Research Article

Structural, Electrical, and Ethanol-Sensing Properties of $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ Nanoparticles

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The nanocrystalline $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ ($0 \leq x \leq 1.0$) powders with orthorhombic perovskite phase were prepared by sol-gel method. The average crystallite sizes of $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ powders are about 20 nm. The resistance and gas-sensing properties of the $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ based sensors were investigated in the temperature range from 160 to 300°C. The results demonstrated that the resistance and response of the perovskite thick films changed with the increase of Nd content.

1. Introduction

There has been much interest in perovskite structured compounds (of general formula ABO_3) because of their catalytic activity, colossal magnetoresistance effects, thermoelectric effects, gas-sensing properties, and so forth [1–8]. Specially perovskite oxides with AFeO_3 structure (A: rare earth) have shown the good gas-sensing properties such as LaFeO_3 , $\text{La}_{1-x}\text{Pb}_x\text{FeO}_3$, $\text{LaMg}_x\text{Fe}_{1-x}\text{O}_3$, $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$, and $\text{SmFe}_{1-x}\text{Ni}_x\text{O}_3$. Among the modified perovskites, $\text{La}_{0.68}\text{Pb}_{0.32}\text{FeO}_3$ showed the best ethanol gas-sensing characteristics; its response to 100 ppm ethanol was more than 80% in the temperature range from 140 to 240°C; it was also found that the $\text{LaMg}_{0.1}\text{Fe}_{0.9}\text{O}_3$ based sensor had the best response and selectivity to ethanol gas; the response to 500 ppm ethanol is 128 at 220°C or the highest response to 500 ppm ethanol gas reaches 57.8 at 260°C for $\text{SmFe}_{0.95}\text{Ni}_{0.05}\text{O}_3$ sensor and so forth [9–12]. Numerous perovskites show p-type semiconductor properties in air. Oxygen adsorption enhances the conductivity of these materials on account of the increased concentration of holes, which are the main charge carrier species in p-type semiconductors. Furthermore, their resistance increases by applying reducing gases, such as ethanol. Interaction

between the reducing gas and the oxygen adsorbed on the metal oxide surface leads to a change in conductance [13–16]. Perovskite powder AFeO_3 , used in thick film gas sensors, can be manufactured by different chemical methods: coprecipitation method, sol-gel method, and hydrothermal method. They are used broadly due to their advantage in which precursors can be admixed at atomic scale. So, the products are pure and homogeneous. The products also have small grain size and great surface area and are compatible in metal oxide semiconductor (MOS) gas sensors.

In this paper, $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ ($0 \leq x \leq 1.0$) perovskite oxides were prepared by a citrate-gel method. The influence of Nd doping on the A site of the crystalline structure of LaFeO_3 and also on their ethanol-sensing characteristics has been investigated in detail.

2. Experimental

Nanopowders of $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ ($0 \leq x \leq 1.0$) were prepared by a sol-gel (citrate-gel) method, which is based on the chelation of the metal cations by citric acid in a solution of water. The specified amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$; and $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was first dissolved

in citric acid solution and then mixture was stirred slowly and kept at a temperature of 70°C until the reaction mixture became clear. To completely create compound matters, ammonium solution was added drop by drop at a time until the pH reached 6 and 7. The complete dissolution of the salts resulted in a transparent solution. After continuously stirring for 2 hours the brown semitransparent sol was produced, and then the solution containing La, Fe, and Nd cations was homogenized; the solution became more viscous as the temperature was continuously kept at 70°C, without showing any visible phase separation. This resin was placed in a furnace and dried to 120°C for 4 h in air to pulverize into powders. The crystalline phase was obtained by heating the powder 500°C for 10 h in air.

Structural characterization was performed by means of X-ray diffraction using a D5005 diffractometer with Cu K α radiation and with 2θ varied in the range of 10–70° at a step size of 0.02°. The particle size and morphology of the calcined powders were examined by SEM (S-4800), Hitachi-Japan.

The fabrication of thick films, structure of sensor prototypes, and measuring conditions were described in [17]. In order to improve their stability and repeatability, the thick film sensors were calcined at 400°C for 2 h in air. The gas sensitivity of LaFe_{1-x}Nd_xO₃ sensors was measured in a temperature range of 100°C–300°C. Their resistance was measured in air with test gas equipment. The response, S , was defined by the following equation:

$$S = \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}}, \quad (1)$$

where R_{air} is the resistance of sensor measured in air and R_{gas} is the resistance of sensors measured in the test gas equipment.

3. Result and Discussion

XRD patterns of the La_{1-x}Nd_xFeO₃ ($0 \leq x \leq 1.0$) samples were shown in Figure 1. All of them are single phase, with orthorhombic structure (space group Pnma). The wide diffraction peaks (in position of 2θ about 32–33°) show that the samples have small grain size. The a -cell parameter versus Nd content is presented in Figure 2, and it can be seen that the a -cell parameter of the samples decreases with the increase of Nd doping concentration. The lattice distortion may be caused by the radius of Nd³⁺ (0.127 Å) that is smaller than one of La³⁺ (0.136 Å). It leads to the decrease of the lattice parameters with increase of the Nd concentration (Figure 2).

The crystalline sizes D (nm) of the samples are calculated by Scherrer formula:

$$D = \frac{k\lambda}{B \cos \theta}, \quad (2)$$

where D is the average size of crystalline particle, assuming that particles are spherical, $k = 0.94$, λ is the wavelength of X-ray radiation, B is full width at half maximum of the diffracted peak, and θ is angle of diffraction.

The cell parameters and the crystalline sizes of La_{1-x}Nd_xFeO₃ powders are shown in Table 1. These small

FIGURE 1: XRD patterns of La_{1-x}Nd_xFeO₃ nanoparticles after annealing in air at 500°C for 10 hours.

FIGURE 2: a -Cell parameter versus Nd content.

grain sizes of the La_{1-x}Nd_xFeO₃ ($0 \leq x \leq 1.0$) nanopowders are favourable for preparing the thick film sensors.

The thick film sensors were prepared by using the nanopowder La_{1-x}Nd_xFeO₃ and their ethanol-sensing characters were studied. The resistance of these sensors was examined with the different temperatures and ethanol concentrations. Figure 3 presents the temperature dependence of resistance of thick film sensors based on the nanosized La_{1-x}Nd_xFeO₃ in the temperature range from 160°C to 300°C in air. It is suggested that the electrical conductivity mechanism is small polaron hopping process [18, 19] following the equation

$$\sigma = \frac{A}{T} \exp\left(-\frac{E_a}{kT}\right), \quad (3)$$

TABLE 1: The cell parameters and crystallite sizes of $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ powders.

x	Compounds	a (Å)	b (Å)	c (Å)	V (Å) ³	D (nm)
0	LaFeO_3	5.5656	5.2544	7.5659	221.256	20.31
0.15	$\text{La}_{0.85}\text{Nd}_{0.15}\text{FeO}_3$	5.5538	5.2432	7.5498	219.850	19.62
0.30	$\text{La}_{0.7}\text{Nd}_{0.3}\text{FeO}_3$	5.54500	5.2350	7.5379	218.811	21.24
0.50	$\text{La}_{0.5}\text{Nd}_{0.5}\text{FeO}_3$	5.5406	5.2308	7.5319	218.280	19.34
1	NdFeO_3	5.5046	5.1967	7.4829	214.050	17.40

TABLE 2: The Activation energy (E_a) of the electrical conduction process.

$\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ ($0 \leq x \leq 1.0$)	$x = 0.0$	$x = 0.15$	$x = 0.3$	$x = 0.5$	$x = 1.0$
E_a (kJ mol ⁻¹)	27	28	26	27	20

FIGURE 3: Resistance versus temperature of $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0.0$ – 1.0) measured in air. FIGURE 4: Electrical conductivity versus temperature of $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0.0$ – 1.0) measured in air.

where A is constant relating to carrier concentration, T is the temperature, k is the Boltzmann constant, and E_a is activation energy. Figure 4 shows the temperature dependent on conductivity and Figure 5 demonstrates the Arrhenius plots of conductivities of the $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ samples. From Figure 5 the activation energy E_a can be calculated (Table 2).

It is noted that the resistance was decreased with increasing temperature due to an intrinsic characteristic of a semiconductor. This would result from the ionization of oxygen vacancies. LaFeO_3 and doped- LaFeO_3 are the kind of p-type semiconductive material [20].

When the sensor is exposed to ethanol, the ethanol reacts with the chemisorbed oxygen, releasing electrons back to the valence band, decreasing the holes concentration, and increasing resistance [16]. Figure 6 depicts the response and recovery curve of $\text{La}_{0.7}\text{Nd}_{0.3}\text{FeO}_3$ when exposed to 0.25 mg/L ethanol at 212°C. The response and recovery times of this

sensor are relatively short. The doping at A site caused a disorder in structure and oxygen deficiency can occur during heating sample at high temperature. On the other hand, $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ interacts with the oxygen, by transferring the electrons from the valence band to adsorbed oxygen atoms, forming ionic species such as O^{2-} or O^- . The electron transferring from the valence band to the chemisorbed oxygen results in an increase in holes concentration and a reduction in resistance of these sensors.

The temperature dependence of the $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ sensor responses to 0.25 mg/L ethanol is shown in Figure 7. We found that the sensors' sensitivity increases with Nd replaced concentration. On the other hand, the temperature, at which sensor responses reach maximum value, decreases with increasing Nd replaced concentrations. All sensors showed excellent ethanol-sensing characteristics. The response of $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ was positive; this suggests that

FIGURE 5: Arrhenius plots of electrical conductivity for $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0.0$ – 1.0).

FIGURE 6: Response and recovery curve of $\text{La}_{0.7}\text{Nd}_{0.3}\text{FeO}_3$ when exposed to 0.25 mg/L ethanol at 212°C.

the semiconductivity is p-type behavior. Mechanism of gas-sensing is based on the oxidation-reduction on the surface of the material. The absorbed O^{n-} accelerates the reaction:

This should give an increase in R_{gas} and thus increase the sensitivity of these sensors [9–13].

Figure 8 presents the dependence of the response upon the concentration of ethanol at 182°C for the $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ sensor. The change of electric resistance of the $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ sensor is strongly affected by an increase in ethanol gas concentration.

FIGURE 7: Temperature dependence of the response in 0.25 mg/L ethanol of $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ sensors.

FIGURE 8: Ethanol concentration dependence of response of $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ at 182°C.

4. Conclusion

The perovskite compounds $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ with orthorhombic perovskite structure were prepared successfully by gel-citrate method. With increasing of the Nd replaced concentrations, both the particle size and a -cell parameter of the samples decrease. The $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ nanocrystallite materials were manufactured thick film sensors and studied ethanol-sensing characters. All sensors showed excellent ethanol-sensing characteristics. The lattice structure of

$\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ is strongly distorted, and this leads to the change of the ethanol-sensing characters as function of replaced Nd concentrations.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] L. Zhang, J. Hu, P. Song, H. Qin, and M. Jiang, "Electrical properties and ethanol-sensing characteristics of perovskite $\text{La}_{1-x}\text{Pb}_x\text{FeO}_3$," *Sensors and Actuators B Chemical*, vol. 114, no. 2, pp. 836–840, 2006.
- [2] V. Caignaert, A. Maignan, and B. Raveau, "Up to 50 000 per cent resistance variation in magnetoresistive polycrystalline perovskites $\text{Ln}_{23}\text{Sr}_{13}\text{MnO}_3$ ($\text{Ln}=\text{Nd}$; Sm)," *Solid State Communications*, vol. 95, no. 6, pp. 357–359, 1995.
- [3] N. Gayathri, A. K. Raychaudhuri, S. K. Tiwary, R. Gundakaram, A. Arulraj, and C. N. R. Rao, "Electrical transport, magnetism, and magnetoresistance in ferromagnetic oxides with mixed exchange interactions: a study of the $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Co}_x\text{O}_3$ system," *Physical Review B*, vol. 56, no. 3, pp. 1345–1353, 1997.
- [4] H. Taguchi, M. Nagao, and M. Shimada, "Mechanism of metal-insulator transition in the systems $(\text{Ln}_{1-x}\text{Ca}_x)\text{MnO}_3$ (Ln : La, Nd, and Gd) and $(\text{Nd}_{0.1}\text{Ca}_{0.9-y}\text{Sr}_y)\text{MnO}_3$," *Journal of Solid State Chemistry*, vol. 97, no. 2, pp. 476–480, 1992.
- [5] Md. A. Choudhury, S. Akhter, D. L. Minh, N. D. Tho, and N. Chau, "Large magnetic-entropy change above room temperature in the colossal magnetoresistance $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$ materials," *Journal of Magnetism and Magnetic Materials*, vol. 272–276, pp. 1295–1297, 2004.
- [6] K. Iwasaki, T. Ito, M. Yoshino, T. Matsui, T. Nagasaki, and Y. Arita, "Power factor of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ and $\text{LaFe}_{1-y}\text{Ni}_y\text{O}_3$," *Journal of Alloys and Compounds*, vol. 430, no. 1–2, pp. 297–301, 2007.
- [7] M.-H. Hung, M. D. M. Rao, and D.-S. Tsai, "Microstructures and electrical properties of calcium substituted LaFeO_3 as SOFC cathode," *Materials Chemistry and Physics*, vol. 101, no. 2–3, pp. 297–302, 2007.
- [8] D. Bayraktar, F. Clemens, S. Diethelm, T. Graule, J. Van herle, and P. Holtappels, "Production and properties of substituted LaFeO_3 -perovskite tubular membranes for partial oxidation of methane to syngas," *Journal of the European Ceramic Society*, vol. 27, no. 6, pp. 2455–2461, 2007.
- [9] X. Liu, B. Cheng, J. Hu, H. Qin, and M. Jiang, "Semiconducting gas sensor for ethanol based on $\text{LaMg}_x\text{Fe}_{1-x}\text{O}_3$ nanocrystals," *Sensors and Actuators B: Chemical*, vol. 129, no. 1, pp. 53–58, 2008.
- [10] H. Suo, F. Wu, Q. Wang et al., "Study on ethanol sensitivity of nanocrystalline $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$ -based gas sensor," *Sensors and Actuators B*, vol. 45, no. 3, pp. 245–249, 1997.
- [11] L. Chena, J. Hua, S. Fanga et al., "Ethanol-sensing properties of $\text{SmFe}_{1-x}\text{Ni}_x\text{O}_3$ perovskite oxides," *Sensors and Actuators B*, vol. 139, pp. 407–410, 2009.
- [12] N. N. Toan, S. Saukko, and V. Lantto, "Gas sensing with semi-conducting perovskite oxide LaFeO_3 ," *Physica B: Condensed Matter*, vol. 327, no. 2–4, pp. 279–282, 2003.
- [13] J. Xu, J. Han, Y. Zhang, Y. Sun, and B. Xie, "Studies on alcohol sensing mechanism of ZnO based gas sensors," *Sensors and Actuators, B: Chemical*, vol. 132, no. 1, pp. 334–339, 2008.
- [14] J. R. Stetter, W. R. Penrose, and S. Yao, "Sensors, chemical sensors, electrochemical sensors, and ECS," *Journal of the Electrochemical Society*, vol. 150, no. 2, pp. S11–S16, 2003.
- [15] H. Suo, J. Wang, E. Wu, G. Liu, B. Xu, and M. Zhao, "Influence of Sr content on the ethanol sensitivity of nanocrystalline $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$," *Journal of Solid State Chemistry*, vol. 130, pp. 152–153, 1997.
- [16] L. Zhang, J. Hu, P. Song, H. Qin, and M. Jiang, "Electrical properties and ethanol-sensing characteristics of perovskite $\text{La}_{1-x}\text{Pb}_x\text{FeO}_3$," *Sensors and Actuators B*, vol. 114, pp. 836–840, 2006.
- [17] H. T. Giang, H. T. Duy, P. Q. Ngan, G. H. Thai, D. T. A. Thu, and N. N. Toan, "Hydrocarbon gas sensing of nano-crystalline perovskite oxides LnFeO_3 ($\text{Ln} = \text{La}$, Nd and Sm)," *Sensors and Actuators B: Chemical*, vol. 158, no. 1, pp. 246–251, 2011.
- [18] M. Hung, M. V. M. Rao, and D. Tsai, "Microstructures and electrical properties of calcium substituted LaFeO_3 as SOFC cathode," *Materials Chemistry and Physics*, vol. 101, no. 2–3, pp. 297–302, 2007.
- [19] S. Komine and E. Iguchi, "Dielectric properties in $\text{LaFe}_{0.5}\text{Ga}_{0.5}\text{O}_3$," *Journal of Physics and Chemistry of Solids*, vol. 68, no. 8, pp. 1504–1507, 2007.
- [20] K. Iwasaki, T. Ito, M. Yoshino, T. Matsui, T. Nagasaki, and Y. Arita, "Power factor of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ and $\text{LaFe}_{1-y}\text{Ni}_y\text{O}_3$," *Journal of Alloys and Compounds*, vol. 430, no. 1–2, pp. 297–301, 2007.