High-$T_c$ superconductors as NO sensor materials: a general investigation

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Abstract

The response of several ceramic high-$T_c$ superconductors to NO and CO in Taguchi-type gas sensors has been investigated. $YBa_2Cu_3O_{6+\delta}$ decomposes in the presence of NO. $Ba_2La_2Cu_3O_{6+\delta}$, and $La_{1.5}Sr_{1.5}CuO_4$ do not show any sensitivity or selectivity of interest. $Nd_{1.5}Sr_{0.5}CuO_{4+\delta}$ exhibits sensitivity to CO, but no sensitivity to NO. These materials are not suitable for NO gas sensors. $Bi_2Sr_2CaCu_2O_{8+\delta}$, $Bi_2Sr_2CaCu_2O_{8+\delta}$, and $Bi_2PbSr_2CaCu_2O_{8+\delta}$ show high selectivity to NO against CO. They are promising materials for Taguchi-type NO sensors. $Bi_2Sr_2CaCu_2O_{8+\delta}$ exhibits the best properties. The sensitivities of composites of $Bi_2Sr_2CaCu_2O_{8+\delta}$, with 0.5, 2, and 10 wt.% $Al_2O_3$, $Bi_2Sr_2CaCu_2O_{8+\delta}$, with 20 wt.% $Fe_2O_3$, $Bi_2Sr_2CaCu_2O_{8+\delta}$, with 20 wt.% $NiO$, $Bi_2Sr_2CaCu_2O_{8+\delta}$, with 20 wt.% $ZrO_2$, $Bi_2Sr_2CaCu_2O_{8+\delta}$, with 50 wt.% $Sb_2O_3$, and the lithium-intercalated compound $Li_{x}Bi_2Sr_2CaCu_2O_{8+\delta}$ to NO and CO at 300 and 350 °C have been studied. While additions of $Al_2O_3$, $ZrO_2$, and $Sb_2O_3$ to $Bi_2Sr_2CaCu_2O_{8+\delta}$ do not improve its selectivity to NO against CO, additions of $Fe_2O_3$ and $NiO$ and lithium intercalation do improve the selectivity.

Keywords: High-$T_c$ superconductors; Nitrogen oxide sensors

1. Introduction

The gas-detection concept of the conductivity-type [1] NO$_2$ sensor is based on chemisorption and/or catalytic activity at the semiconductor surface by monitoring the resistance changes of a thin-film semiconductor caused by charge transfer between semiconductor adsorbent and chemisorbed gas.

SnO$_2$ and other metal oxides, such as In$_2$O$_3$ and ZnO-modified SnO$_2$, have been investigated as NO$_2$ sensor materials for many years [2–7]. V$_2$O$_5$ and its modifications show high sensitivity [8–10]. ATIO$_3$ (A = Al, Nb, Ta, Sb, As, Ga, In, Sc, Mg, Y, Pb, Ca, Sr, Cd, Zn, La and Ba) has been investigated as an NO$_2$ sensor material [11]. α-Fe(OOH), γ-Fe(OOH) and amorphous Fe(III) hydroxide exhibit low-temperature sensitivity for NO$_2$ [12]. In recent years, phthalocyanine has been broadly studied for use in trace-NO$_2$ sensors [13–15].

Mixed metal oxides crystallizing in a perovskite-related structure have long been of interest to solid-state chemists and physicists, because of their technologically important physical properties. These mixed metal oxides are more advantageous and are better catalytic materials than simple oxides because: (i) the crystal structure can accommodate various metal ions, and can stabilize unusual and mixed valence states of active metal ions; (ii) appropriate formulation of these oxides leads to easy tailoring of many desirable properties, such as the distance between active sites, the binding energy, the diffusion of oxygen in the lattice, magnetic and conducting properties; (iii) the catalytic activity can be correlated to solid-state properties, since these are thoroughly understood [16]; (iv) the surface of these oxides can be regenerated by a suitable activation procedure.

Several ceramic high-$T_c$ superconductors with perovskite structure exhibit high catalytic activity for NO$_2$ oxidation or reduction [17–22]. Göpel [23] has suggested that the members of this family are potential sensor materials. Schoonman [24] has suggested that the oxide superconductors may be used as NO$_2$-sensing materials.
We have reported the result of a primary investigation of superconductors as NO\textsubscript{s}-sensing materials [25].

In the present study, the NO\textsubscript{s} and CO\textsubscript{s} sensing behaviour of YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-}\textdelta, Ba\textsubscript{1}La\textsubscript{1-x}Cu\textsubscript{3}O\textsubscript{5}, La\textsubscript{2-x}Sr\textsubscript{x}CuO\textsubscript{3}, Nd\textsubscript{1.4}Ce\textsubscript{0.6}CuO\textsubscript{4-\textdelta}, Bi\textsubscript{2}Sr\textsubscript{2}CaCuO\textsubscript{4+\textdelta} (BSCCO 2201-phase), Bi\textsubscript{2}Sr\textsubscript{2}CaCuO\textsubscript{4+\textdelta} (BSCCO 2212-phase) and Bi\textsubscript{1.8}Pb\textsubscript{0.2}Sr\textsubscript{2}CaCuO\textsubscript{4+\textdelta} (BPSSCO 2223-phase) has been investigated.

The sensitivities of the composites of BSCCO and 0.5, 2, 10 wt.% Al\textsubscript{2}O\textsubscript{3}, BSCCO and 20 wt.% Fe\textsubscript{2}O\textsubscript{3}, BSCCO and 20 wt.% NiO, BSCCO and 20 wt.% ZrO\textsubscript{2} were obtained by mixing the powder of BSCCO with a certain amount of metal oxide, followed by grinding thoroughly and calcining at 850 °C for 20 h.

BSCCO lithium-intercalated compounds were obtained by the electrochemical intercalation method. Electrochemical cells with BSCCO 2212-phase as cathode, metallic lithium as anode and 1 M LiClO\textsubscript{4} in propylene carbonate solution as electrolyte were fabricated. The amounts of lithium 2212 were determined from the discharge capacity per mole BSCCO. The modified BSCCO pellets were washed in dimethyltetrahydrofuran and dried at 400 °C.

Then all the pellets mentioned above were ground in a ball-mill to a particle size of 1–10 μm diameter.

2. Experimental

2.1. Preparation of the starting materials

YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-\textdelta} was prepared by the ceramic processing technique described in Ref. [26].

Ba\textsubscript{2-x}La\textsubscript{x}Cu\textsubscript{3}O\textsubscript{7-\textdelta} (x = 0.5) was prepared from mixtures of Ba(NO\textsubscript{3})\textsubscript{2} (99.4% J.T. Baker), La\textsubscript{2}O\textsubscript{3} (99.98%, Fluka AG) and CuO (> 97%, BDH) with a molar ratio Ba:La:Cu = 1:1:2. Thoroughly ground mixtures were pre-reacted at 900 °C in air for 20 h. The resulting products were ground and subsequently sintered at 1000 °C in air for about 100 h. The sintered material was then ground in a ball-mill to a particle size of 1–10 μm diameter.

La\textsubscript{2-x}Sr\textsubscript{x}CuO\textsubscript{4} (x = 0.15) was obtained from the appropriate mixtures of high-purity La\textsubscript{2}O\textsubscript{3}, SrCO\textsubscript{3} (> 99%, BDH) and CuO (> 97%, BDH) powders, by heating for 100 h at 1000 °C as described in Ref. [27].

The Nd\textsubscript{1.4}Ce\textsubscript{0.6}CuO\textsubscript{4-\textdelta} pellet was prepared from a stoichiometric mixture of metal oxides. The mixed oxides were calcined at 950 °C in air for 20 h, ground and pressed to pellets. After this procedure, the pellet was sintered for 12 h in air at 1150 °C, followed by quenching to room temperature as described by Takagi et al. [28].

BSCCO was prepared from mixtures of Bi(NO\textsubscript{3})\textsubscript{3}·5H\textsubscript{2}O, SrCO\textsubscript{3}, CaCO\textsubscript{3} and Cu(NO\textsubscript{3})\textsubscript{2}·2H\textsubscript{2}O with a molar ratio Bi:Ca:Cu:2:2:1:2. Thoroughly ground mixtures were pre-reacted at 820 °C in air for 20 h. The resulting products were ground and subsequently sintered at 850 °C in air for about 20 h.

BSCCO was obtained by a similar process to that described for BSCCO with a molar ratio Bi:Ca:Cu = 2:2:1. Here, the final sintering time was 168 h.

The structures of all the sintered materials studied were identified by X-ray diffraction (Philips PW1840, Cu Kα).

A variety of composites of BSCCO and metal oxides including BSCCO + 0.5, 2, 10 and 20 wt.% Al\textsubscript{2}O\textsubscript{3}, BSCCO + 20 wt.% Fe\textsubscript{2}O\textsubscript{3}, BSCCO + 20 wt.% NiO, BSCCO + 20 wt.% ZrO\textsubscript{2} and BSCCO + 50 wt.% Sb\textsubscript{2}O\textsubscript{3} were obtained by mixing the powder of BSCCO with a certain amount of metal oxide, followed by grinding thoroughly and calcining at 850 °C for 20 h.

BSCCO lithium-intercalated compounds were obtained by the electrochemical intercalation method. Electrochemical cells with BSCCO 2212-phase as cathode, metallic lithium as anode and 1 M LiClO\textsubscript{4} in propylene carbonate solution as electrolyte were fabricated. The amounts of lithium 2212 were determined from the discharge capacity per mole BSCCO. The modified BSCCO pellets were washed in dimethyltetrahydrofuran and dried at 400 °C.

Then all the pellets mentioned above were ground in a ball-mill to a particle size of 1–10 μm diameter.

2.2. Fabrication of gas sensors

One popular method of preparing a semiconductor powder-based gas sensor is the one used by Taguchi for his original gas sensors. These sensors consist of a ceramic tube with the heater element inside the tube and the semiconductor as a coating on the outside. Au electrical contacts are deposited on the semiconductor coating by sputtering or sputtering.

Usually, thick-film sensors are fabricated using pastes and planar alumina substrates. In the present study, different preparation techniques for thick-film sensors have been employed. The low-temperature sintered pellets exhibited porosity. Their sensitivity to NO and CO was tested, as they provide a first indication of the suitability of the material as an active sensor material. Due to their ease of fabrication, they are suited for research purposes.

2.2.1. Thick films of YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-\textdelta}

Thick films of YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-\textdelta} were prepared by spraying aqueous solutions of Y(NO\textsubscript{3})\textsubscript{3}, Ba(NO\textsubscript{3})\textsubscript{2} and Cu(NO\textsubscript{3})\textsubscript{2} with Y:Ba:Cu = 1:2:3 on a 10 mm × 5 mm single crystal of ZrO\textsubscript{2} (001) as substrate, and heat treated according to the procedure for preparing bulk material [29,30]. The thickness of the film is around 100 μm. Their structure is identified as the orthorhombic phase using X-ray diffraction.

2.2.2. Thick films and porous pellets of BSCCO

Powders of BSCCO were distributed homogeneously on 20 mm × 10 mm Al\textsubscript{2}O\textsubscript{3} substrates, which have been cleaned in acetone. The amount of powder was chosen to obtain films with a thickness of less than 100 μm. Subsequently, the particles on the substrates were melted at 950 °C for 8–10 min. The film was polished to a thickness of about 20–30 μm. These films were then annealed at 850 °C in air for 20 h.

Porous sintered pellets were obtained by pressing the powders of the starting material into pellets with a
diameter of 10 mm and thickness of 2 mm, and subsequently calcining at 500 °C in air for 20 h. A high-porosity thick BSCCO film with a 20 mm × 10 mm Al₂O₃ substrate was prepared by screen printing. The film thickness is 50–100 μm. The high porosity was maintained by sintering at 600 °C.

2.2.3. BSCO thick and thin films

The thick films were prepared by a similar method as used for BSCO, but with shorter annealing times. The thin films of BSCO were obtained by electron-beam (EB) evaporation using a Bio-Rad Turbo Coater with single-phase source material. 20 mm × 10 mm Al₂O₃ plates were used as the substrate. They were annealed at 800 °C for 10 min with subsequent cooling in the furnace to 600 °C, and were kept at this temperature for 20 h. Their thickness is around 1 μm. The structure of the films was identified by X-ray diffraction to be the 2201-phase.

2.2.4. Other pellets

Pellets of Nd₁₋ₓCeₓCuO₂₋ₓ, Ba₁₋ₓLaₓCuO₃, La₁₋ₓSrₓCuO₄, BPSICO, CuO₃ metal oxides + BSCO composites and lithium-intercalated BSCO were obtained by the same technique as described above for BSCO pellets.

2.3. Measurements of sensitivity

The samples were exposed to different NOₓ or CO-containing ambient in the sensor-testing system described previously [31]. The total flow rate of the gases in all experiments was 200 ml min⁻¹.

The electrical resistivity of the materials was measured using a standard four-point measurement and a two-electrode method with Ag paste or sputtered Au to improve the contact of the electrodes. Both methods yield the same value for the electrical resistivity of porous pellets of BSCO 2212-phase. Therefore, at a later stage of the investigation, only the two-electrode method was used to obtain the resistivity of porous pellets. The resistances of thick films made by powder melting, high-porosity thick BSCO film, thin BSCO films prepared by EB evaporation and poorly sintered pellets under the experimental conditions are around 10 mΩ, 80 Ω, 2 × 10⁴ Ω and 100 mΩ, respectively. A Keithley multimeter is convenient to use for the measurements.

The sensitivity to NO and selectivity against CO of these samples were studied at different temperatures.

3. Results and discussion

The sensitivity, S, of the samples to the various gases is defined as

\[ S = \frac{\rho}{\rho_0} = \sigma_0 \]

where \( \rho \) and \( \sigma \) denote the resistivity and conductivity of the sample on exposure to NO or other gases, respectively, while \( \rho_0 \) and \( \sigma_0 \) denote the resistivity and conductivity of the sample in air as a reference.

Usually, the response of the sensor is influenced by the flow rate. An account of this parameter was reported elsewhere [31].

Table 1 shows the sensitivity of Ba₁₋ₓLaₓCuO₃, La₁₋ₓSrₓCuO₄, Nd₁₋ₓCeₓCuO₂₋ₓ, BSCO 2201-phase, BSCO 2212-phase and BPSICO 2223-phase to NO and CO at 300 and 350 °C. [S(A)−1]/[S(B)−1] and [S(C)−1]/[S(D)−1] are used to express the se-

<table>
<thead>
<tr>
<th>Materials</th>
<th>S(A)</th>
<th>S(B)</th>
<th>S(A)−1/S(B)−1</th>
<th>S(C)</th>
<th>S(D)</th>
<th>S(C)−1/S(D)−1</th>
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<td>1 at</td>
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<td>1.210</td>
<td>1.013</td>
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<td>3.6</td>
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<td>1.021</td>
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<td>2.78</td>
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* A: 300 °C, 500 ppm NO in air.
* B: 300 °C, 500 ppm CO in air.
* C: 350 °C, 500 ppm NO in air.
* D: 350 °C, 500 ppm CO in air.
* Porous pellet.
lectivity of the sensors to NO against CO at 300 and 350 °C, respectively. A large value means high selectivity.

3.1. The sensing behaviour of Cu-based superconductors and CuO

The resistivity of all copper-based materials was uninfluenced by the presence of CO₂, which is consistent with theoretical analyses [31].

3.1.1. YBa₂Cu₃O₇−δ

The behaviour of resistivity change of a thick film of YBa₂Cu₃O₇−δ when exposed to 500 ppm NO in air suggests a diffusion-controlled process [25], which is consistent with early reports that this material can absorb large amounts of NO, and may even catalyse the decomposition of NO when the amount of NO absorbed is large enough. This process is reversible [16]. Hence, YBa₂Cu₃O₇−δ is not a suitable material for utilization in NO sensors. Recently, Koshizaki et al. [32] reported that when YBa₂Cu₃O₇−δ is annealed in N₂, it becomes sensitive to NO around 150 °C. Its resistivity decreases when exposed to NO. There was no similar phenomenon observed in this study. The oxygen content and copper valence of this material are determined by the annealing conditions [33], and it is assumed that these parameters influence the sensing behaviour.

3.1.2. Ba–La–Cu–O

The resistivity of Ba₁₋ₓLaₓCu₂O₄ did not change upon exposure to 1% CO₂ in air. The resistivity of this material increased when exposed to NO, NO₂, and CO. The original value of the resistivity was attained on exposure to air again. At 300 °C the sensitivities to NO and CO are almost equal: this material has no selectivity to NO against CO. At 350 °C, its sensitivity to NO is very small as compared to the other copper-based materials. Hence, this material seems to be unattractive for utilization as the active material in a Taguchi-type gas sensor.

3.1.3. La–Sr–Cu–O

Like Ba–La–Cu–O, La₁₋ₓSrₓCu₂O₄ has no sensitivity to CO₂, and its resistivity increases when exposed to NO and CO. Both the selectivity to NO against CO, as well as the sensitivity to NO are low. It was therefore disregarded as a material for an NO sensor.

3.1.4. Nd–Ce–Cu–O

At 294 °C, Nd₁₋ₓCeₓCuO₄−δ, which exhibits n-type conductivity, does not show any resistivity change when exposed to NO and NO₂. For 500 ppm CO in air, S has the value 0.97. This is consistent with electron conductivity, and CO acting as a reductant. At 401 °C, no sensitivity to NO, and CO could be measured. This material is also not suitable for utilization in NO senses.

3.1.5. BSCO (2201-phase)

The response behaviour of a thick film of BSCO and a thin film of BSCO prepared by electron-beam evaporation has been reported before [25]. For the thick film, the baseline of the signal can be recovered when the materials are exposed to air again; this process is reversible. At 300 °C, the film sensitivity to NO reaches saturation when the concentration of NO in air is 300 ppm. For the thin film of BSCO prepared by electron-beam evaporation, the sensitivity to 500 ppm NO in air is lower than that to 300 ppm NO in air at 300 °C, and this was reproducible.

3.1.6. BSCCO (2212-phase)

BSCCO is sensitive to NO. The optimal temperature for sensing NO is 350 °C. At lower temperatures, the response time is too long, although higher sensitivity can be obtained. At 350 °C the sensitivity of a thick film to 500 ppm NO was much higher than that to 500 ppm CO at 350 °C. The low sensitivity of BSCCO to CO₂ has been reported earlier [25]. Fig. 1 shows the time dependence of the response of a high-porosity BSCCO film to NO in air. The response rate should be improved in practical usage. Fig. 2 shows the influence of 500 ppm CO on the sensitivity to 200 ppm NO in air at 350 °C is small. This 2212-phase is sensitive and selective enough for NO detection. The sensitivities of a porous pellet to NO and CO are shown in Fig. 3.

3.1.7. BPSCCO

BPSCCO exhibits no sensitivity to CO₂. Its sensitivity to NO and the selectivity of NO against CO are comparable with the observed responses of BSCO and BSCCO (see Table 1). Fig. 4 presents the temperature dependence of its sensitivity to NO.

Fig. 1. The response behaviour of high-porosity BSCCO film to NO in air.
Fig. 2. The response behaviour of high-porosity BSCCO film in CO(500 ppm)+NO(200 ppm) in air at 350 °C.

Fig. 3. The sensitivity of a porous pellet of BSCCO to NO and CO at 350 °C.

Fig. 4. The temperature dependence of the sensitivity to NO of a porous BPSCCO pellet.

3.1.8 CuO

Because all the ceramics investigated here that exhibit sensitivity to NO contain copper, the sensing behaviour of CuO was investigated for comparison. CuO exhibits a sensitivity to NO that exceeds its sensitivity to CO. CuO is selective to NO against CO, but this selectivity decreases with increasing temperature. In general, the sensitivity of CuO to NO and CO is much lower than the sensitivity of the bismuth-based ceramic superconductors.

Substantial differences in sensitivity exist between sensors comprising a thin film (EB) and a pellet of BSCO, and thick films made by powder melting and poorly sintered, porous pellets of BSCCO. The thick films made by powder melting exhibited the lowest sensitivity. SEM micrographs of the present thick films revealed a grain structure. The width of the necks between the grains is much larger than the Debye length, which is of the order of 100 Å. It is speculated that the conductance is ‘bulk-trap limited’ [34]. This is consistent with the results reported by Xu et al. [35,36], which reveal that the sensitivity can be enhanced by reducing the grain size, and hence the width of the necks. The conductivities of the poorly sintered pellets and the BSCO EB film are speculated to be ‘Schottky-barrier limited’. They show higher sensitivity as discussed elsewhere [31]. The best results should be obtained using ultra-thin films with a ‘surface-trap limited’ conductance.

The Bi-based ceramic superconductors are interesting candidates for application as the active element in Taguchi-type NO gas sensors. Because the detection limit of BSCO is lower than that of BSCCO and BPSCCO, we will focus here on the latter and two-phase composites based on BSCCO. An additional advantage of BSCCO is its ease of preparation.

3.2. The sensing behaviour of modified BSCCO (2212-phase)

In order to improve the selectivity of BSCCO to NO against CO, composites based on BSCCO with several metal oxides including Al₂O₃, Fe₂O₃, NiO, ZrO₂ and Sb₂O₃, have been investigated. In addition, lithium-intercalated BSCCO, prepared by electrochemical intercalation at room temperature, was studied.

Table 2 shows the sensitivity of BSCCO +0.5, 2 and 10 wt.% Al₂O₃, BSCCO +20 wt.% Fe₂O₃, BSCCO +20 wt.% NiO, BSCCO +20 wt.% ZrO₂, BSCCO +50 wt.% Sb₂O₃ and Li₀.₁₃BSCCO to NO and CO at 300 and 350 °C.

3.2.1. BSCCO +0.5 wt.%, 2 wt.% and 10 wt.% Al₂O₃

Considering the difference between the selectivity to NO against CO of the thick film on an Al₂O₃ substrate and the poorly sintered pellet of BSCCO, the question arises as to whether Al₂O₃ has interacted with BSCCO and influenced its selectivity. According to Ishihara et al. [2], V₂O₃ has a low selectivity to NO, against CO, but the addition of Al₂O₃ enhanced its selectivity. The sensing behaviour of the 2212-phase with different amounts of Al₂O₃ was examined. The resistivity of the 2212-phase with 20 wt.% Al₂O₃ turned out to be very large. This composite could not be used in a sensor.
Table 2
The sensitivity of modified BSCCO (2212-phase) to NO and CO at 300 and 350 °C

<table>
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<tr>
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<th>S(A)</th>
<th>S(B)</th>
<th>S(C)</th>
<th>S(D)</th>
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<td>2 wt.% Al$_2$O$_3$</td>
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<td>2.32</td>
<td>1.383</td>
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<td>10 wt.% Al$_2$O$_3$</td>
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<td>50 wt.% Sb$_2$O$_3$</td>
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<td>1.80</td>
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<td>Li$_{0.21}$BiSCCO</td>
<td>1.573</td>
<td>1.101</td>
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<td>1.505</td>
<td>1.040</td>
<td>12.6</td>
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</table>

* A: 300 °C, 500 ppm NO in air.
* B: 300 °C, 500 ppm CO in air.
* C: 350 °C, 500 ppm NO in air.
* D: 350 °C, 500 ppm CO in air.

For amounts of Al$_2$O$_3$ up to 10 wt.% the composites revealed metallic behaviour with $T^\text{onset}_c = 70$–80 K and $T^\text{onset}_e = 30$–40 K. Here $T^\text{onset}_c$ denotes the starting temperature of superconductive conversion and $T^\text{onset}_e$ denotes the highest temperature with zero resistance. The selectivity of the samples with Al$_2$O$_3$ has not changed.

3.2.2. BSCCO + 20 wt.% Fe$_2$O$_3$

The composite of BSCCO and 20 wt.% Fe$_2$O$_3$ exhibited an enhanced selectivity at 350 °C, while the response rate was not affected.

3.2.3. BSCCO + 20 wt.% NiO

The composite material showed metallic behaviour with $T^\text{onset}_c = 70$ K and $T^\text{onset}_e = 37$ K. Its Seebeck coefficient at room temperature is negative, indicating n-type conductivity. The resistivity of the composite increased when it was exposed to CO at 300 °C. Its sensitivity to CO decreases quickly with increasing temperature. The resistivity decreased with CO exposure at 400 °C. Determining whether this composite has the same sensing mechanism as proposed for Al$_2$O$_3$–V$_2$O$_5$ (Al:V = 1:1) by Ishihara et al. [2] needs further work.

The selectivity was substantially enhanced by adding 20 wt.% NiO. However, the response rate was not affected. Fig. 5 shows the sensitivity to NO and CO at different temperatures.

3.2.4. BSCCO + 20 wt.% ZrO$_2$

The addition of ZrO$_2$ did not influence the selectivity and response rate noticeably.

3.2.5. BSCCO + 50 wt.% Sb$_2$O$_3$

The selectivity of this composite decreased as compared to pure BSCCO.

3.2.6. Li$_{0.21}$BiSCCO

Figs. 6 and 7 show the response behaviour of the lithium-intercalated compound. The selectivity of BSCCO to NO against CO is enhanced by lithium intercalation. The sensitivity to NO is not influenced substantially upon lithium intercalation.

4. Conclusions

YBa$_2$Cu$_3$O$_{7-\delta}$ reacts with NO and decomposes. Ba$_{1.3}$La$_{1.5}$Cu$_3$O$_y$ and La$_{1.8}$Sr$_{0.2}$CuO$_y$ did not show any
sensitivity or selectivity of practical interest. Nd_{0.85}Ce_{0.15}CuO_{2+δ} has no selectivity for NO against CO. These are not suitable for the development of NO gas sensors. The present investigation clearly shows that the Bi-family materials are good candidates for the development of Taguchi-type NO gas sensors.

Bi_{2}Sr_{2}CuO_{6+δ}, Bi_{2}Sr_{2}CaCu_{2}O_{8+δ}, and Bi_{1+δ}Pb_{0.2}Sr_{2}Ca_{2}Cu_{3}O_{10+δ} exhibit high selectivity to NO against CO. Bi_{2}Sr_{2}CaCu_{2}O_{8+δ} exhibits the best response behaviour.

It is assumed that the sensitivity of sensors with Bi-based materials can be improved further by optimizing their fabricating method. The investigation of composites based on Bi_{2}Sr_{2}CaCu_{2}O_{6+δ} showed that an improvement of the selectivity to NO against CO can be obtained by metal oxide addition or lithium intercalation. Additions of Al_{2}O_{3}, ZrO_{2} and Sb_{2}O_{3} did not improve the selectivity. The addition of Fe_{2}O_{3} and NiO improved the selectivity. The latter oxide exhibited attractive results for practical applications. Lithium intercalation also improved the selectivity to NO against CO.

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