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Gas Sensing Characteristics of Superconducting Cuprates

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Gas sensing characteristics of $YBa_2Cu_3O_{7-\delta}$, $La_{2-x}Sr_xCuO_4$, and $Bi_2Y_{1-x}Ca_xSr_2Cu_2O_8$ have been examined. $La_{2-x}Sr_xCuO_4$ (x=0.075), and $Bi_2YSr_2Cu_2O_8$ are found to show good sensitivity ($\approx$ 10 ppm) to ethyl alcohol and such vapours.

Superconducting cuprates have recently been found to exhibit interesting catalytic properties especially for oxidation reactions.[1-3] Accordingly $YBa_2Cu_3O_{7-\delta}$ readily oxidizes CO and methanol, while toluene undergoes ammoxidation. $La_{2-x}Sr_xCuO_4$ also shows such catalytic activity.[4] In view of the oxidizing capability of the surfaces of cuprate superconductors, we considered it most worthwhile to investigate whether they had any gas-sensing characteristics as well. Since the cuprate superconductors are metallic in the normal state, we would not expect them to show marked variations in the electrical resistivity on exposure to gases or vapours. It therefore becomes necessary to work with cuprate compositions with electrical resistivities in the right range, showing sensitive changes on exposure to gases, and vapours. Catalytic activity of such compositions could be somewhat lower, but our concern is their gas-sensing sensitivity. We have therefore examined the sensing characteristics of several compositions of $YBa_2Cu_3O_{7-\delta}$, $La_{2-x}Sr_xCuO_4$, and $Bi_2Y_{1-x}Ca_xSr_2Cu_2O_8$ towards various gases and vapours. We report our preliminary findings in this communication.

Fine powders of $YBa_2Cu_3O_{6.9}$, $La_{2-x}Sr_xCuO_4$, and $Bi_2Y_{1-x}Ca_xSr_2Cu_2O_8$ were prepared by the solid state reaction of the appropriate oxides at 1200, 1300, and 1100 K respectively for 24 hours in air followed by O_2 annealing in the case of the first system. $YBa_2Cu_3O_{6.4}$ was prepared by heating $YBa_2Cu_3O_{6.9}$ in nitrogen. Authenticity of the cuprate samples was established by means of x-ray powder diffraction. Pellets of the cuprates (10 mm dia and 2 mm thick) were prepared by applying 20 kPa/cm^2 pressure and sintered for a period of 6 hours and annealed appropriately. Gas sensing properties of these pellets were then examined. Thick films ($\gtrsim$ 30 μm) prepared by screen printing were also examined for gas-sensing

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properties. For the purpose of screen printing, fine powders of the cuprates were mixed with equal amounts of starch, and n-butyl alcohol and made into a form of paste by grinding. The paste was printed on sintered polycrystalline pellets of alumina by using a 300 mesh screen and dried. These films were heated slowly ($YBa_2Cu_3O_{7-\delta}$ to 1170 K, $La_{2-x}Sr_xCuO_4$ to 1250 K, and $Bi_2Y_{1-x}Ca_xSr_2Cu_2O_8$ to 1000 K) and kept for 30 minutes, and cooled in air. The 123 films were annealed in O_2 at 870 K. Electrical contacts were made using conducting silver paint. Both the pellets and films were tested for gas sensitivity by applying a constant voltage (1 Volt D.C.) and monitoring the current passing through the sensor. The sensitivity is expressed as the response ratio, R, which is defined as follows:

$$R = 100\ (R_a - R_g)/R_g, \text{ for n-type sensors}$$
$$R = 100\ (R_g - R_a)/R_g, \text{ for p-type sensors}$$

Here R_g is the resistance of the sensor after exposing it to the gas or vapour and R_a is the resistance in dry air. The response time of the various cuprate films studied by us was generally 6 sec to reach 90% of the sensitivity at 600 K.

We first carried out experiments with $YBa_2Cu_3O_{6.9}$, and found the response ratio of the pellets to be smaller than that of the screen printed films. Both the films and pellets showed p-type behaviour (the resistance increased when exposed to reducing gases or vapours). The films showed reasonable sensitivity to ethanol, but the results were not reproducible. After a few cycles, the sensitivity went down while the oxygen stoichiometry changed from 6.9 to 6.75. In Fig.1 we show the gas-sensing characteristics of the $O_{6.75}$ composition; we see that the response to the various gases, and vapours is not very good. We carried out similar experiments with non-superconducting $YBa_2Cu_3O_{6.4}$. This sample also showed low sensitivity, and a change in oxygen stoichiometry after exposure to ethanol. It became clear that $YBa_2Cu_3O_{7-\delta}$ may not be good for gas sensing purposes because of the marked change in oxygen stoichiometry resulting from the interaction with reducing vapours.

We have examined the temperature dependence of the response ratio of the films of $La_{2-x}Sr_xCuO_4$ with x = 0.0, 0.075, and 0.2 for various gases, and vapours. All the films of $La_{2-x}Sr_xCuO_4$ showed p-type semiconducting behaviour. In Fig.2 we show the variation of the response

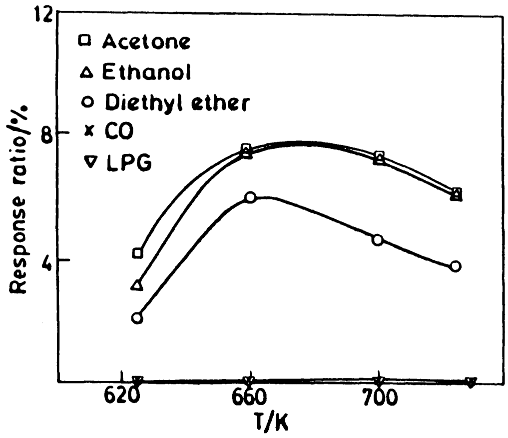

Fig. 1. Temperature-variation of the response ratio of $YBa_2Cu_3O_{6.75}$ films (400 ppm gas or vapour).

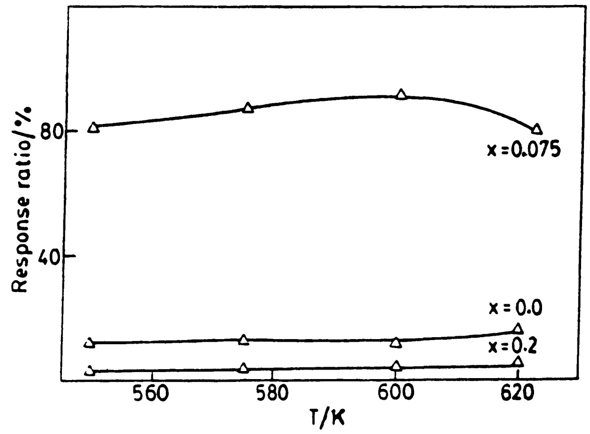

Fig. 2. Temperature-variation of the response ratio of $La_{2-x}Sr_xCuO_4$ (x=0.0, 0.075, and 0.2) films for ethanol vapour (400 ppm).

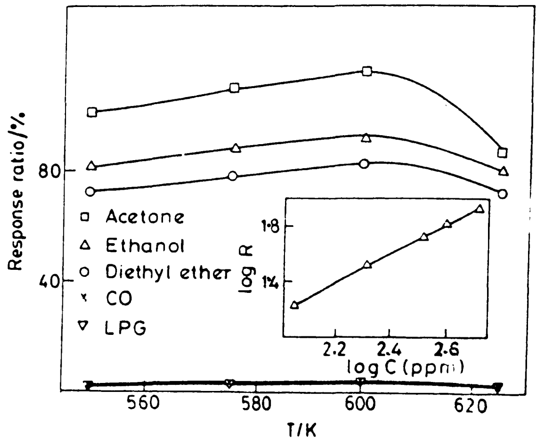

Fig. 3. Temperature-variation of the response ratio of a film of $La_{1.925}Sr_{0.075}CuO_4$ for different gases and vapours (400 ppm). The inset shows the log response ratio-log concentration plot for ethanol vapour at 600 K.

ratio for the insulator (x = 0.0) as well as the superconducting compositions (x = 0.075 and 0.20) for ethanol vapour. The response ratio of the x = 0.0 and 0.2 films was rather low compared to the films of the x = 0.075 composition. The response ratio of all the compositions to CO was negligible. In Fig.3 we show the response ratio of a x = 0.075 film for various gases, and vapours. The response ratio is high at 600 K for ethanol, acetone, and diethyl ether, but very low for LPG and CO. The response ratios for the first three vapours do not vary significantly with temperature, and are good even at 550 K. In the inset of Fig.3 we show the variation of the response ratio with the concentration of ethanol vapour at 600 K. The detection limit of the $La_{1.925}Sr_{0.075}CuO_4$ films for alcohol and diethyl ether is $\simeq$10 ppm or less; these films can, in principle, be used as alcohol sensors at a relatively low temperature of 550 K with a sensitivity of $\lesssim$ 10 ppm.

Films of $Bi_2Y_{1-x}Ca_xSr_2Cu_2O_8$ with x = 0.0 showed a decrease in resistivity on exposure to reducing gases, and vapours (n-type behaviour) whereas the films with x = 0.3 showed p-type behaviour. In Fig.4 we show the temperature dependence of the response ratio of $Bi_2Y_{1-x}Ca_xSr_2Cu_2O_8$ films (x = 0.0 and 0.3) for diethyl ether vapour. The response ratio is highest at 675 K for both the films, but the film of x = 0.0 shows higher response ratio than that of x = 0.3. In Fig.5 we show the sensitivity of $Bi_2YSr_2Cu_2O_8$ films for various gases, and vapours. The response ratio is highest for diethyl ether around 675 K, but very low for all other gases, and vapours studied. The selectivity of these films for diethyl ether is noteworthy. In the inset of Fig.5, we show the

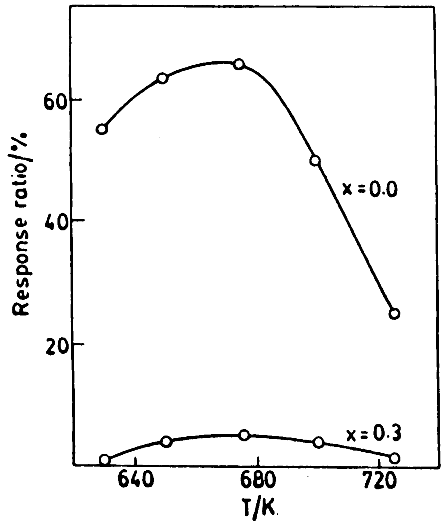

Fig. 4. Temperature-variation of the response ratio of $Bi_2Y_{1-x}Ca_x Sr_2Cu_2O_8$ (x=0.0 and 0.3) films for diethyl ether vapour (400 ppm).

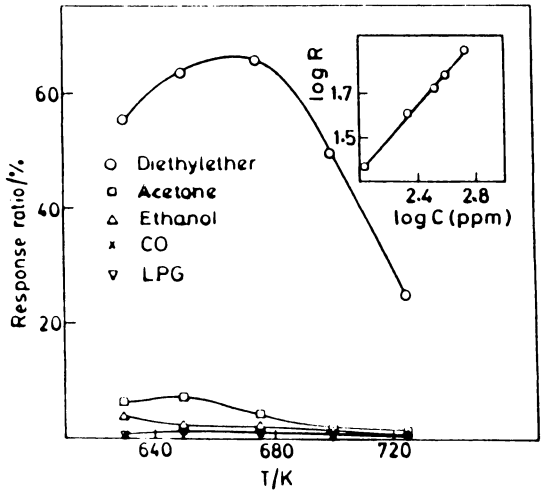

Fig. 5. Temperature-variation of the response ratio of $Bi_2YSr_2Cu_2O_8$ films for different gases and vapours (400 ppm). The inset shows the log response ratio-log concentration plot for diethyl ether vapour at 675 K.

variation of the response ratio to the concentration of diethyl ether vapour at 675 K. The detection limit for diethyl ether vapour is around 10 ppm. The gas-sensing characteristics of Bi-Y-Ca-Sr-Cu-O and La-Sr-Cu-O films were studied repeatedly on the same sample over 50 cycles, and found to be reproducible.

Obayashi et al.[5] have found $LaNiO_3$ to be a reasonably good ethanol sensor (≈ 200 ppm with 25% response ratio at 540 K) while Arakawa et al.[6] have found $SmCoO_3$ to be a methanol sensor. The La-Sr-Cu-O system examined by us is as good or better than $LaNiO_3$, although at a slightly higher temperature. The Bi-Y-Sr-Cu-O system is good for diethyl ether, for which La-Sr-Cu-O also shows sensitivity. Further studies on the gas sensing characteristics of cuprate superconductors are in progress, and will be reported in due course.

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