Cathodoluminescence of high-temperature Y–Ba–Cu–O superconductors

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A revision of data on the cathodoluminescence of high-temperature Y–Ba–Cu–O superconductors is reported. The luminescence of Y–Ba–Cu–O high-temperature superconductors with a gadolinium admixture has been studied for the first time.

The cathodoluminescence of the new Y–Ba–Cu–O high-temperature superconductors has recently been the subject of active research,[1–5] but the data reported by different investigators do not agree. For example, in Ref. 2, where the narrow line at 3.36 eV was observed for the first time, the intensification of this line with decreasing temperature was noted at 50 K in a high-temperature superconductor with a transition temperature $T_c = 93$ K, while in Ref. 5 the intensification of this line (called the "α line") was linked with specifically the temperature $T_c = T_c(0.5R) = 98$ K (in Refs. 2–5, T_c was determined from the decrease in the resistance). Eremenko *et al.*[5] observed a hysteresis: The intensity of the α line behaved in different ways, depending on whether the sample was being heated or cooled. Lushchik *et al.*[4] suggested that the α line stems from the emission of the ZnO phase in the samples, while Eremenko *et al.*[5] are inclined to regard this line as intrinsic emission of the $YBa_2Cu_3O_7$ phase. Bands about 0.5 eV wide with peaks at 400 nm and ~270 nm (Ref. 4) and a continuum stretching from ~210 to >730 nm (Ref. 5) were linked by the researchers who observed them with an intrinsic luminescence of the superconducting phase, while it was asserted by Andreev *et al.*[1] that the cathodoluminescence of these samples is a consequence of the presence of nonsuperconducting insulating phases in them. Andreev *et al.*[1] studied the cathodoluminescence in the region 400–700 nm; that region did not include the narrow α and β lines which were observed in Refs. 2–5; those lines peak at $\lambda_\alpha = 368.5$ nm and $\lambda_\beta = 374.3$ nm.

We have studied ceramic samples of an Y–Ba–Cu–O high-temperature superconductor, including samples containing admixtures of gadolinium (the gadolinium was added in order to determined whether it could be used as a luminescent probe), synthesized by the standard method[6] and pressed into tablets. The luminescence was excited by an electron beam with an energy of 2–8 keV and a current density (at the sample) of 20–50 μA/cm^2, in a vacuum between $(2–3)\times 10^{-6}$ and $(2–3)\times 10^{-7}$ torr. The emission at 85–300 K was detected over the spectral region 500–220 nm with an FÉU-106 photomultiplier through an MDR-2 monochromator with a slit spectral width of 0.6 nm.

Figure 1a shows emission spectra of a $Y_{0.99}Gd_{0.01}Ba_2Cu_3O_{7-x}$ sample [$T_c(0.5R) = 92.3$ K, $\Delta T_c = 1.8$ K inductive $T_c = 83$ K] recorded under various conditions. From a freshly cleaved sample we observe a very faint continuous back-

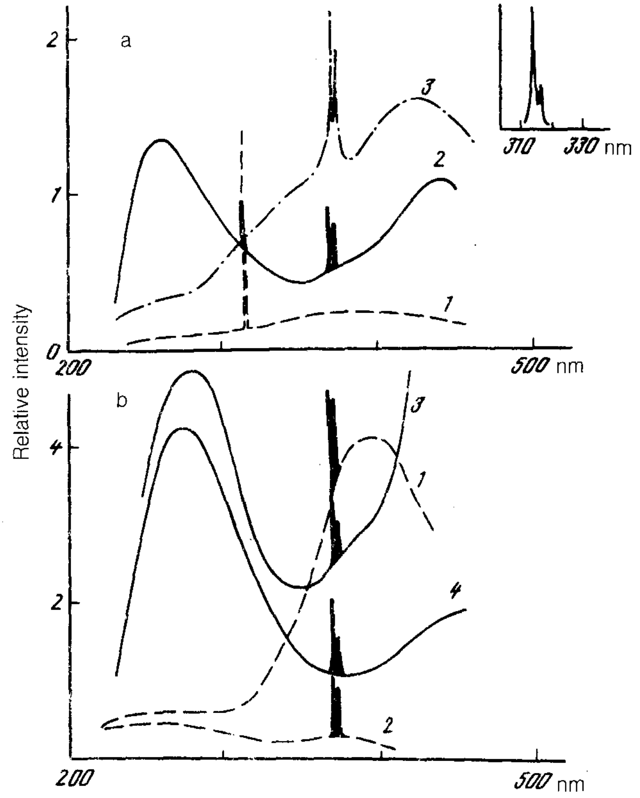

FIG. 1. Cathodoluminescence spectra (electron energy of 8 keV, $T = 90$ K). a: Ceramic $YBa_2Cu_3O_{7-x}$-Gd (1%) high-temperature superconductor. 1–Freshly cleaved; 2–old surface; 3–the same, after half a year. The inset shows the gadolinimum doublet of metallic indium. b: 1, 2–Freshly cleaved; 3, 4–soldered with $ZnCl_2$ flux to a holder; 2, 4–after heating.

ground and a doublet of lines at 314 and 316 nm which are more intense by about an order of magnitude. These lines have the instrumental width and are evidently due to an emission of Gd^{3+} (as is implied by their spectral position and the absence of these lines from samples without gadolinium). The spectrum from a surface which had spent a substantial length of time in air was different. In addition to the wide-band spectrum, in this case we saw narrow lines, whose wavelengths, 369.5 and 375 nm, agreed within the error (± 1 nm) with λ_α and λ_β. The intensities of the lines and also of the broad bands depend on the history of the sample, the position on the sample, and the vacuum in the cryostat. Under the conditions prevailing during the recording of spectrum 3 in Fig. 1a, an increase in the sample temperature from 90 K to 160 K reduced the intensity of the α and β lines by a factor of about two. These lines were absent at room temperature.

We carried out the following experiments. After removing a sample from the cryostat, we (1) placed a freshly cleaved plate of metallic indium in its place and (2) soldered indium to the holder with $ZnCl_2$ flux. In the cathodoluminescence spectra in both cases we observed broad bands and intense narrow lines, at the positions of the α and β lines (Fig. 1b; note that the sensitivity of the recording apparatus here was half that for part a). On freshly cleaved indium these lines do not appear immediately, as in the case of the soldered indium, but after several hours. The intense long-wave continuum is eliminated after the sample is heated in the cold cryostat to room temperature, while the lines and the short-wave band at ~275 nm—which is particularly intense for the soldered indium—remain (Fig. 1b). These facts suggest that the α and β lines and at least some of the broad bands in the cathodoluminescence of this high-temperature superconductor stem from an adsorbed layer of contaminants. It may be that the zinc flux used in the soldering of the cryostat is dominating the situation here.

Are the intense emission of gadolinium and the faint background the intrinsic luminescence of the superconducting phase? The intensity of this luminescence and the spectral shape of the background depend on the position on the sample. A ceramic $YBa_2Cu_3O_{7-x}$ sample may be nonuniform because of both variations in x over the volume[7] and inclusions of other phases. Even in a carefully prepared sample, the insulating green phase of Y_2BaCuO_5 is usually present.[8] We recorded a cathodoluminescence spectrum of a freshly cleaved sample of the green phase of Y_2BaCuO_5–Gd (1%), which was synthesized especially for the purpose. In this spectrum we see a background of roughly the same intensity as that for the high-temperature superconductor, and we see an emission of gadolinium which is about two orders of magnitude more intense than that in the high-temperature superconductor $YBa_2Cu_3O_{7-x}$–Gd (1%). Its spectrum consists of the same doublet, at 314 and 316 nm. Consequently, gadolinium which has entered inclusions of an accompanying green phase emits in a high-temperature Y–Ba–Cu–O superconductor to which gadolinium has been added. The intensity of this luminescence increases sharply during cooling to temperatures near T_c. Whether the luminescence of the gadolinium can serve as a marker of the superconducting transition requires further study. With regard to the weak continuous background, we note that it appears to be a consequence of inclusions of foreign phases, which are common to the high-temperature superconductor and green phase. Further evidence for this conclusion comes from the picture observed in a luminescence microscope: Samples of both the high-temperature superconductor and the green phase luminesce at distinct points during UV excitation.

CONCLUSIONS

1) The narrow lines at 3.36 eV and 3.31 eV which have been observed previously[2–5] in the cathodoluminescence of high-temperature Y–Ba–Cu–O superconductors stem from surface-adsorbed contaminants. 2) The luminescence of freshly cleaved samples of the high-temperature superconductors stems from inclusions of foreign phases, in confirmation of the conclusion reached in Ref. 1. 3) The introduction of gadolinium ions, which luminesce intensely, may serve as an indicator of extremely small amounts of the green phase in high-temperature superconductors.

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