Available online at www.sciencedirect.com
ScienceDirect
JOURNAL OF RARE EARTHS, Vol. 35, No. 7, Jul. 2017, P. 690
JOURNAL OF RARE EARTHS
www.re-journal.com/en/

Nanocrystalline $Gd_{1-x}Ca_xFeO_3$ sensors for detection of methanol gas

WANG Xiaofeng (王小凤)[1,*], MA Wei (马 威)[1], SUN Kaiming (孙凯铭)[1], HU Jifan (胡季帆)[2], QIN Hongwei (秦宏伟)[2]

(1. School of Mathematics and Physics Science, Dalian University of Technology, Panjin 124221, China; 2. State Key Laboratory for Crystal Materials, School of Physics, Shandong University, Jinan 250100, China)

Received 28 September 2016; revised 5 December 2016

Abstract: The sol-gel method was used to prepare the nanocrystalline $Gd_{1-x}Ca_xFeO_3$ (x=0–0.4) powders. The XRD results showed that all the $Gd_{1-x}Ca_xFeO_3$ (x=0–0.4) compounds crystallized as perovskite phase with orthorhombic structure. The doping of Ca in $GdFeO_3$ not only reduced the resistance, but also enhanced the response to methanol. The $Gd_{0.9}Ca_{0.1}FeO_3$ showed the best response to methanol among $Gd_{1-x}Ca_xFeO_3$ sensors. Besides, it showed good selectivity to methanol among methanol, ethanol, CO and formaldehyde gases. The responses at 260 ºC for $Gd_{0.9}Ca_{0.1}FeO_3$-based sensor to 600 ppm methanol, ethanol and CO gases were 117.7, 72.7 and 31.9, respectively. Even at quite low gas concentrations, $Gd_{0.9}Ca_{0.1}FeO_3$-based sensor had an obvious response. At 260 ℃, the response of 1.54 was obtained to be 45 ppm methanol. The experimental results showed that nanocrystalline $Gd_{0.9}Ca_{0.1}FeO_3$ based sensor can be used to detect methanol gas.

Keywords: gas sensor; methanol; electrical properties; perovskite; rare earths

Methanol (methyl alcohol) is an organic solvent, which is broadly applied in many fields such as industry, fuel, medicine and other chemicals. It is necessary to develop a reliable and selective methanol sensor. Semiconductor materials are an important class of functional materials which have received considerable interest due to their applications in catalysis[1,2], gas sensors[3–6], electrodes and electrolytes of fuel cells[7,8]. The metal oxide semiconductor such as SnO_2 was early used in detecting toxic and harmful gases. However, both gas selectivity and stability of SnO_2 sensors at high temperature are poor. It was reported that the response of SnO_2 thin film sensor to 1000 ppm methanol was very small (about 2.5 at 350 ºC)[9]. Patel et al.[10] reported that the response to 200 ppm methanol for ITO films was 2 at room temperature. Comini et al.[11] presented that TiO_2 film doped with 1% Nb and 0.5% Pt showed good selectivity to ethanol. The sensor response to 500 ppm ethanol was as high as 23.7 at 300 ºC but that to methanol was quite low. Jiang et al.[12] found that polypyrrole (PPy) sensors can detect methanol at room temperature, the response of PPy sensor was 1.026 to 49 ppm methanol. Mabrook et al.[13] showed that TiO_2 powders dispersed in the vinylidenfluride show a response of 1.32 to 350 ppm methanol at room temperature. Sahay and Nath[14] reported that the 0.5 at.% Al-doped ZnO film showed the maximum response 1.44 at 275 ºC to 500 ppm of methanol vapour in air. Neri et al.[15] found that CeO_2-Fe_2O_3 thin film showed the best response of 11 to 200 ppm at 500 ºC. Sun et al.[16] found that $La_{0.75}Ba_{0.25}FeO_3$ showed the response of 180 to 500 ppm ethanol at 240 ºC but only 10 to 500 ppm methanol at 220 ºC. Doroftei et al.[17] found that $La_{0.8}Pb_{0.2}FeO_3$ showed a good response to methanol, but had inverse selectivity for methanol and ethanol at different operating temperature. Chen et al.[18] reported that responses of $SmFe_{0.95}Ni_{0.05}O_3$ sensor to 500 ppm ethanol and methanol at 260ºC were 57.8 and 8, respectively. Niu et al.[19] presented that nanometer $GdFeO_3$ sensor showed a good sensing response (about 45) to 50 ppm gasoline at 340 ºC. At 340 ºC, the $GdFeO_3$ sensor showed a response of 90.8 to 1000 ppm ethanol[45]. Arakawa et al.[20] found that for $LnFeO_3$ oxides the methanol sensing activity increased as the radius of the rare-earth ion decreased, and the sequence of the activity for $LnFeO_3$ was Gd>Eu>Sm>Nd>Pr>La. In the present work, we presented the methanol sensing characteristics of $GdFeO_3$ sensor. In usual, the resistances of $LnFeO_3$ compounds are large. As alkaline earth elements are frequently substituted by part of Ln in $LnFeO_3$ in order to decrease the resistance. The effects of Ca substitution on the methanol sensing properties for $GdFeO_3$ were also investigated.

1 Materials and methods

The $Gd_{1-x}Ca_xFeO_3$ (x=0–0.4) powders were prepared

Foundation item: Project supported by National Natural Science Foundation of China (51602035, 51472145, 51272133) and the Fundamental Research Funds for the Central Universities (DUT16RC(4)69)

* **Corresponding author:** WANG Xiaofeng (**E-mail:** wangxf@dlut.edu.cn; **Tel.:** +86-427-2631105)

DOI: 10.1016/S1002-0721(17)60965-7

by sol-gel method. Firstly, Gd_2O_3 (99.99%) was dissolved in an appropriate amount of concentrated nitric acid to prepare $Gd(NO_3)_3$ solution, and then mixed completely with stoichiometric $Ca(NO_3)_2{\cdot}4H_2O$ (99.0%) and $Fe(NO_3)_3{\cdot}9H_2O$ (98.5%) in deionized water. After adding some polyethylene glycol (PEG; molecular weight over 20000), the solution was well stirred for several hours until the sol was formed. Then the sol was dried to gel and crushed into powders, which were subsequently annealed in an oven at 800 ºC for 4 h. The structure of resultant powders was characterized by X-ray diffraction with Cu Kα radiation.

The prepared $Gd_{1-x}Ca_xFeO_3$ powders were mixed with terpineol and ground into paste. The paste was packed into a ceramic tube with two electrodes installed at each end. The tube was calcined at 400 °C for 3 h. The gas sensing properties of the $Gd_{1-x}Ca_xFeO_3$ sensors were measured. The schematic diagram of the testing principle[21] is shown in Fig. 1. The voltage V_h is the heating voltage supplied to the coils, while the circuit voltage V_c is supplied across the sensors and the load resistor (R_L) connected in series. In order to derive the resistance of the sensor, the signal voltage V_{out} across the load resistor was measured by a digital voltmeter HB-408. Its response can be defined as R_g/R_a, where R_g is the resistance measured in testing gas under the background of dry air, while R_a is the resistance in dry air.

2 Results

Fig. 2 shows the XRD patterns of $Gd_{1-x}Ca_xFeO_3$ powders calcined at 800 ºC for 4 h. All the $Gd_{1-x}Ca_xFeO_3$ (x=0–0.4) compounds crystallize as perovskite phase with orthorhombic structure. All of the five XRD patterns are quite similar, indicating that Ca doping does not change the crystal phase of $GaFeO_3$. With the help of MDI Jade software, differences of peak intensity and width of the five XRD patterns can be seen. The mean

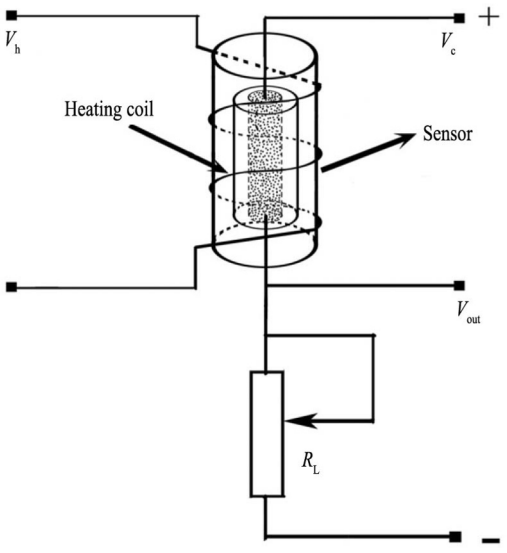

Fig. 1 Schematic diagrams of testing principle

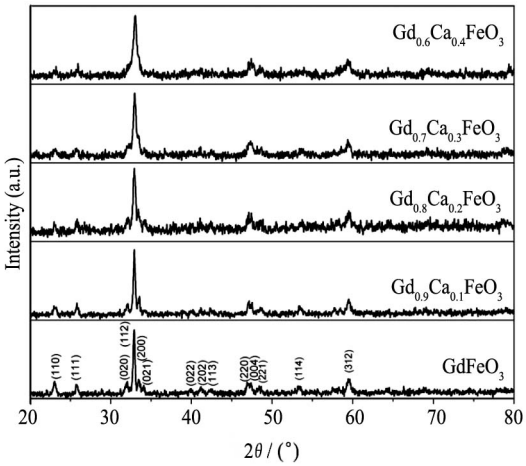

Fig. 2 XRD patterns for $Gd_{1-x}Ca_xFeO_3$ calcined at 800 °C

crystalline sizes can be calculated from these peaks. The mean crystalline sizes of $Gd_{1-x}Ca_xFeO_3$ powders calculated with Scherrer method are about 37.6 nm (x=0), 35.1 nm (x=0.1), 34.2 nm (x=0.2), 32.9 nm (x=0.3) and 25.7 nm (x=0.4), respectively. The Ca^{2+} doping suppresses the growth of crystallite size during the high temperature synthesis. The small crystallite size with large specific surface area would provide more adsorption sites.

Fig. 3 shows the temperature dependence of resistances for $Gd_{1-x}Ca_xFeO_3$-based sensors in dry air. In the whole temperature range, the resistances of all sensors decrease with an increase of temperature, which is the intrinsic characteristic of semiconductor. The $GdFeO_3$ sensor has very large resistance near room temperature[19]. The Ca doping in $GdFeO_3$ decreases the resistance. As we know, the compound $GdFeO_3$ is a p-type semiconductor, and its charge carriers are holes ($h^{\bullet}$) which are produced by the ionization of the Gd^{3+} vacancy defects [V_{Gd}^{x}]:

$$V_{Gd}^{x} \rightarrow V_{Gd}^{'''} + 3h^{\bullet} \quad (1)$$

When Gd^{3+} ions in $GdFeO_3$ are replaced by some Ca^{2+} ions, holes are produced due to the ionization of [Ca_{Gd}^{x}]:

$$Ca_{Gd}^{x} \rightarrow Ca_{Gd}^{'} + h^{\bullet} \quad (2)$$

which increases the conductivity of p-type $Gd_{1-x}Ca_xFeO_3$.

In fact, similar to that in $La_{1-x}M_xFeO_3$ system (M=Pb,

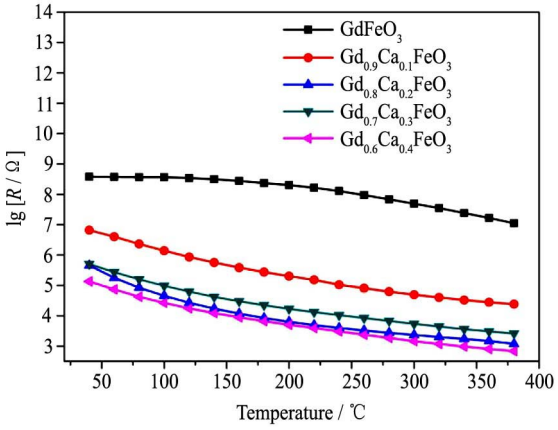

Fig. 3 Temperature dependence of resistance for $Gd_{1-x}Ca_xFeO_3$