JOURNAL OF MATERIALS SCIENCE **36** (2001) 2287–2290

Effect of Fe_2O_3 crystallite size on its mechanochemical reaction with La_2O_3 to form $LaFeO_3$

QIWU ZHANG, FUMIO SAITO
Institute for Advanced Materials Processing, Tohoku University,
2-1-1, Katahira, Aoba-ku, Sendai 980-8577. Japan
E-mail: zqw@iamp.tohoku.ac.jp

Fe_2O_3 powders with different crystallite sizes prepared by heating FeOOH at various temperatures were ground with La_2O_3 powder using a planetary ball mill to investigate the effect of crystallite size on mechanochemical synthesis of $LaFeO_3$. Fe_2O_3 powder with smaller crystallite size obtained by heating at lower temperature reacts more easily with La_2O_3 than that with larger size. The mechanochemical reaction proceeds with an increase in grinding time. Specific surface area of the $LaFeO_3$ powder synthesized has a large value of over 11 m^2/g. The mechanochemical process can be also applied to synthesize other iron complex oxides with rare earth elements such as Pr, Nd and Sm.

1. Introduction

Perovskite-type complex oxides, $RMeO_3$ (R = rare earth elements, Me = transition metals such as Mn, Fe, Co, Cr), have been studied for utilization as functional materials such as catalysts [1, 2], magnetic materials [3, 4], sensing materials [5–8], electrode materials for solid-oxide fuel cell [9, 10]. In the case of Fe as a transition metal, investigations have been intensively conducted on oxidation catalysis and gas sensing ability for NO_x [11, 12] and CO [13, 14]. It is well known that the properties of these materials depend on their synthesis processes and preparation of ultrafine homogeneous powders is of primary importance. Besides the conventional method based on solid-state reaction between R_2O_3 and Fe_2O_3 at high temperature, much effort has been paid on the development of innovative chemical solution methods, namely thermal decomposition of wet-chemically precipitated precursors to synthesize $RFeO_3$ [15–20]. These methods can provide products of fine and homogeneous particles, but their processes of formation are generally complicated and the reagents used are expensive. Although the solid-state reaction method has some drawbacks such as large particle size and limited degree of chemical homogeneity, it is a simple operation and use inexpensive oxides as starting materials. Another route for preparation of these fine particles may be a mechanochemical method. The authors have attempted to synthesize $LaFeO_3$ by grinding the mixture of La_2O_3 and Fe_2O_3 powders by a high-energy ball mill at room temperature. It has been found that the crystal state of the starting Fe_2O_3 sample is of much importance in completion of the mechanochemical solid reaction.

The main purpose of this paper is to provide the basic information about the effect of both Fe_2O_3 crystallite size and grinding time on the mechanochemical reaction for synthesizing $LaFeO_3$. In addition, this paper indicates the possibility of synthesizing other rare earth and iron complex oxides, $RFeO_3$ (RE = Nd, Pr, Sm).

2. Experimental

Rare earth oxide samples used in the experiment were La_2O_3, Nd_2O_3, Pr_6O_{11}, Sm_2O_3, with purity of 99.9%, supplied from Shin-Etsu Chemical Co., Ltd. Japan. Fe_2O_3 powder was prepared by heating iron hydroxide oxide (FeOOH, Kanto Chemicals Ltd., Japan), at 6.67°C/min up to different temperatures from 200°C to 1000°C. The heated samples were cooled down naturally. The Fe_2O_3 sample was mixed with the La_2O_3 powder at equivalent molar ratio to be starting mixtures for grinding.

A planetary ball mill (Fritsch Pulverisette-7, Germany) was used to grind the starting mixtures. 3 grams of the mixture were put in a zirconia pot of 45 cm^3 inner volume with 7 zirconia balls of 15 mm diameter. The grinding was operated in air at approximately 650 rpm for different periods of time.

The ground products were characterized by X-ray diffraction (XRD) (RAD-B system, Rigaku, Japan) using Cu-K_α radiation to identify phases formed after grinding. Morphology of the ground sample was observed by a scanning electron microscope (SEM, S4100, Hitachi, Japan). Specific surface area (SSA) of the samples was measured by a nitrogen gas adsorption instrument (ASAP2010, Micromeritics, Shimadzu, Japan) based on the BET method.

0022–2461 © *2001 Kluwer Academic Publishers*

3. Results and discussion

3.1. Formation of $LaFeO_3$

All the heated samples from FeOOH powders were confirmed to be the hematite phase of Fe_2O_3 by XRD analysis. The crystallite size of the prepared sample was calculated based on the half-width of (104) peak using the Scherrer equation. Fig. 1 shows the change in crystallite size of Fe_2O_3 with the heating temperature. It is clear that the crystallite size increases rapidly with an increase in heating temperature. Fig. 2 shows XRD patterns of 120 min ground mixtures of La_2O_3 and Fe_2O_3 with different crystallite size. When the Fe_2O_3 sample with crystallite size less than 20 nm is used, a single phase of $LaFeO_3$ (JCPDS No.: 37-1493) is obtained. This result indicates that the following solid reaction has taken place mechanochemically.

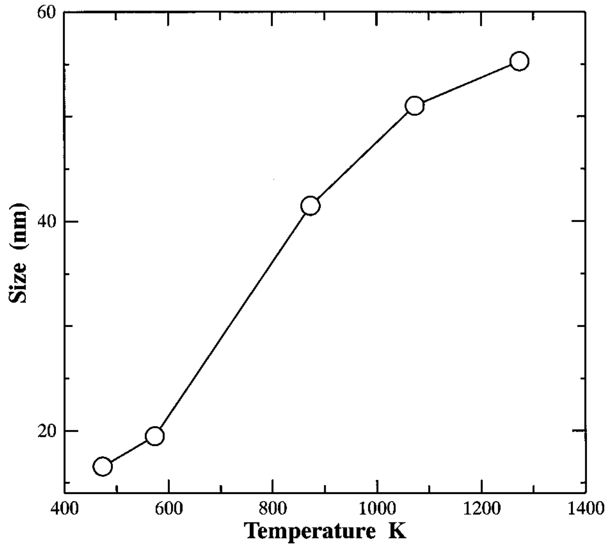

Figure 1 Change in crystallite size of Fe_2O_3 sample with the heating temperature.

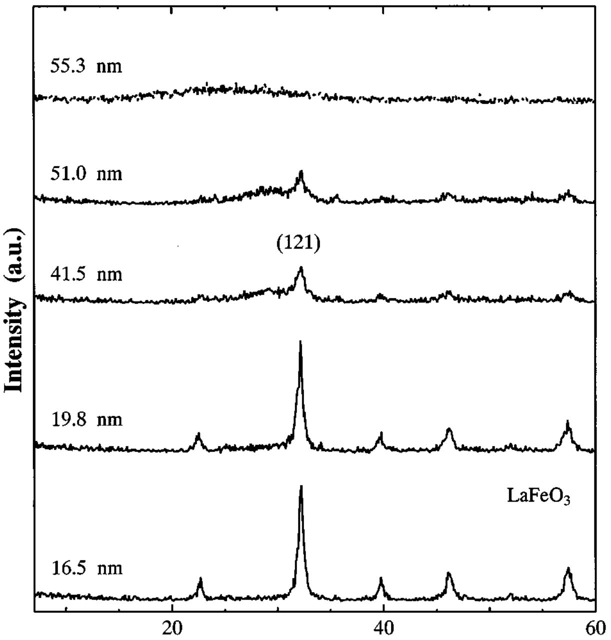

Figure 2 XRD patterns of the 120 min ground mixture of La_2O_3 and Fe_2O_3 with different grain sizes.

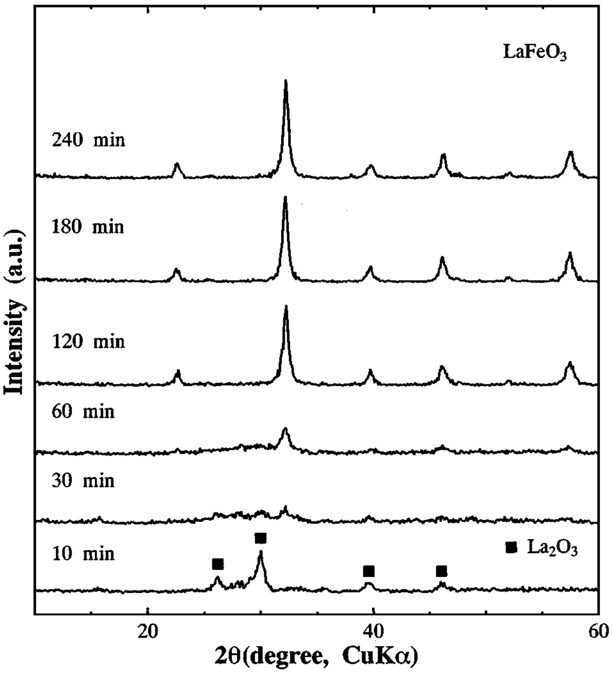

Figure 3 XRD patterns of the La_2O_3 and Fe_2O_3 (16.5 nm) mixture ground for different times.

$$La_2O_3 + Fe_2O_3 = 2LaFeO_3 \qquad (1)$$

When the Fe_2O_3 sample with crystallite size around 40 nm is used, a weak peak from (121) reflection of $LaFeO_3$ has appeared in a nearly amorphous pattern. This suggests that the reactivity of the Fe_2O_3 sample becomes low and the reaction given by Equation (1) to form $LaFeO_3$ has partly taken place. When the sample with larger crystallite size over 55 nm is used, no formation of $LaFeO_3$ is obtained.

Fig. 3 shows the XRD patterns of the La_2O_3 and Fe_2O_3 mixture ground for different times, where the Fe_2O_3 sample with crystallite size of 16.5 nm was used. Only peaks of the starting oxide were observed in the pattern of the mixture ground for 10 min, and the peak intensity decreases with an increase in grinding time. A new peak appears in the patterns of the mixture ground for 60 min or more due to the formation of $LaFeO_3$, and its intensity increases as the grinding progresses. Prolonged grinding over 120 min enables us to synthesize $LaFeO_3$ of single phase.

Fig. 4 shows an SEM picture of the sample ground for 240 min. In the photo A, the product seems to be agglomerated having sizes of several microns. It is found from the photo B that these agglomerates consist of fine primary grains with about 100 nm order in size.

Fig. 5 shows specific surface area (SSA) of the ground samples, shown in Fig. 3 as a function of grinding time. In the early stage of grinding operation, the SSA decreases rapidly and reaches about 3.2 m^2/g at 30 min grinding. This value is maintained till 60 min and increases gradually up to 11.1 m^2/g at 240 min grinding. Rapid decrease in SSA indicates that agglomeration of the starting powders proceeds predominantly in the early stage of grinding. The leveling off of SSA in the range from 30 to 60 min indicates a kind equilibrium state between the agglomeration and disagglomeration.

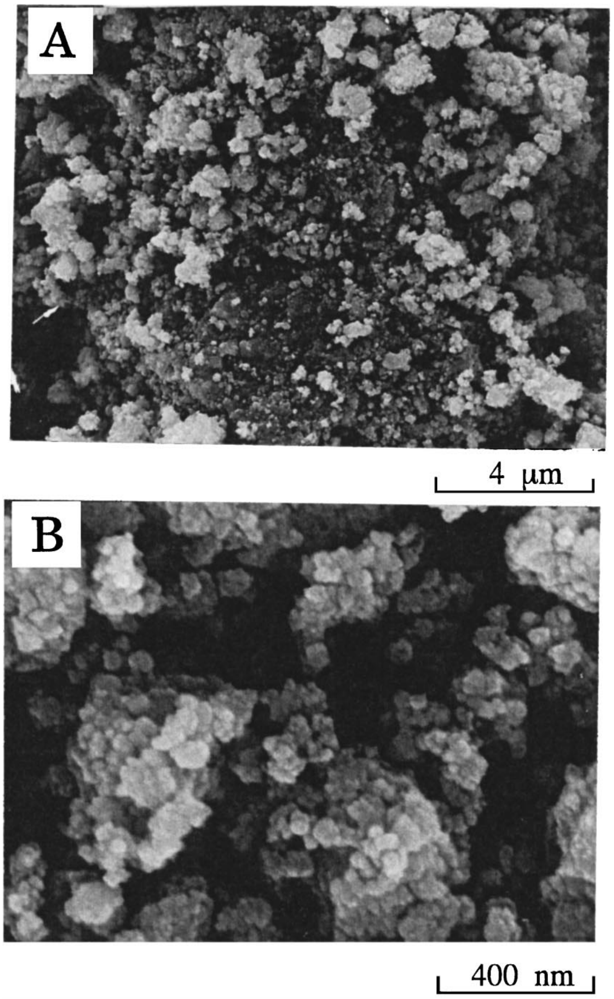

Figure 4 SEM photographs of the 240 min ground sample.

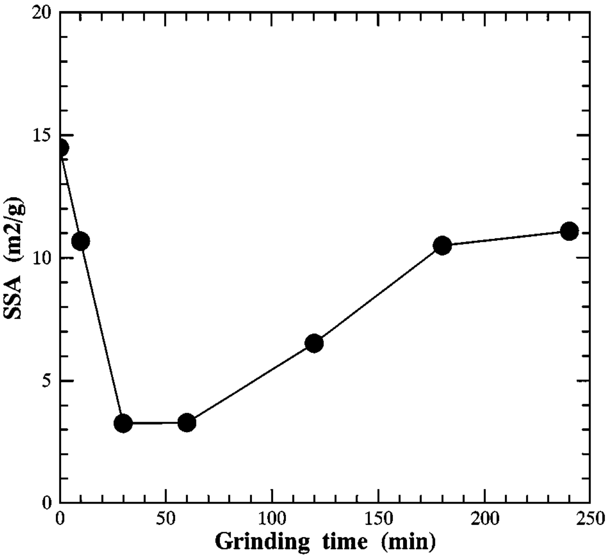

Figure 5 Change in specific surface area (SSA) of the sample with grinding time.

Then, $LaFeO_3$ is formed through the recrystallization of the deeply mixed composite through the repeated agglomeration and regrinding. As to the reason of increase in SSA again by the prolonged grinding, disagglomeration due to grinding will become the main action against agglomeration, when $LaFeO_3$ becomes the main composition in the ground sample. This is under the consideration that agglomeration between the same $LaFeO_3$ particles will take place not so heavily compared with that between the heterogeneous fine particles in the early stage of grinding. Therefore the SSA increases gradually again. The final $LaFeO_3$ product of 240 min ground sample gives out a large SSA value over 11 m^2/g. This value is comparable to that by some chemical solution methods.

3.2. Formation of $RFeO_3$ ($R = Nd$, Pr, and Sm)

Complex oxides of Fe and other rare earths (R), namely, $RFeO_3$, have the perovskite structure and show similar physico-chemical properties to that of $LaFeO_3$. Synthesis of $RFeO_3$ ($R = Nd$, Pr and Sm) was examined by the mechanochemical method. The grinding operation was conducted at the same condition as that for the synthesis of $LaFeO_3$, using Fe_2O_3 sample with crystallite size of 16.5 nm. Since praseodymium oxide exists as Pr_6O_{11} [21] in air, it was mixed with the Fe_2O_3 powder in molar ratio of 1 : 3. The other oxides, R_2O_3, were mixed with the Fe_2O_3 powder at equimolar ratio. Fig. 6 shows the XRD patterns of the mixed samples ground for 180 minutes. All cases give us the new patterns of $NdFeO_3$ (JCPDS No.25-1149), $PrFeO_3$ (JCPDS No.15-134) and $SmFeO_3$ (JCPDS No.39-1490), respectively. The XRD analysis has confirmed that the rare earth oxides Nd_2O_3 and Sm_2O_3 react with the Fe_2O_3 powder to form $NdFeO_3$ and $SmFeO_3$ in the similar manner as the case of La_2O_3 by the grinding operation according to the following two reactions:

$$Nd_2O_3 + Fe_2O_3 = 2NdFeO_3 \quad (2)$$

$$Sm_2O_3 + Fe_2O_3 = 2SmFeO_3 \quad (3)$$

However, in the case of Pr_6O_{11}, The solid reaction seems to proceed in a different way as follows. The

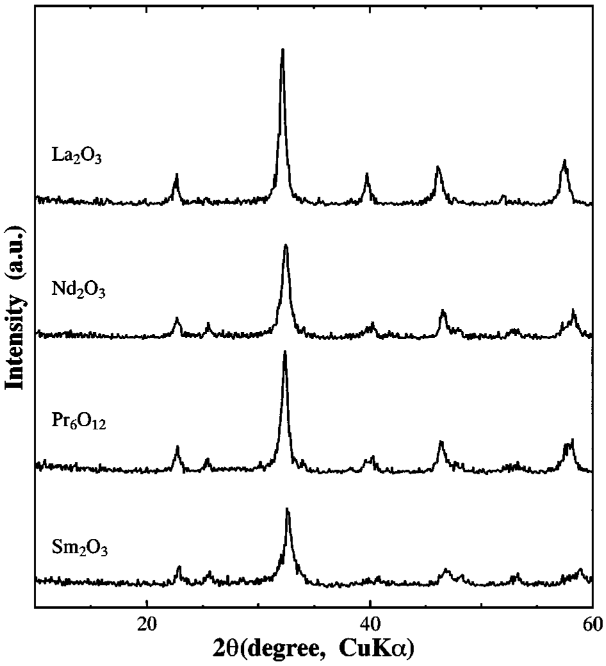

Figure 6 XRD patterns of the R_2O_3 and Fe_2O_3 mixture ground for 180 min.

reaction will involve the release of oxygen, which was confirmed during the experiment. Gas release was observed when the pot was opened after grinding.

$$1/3\mathrm{Pr_6O_{11}} + \mathrm{Fe_2O_3} = 2\mathrm{PrFeO_3} + 1/3\mathrm{O_2} \qquad (4)$$

SSA of the prepared $RFeO_3$ samples are found in the range of 8–10 m^2/g, indicating that the grinding method is useful to prepare fine and homogeneous $RFeO_3$ materials.

4. Conclusions

The following conclusions can be made from the present experiment.

(1) $LaFeO_3$ powder can be simply synthesized mechanochemically by room temperature grinding of La_2O_3 and Fe_2O_3 powders when the Fe_2O_3 sample with crystallite size less than 20 nm is used. This solid reaction tends to be difficult with the increase in crystallite size of Fe_2O_3 powder. The synthesis reaction proceeds with an increase in grinding time.

(2) The obtained $LaFeO_3$ powder sample consists of agglomerates with fine grains of nanometer size. It gives a relatively high value in specific surface area of about 11 m^2/g.

(3) This mechanochemical method can be also applicable to the synthesis of iron complex oxides with other rare earths such as Pr, Nd and Sm.

Acknowledgment

The authors are grateful to Shin-Etsu Chemical Co., Ltd. Japan for kindly supplying the rare earth oxides samples.

References

1. W. F. LIBBY, *Science* **171** (1971) 449.
2. N. YAMAZOE and Y. TERAOKA, *Catalysis Today* **8** (1990) 175.
3. A. ASAMITSU, Y. MORITOMO, Y. TOMIOKA, T. ARIMA and Y. TOKURA, *Nature* **373** (1995) 407.
4. C. N. R. RAO and B. RAVEAU (Eds.), "Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides" (World Scientific Publishing Co. Pte, Ltd., Singapore, 1998) p. 189.
5. T. ARAKAWA, H. KURACHI and J. SHIOKAWA, *J. Mater. Sci.* **4** (1985) 1207.
6. T. ARAKAWA, K. TAKADA, Y. TSUNEMINE and J. SHIOKAWA, *Sens, Actuators* **14** (1988) 215.
7. J. P. LUKASZEWICZ, *Sens. Actuators B* **4** (1991) 227.
8. Y. MATSUURA, S. MATSUSHIMA, M. SAKAMOTO and Y. SADAOKA, *J. Mater. Chem.* **3** (1993) 767.
9. H. TAIMATSU, K. WADA and H. KANEKO, *J. Amer. Ceram. Soc.* **75** (1992) 401.
10. L. KINDERMANN, D. DAS, H. NICKEL and K. HILPERT *J. Electrochem. Soc.* **144** (1997) 717.
11. E. TRAVERSA, S. MATSUSHIMA, G. OKADA, Y. SADAOKA, Y. SAKAI and K. WATANABE, *Sens. Actuators B* **25** (1995) 661.
12. E. TRAVERSA, S. VILLANTI, G. GUSMANO, H. AONO and Y. SADAOKA, *J. Amer. Ceram. Soc.* **82** (1999) 2442.
13. W. B. LI, H. YONEYAMA and H. TAMURA, *Nippon Kagaku Kaishi* (1982) 761.
14. Y. TAKAHASHI and H. TAGUCHI, *J. Mater. Sci. Lett.* **3** (1984) 251.
15. M. P. PECHINI, U.S. Patent no. 3.330.697 (1967).
16. P. K. GALLAGHER, *Mater. Res. Bull.* **3** (1968) 225.
17. H. M. ZHANG, Y. TERAOKA and N. YAMAZOE, *Chem. Lett.* (1987) 665.
18. C. D. CHANDLER, C. ROGER and M. J. HAMPDEN-SMITH, *Chem. Rev.* **93** (1993) 1205.
19. Y. SADAOKA, K. WATANABE, Y. SAKAI and M. SAKAMOTO, *J. Alloys Compounds* **224** (1995) 194.
20. E. TRAVERSA, M. SAKAMOTO and Y. SADAOKA, *J. Amer. Ceram. Soc.* **79** (1996) 1401.
21. G. ADACHI and N. IMANAKA, *Chem. Rev.* **98** (1998) 1479.

Received 22 February
and accepted 2 August 2000