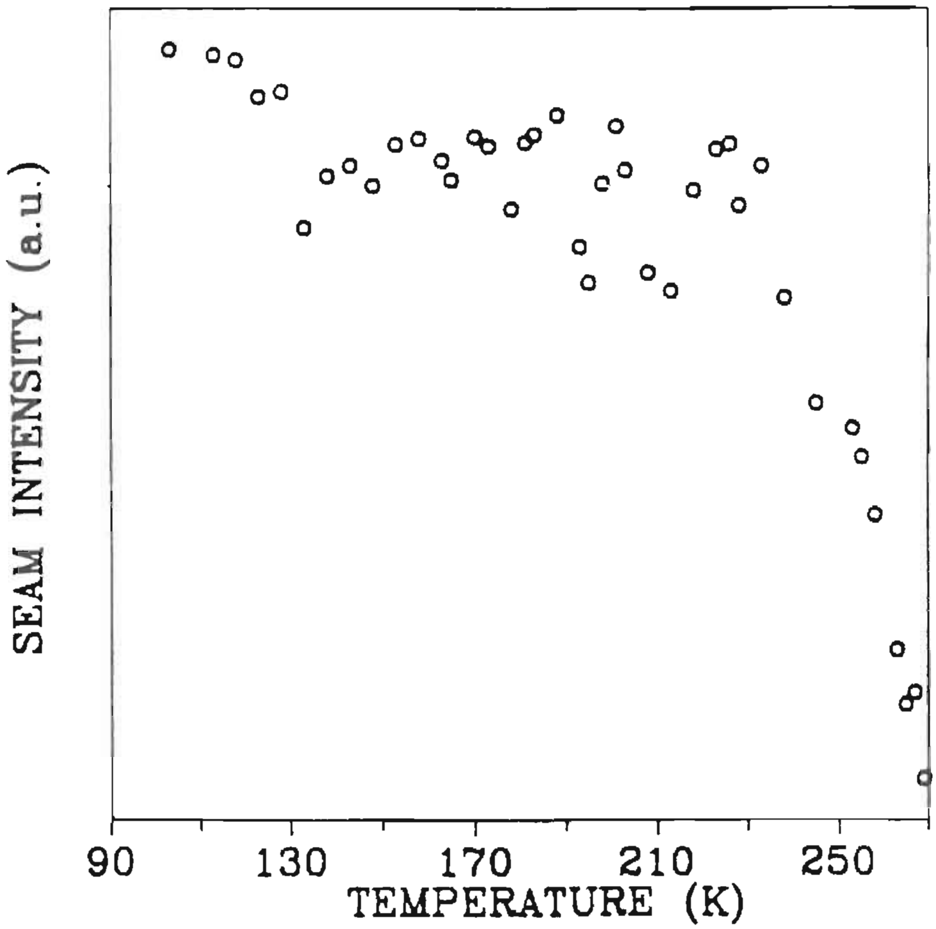

Figure 6. Temperature dependence of SEAM signal intensity for a $YBa_2Cu_3O_{7-x}$ sample.

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