

Ethanol Sensing of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x=0, 0.1$ and 0.3) Prepared by Metal-Organic Complex Decomposition

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ABSTRACT

The perovskite $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x=0, 0.1$ and 0.3) powders were successfully prepared by the decomposition of metal-organic complexes which were synthesized from the reaction of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ at 190°C in ethylene glycol solvent. The amounts of strontium nitrate used as a dopant were varied by 0, 10.0 and 30.0 mol%. The $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ powders were obtained by calcination of metal-organic complexes at 850°C for 4 h and then were characterized by FTIR, XRD, SEM and BET. Based on semiconducting properties $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ films prepared by spin coating were investigated for ethanol sensing. The results showed that 10% Sr(II) doped LaFeO_3 -based sensor, $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$, exhibited the highest sensitivity to ethanol vapour with a minimum concentration of 100 ppm at an operating temperature of 300°C .

Key words: LaFeO_3 , ethanol-sensing, gas sensor, metal-organic complex, $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ powders

INTRODUCTION

Monitoring and controlling ethanol gas is undertaken in many fields, such as fuel cell and fuel ethanol industries, alcoholic beverages production and breath analysis for drunk driving. Among the many types of sensors used to detect ethanol gas, metal oxide semiconducting gas sensors (MOGs) have been of wide interest due to their low cost, high sensitivity and simplicity of function and work mode (Korotcenkov, 2007). In principle, when MOG is exposed to oxidizing or reducing gases, the redox reactions between gas molecules and the surface of the metal oxide cause a change in its resistance by consumption or

donation of electrons from the metal oxide surface and produce electrical signals with a magnitude proportional to the concentration of gas.

The sensitivity of MOG depends on the material used for gas sensing, with many oxides used as the ethanol sensor, such as Fe_2O_3 , SnO_2 , ZnO , In_2O_3 , WO_3 and CuO (Wang *et al.*, 2008). LaFeO_3 has been proposed as the sensing material to detect ethanol and other gases (Toan *et al.*, 2003; Liu *et al.*, 2006) because its perovskite structure usually has structural defects caused by fluctuation between two stable oxidation states of iron, causing the electrical balance by insertion of O^{2-} in the lattice from environmental O_2 or the occurrence of oxygen vacancies (Delmastro *et al.*,

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2001; Liu *et al.*, 2008). In spite of the fact that LaFeO_3 can detect various kinds of gas with high sensitivity, it has a longer response time and has low selectivity. The response time and selectivity can be improved by addition of other metals such as Pb(II) or Ca(II) (Kong and Shen, 1996; Song *et al.*, 2005) at the lanthanum site or another of the transition metals, such as Co(II) at the iron site (Song *et al.*, 2006) to enhance the conductivity and catalytic activity of LaFeO_3 .

In addition, the physical and gas sensing properties of LaFeO_3 powder strongly depend on the preparation method, which can be solid state reaction, wet combustion synthesis, sol-gel, co-precipitation or thermal decomposition. Among these methods, thermal decomposition has been of interest because of its low processing temperature, low cost and low number of preparation steps. Therefore, in this work, LaFeO_3 powder was prepared by thermal decomposition of a metal-organic complex using triethanolamine as a ligand. Amounts of Sr(II) ion were doped at the lanthanum site of LaFeO_3 at 10 and 30% mole ratio in order to improve the conductivity and surface activity of the powder, and subsequently, the ethanol sensing properties of prepared $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x=0, 0.1$ and 0.3) were investigated.

MATERIALS AND METHODS

Materials

Lanthanum(III) nitrate hexahydrate ($\text{La(NO}_3)_3 \cdot 6\text{H}_2\text{O}$), iron(III) nitrate nonahydrate ($\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and strontium(II) nitrate ($\text{Sr(NO}_3)_2$) were purchased from Fisher Scientific, Ajax Finechem and HIMEDIA, respectively. Triethanolamine (TEA, $\text{N(CH}_2\text{CH}_2\text{OH)}_3$) was supplied by UNILAB. Ethylene glycol (EG, $\text{HOCH}_2\text{CH}_2\text{OH}$) was obtained from UNILAB, and distilled before use. Triton X-100 and acetylacetone were purchased from Fluka.

Preparation of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ powders

Firstly, $\text{La(NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and TEA with a molar ratio of $\text{La(III)} : \text{Fe(III)} : \text{TEA} = 1 : 1 : 3$ were mixed in a round bottom flask at room temperature. Ethylene glycol (EG) was then added. The reaction mixture was distilled at 190°C for 6 h with continuous stirring. Distillation was carried out until nearly 66% of the EG had been evaporated.

Sr(II) doped metal-organic complexes were prepared in a similar manner. To obtain 10 or 30% Sr(II) doped complexes, stoichiometric molar quantities of $\text{La(III)} : \text{Sr(II)} = 0.9 : 0.1$, or $0.7 : 0.3$ were added to the $1 : 3$ molar ratio of $\text{Fe(III)} : \text{TEA}$. The as-prepared metal-organic complexes were characterized by TGA (761 Connecticut 06859 Perkin Elmer, heating rate of 10°C/min over a 50°C to 1000°C temperature range).

Metal-organic complexes were converted to $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ by calcination at 850°C for 4 h under atmospheric conditions. The phase formation of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ powders was characterized by XRD analysis using $\text{CuK}\alpha$ radiation (Bruker-AXS Advance D8 X-ray powder diffractometer, operated at 40 kV and the scan step was 0.04°). The specific surface areas of powders were measured by the Brunauer-Emmett-Teller (BET) nitrogen gas absorption method. The powder microstructure was identified by scanning electron microscope (SEM, 145 OVP LEO).

Fabrication and gas sensing measurement of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ sensors

The $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ films were deposited on alumina substrates (3×2 mm) with gold interdigitated electrodes by a spin coating technique. Triton X-100 binder and $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ powders were mixed and ground in acetyl acetone to form pastes. The pastes were dropped onto alumina substrates and spun by spin coater with a rate of 3,000 rounds/min for 30 seconds to form films. The $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ films were then annealed at 400°C for 3 h to remove organic content.

In a gas-testing chamber, the electrodes of the $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ sensors were connected with the probe on a heating state. Voltage was applied to two Ni-Cr coils under the heating state to heat the sensors and operating temperatures of 200–350°C were detected by thermo couple. For gas testing, the resistances of the films were measured in air (R_A). Then, various concentrations of ethanol gas (100, 200, 300, 500 and 1000 ppm) were continuously flowed into the chamber using a mass flow controller and the gas sensor resistance (R_E) at different temperatures was measured. The sensitivity of the $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ -based sensor to ethanol gas was expressed in term of response (R) defined as $R = R_E/R_A$.

RESULTS AND DISCUSSION

Characterization of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ powders

To obtain $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0, 0.1$ and 0.3) powders, the metal-organic complexes were calcined to remove the organic contents. The calcination temperature was determined by studying the TGA thermogram of the metal-organic complexes. There were three regions of weight loss in the TGA thermogram (Figure 1). The first weight loss occurred from 50°C to 200°C and was involved in the decomposition of

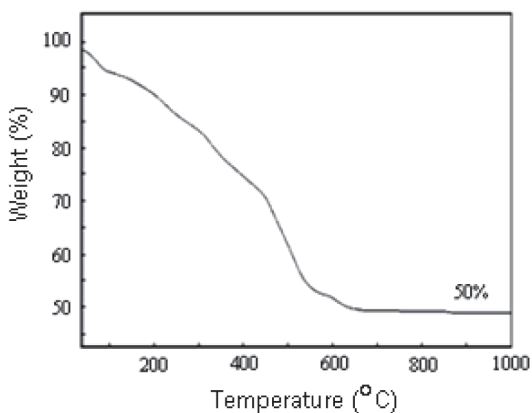


Figure 1 Representative TGA thermogram of metal-organic complexes.

water and organic solvents. The second weight loss from 200°C to 500°C corresponded to oxidation of the organic contents. The final weight loss that occurred from 500°C to 700°C was attributed to carbon-residue decomposition. After 700°C, no weight loss was observed.

To ensure that all the organic contents were removed for preparing $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0, 0.1$ and 0.3) powders, the metal-organic complexes were calcined at 850°C for 4 h. Figure 2 shows XRD patterns of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ complexes calcined at 850°C for 4 h. It was found that all of the $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0, 0.1$ and 0.3) powders were perovskite phases with orthorhombic structures. The diffraction peaks agreed well with JCPDS file no. 37-1493 and shifted to higher 2-theta values when the Sr(II) increased. The crystallite sizes of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0, 0.1$ and 0.3) powders calculated from Scherrer's equation were 28.59, 26.19 and 20.70 nm, respectively. It was suggested that Sr(II) ions interfered with the crystal growth of LaFeO_3 (Song *et al.*, 2005).

FTIR spectra of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ recorded in the 400–4000 cm^{-1} region are shown in Figure 3. The results corresponded to the XRD analysis that all of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0, 0.1$ and 0.3) powders

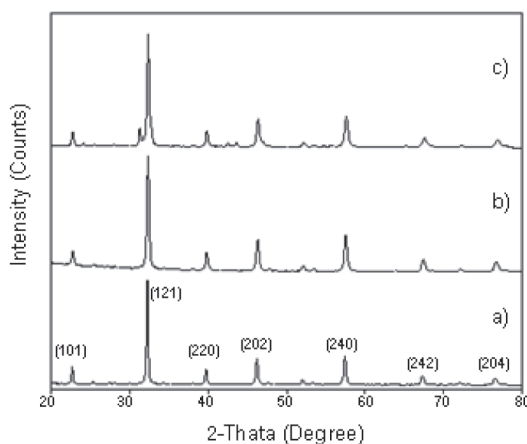


Figure 2 XRD patterns of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ calcined at 850°C for 4 h
(a) $x = 0$, (b) $x = 0.1$ and (c) $x = 0.3$.

were perovskite phases, as was indicated by the strong and sharp peak at 560-579 cm^{-1} referring to antisymmetric stretching vibration of Fe-O in the BO_6 octahedral unit of perovskite oxide ABO_3 (Li *et al.*, 2007).

The morphology of all calcined powders revealed rather homogeneous microstructures with the assembly of regular size particles as shown in Figure 4, $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$ powder. The specific surface areas of 0, 10 and 30% of Sr(II) doped

LaFeO_3 were 11.41, 7.88 and 10.18 m^2/g , respectively.

Gas sensing properties of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ -based sensors

It is well known that the operating temperature influences the sensitivity of the semiconducting gas sensor. In order to acquire the optimum operating temperature, the relationship between different operating temperatures and the sensitivity of the sensor to 1,000 ppm ethanol was investigated and the result is shown in Figure 5.

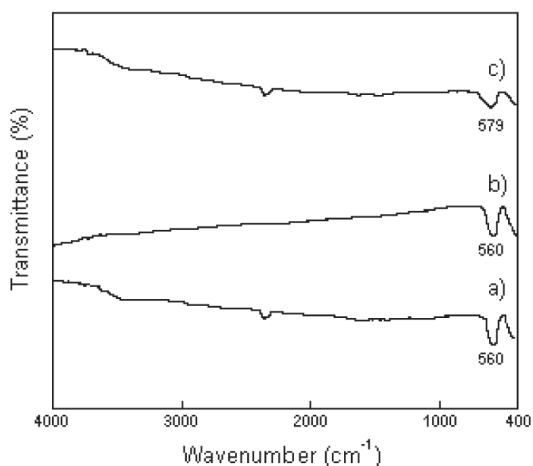


Figure 3 FTIR spectra of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ calcined at 850°C for 4 h
(a) $x = 0$, (b) $x = 0.1$ and (c) $x = 0.3$.

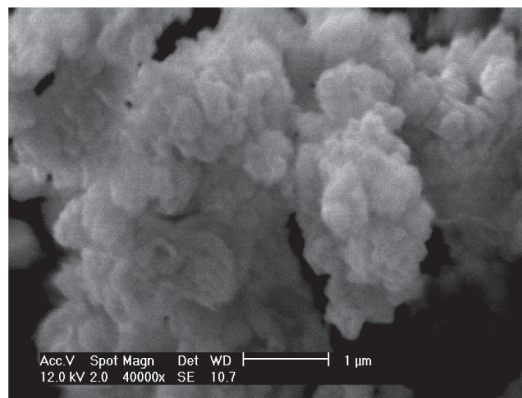


Figure 4 SEM micrograph of the $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$ powder.

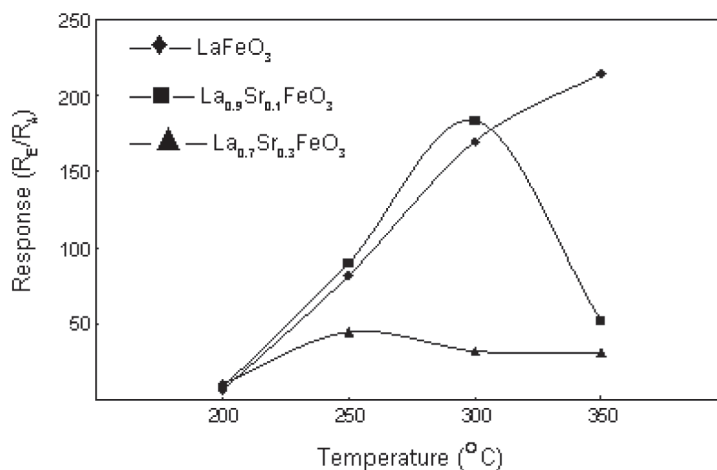


Figure 5 The effects of operating temperature on the sensitivity of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ -based sensors at 1,000 ppm ethanol.

The $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$ -based sensor exhibited the highest sensitivity at 300 °C and dropped at higher temperature. On the other hand, the LaFeO_3 -based sensor showed the highest sensitivity at an operating temperature up to 350 °C, but the higher the temperature used, the more energy was consumed.

The responses of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x=0, 0.1$ and 0.3) to various concentrations of ethanol gas were therefore, determined at 300 °C and the sensor responses as a function of concentration are

presented in Figure 6. It can be seen that the responses of $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$ and the LaFeO_3 sensors significantly increased with increasing ethanol concentration. The better response was observed in $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$, indicating that Sr(II)-doping can improve the sensitivity to ethanol gas. However, in the case of higher Sr(II)-doping, $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_3$, the sensitivity was significantly lower.

The sensing behavior of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ -based sensors in Figure 7 indicated that all of the

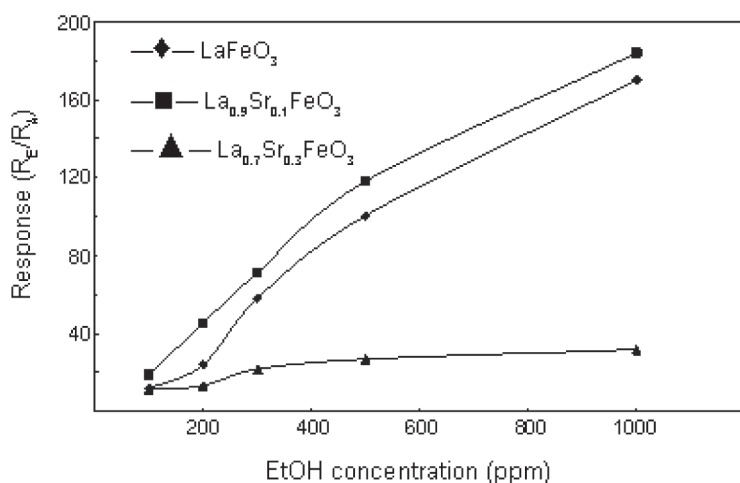


Figure 6 The effects of ethanol concentration on the sensitivity of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ -based sensors at 300 °C.

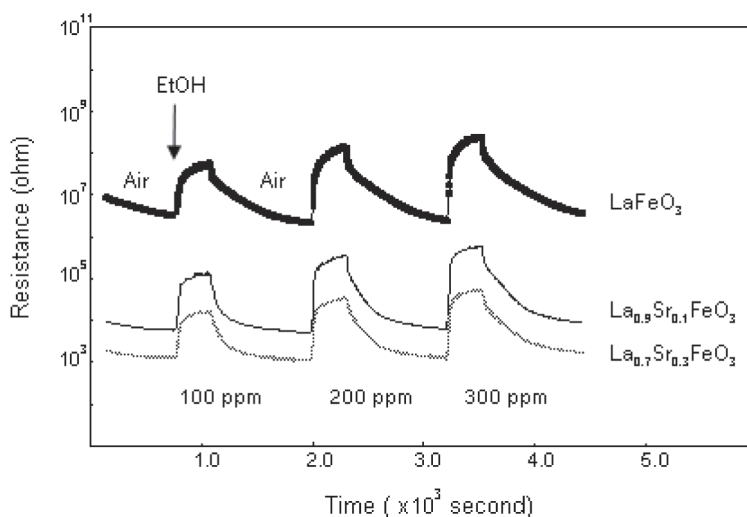


Figure 7 Response characteristics of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ -based sensors to 100, 200 and 300 ppm ethanol operated at 300 °C.

$\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0, 0.1$ and 0.3) were p-type semiconductors (Liu *et al.*, 2006). When $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ -based sensors were exposed to ethanol reducing gas, their resistances increased because of the recombination of holes in the p-type $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ and extra electrons from oxidation of ethanol. Furthermore, the conductivity of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ increased with an increase in Sr(II) dopant; consequently, the time to respond to ethanol gas was lower. In this experiment, the response times to 100 ppm of ethanol gas concentration at 300°C defined by the time to reach 90% at final resistance (Wang *et al.*, 2008) were approximately 256, 200 and 245 sec for the content of 0, 10 and 30% Sr(II) dopant, respectively. From overall results, it can be concluded that 10% Sr(II) was the proper amount of dopant for improving the ethanol sensing properties of the LaFeO_3 -based sensor.

CONCLUSION

$\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ ($x = 0, 0.1$ and 0.3) was successfully prepared by thermal decomposition of metal-organic complexes. XRD patterns showed that all compounds were perovskite phase with orthorhombic structure. The characteristics of a gas sensor on thick films of these compounds prepared by spin coating were investigated. The results showed that an $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$ -based sensor exhibited the highest sensitivity to ethanol gas at 300°C in the 100-1,000 ppm concentration range.

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LITERATURE CITED

- Delmastro, A., D. Mazza, S. Ronchetti, M. Vallino, R. Spinicci, P. Broveto and M. Salis. 2001. Synthesis and characterization of non-stoichiometric LaFeO_3 perovskite. **Mater. Sci. Eng. B.** 79: 140-145.
- Kong, L. and Y. Shen. 1996. Gas-sensing property and mechanism of $\text{Ca}_x\text{La}_{1-x}\text{FeO}_3$ ceramics. **Sens. Actuators B.** 30: 217-221.
- Korotcenkov, G. 2007. Metal oxides for solid-state gas sensors: What determines our choice? **Mater. Sci. Eng. B.** 139: 1-23.
- Li, S., L. Jing, W. Fu, L. Yang, B. Xin and H. Fu. 2007. Photoinduced charge property of nanosized perovskite-type LaFeO_3 and its relationships with photocatalytic activity under visible irradiation. **Mater. Res. Bull.** 42: 203-212.
- Liu, X., H. Ji, Y. Gu and M. Xu. 2006. Preparation and acetone sensitive characteristics of nano- LaFeO_3 semiconductor thin films by polymerization complex method. **Mater. Sci. Eng. B.** 133: 98-101.
- Liu, X., B. Cheng, J. Hu, H. Qin and M. Jiang. 2008. Semiconducting gas sensor for ethanol based on $\text{LaMg}_x\text{Fe}_{1-x}\text{O}_3$ nanocrystals. **Sens. Actuators B.** 129: 53-58.
- Song, P., H. Qin, L. Zhang, K. An, Z. Lin, J. Hu and M. Jiang. 2005. The structure, electrical and ethanol-sensing properties of $\text{La}_{1-x}\text{Pb}_x\text{FeO}_3$ perovskite ceramics with $x \leq 0.3$. **Sens. Actuators B.** 104: 312-316.
- Song, P., H. Qin, X. Liu, S. Huang, R. Zhang, J. Hu and M. Jiang. 2006. Structure, electrical and CO-sensing properties of the $\text{La}_{0.8}\text{Pb}_{0.2}\text{Fe}_{1-x}\text{Co}_x\text{O}_3$ system. **Sens. Actuators B.** 119: 415-418.
- Toan, N.N., S. Saukko and V. Lantto. 2003. Gas sensing with semiconducting perovskite oxide LaFeO_3 . **Phys. B.** 327: 279-282.
- Wang, Y., Y. Wang, J. Cao, F. Kong, H. Xia, J. Zhang, B. Zhu, S. Wang and S. Wu. 2008. Low-temperature H_2S sensors based on Ag doped $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles. **Sens. Actuators B.** 131: 183-189.