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LETTER

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CO Sensing Properties of La-added $MgFe_2O_4$ Powders

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La-added $MgFe_2O_4$ ($MgFe_{2-x}La_xO_4$, $0.05 \leq x \leq 0.20$) and pure $MgFe_2O_4$ powders were prepared using a malic acid complex, and their CO sensing properties were examined in dry air in the temperature range of 300–500 °C. It was observed that when the measurement atmosphere was changed from air to CO, the electrical resistance of the $MgFe_2O_4$ sensor decreased, whereas that of the $MgFe_{2-x}La_xO_4$ sensor increased, indicating that the $MgFe_{2-x}La_xO_4$ sensor is a p-type semiconductor. It was also observed that the addition of La significantly improved the CO sensitivity of the $MgFe_2O_4$ sensor. Among the $MgFe_{2-x}La_xO_4$ sensors examined, the $MgFe_{1.85}La_{0.15}O_4$ sensor exhibited the highest response to CO at 300 °C, and its value was 11.2 times higher than that of the pure $MgFe_2O_4$ sensor. However, the $MgFe_{1.85}La_{0.15}O_4$ sensor did not exhibit a rapid response or steady-state electrical resistance in a CO atmosphere at 300 °C. Conversely, at 400 °C, the $MgFe_{1.90}La_{0.10}O_4$ sensor exhibited a higher response to CO than the $MgFe_{1.85}La_{0.15}O_4$ sensor and showed a quick response and a steady-state resistance. Therefore, it can be concluded that the $MgFe_{1.90}La_{0.10}O_4$ sensor exhibited the best CO detection characteristics among the sensors examined.

$MgFe_2O_4$ is an environmentally friendly oxide and has attracted attention as a suitable material for meeting some of the recently adopted sustainable development goals (SDGs).[1] The SDGs comprehensively deal with various environmental, social, and economic issues, with 17 goals and 169 targets that humankind should achieve.

$MgFe_2O_4$ powders have been used in applications such as catalysts,[2] absorbents,[3] humidity sensors,[4] fuel cells,[5] drug delivery systems,[6] and so forth.[7–9] Additionally, $MgFe_2O_4$ exhibits n-type semiconductor characteristics; thus, it can be applied as a gas sensor material.[10] Among the various types of gas sensor, semiconductor-based gas sensors exhibit very high gas sensitivity despite their simple structure. Therefore, many semiconductor gas sensors capable of detecting various gas molecules have been developed and are currently used for practical applications such as gas-leak alarms.[11–16]

The gas sensing mechanism of a semiconductor gas sensor is based on a change in the semiconductor conductivity, which is caused by the reaction between the oxygen adsorbed by the semiconductor surface and the gas to be detected.[17–19] To improve the sensitivity of a semiconductor gas sensor, it is important to synthesize a semiconductor powder having a large

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specific surface area.[20–24] The authors have focused on $MgFe_2O_4$ to which a heteroatom was added, and have investigated the change in the specific surface area of $MgFe_2O_4$ due to the addition of a heteroatom. It was found that when Si, La, and Al were added, the crystallite growth of $MgFe_2O_4$ was suppressed and fine $MgFe_2O_4$ particles were obtained.[25–28] In particular, upon adding La, the crystallite size of $MgFe_2O_4$ was approximately 10 nm even after heating at 600 °C in dry air. Compared with the $MgFe_2O_4$ before La addition, the crystallite size of the La-added $MgFe_2O_4$ was an order of magnitude smaller.

In this work, La-added $MgFe_2O_4$ (i.e., $MgFe_{2-x}La_xO_4$) and pure $MgFe_2O_4$ powders were prepared using a malic acid complex, and their CO sensing properties in dry air were examined. Consequently, we determined the optimum amount of La that should be added to achieve a high and quick response to CO; the details of this work are given below.

$MgFe_2O_4$ powders were prepared using a malic acid complex. $Mg(NO_3)_2 \cdot 4H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, and malic acid were dissolved in deionized water in the molar ratio 1:2:3.[25] La atoms were added to $MgFe_2O_4$ using $La(NO_3)_3 \cdot 6H_2O$. The amount of La atoms doped was set to 2.5 mol% ($x = 0.05$), 5 mol% ($x = 0.10$), 7.5 mol% ($x = 0.15$), or 10 mol% ($x = 0.20$) with respect to Fe. The malic acid solution was heated on a hot plate to prepare the precursor powder of $MgFe_2O_4$. The precursor was calcined at 800 °C for 2 h in dry air. The heating rate was 10 °C min^{-1} for all cases. Powder X-ray diffraction (XRD) measurements were performed to analyze the crystal phase of the prepared powders. The XRD patterns were corrected using Cu–Kα radiation with a sweep rate of 2 °C/min and an apparent electrical power of 30 kV × 20 mA. Powder diffraction files (PDFs) were employed to identify the crystal phases.

Figure 1 shows a schematic illustration of the sensor element and measuring circuit used in this study. $MgFe_2O_4$ and $MgFe_{2-x}La_xO_4$ ($x = 0.05$, 0.10, 0.15, and 0.20) powders were mixed with α-terpineol containing 10 wt% ethyl cellulose. The resulting paste was applied on an alumina substrate, which employed a pair of interdigitated Au electrodes, as shown in Fig. 1. The sensor element was fabricated by heating the entire assembly at 600 °C for 2 h in dry air. The CO sensing properties of the sensor element were investigated in a conventional gas-flow apparatus equipped with heating facilities in the temperature range of 300–500 °C. The CO gas concentration was varied in the range of 0–500 ppm by diluting 500 ppm of CO gas in dry air. The sample gases were allowed to flow over the sensor element at a rate of 0.1 dm^3 min^{-1}. The magnitude of the change in electrical resistance of the sensor to CO was defined as

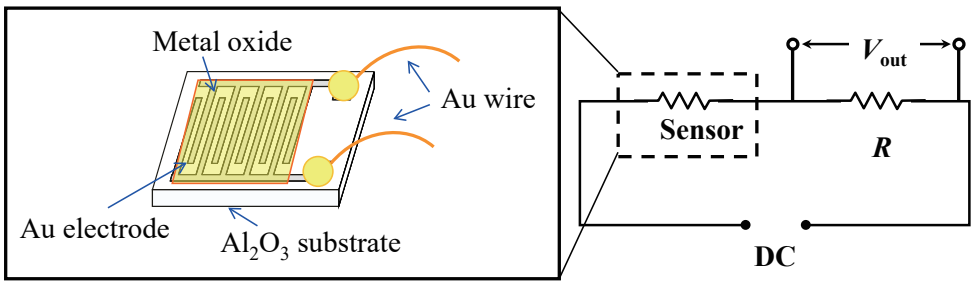


Fig. 1. (Color online) Schematic illustration of the CO sensor using $MgFe_2O_4$-based material and measuring circuit.

$\lambda = (R_{air} - R_{CO})/R_{air} \times 100$ (%), where R_{air} and R_{CO} are the electrical resistances of the sensor element in dry air and in CO gas, respectively. The measurement of the electrical resistances was based on a conventional circuit, where the sensor element was connected in series with an external resistor.

Initially, the relationship between the electrical resistance and the temperature of the $MgFe_2O_4$ and $MgFe_{2-x}La_xO_4$ (x = 0.05, 0.10, 0.15, and 0.20) sensors was investigated to find a reasonable temperature range for the CO sensing properties. As shown in Fig. 2, the electrical resistance of the $MgFe_2O_4$ and $MgFe_{2-x}La_xO_4$ sensors decreased as the temperature increased. The electrical resistance of the $MgFe_2O_4$ sensor was very high (higher than 10^7 Ω even at 450 °C in dry air). Upon adding La, the electrical resistance decreased by approximately an order of magnitude. As reported previously, by adding La, a $LaFeO_3$ phase was formed via the $MgFe_2O_4$ phase, but other phases were not observed.[27] Since $LaFeO_3$ exhibits a smaller electrical resistance than $MgFe_2O_4$, the electrical resistance of the La-added $MgFe_2O_4$ sensor is considered to be smaller than that in the unadded case.[4,29,30] On the basis of the preliminary examination, the gas sensing properties of $MgFe_{2-x}La_xO_4$ sensors were mainly investigated in the temperature range of 300–500 °C, and those of pure $MgFe_2O_4$ were measured in the temperature range of 450–500 °C.

Figure 3 shows the transient responses to 500 ppm CO of the $MgFe_{2-x}La_xO_4$ (x = 0.05, 0.10, 0.15, and 0.20) and pure $MgFe_2O_4$ sensors in the temperature range of 300–500 °C in dry air. Before La addition, when the atmosphere in the measurement chamber was switched from air to 500 ppm CO, the electrical resistance of the $MgFe_2O_4$ sensor decreased. Upon switching from 500 ppm CO to air again, the resistance of the sensor increased to its initial value. These results clearly indicate that the $MgFe_2O_4$ sensor exhibited a reversible response to CO. As described above, when an n-type semiconductor, such as $MgFe_2O_4$, is exposed to a reducing gas, such as

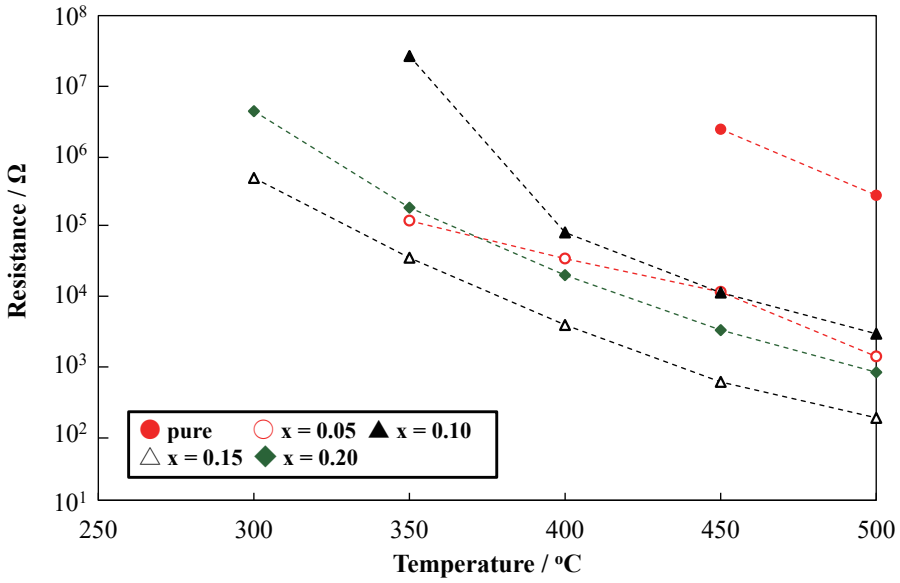


Fig. 2. (Color online) Operating temperature dependence of the electrical resistance of the $MgFe_{2-x}La_xO_4$ powders in dry air.

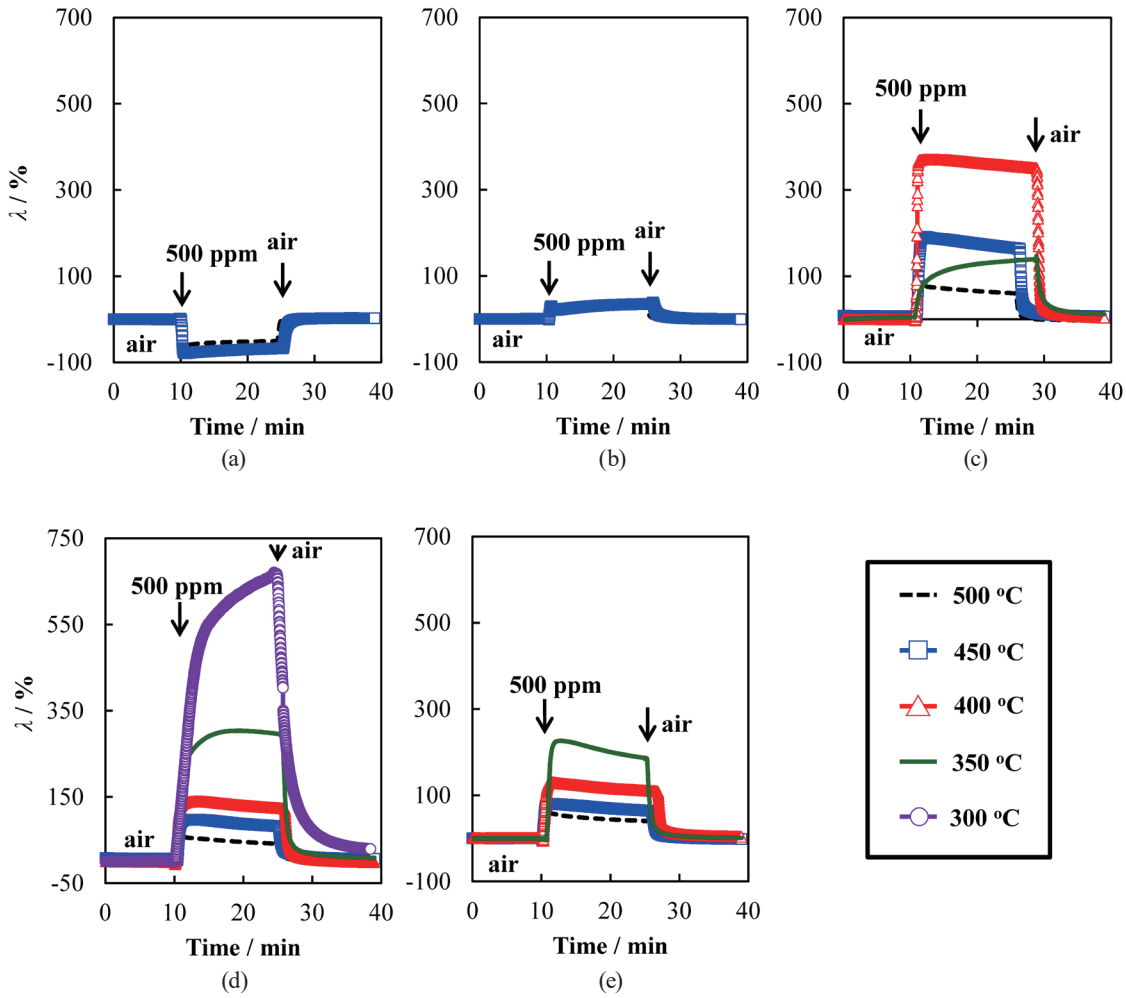


Fig. 3. (Color online) Transient responses of the $MgFe_{2-x}La_xO_4$ (x = 0.05, 0.10, 0.15, 0.20) and pure $MgFe_2O_4$ sensors to 500 ppm CO in dry air. (a) x = 0, (b) x = 0.05, (c) x = 0.10, (d) x = 0.15, and (e) x = 0.20.

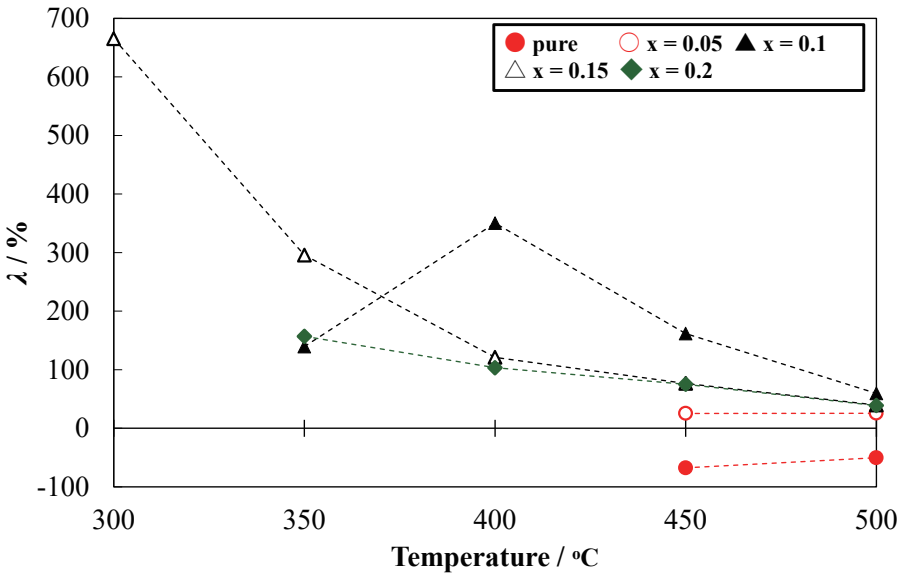
CO, the negatively charged oxygen adsorbed by the surface of the semiconductor is removed through its reaction with CO. During this time, electrons are transferred from the negatively charged adsorbed oxygen to the semiconductor. As a result, the electrical resistance of the sensor decreases.

Conversely, in the $MgFe_{2-x}La_xO_4$ sensor, the electrical resistance of the sensor increased when switching from air to a 500 ppm CO atmosphere. This result is attributed to the fact that $LaFeO_3$ is a p-type semiconductor;[29,30] that is, when oxygen in the gas phase is adsorbed by the $LaFeO_3$ surface, it collects electrons from the semiconductor's surface. As a result, the hole concentration in $LaFeO_3$ increases. When the adsorbed oxygen reacts with CO and is consumed, electrons move from the adsorbed oxygen to $LaFeO_3$, reducing the hole concentration. Also, it is found that the addition of La not only improves λ but also makes it possible to detect CO at a lower temperature compared with that before La addition.

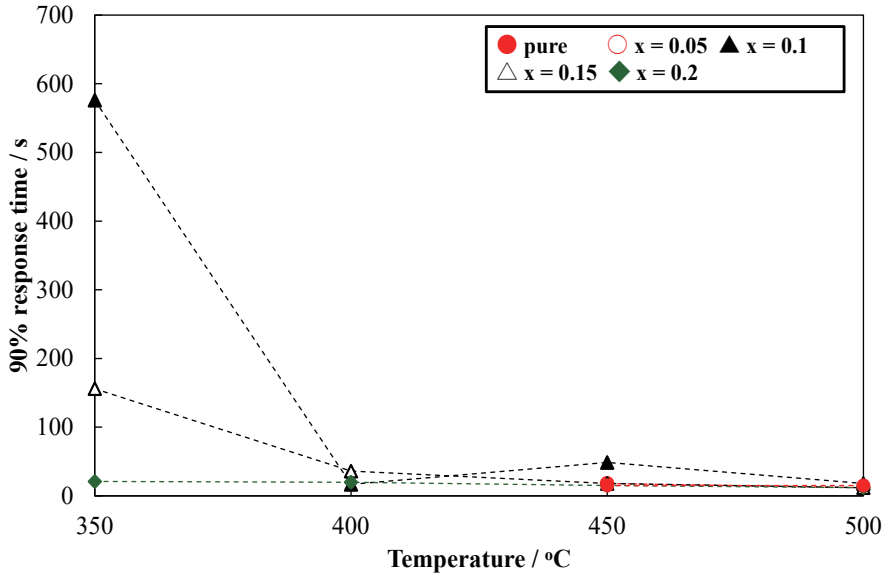
Among the $MgFe_{2-x}La_xO_4$ sensors examined, the $MgFe_{1.85}La_{0.15}O_4$ sensor exhibited the highest λ at 300 °C. However, at 300 °C, when the atmosphere in the measurement chamber was

switched from air to CO, the response of the $MgFe_{1.85}La_{0.15}O_4$ sensor gradually changed and did not reach a steady-state value. Above 350 °C, the response of the sensor quickly reached its steady-state value in the CO atmosphere, but the value was much smaller than that at 300 °C. At 400 °C, the $MgFe_{1.90}La_{0.10}O_4$ sensor showed the highest sensitivity among the $MgFe_{2-x}La_xO_4$ sensors examined.

Figure 4 shows the temperature dependence of the λ value and t_{90} response time of the $MgFe_{2-x}La_xO_4$ (x = 0.05, 0.10, 0.15, and 0.20) and pure $MgFe_2O_4$ sensors to 500 ppm CO in dry



(a)



(b)

Fig. 4. (Color online) (a) λ values and (b) t_{90} response time of the $MgFe_{2-x}La_xO_4$ (x = 0.05, 0.10, 0.15, 0.20) and pure $MgFe_2O_4$ sensors in the temperature range of 300 to 500 °C.

air. As mentioned above, the $MgFe_{1.85}La_{0.15}O_4$ sensor exhibited the highest λ at 300 °C and its value was 11.2 times higher than that of the $MgFe_2O_4$ sensor. However, the λ value did not reach a steady-state value and the t_{90} response time was long when the atmosphere in the measurement chamber was switched from air to CO at 300 °C. On the other hand, the $MgFe_{1.90}La_{0.10}O_4$ sensor showed the highest sensitivity among the $MgFe_{2-x}La_xO_4$ sensors examined and its t_{90} response time was also the shortest at 400 °C. Therefore, the response characteristics of the $MgFe_{1.90}La_{0.10}O_4$ sensor were tested in detail.

Figure 5(a) shows the response curve of the $MgFe_{1.90}La_{0.10}O_4$ sensor when the CO concentration was changed stepwise from 0 to 500 ppm at 400 °C. In this figure, it can be observed that when the CO gas concentration increased from 0 to 500 ppm, λ of the $MgFe_{1.90}La_{0.10}O_4$ sensor increased linearly with the logarithm of the CO concentration, as shown in Fig. 5(b). Also, t_{90} was estimated to be below 60 s at 400 °C. The response time decreased as the measured temperature increased, but λ decreased sharply. Therefore, the optimum operating temperature of the $MgFe_{1.90}La_{0.10}O_4$ sensor is considered to be 400 °C.

In conclusion, it was found that the La-added $MgFe_2O_4$ sensor exhibited higher λ value to CO in dry air than that exhibited by a pure $MgFe_2O_4$ sensor. Also, the $MgFe_{1.90}La_{0.10}O_4$ sensor exhibited a high λ value and a fast response at 400 °C. In addition, a linear relationship between the CO concentration and the change in the resistivity of the sensor was found.

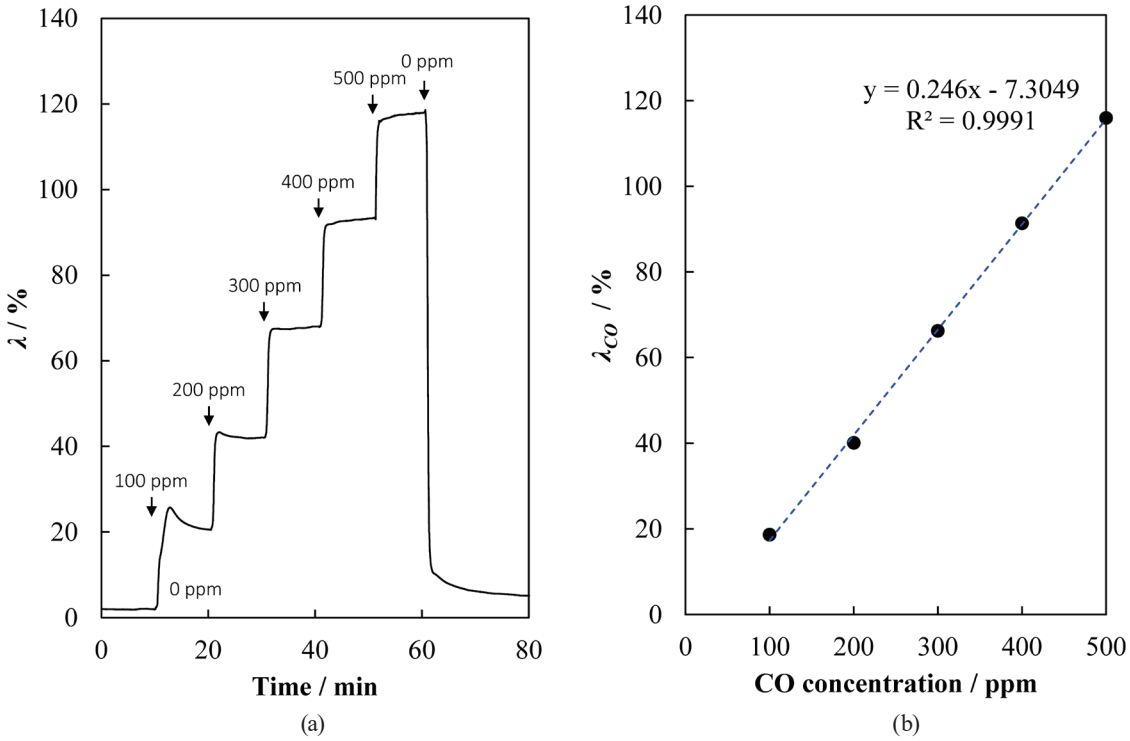


Fig. 5. (a) Transient response and (b) λ relative to stepwise changes in CO concentration for $MgFe_{1.90}La_{0.1}O_4$ powder at 400 °C in dry air.

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