High Conductivity $La_{2-x}Sr_xCu_{1-y}(Mg, Al)_yO_4$ Solid State Metal Oxide Gas Sensors with the K_2NiF_4 Structure

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Materials of the K_2NiF_4 structure type have been identified as new highly conducting conductometric gas sensors. The materials of interest are based on substituted La_2CuO_4, a known superconducting material at low temperatures. La_2CuO_4 has been substituted with Sr for La and with Al or Mg for Cu, and sensitivity was demonstrated toward CO, NH_3, and NO_2 gases at temperatures in the range 300−600 °C. The level and type of substitution can be adjusted to enhance selectivity and minimize humidity interference. As a result of the relatively high conductivity of these sensor materials there is great potential for miniaturization of devices for use in small area applications. Uncomplicated electrode requirements also mean a simplification of the manufacturing of these new devices.

Introduction

Accurate and reliable gas sensors are essential in both the industrial and the domestic environments where the presence of noxious gases at very low levels (i.e., a few parts per million) is increasingly of concern. This concern has given rise to stringent environmental legislation;[1] hence, the accurate monitoring of emissions, such as carbon monoxide and nitrogen oxides, is very important in a wide variety of industries from steel and glass production to the automotive and aerospace sectors. Further requirements for gas sensing include the detection of H_2 and hydrocarbons, particularly with the advent of renewable energy technology such as fuel cells, and also in the nuclear industry where reprocessing also requires detection of hydrogen and hydrocarbons among many other gaseous species. In these applications the monitoring is often undertaken under very difficult and aggressive conditions such as high ambient temperatures. The food industry also requires highly accurate sensors for the detection of gases at low concentrations such as ammonia at down to parts per million levels, as ammonia is increasingly used as an alternative to chlorofluorocarbons in refrigeration. In addition to these examples there are numerous other gases that require accurate detection, including hydrogen sulfide and sulfur dioxide.

There are a number of commercial semiconducting oxide gas sensors currently available for the detection of the majority of these gaseous species based mainly on tin oxide[2−7] as manufactured by Figaro and FIS in Japan or chromium titanium oxide[2,8−10] manufactured by City Technology, Ltd., in the United Kingdom. These sensor materials, although adequate, can exhibit deficiencies in operation including poor sensitivity and thermal stability and, importantly, poor selectivity of gases. Indeed many current gas sensors are affected by the presence of moisture, giving inaccurate readings as a result of loss of sensitivity. Hence, there is a requirement for highly sensitive, highly accurate, environmentally stable gas sensors that can overcome these limitations. For this reason we have investigated mixed conducting oxides with perovskite and perovskite related structures.

Perovskite related oxide materials that adopt the K_2NiF_4 structure, the first member of the Ruddlesden−Popper ($A_{n+1}B_nO_{3n+1}$) series, have been studied for some time for their catalytic and electrocatalytic properties.[11−17] Of par-

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ticular interest have been the oxygen excess mixed conducting materials with the general formula $A_2BO_{4+\delta}$ where the A site is occupied by a rare earth cation and the B site is occupied by a transition metal. It has been shown that this excess oxygen is highly mobile and that the materials can be used as solid oxide fuel cell cathodes[18–20] and are potentially excellent candidates for use in oxygen separation membranes.[21] The surfaces of these materials have also been shown to be highly active for oxygen exchange,[18] and for this reason it is anticipated that the conducting K_2NiF_4 type oxides would show sensitivity toward reducing gases.

Previous studies of the oxygen deficient K_2NiF_4 type oxides have demonstrated catalytic behavior toward the decomposition of NO_x and suggest that cuprate based materials would be suitable for this application in the automotive industry.[15–17,22] No further studies of these or related materials have been reported as demonstrating sensitivity toward other gaseous species, but there have been reports of the use of both $ZnO-La_2CuO_4$ and $SnO_2-La_2CuO_4$ hetero-contacts to detect H_2 and CO.[23–26] Unfortunately these preliminary reports do not develop the studies further by investigating substituted compositions. In this work we report on the study of substituted $La_2CuO_{4\pm\delta}$ as a potential gas sensing material that demonstrates good sensitivity and encouraging response time when compared with existing sensor materials.

Experimental Section

Each of the materials was produced using the high-temperature ceramic synthesis route using the appropriate oxides and carbonates. Six compositions of general formula $La_{2-x}Sr_xCu_{1-y}(Mg, Al)_yO_4$, where $x = 0$, 0.05, and 0.1 and $y = 0.05$, were produced, substituting Sr for La and Mg or Al for Cu, and one composition with a double site substitution where both A and B sites were co-doped was produced. The starting materials were homogenized under acetone, dried, pressed, and fired at temperatures of around 1050 °C with intermediate grinding and pressing. Phase determination was performed using X-ray powder diffraction (XRD) on a Philips PW1700 series diffractometer with Cu Kα radiation and a secondary graphite single-crystal monochromator.

Prior to deposition on the sensor substrates inks of the relevant ceramic powder were prepared. Each powder was mixed with an organic vehicle for 20 min (ESL400, Agmet, U.K.) using a triple roll mill (Pascall Engineering) producing an ink suitable for screen printing onto the sensor substrates, using a DEK 1202 hybrid printer, to a thickness of approximately 10 μm. The sensors were then fired at 700 °C for 1 h to remove the residual organic vehicle and partially sinter the material. The sensor chips were finally spot welded with Pt wires to sensor housings for testing. The sensor substrates are made of alumina tiles with interdigitated gold electrodes on the top and a platinum meander on the back, which serves as a microheater. The platinum heater track of each sensor also formed one arm of a Wheatstone bridge, which allowed the resistance and, hence, the heater temperature to be both regulated and programmed.[27]

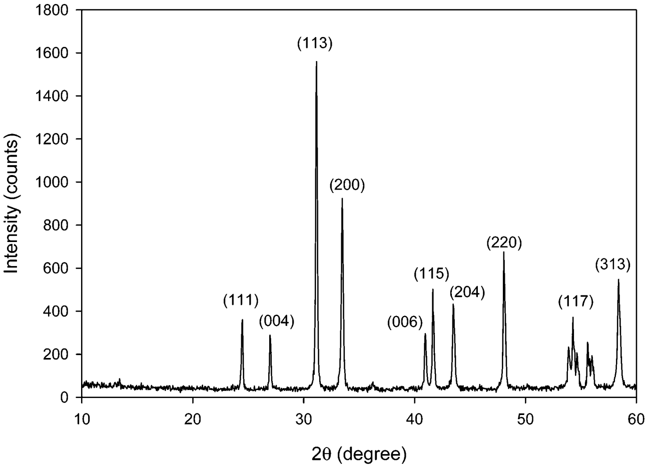

Figure 1. XRD data recorded from the $La_{1.9}Sr_{0.1}CuO_4$ sample with selected peak indices labeled. Lattice parameters $a = 5.345(3)$, $b = 5.351(4)$, and $c = 13.207(8)$ Å.

The gas sensing setup comprised a stainless steel test chamber[27] to which gases (BOC special gases) were streamed through PC controlled mass flow controllers (Tylan General). Gases were delivered to the sample via poly(tetrafluoroethylene) tubing with stainless steel Swagelock fittings. Two terminal resistance measurements in varying gas atmospheres were performed using an in-house constructed test rig which has been described previously.[27] Automated resistance readings were made every 60 s with a multiplexed Keithley Digital Multimeter. Humidity was measured using a commercial humidity sensor at the gas outlet. The devices were initially allowed to stabilize for 24 h at their operating temperatures before any measurements were taken. The response to a given concentration of test gas was calculated from the ratio $(R_g - R_a)/R_a$, where R_a is the resistance of the sensor in air and R_g is the resistance in the test gas.

Results and Discussion

The materials investigated, of general composition $La_{1-x}Sr_xCu_{1-y}B_yO_{4\pm\delta}$, where B is either Al or Mg, were selected for screening because of the effect of the cation substitutions on the relative oxygen stoichiometry, with Sr and Mg additions reducing and Al additions increasing the typical oxygen stoichiometry. In each case XRD analysis of the resulting materials revealed a single-phase material of K_2NiF_4-type character with no evidence of any secondary phase present. A typical diffraction pattern is shown in Figure 1 for the 20% Sr substituted sample. The room-temperature direct current bulk electrical conductivity, Table 1, of each material was measured under ambient conditions with pelletized samples using the van der Pauw method and was

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Table 1. Conductivity of Sensor Materials Recorded at 25 °C

sample	σ, S cm^{-1}
La_2CuO_4[28]	10.0
$La_{1.95}Sr_{0.05}CuO_{4+\delta}$	0.43
$La_{1.90}Sr_{0.10}CuO_{4+\delta}$	0.31
$La_{1.95}Sr_{0.05}Cu_{0.95}Mg_{0.05}CuO_{4\pm\delta}$	0.24
$La_2Cu_{0.95}Mg_{0.05}O_{4+\delta}$	0.27
$La_2Cu_{0.95}Al_{0.05}O_{4+\delta}$	0.21

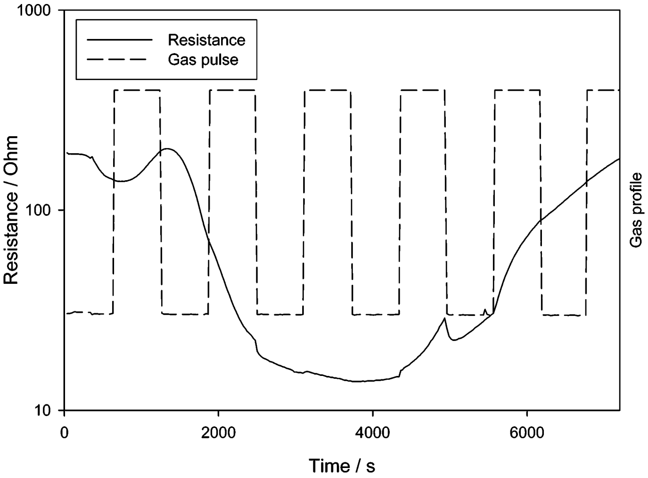

Figure 2. Temperature profile of the LCO12 sensor from 25 to 600 °C in 1000 ppm CO. Temperature was ramped from 25 to 600 °C and subsequently cooled to 25 °C during the time period shown.

found to be in the range 0.2−0.45 S cm^{-1}. Only the end member La_2CuO_4 had a reported bulk conductivity outside of this range.[28]

Each of the materials produced was then tested in a selection of gases: CO, NH_3, and NO_2 initially under dry conditions at a concentration of 2000 ppm.[27] This concentration was gradually reduced until a minimum of 1 ppm was used for testing the response of ammonia. Each of these experiments was then repeated in a gaseous atmosphere with 50% relative humidity (RH). The response of these metal oxide sensor materials to each of the test gases will be now be discussed.

(i) Sensor Response to Carbon Monoxide (CO). Initial test runs were performed on each sensor material over a range of temperatures from 25 to 600 °C using 1000 ppm pulses of CO in air at 0% RH and 50% RH. This preliminary investigation, Figure 2, indicated that the sensors showed maximum response to CO at a temperature of around 300 °C. Hence, all CO gas testing was subsequently carried out at 300 °C, and the sensors were then exposed to three concentrations of CO: 200, 500, and 2000 ppm at both 0% RH and 50% RH. For these sensors the response increased with CO concentration; however, the presence of moisture was found to reduce the response and shift the baseline. This may be due to the competitive adsorption of H_2O molecules on the active sites of the sensors thereby reducing the sites for CO adsorption. The response of $La_2CuO_{4+\delta}$ to a relatively high concentration of CO, 2000 ppm, at 300 °C was calculated to be 0.17 in 0% RH and 0.07 in 50% RH. Of the six compositions tested for CO, only $La_2CuO_{4+\delta}$, $La_{1.95}Sr_{0.05}CuO_{4+\delta}$, and $La_2Cu_{0.95}Al_{0.05}O_{4+\delta}$ showed appreciable response, the responses being 0.17, 0.12, and 0.34, respectively, when measured in 2000 ppm of CO at 300 °C and 0% RH. The response times, T_r, calculated as the time taken to reach 90% of the signal, were determined to be 433, 202, and 347 s, respectively, under the same conditions. Note that the signal at 100% response is not exact as the responses had not fully reached a plateau in all cases.

Table 2. Comparison of Sensitivity, $(R_g - R_a)/R_a$, and Response Time, T_r, of K_2NiF_4 Type Sensors in Dry Atmospheres with Current Sensor Materials[a]

	sensitivity	reponse time, s
2000 ppm NH_2 at 400 °C		
La_2CuO_4	1.48	188
$La_{1.95}Sr_{0.05}CuO_4$	0.26	279
$La_{1.90}Sr_{0.10}CuO_4$	0.11	405
$La_2Cu_{0.95}Mg_{0.05}O_4$	0.37	124
$La_{1.95}Sr_{0.05}Cu_{0.95}Mg_{0.05}O_4$	0.14	91
$La_2Cu_{0.95}Al_{0.05}O_4$	0.95	111
CuO	0.46	292
$Cr_{2-x}Ti_xO_{3-y}$	4.52	398
2000 ppm CO at 300 °C		
La_2CuO_4	0.17	433
$La_{1.95}Sr_{0.05}CuO_4$	0.12	202
$La_2Cu_{0.95}Al_{0.05}O_4$	0.34	347
CuO	0.5	287

[a] In each case the maximum resitance attained was selected for the calculation of the response time.

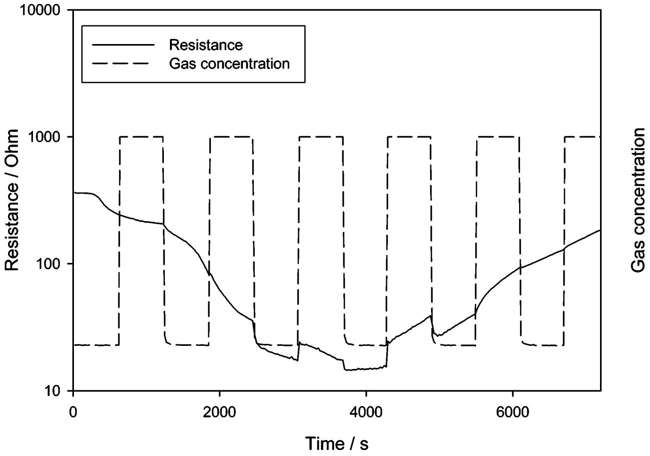

Figure 3. Temperature profile for LCO12 in 1000 ppm NH_3 ramped from 25 to 600 °C. Temperature was ramped from 25 to 600 °C and subsequently cooled to 25 °C during the time period shown.

To compare the performance of the sensors under investigation with a p-type material of simpler composition, a screen printed CuO sensor was tested under identical conditions in CO and the sensitivity and response time were calculated to be 0.50 and 287 s, respectively, when measured in 2000 ppm of CO at 300 °C and 0% RH, Table 2. From these data it is evident that the materials reported are competitive with existing known materials,[29] and through improvements to the particle morphology and porosity significant improvements in performance could be achieved.

(ii) Sensor Response to Ammonia (NH_3). As mentioned previously, an initial test run, Figure 3, was used to establish the optimal temperature of operation for these materials in a NH_3 environment, and it was found that the sensors under investigation showed maximum sensitivity at a temperature

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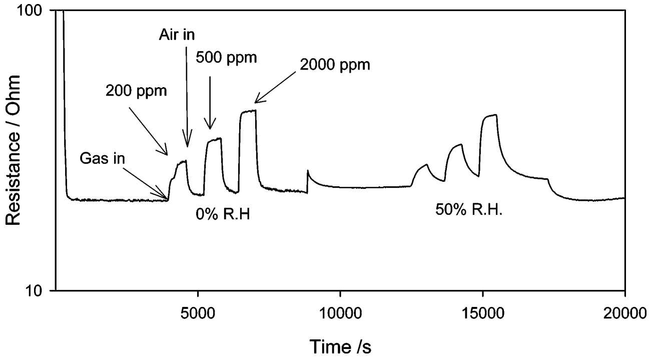

Figure 4. Response of $La_2Cu_{0.95}Al_{0.05}O_4$ to NH_3 at 400 °C at 0% and 50% RH.

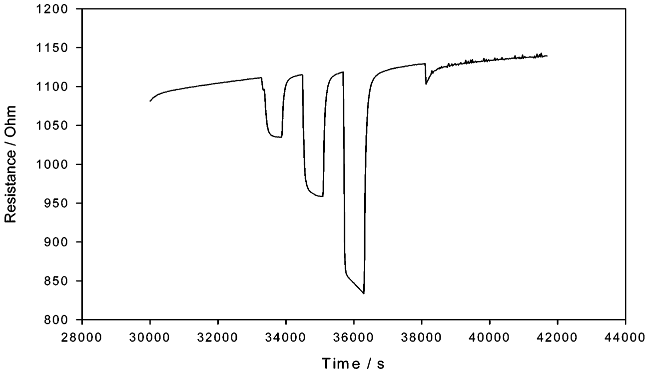

Figure 5. $La_2CuO_{4+\delta}$ sensor exposed to 10, 25, and 100 ppm NO_2 at 600 °C and 50% RH.

of around 400 °C. Therefore, all subsequent testing in NH_3 was carried out at this temperature. Figure 4 shows the response of the 5% Al doped $La_2CuO_{4+\delta}$ at a constant temperature (400 °C) to differing concentrations of NH_3 at both 0 and 50% RHs. In each case the test gas was switched on/off every 10 min.

Each of the $La_2CuO_{4+\delta}$-based sensors showed sensitivity to NH_3 with the sensitivity factor and the response time of these sensors given in Table 2. To compare the performance of the K_2NiF_4 oxides with p-type materials used in commercial sensors, a commercial screen printed sensor made from $Cr_{2-x}Ti_xO_{3+y}$ (CTO) on similar sensor substrates, supplied by City Technology, Ltd.,[8,30] was included for comparison. The CuO sensor described earlier was also studied under the same conditions. From these data it can be inferred that both $La_2CuO_{4+\delta}$ and $La_2Cu_{0.95}Al_{0.05}O_{4+\delta}$ have better sensitivity and response time than the CuO sensors. The sensitivity of the K_2NiF_4 materials was almost half that observed for the CTO; however, the response time was found to be superior to that of the CTO based system. An interesting observation was that the presence of humidity amplifies the signal for the CTO sensor, but it has a negative effect for K_2NiF_4 sensors. However, the shift in the baseline with humidity is much larger for CTO when compared to the K_2NiF_4 oxides, which may be an advantage. Further, when the operating temperature of the K_2NiF_4-type sensors was increased from 400 °C to 500 °C, the influence of humidity on the sensitivity was minimized and the shift in the baseline was almost negligible, thus offering the possibility of tailoring the sensor operating conditions for use in environments where wide humidity variations are likely.

In a further preliminary measurement $La_2CuO_{4+\delta}$ was found to have sensitivity to NO_2, particularly in a humid atmosphere. The response of this material to 10, 25, and 100 ppm of NO_2 at 600 °C in 50% RH is given in Figure 5. A stable baseline was observed under these conditions. However, the calculated sensitivity values were low and could possibly be due to the fact that the doped and undoped $La_2CuO_{4+\delta}$ sensors are in a fully oxidized form, rendering them less sensitive to an oxidizing gas such as NO_2. This contrasts with the fact that materials which are normally in a slightly reduced form, such as WO_3, are much more sensitive to oxidizing gases than to reducing gases.[31] Earlier work by Yasuda et al.[17,22] and Ho et al.[15,16] indicated that the cuprate based materials were catalytically active to NO decomposition at relatively high concentrations of 500 ppm but did not report the performance relative to NO_2 or indeed the performance of these materials as sensors. Ho et al.[16] did, however, suggest a possible mechanism for gas sensing in the analogous Nd_2CuO_{4-y} based on X-ray photoelectron spectroscopy studies that evidenced NO_2 adsorption on the Cu−O surface, resulting in NO_3^- species. No studies of the effect of humidity on the surface adsorption or sensor response have been reported. Ho et al. observed an increase in conductance, G, on introduction of the NO_2 gas. In the current work on La_2CuO_4 based materials a decrease in resistance is noted on introduction of NO_2 at significantly lower concentrations than those reported for the Nd_2CuO_{4-y} material. Of further interest is that although the stoichiometry is similar for both cuprates they are structurally distinct with the Nd analogue possessing a square planar B site coordination whereas La_2CuO_4 possesses an octahedral B site coordination. These structural differences are likely to extend to the surface structure, and, therefore, it is conceivable that the sensor mechanisms in these two materials will differ. Indeed differences in surface structure have been proposed by Kenway et al.,[32] suggesting that the {001} surface terminating in CuO_2 with half monolayer coverage of both Cu and O vacancies is more stable in the Nd analogue. By contrast in the La_2CuO_4 material it is the {100} surface that is most stable, terminating in La_2O_2 layers. Evidently these differences will have a significant effect on the surface adsorption sites, and the mechanisms proposed for the Nd_2CuO_4 case cannot, therefore, be directly inferred for the La analogue.

The demonstrated low sensitivity to oxidizing gases could be considered as an advantage when using a sensor for reducing gases, as a high sensitivity to oxidizing gases would result in a "negative" response. Thus, the combined presence of the target reducing gas and an oxidizing gas could give a false low reading. Conversely, interference from other reducing gases gives a false high reading, that is, the sensor would tend to "fail safe".

Of significance in these sensor materials is the sensing mechanism, and as discussed above previous studies have

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attempted to address this issue in the case of NO_2. As no studies have investigated the use of these or related materials for sensing NH_3 or CO, no definitive statements can be made as to the sensor mechanism. However, from preliminary measurements of the sensor responsive to NH_3 it appears that oxidizing species were present in the effluent gas after exposure to the sensor material as determined by gas chromatography. This suggests that a reaction involving the loss/gain of chemisorbed oxygen species is involved, and in the case of the ammonia sensor it could be formulated as

$$4NH_3 + 7O_2^- \rightarrow 4NO_2 + 6H_2O + 7e^-$$

Because the sensing material is p-type, the electrons released lower the number of charge carriers (holes) giving rise to an increase in resistance.[33,34] To confirm this hypothesis and elucidate the mechanism involved in the sensors responsive to either CO or NO_2 further testing is underway.

It should be noted that each of the sensor materials discussed was tested on substrates with 400 μm wide electrode gaps, optimized for moderately resistive gas sensor materials and thus is not optimal for these highly conducting materials. Hence, the data obtained are highly significant in that competitive response times and sensitivities were obtained, and as such there is great potential to further develop these materials with modified electrodes. Furthermore, there has been no optimization of the particle morphology of the sensor materials, and as shown in Figure 6, there is a wide variation in morphology, leaving considerable scope for improvement. Studies of sintering conditions and the resultant sensing layer porosity will be invaluable. Further optimization is, therefore, required to obtain the maximum sensitivity with minimum humidity interferene, and with modified electrodes and optimized compositions, these new sensor materials offer tremendous opportunities for device miniaturization and simplification.

It is of particular interest that the ammonia sensing performance of the materials compares very favorably with that of chromium titanate,[35] a material which has been used commercially for more than 10 years and which is known to have greatly superior ammonia sensing performance to that of traditional tin oxide sensors. Another noteworthy factor is that, like chromium titanate and copper oxide, the materials studied here are p-type. Tin oxide is n-type; that is, its response to reducing gases is a resistance decrease. n-type sensors are inherently not fail safe, because the most common failure modes in metal oxide sensors, such as heater failure of broken connections, result in a resistance increase. The advantage of p-type sensors is that such failures result in the sensor reading artificially high; that is, they fail safe.

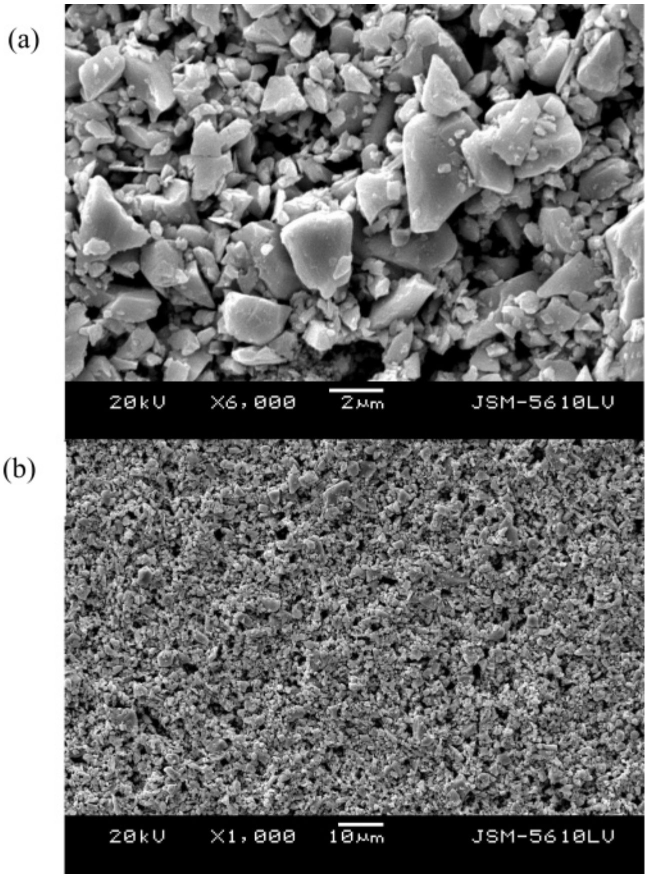

Figure 6. Typical microstructure of La_2CuO_4 sensors at two different magnifications.

Conclusions

Materials of the K_2NiF_4 structure type have been identified as highly conducting solid-state metal oxide gas sensors. The materials of interest are based on La_2CuO_4 substituted with Sr for La and with Al or Mg for Cu and have demonstrated sensitivity toward CO, NH_3, and NO_2 at temperatures in the range 300−600 °C. The level and type of doping has been found to enhance selectivity, and the humidity interference was found to be at a minimum. As a result of the relatively high conductivity of these sensor materials there is great potential for miniaturization of devices for use in small area applications. Relatively simple electrode requirements also mean a simplification of the manufacturing of these new devices.

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