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CO_2 gas sensors based on $Yb_{1-x}Ca_xFeO_3$ nanocrystalline powders

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Abstract: In this study, the $Yb_{1-x}Ca_xFeO_3$ ($0\le x\le 0.3$) nanocrystalline powders were prepared by sol-gel method. We used the method of quantitative analysis to research the gas-sensitive properties for $Yb_{1-x}Ca_xFeO_3$ to CO_2. Also, we investigated the effects of various factors on gas sensing properties by simple variable method. The doping of Ca could not only decrease the resistance of $YbFeO_3$, but also enhance its sensitivity to CO_2. When the Ca content x=0.2, $Yb_{1-x}Ca_xFeO_3$ showed the best response to CO_2. The response R_g/R_a to 5000 ppm CO_2 for $Yb_{0.8}Ca_{0.2}FeO_3$ at its optimal temperature of 260 °C with the room temperature humidity of 28%RH was 1.85. The response and recovery time decreased with an increase of the operating temperature for $Yb_{0.8}Ca_{0.2}FeO_3$ sensor to 5000 ppm CO_2. Furthermore, with an increase of CO_2 concentration from 1000 to 50000 ppm, the response time of $Yb_{0.8}Ca_{0.2}FeO_3$ became shorter, and meanwhile the recovery time was longer. CO_2-sensing response for $Yb_{0.8}Ca_{0.2}FeO_3$ increased with the increase of relative humidity. The response for $Yb_{0.8}Ca_{0.2}FeO_3$ in the background of air (with the room temperature humidity of 39%RH) at 260 °C could reach 2.012 to 5000 ppm CO_2, which was larger than the corresponding value (1.16) in dry air.

Keywords: gas sensor; CO_2; perovskite; rare earths

As the primary greenhouse gas, carbon dioxide (CO_2) emitted by factories and human activities, is causing more and more serious global warming problems. Thus, it is of great necessity to seek for effective techniques and methods to detect and control the concentrate of CO_2 in the air[1]. The problems of global warming promote the researches on the detection of CO_2[2]. Up to now, some kinds of CO_2 sensors, such as infrared[3], surface acoustic wave[4], solid electrolyte[5–7], capacitive and resistive[8–14], have been found. The resistive CO_2 sensor is based on the change of the conductance or resistance of semiconductors when being exposed to CO_2 in the air[15–20]. According to the report, some composite or single phase oxides can be adopted as the resistive CO_2 sensors[21–26].

~~Due to their widely practical~~ applications in multiple fields, perovskite-type compounds (ABO_3) have drawn more and more attention[27–32]. The general formula of perovskite-type oxides is ABO_3, in which A represents a large cation (usually a rare earth ion), while B refers to a smaller one[28,33]. In general, many gas sensors based on ABO_3 and its derivatives show high gas-selectivity and great working stability. However, the large resistance of ABO_3 sensors limits their application. Thus, many efforts have been made to promote the sensing behaviors of ABO_3. According to recent finding, the response $S=R_{gas}/R_a$ for $La_{0.8}Sr_{0.2}FeO_3$ to 4000 ppm CO_2 is 2.0[1], for $BaTiO_3$ to 10000 ppm CO_2 is 1.2[34], for $LaCrO_3$ to 300000 ppm CO_2 is 1.048[23]. Moreover, it has been reported that $La_{0.2}Sr_{0.8}FeO_3$ sensor shows larger CO_2 response in oxygen than in air[1], indicating that the oxygen adsorbed on the surface of semiconductor may be related to the sensing process of CO_2 in the air. The CO_2 sensing mechanism was initially suggested to be associated with the formation of carbonates in CuO-$BaTiO_3$ system[35]. Furthermore, the formation of the carbonation would change the height of potential barrier and result in an increase of resistance of p-type semiconductor oxides.

In this paper, the gas-sensor based on $Yb_{1-x}Ca_xFeO_3$ could sensitively detect CO_2 gas. Besides, Ca was used to partially replace Yb for improving its microstructure as well as gas sensing performance. This experiment utilized a sol-gel method with annealing temperature at 950 ºC for 4 h to prepare nanocrystalline $Yb_{1-x}Ca_xFeO_3$ sensitive material. Also, their phase composition, resistances and CO_2 gas sensing properties were studied.

1 Experimental

The $Yb_{1-x}Ca_xFeO_3$ powders were prepared by sol-gel method. Firstly, a mixed solution was prepared at stoichiometric ratio of $Yb(NO_3)_3$:$Ca(NO_3)_2$:$Fe(NO_3)_3$=(1–x):x:1, and the citrate acid was added at a ratio of (Yb^{3+}+Ca^{2+}+Fe^{3+}):(citrate acid)=1:2 into the solution. Besides, the mixture was heated in water bath at 80 ºC. Then, 10% (wt.%) polyethylene glycol (PEG; molecular weight 20000) was added into the solution through con-

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stant stirring. The solution was continuously stirred for several hours until the sol was formed. Furthermore, sol was dried into a gel, and the obtained gel was completely dried into pieces in a baking box. Subsequently, the pieces were ground to powder sample. Lastly, the samples were annealed in an oven at 950 ºC for 4 h. Also, the obtained powder was characterized by X-ray diffraction (XRD) to determine its phase composition, and the microstructure was observed by a field emission scanning electron microscope (FE-SEM).

The prepared powders were mixed with an amount of adhesive (deionized water was utilized in this paper) until it became a paste. Furthermore, the mixture was packed into an alumina ceramic tube where there are two Au electrodes on both sides. The size of ceramic tube was about 1.2 mm in diameter and 4 mm in length, attached with a pair of Au electrodes and Pt wires. Moreover, a Ni-Cr heating wire was inserted into the ceramic tube. For improving their repeatability and stability, the sensors were dried at about 100 ºC for 6 h. Fig. 1 shows the photo of sensor we prepared and the structure diagram of sensor. Subsequently, the sensors were aging 48 hours on the aging equipment in air. In the end, we tested the gas-sensing properties of $Yb_{1-x}Ca_xFeO_3$ in a temperature ranging from 160 to 340 ºC.

2 Results and discussion

As shown in Fig. 2, the X-ray diffraction patterns of $Yb_{1-x}Ca_xFeO_3$ (x=0, 0.1, 0.2 and 0.3) powders annealed at 950 ºC for 4 h. From the figure, it can be seen that the $Yb_{1-x}Ca_xFeO_3$ (x=0, 0.1, 0.2 and 0.3) powders show orthorhombic perovskite structure, suggesting that the Yb^{3+} was partially substituted by Ca^{2+} in the $YbFeO_3$ crystal lattice. Table 1 lists the corresponding crystalline parameters of $Yb_{1-x}Ca_xFeO_3$ (x=0, 0.1, 0.2 and 0.3). According to the table, it can be found that the values of unit cell increase with the increase of Ca content x. This results from the fact that the radius of Ca^{2+} (100 pm) is larger than that of Yb^{3+} (86.8 pm). We investigated the morphology of the obtained $Yb_{1-x}Ca_xFeO_3$ (x=0, 0.1, 0.2 and 0.3) samples with FE-SEM technique. The SEM micrograph on the surfaces of the $Yb_{1-x}Ca_xFeO_3$ (x=0, 0.1, 0.2 and 0.3) powders are shown in Fig. 3. It can be seen that the morphology of the prepared $Yb_{1-x}Ca_xFeO_3$ (x=0, 0.1, 0.2 and 0.3) samples are nanoparticles with somewhat agglomeration. Besides, the average grain sizes D were estimated as about 40, 38, 36.4 and 36 nm for x=0, 0.1, 0.2 and 0.3. The crystallite size decreases with the increase of the doping amount x, indicating that during the high temperature treatment, Ca^{2+} doping might prevent the $YbFeO_3$ particle size from growing.

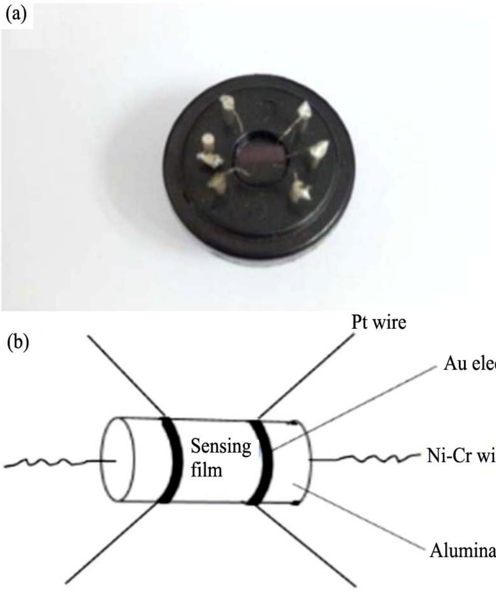

Fig. 1 (a) Photo of the sensor we prepared; (b) the structure diagram of sensor

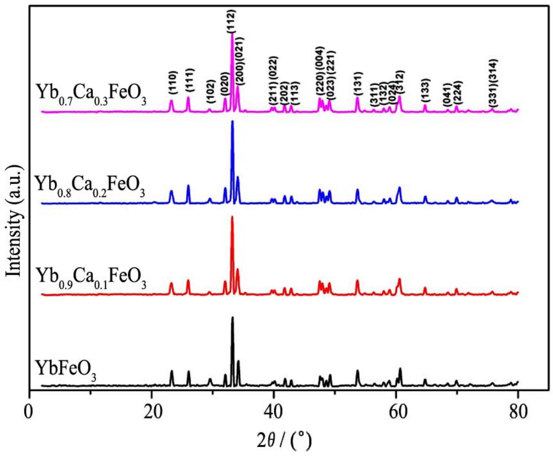

Fig. 2 X-ray diffraction patterns of $Yb_{1-x}Ca_xFeO_3$ (x=0, 0.1, 0.2 and 0.3) powders

Table 1 Corresponding lattice parameters of $Yb_{1-x}Ca_xFeO_3$ for x=0, 0.1, 0.2 and 0.3

x	a/nm	b/nm	c/nm	$V/10^3$ nm^3
0	0.50054	0.59446	0.76276	0.22696
0.1	0.50129	0.59482	0.76229	0.22750
0.2	0.50218	0.59507	0.76385	0.22826
0.3	0.50462	0.59630	0.76521	0.23026

Fig. 4 shows the Ca content x dependence of resistance of $Yb_{1-x}Ca_xFeO_3$ (x=0, 0.1, 0.2 and 0.3) sensors at different operating temperatures (200, 240, 260 and 280 ºC) in the background of ambient air (with the room temperature humidity of 28%RH). It can be seen that the resistances of $Yb_{1-x}Ca_xFeO_3$ (x=0, 0.1, 0.2 and 0.3) sensors decrease with the increase of temperature. Also, with an increase of Ca content x, the resistances of sensors firstly decrease, undergo a minimum at approximately x=0.1, and then increase again.

When the Yb^{3+} in $YbFeO_3$ is partly replaced by Ca^{2+}, the following compensation processes would occur in $Yb_{1-x}Ca_xFeO_3$. To be specific, the first process is electrical valence compensation, which is dominated at low Ca concentration. When Yb^{3+} is partly replaced by Ca^{2+} in