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Impedancemetric Acetylene Sensor Besed on Perovskite-Type Oxide $Sm_{1-x}Ca_xFeO_3$ (x = 0, 0.05, 0.20, 1.0) Thick-Film

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Abstract

Perovskite-type oxide $Sm_{1-x}Ca_xFeO_3$(x = 0, 0.05, 0.20, 1.0) powders were prepared by a wet-chemical route using a polymer precursor method at 750 ºC and a screen-printed oxide thick films were applied as an acetylene sensor which outputs were measured by an AC impedance spectroscopy. Although the conductance of Ca^{2+}-substituted $SmFeO_3$ device was high, the amount of impedance change to C_2H_2 in PO_2 = 0.21 atm was low, compared with $SmFeO_3$.

Key words: Polymer precursor, Perovskite-type oxide, Hydrocarbon, Impedance, Gas sensor, Thick-film

Introduction

Perovskite-type oxides have been well-known as functional inorganic materials having a wide range of application. Also, the properties are further improved by substituting other metal in A- and/or B-site, and then these above materials could be used in many fields such as oxidation catalyst,[1-4] photocatalyst,[5,6] electrode device,[7] and electrolyte.[8-10] In addition, the materials are able to be applied for a sensing material for detection of CO,[11] NO_X,[12] NH_3,[13] hydrocarbon,[14] and VOC.[15] So far a mixed metal oxide like perovskite-type has been prepared by solid reaction method, however a high temperature sintering and a homogenously crushing method has been required. A thermal decomposition such as cyano-complex decomposition reported by E. Travelsa et al. could be prepared homogeneously nano-powder at lower temperature.[16] Moreover, a polymer precursor, a coprecipitation and a reverse coprecipitation are also need the low temperature with thermal decomposition route. M. Mori et al. reported that catalyst properties of $SmFeO_3$ were affected by synthesis method and sintering temperatures.[17]

Recently, development of a hydrocarbon sensor is accelerating with tightening regulations for hydrocarbon gases, such as Euro 6. Also, the rules for gases generating from industry and building-products have been stricter. C_2H_2 which is the aim of detection in this study is important industry gas, as it could be used for a lot of fields such starting material of benzene and poly-acetylene, fuel of metal welding and so on. Moreover, as acetylene gas is to be generated from insulating oils of oil-immersed transformer, thus acetylene gas sensor could be utilized as a maintenance's marker of the transformer. Therefore there are still strong needs to detect acetylene as combustible gas.

In this study, the oxide thick-film device using perovskite-type oxide powder synthesized by a polymer precursor was prepared by a screen-printing, and then the sensing properties to C_2H_2 of the device were evaluated, finally investigated about the response mechanism.

Experimental

The perovskite-type oxide $Sm_{1-x}Ca_xFeO_3$(x = 0, 0.05, 0.20, 1.0) powders were prepared by a polymer precursor method.[18, 19] Metal nitrates were dissolved in ethylene glycol (EG) solvent with acetylacetone (AcAc) and polyvinylpyrrolidone (PVP), as a coordination agent and a polymer additive, respectively. The solution thus prepared was evaporated at 120 ºC, precalcined at 300 ºC, and finally sintered at 750 ºC to form powder. The sintering temperature was determined from TG-DTA of xerogel powder evaporated at 120 ºC with the precursor solution. The paste mixed with oxide powder, PVP and α-terpineol were uniformly screen-printed on Au-interdigitated electrodes and heat-treat at 800 ºC for 2 h. Finally, Au lead wires attached with a silver paste covered with an inorganic adhesive were connected to LCR meter (HIOKI 3532-50).

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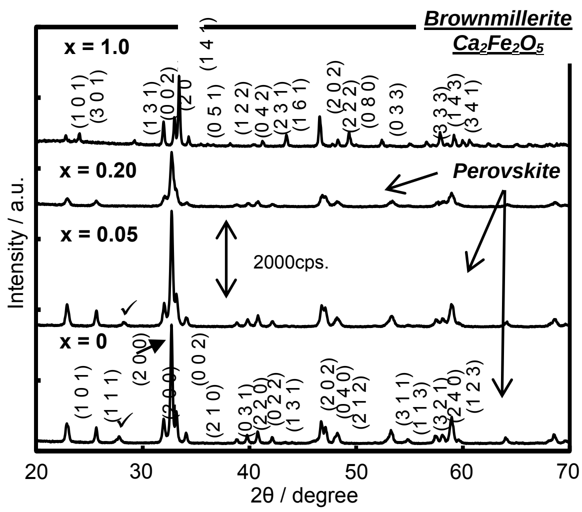

Fig. 1. XRD paterns of $Sm_{1-x}Ca_xFeO_3$ (x = 0, 0.05, 0.20, 1.0) powders sintered at 750 ºC.

The oxide powders were characterized by XRD (JEOL: JDX3500K) and BET surface area (BEL JAPAN, INC.: Bel sorp-mini-II-ss) measurements. Gas sensing properties of the device were investigated by AC impedance method between 50 Hz and 5 MHz at 400 ºC. Concentration of sample gases were controlled by diluting with nitrogen at fixed PO_2 = 0.21 atm. Then, sample gases and based gas (synthesized air) were flowed at a total flow rate of 100 cm^3 / min.

Results and discussion

Figure 1 shows XRD patterns of $Sm_{1-x}Ca_xFeO_3$ (x = 0, 0.05, 0.20, 1.0) powders sintered at 750 ºC. Although brownmillerite phase was formed in x = 1.0, perovskite phase were obtained for x = 0 ~ 0.20. BET surface area of the Ca-substitution x = 0 ~ 0.20 formed perovskites were 8.7 m^2 / g (x = 0), 9.2 m^2 / g (x = 0.05) and 11.3 m^2 / g (x = 0.20), respectively, so these increased with increasing Ca-substitution. Particles could not be grown up because the grain size was decreased with increasing Ca-substitution. This can be attributed that diffusion speed of Ca^{2+} is slower than that of Sm^{3+} at same sintering temperature, because ion radius of Sm^{3+} and Ca^{2+} are 1.24 and 1.34 Å, respectively.[20]

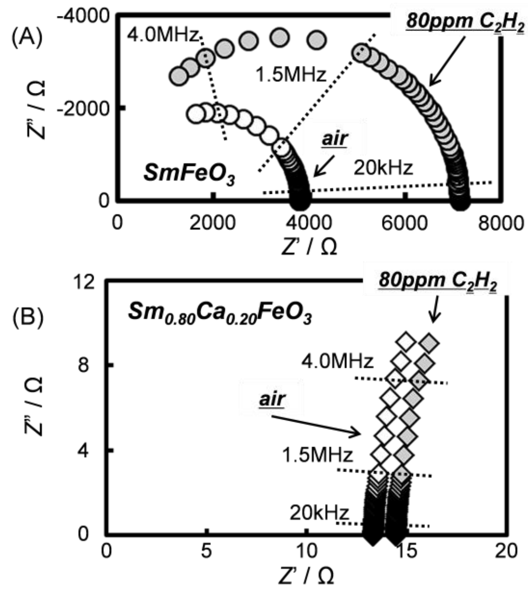

Fig. 2. Nyquist's plots of (A) $SmFeO_3$ and (B) $Sm_{0.80}Ca_{0.20}FeO_3$ thick-film device to air or 80 ppm C_2H_2 at 400 ºC in P_{O_2} = 0.21 atm.

Nyquist's plots of the $SmFeO_3$ and $Sm_{0.80}Ca_{0.20}FeO_3$ devices at 400 ºC are shown in Fig. 2. $SmFeO_3$ device showed a capacitative semicircle which draw negative angle in phase angle, on the other hand, $Sm_{0.80}Ca_{0.20}FeO_3$ device showed an inductive plots which draw positive angle in that. The $SmFeO_3$ device draw a typical capacitative semicircle and had a frequency property of parallel equivalent circuit consisted of resistance *R* and capacitance *C*. Also, the $Sm_{0.80}Ca_{0.20}FeO_3$ device largely increased the conductivity by generated an oxygen defect which came from Ca^{2+} substituted in A-site. Then, the obtained Nyquist's plots of the $Sm_{0.80}Ca_{0.20}FeO_3$ device showed the positive angle plots caused by inductance *L* of Au lead-wires. Both devices showed increasing impedance in all frequencies from air to 80 ppm C_2H_2. According to the response, it seems to come from oxidation reaction between C_2H_2 and negative surface adsorbed oxygen. Electron (e^-) generated in this reaction vanished hole ($h^•$) in conduction band, as in reactions (1).

$$C_2H_2 + 5O^-_{ads} \rightarrow 2CO_2 + H_2O + 5e^- \qquad (1)$$

In lower (20 kHz) and higher (4 MHz) frequency, sensing properties of both devices to various C_2H_2 concentrations are shown in Fig. 3. The $SmFeO_3$ device could not detect C_2H_2 at 20 kHz in the capacitance due to environmental noise, however it could detect good response and concentration dependences of the resistance. On the other hand, resistance of the $Sm_{0.80}Ca_{0.20}FeO_3$ device was decreased by improving conductance, and good concentration dependences were shown in resistance and capacitance components, especially large charge was observed at 20 kHz.

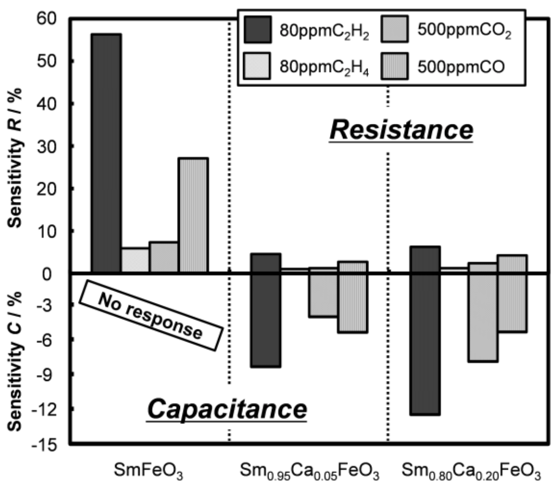

Fig. 4. Selectivities of $Sm_{1-x}Ca_xFeO_3$ (x=0, 0.05, 0.20) thick-film devices to various sample gases at 400 ºC and 20 kHz.

This could be attributed that AC current increased under constant applied voltage by substituted Ca^{2+} in A-site. And then, the 90 % response time to 80 ppm C_2H_2 of $SmFeO_3$ and $Sm_{0.80}Ca_{0.20}FeO_3$ were 10s and 22s, respectively, so there are not effects by the measurement frequency.

Selectivities of the $Sm_{1-x}CaFeO_3$ (*x* = 0, 0.05, 0.20) thick-film devices to various gases such as 80 ppm C_2H_2, 80 ppm C_2H_4, 500 ppm CO_2 and 500 ppm CO at 20 kHz and 400 ºC are shown in Fig. 4. Here, the sensor sensitivity is defined as eq. (2),

$$S_{R,C}\,[\%] = \frac{(R,C_{gas} - R,C_{air})}{R,C_{air}} \times 100 \qquad (2)$$

Where *R* and *C* are resistance and capacitance components in air or sample gas which are written as a subscript notation as "air" and "gas", respectively. The all sensors showed excellent selectivity to 80 ppm C_2H_2. That is to say, the response order in resistance response to sample gases are 80 ppm C_2H_4 < 500 ppm CO_2 < 500 ppm CO < 80 ppm C_2H_2. The x = 0.05 and 0.20 sensors had high selectivity to 80 ppm C_2H_2, however, the resistive sensitivity decreased for the substituted Ca^{2+} device. The reason why thus phenomenon appeared is because x = 0.05 and 0.20 sensor improved the conductivity compared with x = 0 ($SmFeO_3$).

In conclusion, $Sm_{1-x}Ca_xFeO_3$ (*x* = 0, 0.05, 0.20, 1.0) as a sensor material to detect C_2H_2 were prepared by a polymer precursor method. XRD patterns of the oxide showed perovskite- and brownmillerite-phase in *x* = 0 ~ 0.20 and *x* = 1.0, respectively. Sensing properties to C_2H_2 of the devices revealed that $SmFeO_3$ device showed high sensitivity in resistance, and $Sm_{0.80}Ca_{0.20}FeO_3$ showed response in capacitance compared.

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