

O₃ and NO₂ sensing properties of SmFe_{1-x}Co_xO₃ perovskite oxides

Yoshiteru Itagaki, Masami Mori, Yuuki Hosoya, Hiromichi Aono, Yoshihiko Sadaoka*

*Department of Materials Science and Biotechnology, Graduate School of Science and Engineering, Ehime University,
3 Bunkyo-cho, Matsuyama 790-8577, Japan*

Received 19 January 2006; received in revised form 1 June 2006; accepted 1 June 2006
Available online 17 July 2006

Abstract

Novel sensing materials of tri-metallic perovskite oxides, SmFe_{1-x}Co_xO₃ ($x=0-1.0$), were applied for a conductometric O₃ and NO₂ gas sensor. Fine particles of the oxides were prepared by pyrolysis of corresponding cyano-complexes, Sm[Fe_{1-x}Co_x(CN)₆] \cdot 4H₂O. The conductivity in air increased with an increase in the Co content. This increment in the conductivity reduced the operating temperature for a reliable conductivity measurement from 250 °C for $x=0$ to 150, 100 and 80 °C for $x=0.05, 0.1$ and 0.15 , respectively. Furthermore, the measurement at room temperature was possible for $x \geq 0.2$. In 0.4 ppm O₃, a large response ($S > 100$) was obtained for $x=0-0.15$ at the above operating temperatures. While in 10 ppm NO₂, the elements of $x=0.05-0.5$ exhibited the maximal response at 200 °C. The Co-added oxides showed good response and recovery behavior, compared to SmFeO₃ even at low temperature.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Perovskite oxides; Semiconductor gas sensor; Operating temperature; Oxidative gases

1. Introduction

A semiconductor gas sensor is one of the most promising devices to detect a variety of pollutants with high sensitivity and stability [1]. Furthermore, this can be a dramatically cheaper technique than the analytical methods currently accepted for environmental monitoring systems. The semiconductor sensor exhibits a change in conductivity corresponding to adsorption of objective gasses and a charge transfer process. Perovskite-type oxides (ABO₃) are expected to be a promising material for chemical sensors as well as other electric devices. So far, the sensing properties of LnFeO₃ (Ln = La, Sm) perovskite oxide materials have been intensively demonstrated to exhibit good sensitivity to CO and NO₂ [2–7]. Since the LnFeO₃ oxides generally possess a p-type feature, they are more suitable for detecting oxidative gases than n-type oxides. Furthermore, we reported the formation of nano particles of LnFeO₃ oxides by pyrolysis of corresponding hexacyano-complexes, Ln[Fe(CN)₆] \cdot n H₂O [3,4]. Using the nano particles of SmFeO₃ gave rise to significantly good sensing features, compared to those prepared by solid-state reaction of Sm₂O₃ and Fe₂O₃ [3]. In order to

obtain a stable response, this type of sensor elements should be heated to be in a measurable conductivity. For example, conductance of SmFeO₃ at 250 °C is still as low as $\sim 10^{-10}$ S, and reducing the operating temperature is difficult to obtain a reliable output. The problems associated with the operating temperature can be overcome by using semiconductive materials having a higher conductivity. Previously the electrical property of SmCoO₃ was reported and its conductivity was four to five orders of magnitude higher than that of SmFeO₃ [8]. On the other hand, such excessively high conductivity causes a low sensitivity of a sensor and over-reducing the operating temperature gives rise to a slow response and instability. In this study we prepared tri-metallic perovskite oxides of SmFe_{1-x}Co_xO₃ with various Co/Fe ratios. By using such intermediate species between SmFeO₃ and SmCoO₃, the conductivity of the sensors could be adjusted within a suitable region for a low temperature and high sensitivity sensing. We thus examined these oxides as novel sensing materials to oxidizing gases such as ozone and NO₂.

2. Experimental

The perovskite oxides of SmFe_{1-x}Co_xO₃ with $x=0, 0.05, 0.1, 0.15, 0.2, 0.5$ and 1.0 were prepared by the pyrolysis of

* Corresponding author.

E-mail address: sadaoka@eng.ehime-u.ac.jp (Y. Sadaoka).

synthesized $\text{Sm}[\text{Fe}_{1-x}\text{Co}_x(\text{CN})_6]\cdot 4\text{H}_2\text{O}$ hetero-nuclear complexes in air at 800°C for 1 h. Sm_2O_3 (99.9%) was dissolved in an appropriate amount of concentrated nitric acid at room temperature to prepare $\text{Sm}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$. Then the formed $\text{Sm}(\text{NO}_3)_3$ solution was diluted with deionized water to be a 1.0 mol% aqueous solution. The stoichiometric amount of the solution was dropped at room temperature into an aqueous solution containing the prescribed molar ratio of $\text{K}_3[\text{Fe}(\text{CN})_6]$ (Hayashi pure chemical, $\geq 99.0\%$) and $\text{K}_3[\text{Co}(\text{CN})_6]$ (Aldrich, Special grade) with continuous stirring. The resulting precipitate was collected by suction filtration and then washed by water, ethanol and diethyl ether. After that the complex was dried in air before the above described heat treatment. The complex and final product were identified by X-ray diffraction (XRD) (Rigaku Rint 2000) and fluorescent X-ray analyses (Rigaku RIX 2100). A proper quantity of α -terpineol was added into the $\text{SmFe}_{1-x}\text{Co}_x\text{O}_3$ powders and mixed in a mortar, and the obtained slurries were screen-printed on an alumina substrate with Au comb type electrodes. Thickness of the oxide films was approximately $50\ \mu\text{m}$. The thick films were fired at 200, 400 and finally 900°C for 1 h, respectively, to obtain the sensor elements. The sensor elements were inserted into a quartz glass tube set in a tubular furnace and examined at various temperatures. As the objective gases, 0.4 ppm O_3 and 10 ppm NO_2 were introduced in the glass tube with alternately changing to compressed air in a 20 min interval. The O_3 gas was generated from compressed air (5.0 L/min) with an ozone gas generator (Funatech SO-250; ozone gas yield is 0.25 g/h at 5.0 L/min air flow), and the produced gas was diluted with compressed air to obtain 0.4 ppm O_3 gas. While, 10 ppm NO_2 was prepared with a gas permeator using a NO_2 permeation tube (GASTECH PD-1B) and compressed air. The flow rate of the gases introduced to the sensor was 1.0 L/min for O_3 and 1.6 L/min for NO_2 . Conductance of the elements was monitored by an ultra high resistance meter (Advantest R8340) applying a dc voltage of 0.10 V. Gas response of the sensors were monitored as $S = \sigma_{\text{gas}}/\sigma_{\text{air}}$, where σ_{gas} and σ_{air} were the conductance in an objective gas and compressed air, respectively.

3. Results and discussion

3.1. Characterization of the oxides

From the fluorescent X-ray analysis, it was confirmed that the oxides were composed of Sm, Fe and Co atoms with the corresponding feed ratios. Fig. 1 shows XRD powder patterns of the $\text{SmFe}_{1-x}\text{Co}_x\text{O}_3$ perovskite oxides. All the XRD patterns were similar to those of SmFeO_3 and SmCoO_3 previously assigned to an orthorhombic structure (Space group $Pnma$) [3,9]. In some oxides, a minor contribution was seen from the Sm_2O_3 impurity. The corresponding signals shifted to higher angles with the increase in x from 0 to 0.05 and from $x = 0.2$ to 1.0. Between $x = 0.05$ and 0.2 the signal positions were very close to each other. This signal shift is due to the increase in the effective ionic radius of B^{3+} defined as $r_{\text{eff}} = \{(1-x)r_{\text{Fe}} + xr_{\text{Co}}\}$. The fact that the positions of the detected signals of $x = 0.05$ –0.5 are situated between the corresponding positions observed for the $x = 0$

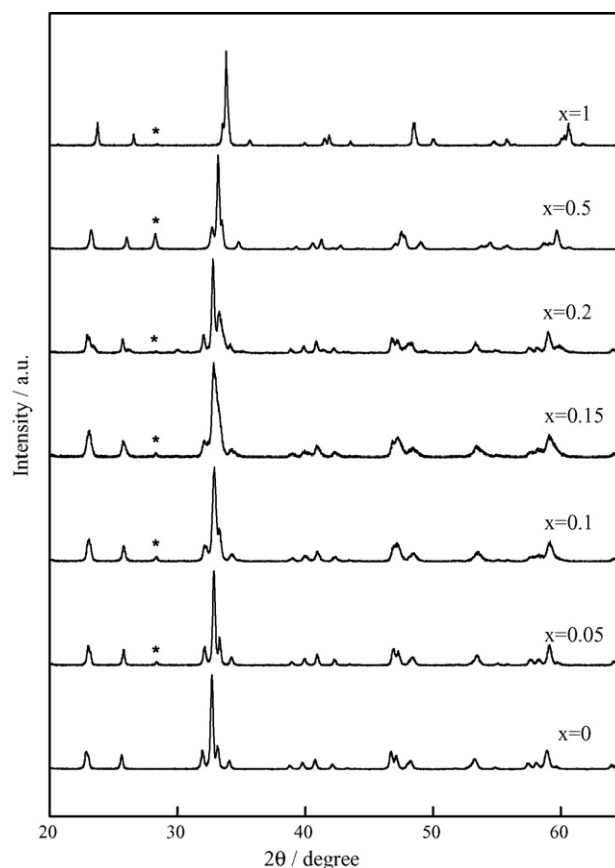


Fig. 1. XRD patterns of the $\text{SmFe}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0, 0.05, 0.1, 0.15, 0.2, 0.5$ and 1.0) powders used in this study. The signals marked with asterisks are those from Sm_2O_3 .

and 1 oxides clearly indicates that the decomposed products are not a mixture of SmFeO_3 and SmCoO_3 but a single phase of hetero-nuclear composite perovskite oxides, $\text{SmFe}_{1-x}\text{Co}_x\text{O}_3$. The specific surface areas of the fine powders examined by BET analysis using N_2 adsorbent were 3.05, 3.85, 3.54, 2.75, 3.51, 3.50 and $1.59\ \text{m}^2/\text{g}$ for $x = 0, 0.05, 0.1, 0.15, 0.2, 0.5$ and 1.0 , respectively.

3.2. The conductivity in air

The elements were exposed to air before introducing the objective gases and their conductance was measured at various temperatures. Fig. 2 shows the temperature dependence of the conductivities of the $x = 0$ –1.0 elements. For all the sensor elements, the Arrhenius type behavior was observed within the temperature region measured. The conductivity apparently increased with an increase in the x value. Furthermore, the activation energy (E_a) decreased with an increase in the Co content and it became nearly constant at $x \geq 0.2$. For this reason, the difference of the conductance was enlarged in a low temperature region. The measurable value of conductance was down to the order of 10^{-10} S for the present by using the ultra high resistance meter with an applied voltage of 0.10 V. For this limitation, the lowest operating temperature for $x = 0$ was 250°C , where the base conductivity was 6.80×10^{-10} S, but with increasing in the

Download English Version:

<https://daneshyari.com/en/article/744734>

Download Persian Version:

<https://daneshyari.com/article/744734>

[Daneshyari.com](https://daneshyari.com)