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Preparation of nanosized La_2CuO_4 perovskite oxide using an amorphous heteronuclear complex as a precursor at low-temperature

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Abstract

The amorphous precursor of $La_2Cu(DTPA)_{1.6}\cdot 6H_2O$ was synthesized by a simple inorganic reaction, and nanosized La_2CuO_4 cuprate oxide with a perovskite structure was prepared by the decomposition of the amorphous precursor at a low temperature in air. DTA and TGA analysis indicates that the precursor of $La_2Cu(DTPA)_{1.6}\cdot 6H_2O$ can completely be decomposed into cuprate oxide at a temperature above 500°C. XPS reveals that the decomposed species is composed of La_2CuO_4 cuprate oxide after the precursor is calcined at 500°C for 2 h. XRD demonstrates that La_2CuO_4 cuprate oxide formed at 500°C is amorphous. Nanosized La_2CuO_4 crystalline powder with a perovskite structure is formed after the calcination temperature is increased to 650°C. TEM shows that the decomposed oxide has a plate texture when the calcination temperature is 500°C. After the calcination temperature is increased to 650°C, the La_2CuO_4 cuprate oxide exists as particles and the dispersion is homogenous. The average crystal size is about 28.7 nm and does not change too much with the increase of calcination time. The temperature also has few effects on the particle size after the crystal is formed above 650°C. The above results demonstrate that this is a useful way to synthesize nanosized perovskite oxides using an amorphous complex as the precursor.

Keywords: La_2CuO_4; Nanosized; Perovskite structure; Cuprate oxide; Amorphous heteronuclear complex

1. Introduction

There is great interest in perovskite oxides and they have been widely studied for their various properties and applications in recent decades. They can be used as superconductors, as their critical temperature decreases linearly with increasing A-site disorder, as quantified by the variance in the distribution of A-site cation radii. The critical temperature is also very sensitive to lattice strains [1]. $(RE)_2CuO_4$ perovskites have variety in their magnetic and electrical characteristics. They show semiconductor behavior below room temperature [2,3]. The catalytic properties of the perovskite oxides also make them effective in various oxidation and reduction reactions [4]. They have been considered as promising substitutes to the classical Pt/Rh-based catalysts applied to automotive pollution control [5–7]. In addition, perovskite oxides are also good materials for electrodes of secondary batteries and fuel batteries [8,9].

Different preparation methods of the perovskite oxides result in different properties of these materials. Such methods include co-melting, freeze-drying, spray-drying, precipitation, sol–gel, etc. [10,11]. It has been reported that the catalytic activity of some materials prepared by the different methods has the following sequence: freeze-drying>spray-drying>precipition [12]. Nanosized particles and thin films are not easily obtained by the traditional methods. It has been shown that the co-melting method by the solid state reaction needs temperatures as high as about 1050°C. It is difficult to synthesize nanosized materials by this method. The sol–gel method has been widely used to prepare nanosized materials, but its application is limited by the stability of its precursor system and it is difficult to control the chemical composition of complex oxides [13].

In this paper, the nanosized perovskite oxide La_2CuO_4 was prepared using an amorphous heteronuclear complex as a precursor. The crystalline phase with a perovskite structure can be obtained after the precursor is calcined at 650°C for 1 h. The average crystal size does not change too much with the calcination temperature and time. It has

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been proved that the heteronuclear complex can be decomposed and form oxides at relatively low temperatures. It is much easier to prepare complex oxides using complex precursors because they can be synthesized more easily and the chemical composition can be controlled more quantitatively.

2. Experimental

2.1. The synthesis of the $La_2Cu(DTPA)_{1.6}\cdot 6H_2O$ precursor

Firstly, a 1.0 mol/l NaOH solution was added in drops into the mixture/solution of $La(NO_3)_3$ and $Cu(NO_3)_2$ to prepare fresh $La(OH)_3$ and $Cu(OH)_2$ depositions. Then, diethylenetriaminepentaacetic acid (H_5DTPA) in a calculated molar ratio was mixed with $La(OH)_3$ and $Cu(OH)_2$ in water to synthesize the complex precursor. The mixture was stirred and heated to 80°C to promote the reaction of the mixture. After the mixture became a dark-blue transparent solution, it was vaporized slowly at room temperature until a piece of transparent glass-like material formed. The precursor was obtained after the solution was dried completely. XRD patterns demonstrated that the complex precursor was amorphous. The ICP result showed that the ratio of La:Cu in this compound was almost 2:1.

2.2. The preparation of the La_2CuO_4 cuprate compound

The La_2CuO_4 cuprate oxide was prepared by decomposing the precursor in air. At first, the temperature was raised to 450°C at a slow heating rate (6°C/min). The sample was kept at this temperature for 90 min to promote the decomposition of organic components. Then, the temperature increased to various pre-set temperatures and maintained for a definite period of time to promote the formation of cuprate oxide.

2.3. Experimental techniques

XRD experiments were carried out using a Rigaku DMAX-2400 diffractometer with Cu Kα radiation. The grain size was measured using a Hitachi H-800 transmission electron microscope (TEM). The accelerating voltage of the electron beam was 200 kV. TGA and DTA analyses were performed on a Dupond 1090 thermal analyzer. The atmosphere was air, and the heating rate was 10°C/min. The XPS spectra were measured in a PHI 5300 ESCA system. An Al Kα X-ray source with a power of 250 W was used. The pass energy of the analyzer was set at 37.25 eV and the base pressure of the analysis chamber was better than 4×10^{-8} Torr. The charge effect was calibrated using the binding energy of C 1s [14].

3. Results and discussion

3.1. The thermal decomposition

The thermal analysis results of TGA for the $La_2Cu(DTPA)_{1.6}\cdot 6H_2O$ complex are shown in Fig. 1. The change of residual weight with temperature is shown by the solid curve and the dashed curve shows the differential of the weight loss. With the temperature rising, five weight loss regions were observed in the solid curve. According to the quantity calculation of the weight loss in each region, the thermal decomposition processes were distinguished as follows: The weight loss peak at 63.2°C resulted from the loss of coordinated water. The peaks at 260.1 and 326.1°C were attributed to the decomposition of a CH_x organic component and the decomposition of the amino-group, respectively. One strong weight loss peak at 377.8°C was produced by the decomposition of the carboxyl copper group and the other strong weight loss peak at 463.7°C was resulted from the decomposition of the carboxyl lanthanum group. No further peak or weight loss appears thereafter, indicating that all organic components have been eliminated after the sample was calcined above 500°C.

The DTA result is showed in Fig. 2. Two exothermic peaks were observed on the DTA curve. The temperature region from 20 to 400°C is amplified five times. The peak at 307.5°C was produced by the burning of the CH_x and amino-groups. The peak at 365.2°C was produced by the decomposition of the carboxyl copper group. The peak at 474.3°C was very strong, which contained both the exothermic contribution from the decomposition of the carboxyl lanthanum group and the formation of the La_2CuO_4 complex oxide. Because the exothermic heat of the carboxyl group was little, most of the exothermic heat came from the formation of the cuprate. The above results

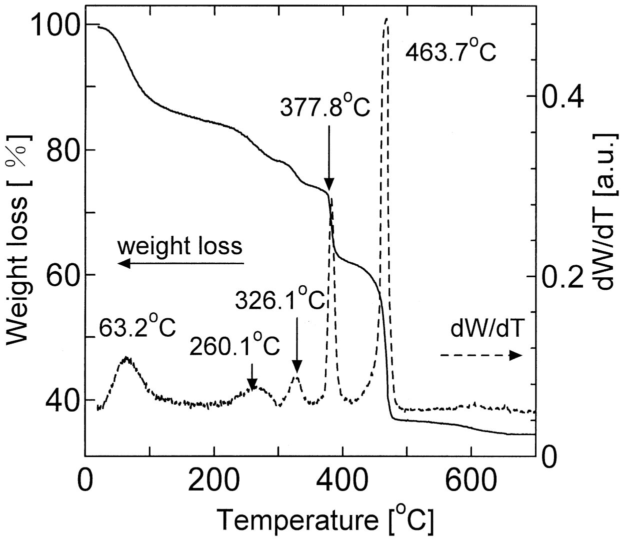

Fig. 1. The TGA spectrum of the $La_2Cu(DTPA)_{1.6}\cdot 6H_2O$ precursor.

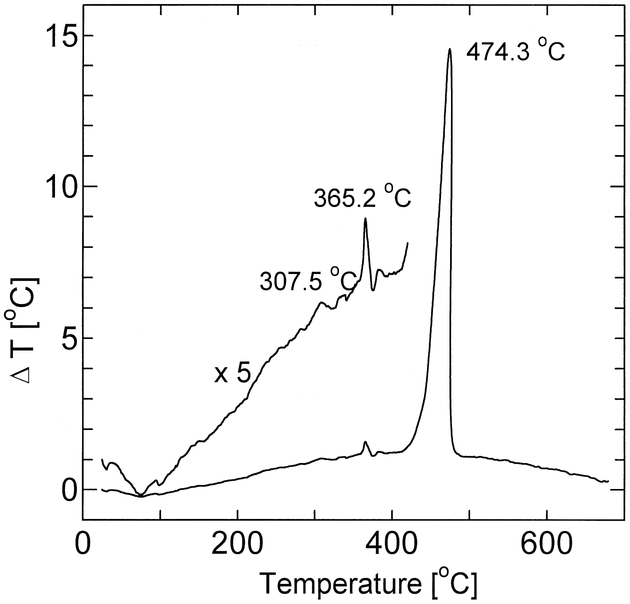

Fig. 2. The DTA spectrum of the $La_2Cu(DTPA)_{1.6}\cdot 6H_2O$ precursor.

suggest that the La_2CuO_4 oxide can be formed below 500°C by decomposing the amorphous complex of $La_2Cu(DTPA)_{1.6}\cdot 6H_2O$.

3.2. The crystallization of the La_2CuO_4 compound

The influence of the calcination temperature on the formation of the La_2CuO_4 crystalline phase was investigated using XRD. The XRD patterns of the La_2CuO_4 samples calcined at different temperatures are shown in Fig. 3. After the precursor was calcined at 500 or 600°C for 2 h, it was showed that the sample was turned into a quasi-crystalline phase. The main peaks were similar with that of the La_2CuO_4 crystalline phase except that the peaks shifted to the low diffraction angle. The peak at 35.6° (2θ) was due to some kind of intermediate. Several sharp peaks were observed after the precursor was calcined at 650°C even for 1 h. According to the XRD standard spectrum of the La_2CuO_4 crystal, these peaks are attributed to the pure perovskite-type La_2CuO_4 crystal. This result indicates that La_2CuO_4 with a pure perovskite structure can be synthesized by this method at 650°C. With the calcination temperatures rising, the peak intensity does not change significantly. This can be explained by the crystalline phase of La_2CuO_4 not growing up with the calcination temperature.

The influence of the calcination time on the formation of the La_2CuO_4 crystalline phase was also studied by XRD, as shown in Fig. 4. Even after the precursor was calcined at 650°C for 1 h, the perovskite crystalline phase was formed. The XRD patterns were unchanged with increasing calcination time. This result shows that the calcination time also has a weak influence on the crystalline phase.

These results indicate that the La_2CuO_4 crystalline phase can be formed at a relatively low temperature (650°C) using an amorphous complex as a precursor. The influence of the calcination temperature is as weak as that of the calcination time after the crystalline phase is formed.

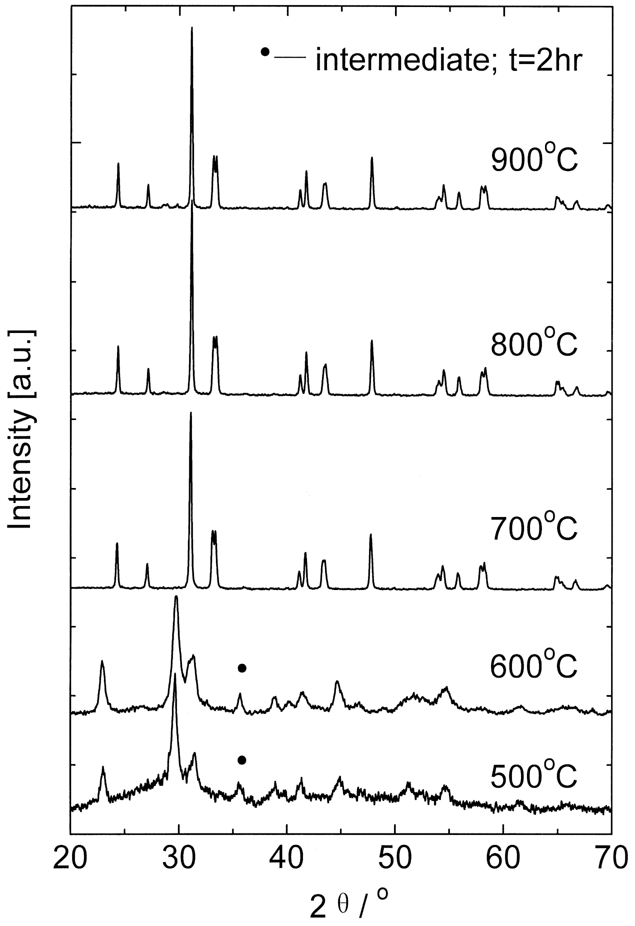

Fig. 3. The XRD patterns of samples calcined at different temperatures for 2 h.

3.3. The identification of the La_2CuO_4 species

The chemical composition of the decomposed samples were determined using XPS. The spectra of Cu 2p in the decomposed samples calcined at 500 and 800°C for 2 h are shown in Fig. 5. The binding energies of Cu $2p_{3/2}$ in CuO and pure Cu are 933.6 and 932.4 eV, respectively [14]. The binding energy of Cu $2p_{3/2}$ in the decomposed sample of 500°C was 933.0 eV, which was lower than that in copper oxide. The binding energy of Cu $2p_{3/2}$ in the decomposed sample of 800°C was 932.6 eV, which was a little higher than that in pure copper. This result indicated that Cu atoms did not exist as either simple copper oxides or pure copper in the decomposed samples. Furthermore, the line shape of Cu 2p in the decomposed species was different from that in the CuO and Cu_2O compounds, and it was closed to that in pure copper. From the results of Cu 2p, it can be considered that Cu existed as the cuprate compound

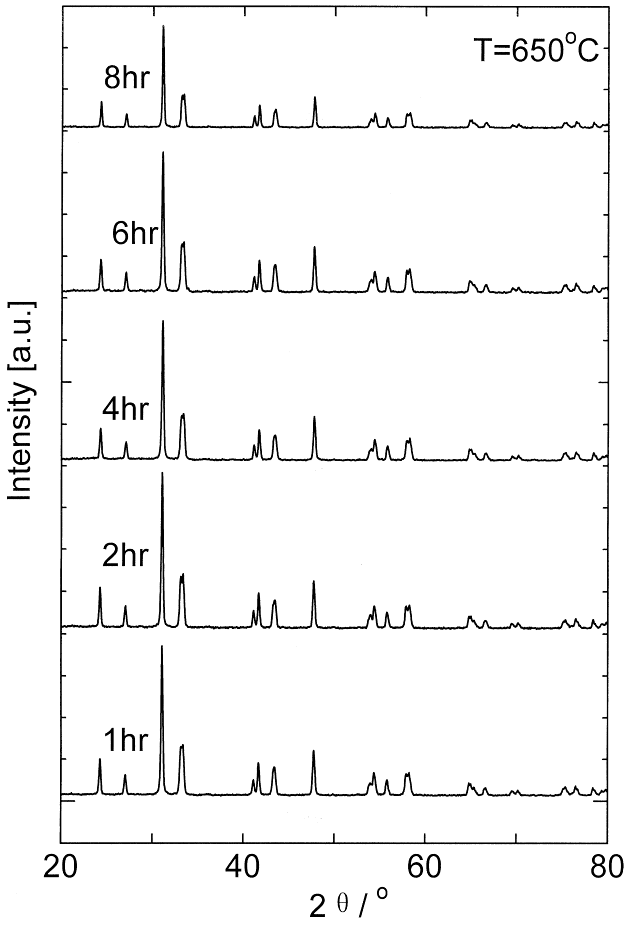

Fig. 4. The XRD patterns of samples calcined at 650°C for different periods of time.

in the decomposed samples, implying that the precursor has decomposed into the La_2CuO_4 compound after it was treated at 500°C for 2 h. The shake-up peaks of Cu 2p in calcined samples at low-temperature were stronger. They decreased with the rising of the calcination temperature, suggesting that the shake-up peak resulted from the carboxyl copper.

The O 1s spectrum consists of two distinct oxygen peaks. The binding energies are 528.7 and 531.4 eV, respectively, in the sample decomposed at 800°C, which are both different from that of La_2O_3 (528.6 eV) and those in the simple oxides of CuO (529.6 eV) and Cu_2O (530.3 eV) [14]. This result shows that there are two chemical environments of the O element in this perovskite oxide. The binding energies of La 3d in pure La and La_2O_3 compounds were 835.8 and 833.7 eV, respectively [14]. The binding energy of La 3d in the decomposed sample annealed at 500°C for 2 h was 833.4 eV and that of the sample of 800°C 2 h was 833.6 eV. These two values were close and the line shapes were also alike. It shows that the La element in the perovskite oxide has a stronger polarization ability and a more remarkable relaxation phenomenon.

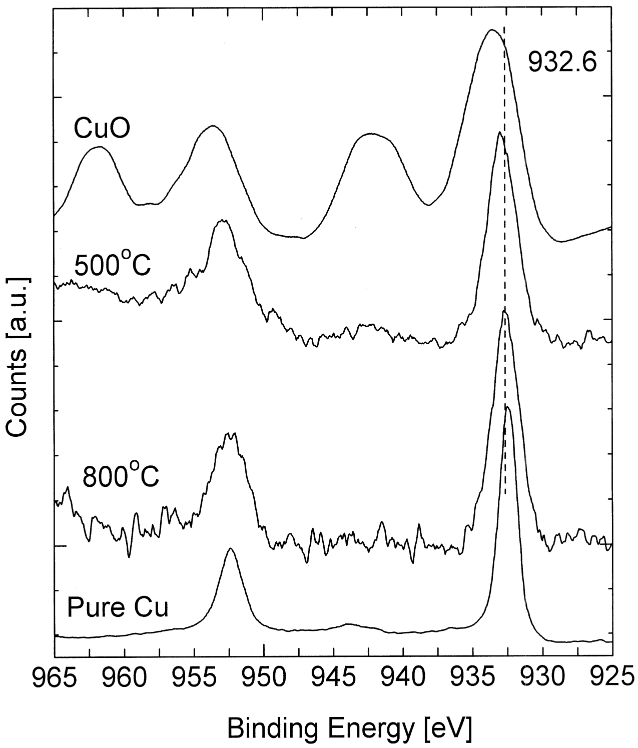

Fig. 5. The Cu 2p spectra of the sample calcined at 500 and 800°C for 2 h.

This result suggests that the decomposed sample is cuprate oxide. It can be concluded from the above results that the precursor can be decomposed into La_2CuO_4 oxide after calcinated at temperatures above 500°C in air.

3.4. The grain size and crystal size of the La_2CuO_4 species

The grain size of the La_2CuO_4 compound varied with calcination temperatures was studied using TEM as shown in Fig. 6. The grain edge of the sample calcined at 600°C for 2 h was a little dim as Fig. 6a shows, indicating that the sample was quasi-crystal after it was calcined at this temperature. This result agrees with that of XRD. The photos also show that the grain size was homogenous and fairly small when the sample was obtained at the calcination temperature of 800°C. The grain size did not grow when the precursors were calcined at the much higher temperature of 900°C for 2 h (Fig. 6b). The grain size kept at about 25 nm.

The dependence of the average grain size on the heat-treatment time was also investigated at 650°C. The TEM photos show that the heat-treatment time also has a weak effect on the grain size. The samples calcined for 1–8 h separately have a similar grain size, which is about 100 nm. This result shows that the calcination time has little influence on the grain size.

The average crystal sizes can be determined from the

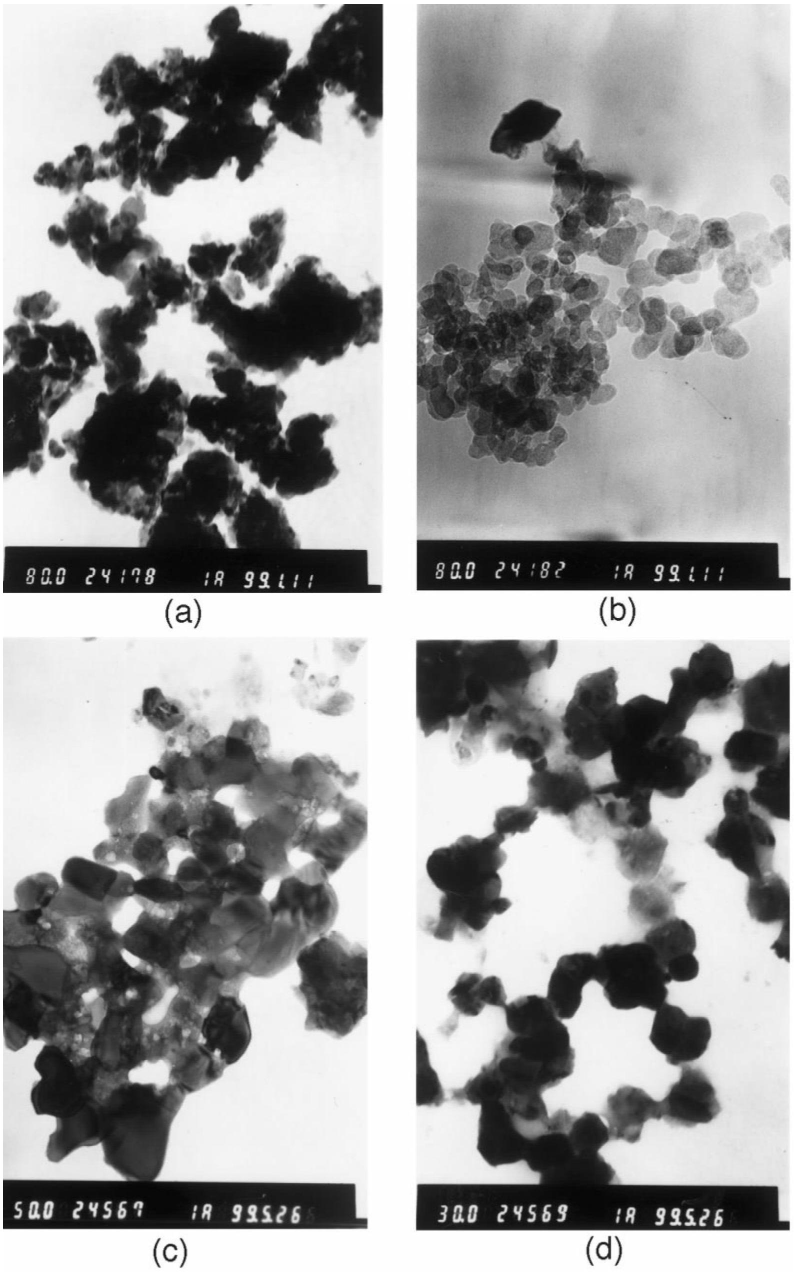

Fig. 6. The TEM photos of the calcined samples. (a) The sample calcined at 600°C for 2 h (80 000 times); (b) the sample calcined at 900°C for 2 h (80 000 times); (c) the sample calcined at 650°C for 2 h (50 000 times); (d) the sample calcined at 650°C for 8 h (30 000 times).

XRD pattern parameters according to the Scherrer equation: $D_c = K\lambda/\beta \cos\theta$. D_c is the average crystal size, K is the Scherrer constant equal to 0.89, λ is the X-ray wavelength equal to 0.1542 nm and β is the full width at half-maximum (FWHM) and θ is the diffraction angle [11]. It is calculated according Figs. 3 and 4 that the species calcined above 650°C have a similar crystal size of about 28.7 nm. It is revealed that the calcination temperature has as little influence on the average crystal size as the calcination time does.

4. Conclusions

1. Nanosized La_2CuO_4 cuprate oxide was synthesized using the amorphous heteronuclear complex $La_2Cu(DTPA)_{1.6} \cdot 6H_2O$ as a precursor at a relatively low calcination temperature. To form the perovskite crystalline phase of La_2CuO_4, the calcination temperature should be higher than 650°C. This work showed that it was an effective method to synthesized the

nanosized La_2CuO_4 oxide using an amorphous heteronuclear complex as a precursor.

2. The grain size was in nano-scale even though the precursor was calcined at 900°C. The crystal size did not change with the calcination temperature above 650°C and the calcination time also had little influence on the crystal size.

References

[1] J.P. Attfield, A.L. Kharlanov, J.A. McAllister, Nature 394 (1998) 157.

[2] K. Asai et al., Phys. Rev. B50 (1994) 3025.

[3] S. Yamaguchi, Y. Okimoto, Y. Tokura, Phys. Rev. B54 (1996) 11 022.

[4] L.G. Tejuca, J.L.G. Fierro, J.M.D. Tascon, in: Adv. Catal., Academic Press, San Diego, 1998, p. 237.

[5] D.B. Meadowcroft, Nature 226 (1970) 847.

[6] N. Mizuno, M. Yamato et al., J. Catal. 132 (1991) 560.

[7] J.A. Anderson, J.L.G. Fierro, J. Solid State Chem. 108 (1994) 305.

[8] S.B. Adler, J.A. Lane, B.C.H. Steele, J. Electrochem. Soc. 143 (11) (1996) 3554.

[9] D.W. Johnson Jr., P.K. Gallagher, F. Schrey, W.W. Rhodes, Am. Ceram. Soc. Bull. 55 (1976) 520.

[10] L. Simonot, F. Garin, G. Maire, Appl. Catalysis B: Environ. 11 (1997) 181.

[11] G. Xiong, Z.-L. Zhi, X.J. Yang et al., J. Mater. Sci. Lett. 16 (1997) 1064.

[12] N. Mizuno, Catal. Today 8 (1990) 221.

[13] M. Guglielmi, G. Carturan, J. Non-Crystalline Solids 100 (1988) 16.

[14] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, in: J. Chastain (Ed.), Handbook of X-Ray Photoelectron Spectroscopy, Perkin-Elmer Corporation, Eden Prairie, MN, 1992.