ELSEVIER

Journal of Alloys and Compounds 408–412 (2006) 480–483

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Absorption and desorption of carbon dioxide in the rare earth oxide-doped Bi_2O_3 powder

Takao Esaka *, Kouichi Motoike

Department of Materials Science, Faculty of Engineering, Tottori University, Minami 4-101, Koyamacho, Tottori 680-0945, Japan

Received 30 July 2004; received in revised form 19 November 2004; accepted 15 December 2004

Abstract

The rare earth oxide-doped Bi_2O_3 powders were prepared by mechanical alloying (MA) method using a planetary ball-milling machine and their CO_2-absorbing/desorbing properties were investigated by TG–DTA. As a result, the sample powders were found to absorb CO_2 gas around 400–500 °C. However, the CO_2-absorption and desorption changed depending on doped rare earth oxide and sample composition; the Y_2O_3-doped Bi_2O_3 did not show absorbing and desorbing cycleability at all. Absorbed and desorbed CO_2 contents also varied with MA time. In the La_2O_3-doped Bi_2O_3, the 72 h MA'ed $(Bi_2O_3)_{0.70}(La_2O_3)_{0.30}$ was found to be the material with highest performance as for CO_2 content and cycleability.

Keywords: Disorder system; Mechanical alloying; X-ray diffraction; Thermal analysis

---

1. Introduction

Some studies have been recently carried out as to CO_2-absorbing agents in the viewpoint of energy-saving materials to eliminate carbon dioxide locally. Up to date, a few materials such as Li_2ZrO_3 [1,2] and Li_4SiO_4 [3] have been reported to have high absorbing efficiency and repeat absorption and desorption. However, the compounds could release CO_2 at high temperatures over 800 °C. Considering the total energy consumption, it is desirable for CO_2 to repeat absorption and desorption at lower temperatures. Thus, we need the materials that have high absorption rate at lower temperatures and good cycleability. We have found that the Bi_2O_3–Y_2O_3 powder can easily react with CO_2 when they were prepared by mechanical milling [4], which meant that this type of material could be a candidate for CO_2 absorbates with cyclic performance. In this study, the CO_2-absorbing and desorbing properties were investigated as to the rare earth oxide-doped Bi_2O_3 powders.

2. Experimental

After mixing Bi_2O_3 (99.9%, Wako Pure Chemicals) with Y_2O_3 (99.99%, Wako Pure Chemicals) or La_2O_3 (99.99%, Kishida chemicals) in a defined ratio, the powder was put in a zirconia pot (80 ml) with 3 ml ethanol and five zirconia balls (Ø 15). The weight ratio of the sample powder to balls was about 1:10. Milling was done using a high-energy planetary ball mill (Fritsch Pulversette5 or Itoh LP-4/2) at 260 rpm and at room temperature.

To identify phases of mechanically milled samples, X-ray diffraction (Shimadzu, XRD-6000) was carried out using Cu Kα radiation with a nickel filter. The CO_2-absorption and desorption properties of the samples were examined using differential thermal analysis (DTA) with a Shimadzu DTA-50 in a flow of argon, CO_2 or N_2–O_2 mixture gas. The heating rate was $10\,^{\circ}C\,min^{-1}$. The powder sample morphology and the particle size distribution were observed by scanning electron microscopy (SEM) and a laser diffraction method (Shimadzu, SALD-2100), respectively. Furthermore, the sample specific surface area was measured using Coulter SA3100.

---

* Corresponding author. Tel.: +81 857 31 5264; fax: +81 857 31 5264.
E-mail address: esaka@chem.tottori-u.ac.jp (T. Esaka).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2004.12.095

3. Results and discussion

Considering our previous results [4], we started to study the powder samples in the system Bi_2O_3–Y_2O_3. As a result, the obtained sample showed almost the same powdery state as the previous; α-Bi_2O_3-type solid solution seemed to be formed by 24 h MA and some amorphousness was occurred by subsequent milling.

As to a typical dry sample of $(Bi_2O_3)_{0.75}(Y_2O_3)_{0.25}$ obtained by 72 h MA, TG–DTA measurement was carried out in different atmospheres (air, Ar and CO_2). As shown in Fig. 1, sample weights generally decreased with increasing temperature in any conditions. Weight decreases in lower temperatures would be due to vaporization of some residual volatile components such as water and/or ethyl alcohol used for mixing. At the same time, exothermic peaks were observed around 200–400 °C in any cases. Considering those matters in Ar and CO_2, they might mean not only combustion of the alcohol but also phase changes from amorphous to crystalline states. A weight increase accompanying another exothermic reaction was observed above 400 °C on heating only in CO_2, which was considered to correspond to CO_2 adsorption. Furthermore, a weight decrease with an endothermic peak was observed at about 550 °C, which meant CO_2 desorption. These results indicated that $(Bi_2O_3)_{0.75}(Y_2O_3)_{0.25}$ is a material that absorbs and desorbs CO_2 at lower temperatures. However, CO_2 could not be absorbed even under the CO_2 atmosphere in the decreasing temperature. In order to avoid the sample sintering and/or the surface area shrinking, of course, the maximum measuring temperature was changed from 800 to 550 °C. Nevertheless, the sample did not show a repeated CO_2 absorption and desorption.

Next, we prepared the Bi_2O_3 powder mixed with La_2O_3, which has higher basicity than Y_2O_3. From the XRD patterns measured for the typical sample of $(Bi_2O_3)_{0.70}(La_2O_3)_{0.30}$ every 24 h MA, α-Bi_2O_3-type solid solution was found to be formed. As same as the case of $(Bi_2O_3)_{0.75}(Y_2O_3)_{0.25}$, the XRD peaks weakened and broadened with continuing MA for longer than 48 h. However, this did not coincide with the particle size measurement of the obtained powders; each sample had almost the same particle distribution profile centered around 0.2–0.3 μm.

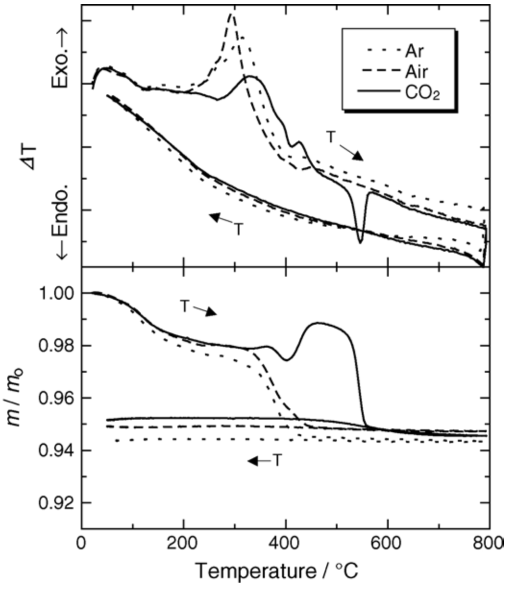


Fig. 1. TG–DTA curves measured in air, Ar and CO_2 for $(Bi_2O_3)_{0.75}(Y_2O_3)_{0.25}$ powder samples MA'ed for 72 h.

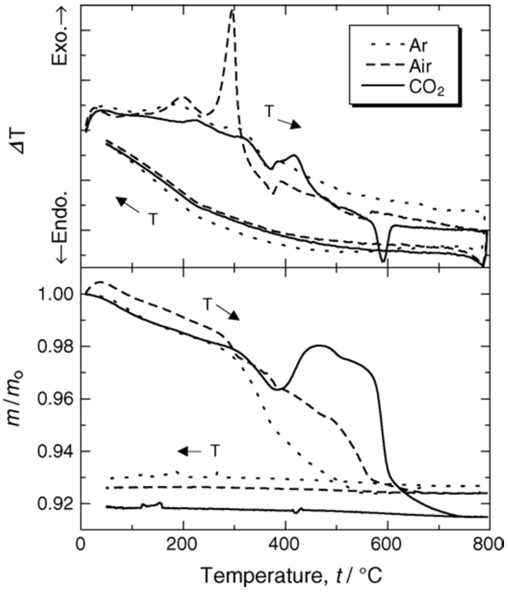


Fig. 2. TG–DTA curves measured in air, Ar and CO_2 for $(Bi_2O_3)_{0.70}(La_2O_3)_{0.30}$ powder samples MA'ed for 72 h.

For dry $(Bi_2O_3)_{0.70}(La_2O_3)_{0.30}$ obtained by 72 h MA, TG–DTA measurement was carried out. As shown in Fig. 2, sample weights were generally apt to decrease with increasing temperature in any atmospheres. A weight increase accompanying an exothermic reaction was observed on heating to 400 °C only in CO_2. Furthermore, weight decrease with an endothermic peak was observed over 600 °C, These were almost the same result as the case of $(Bi_2O_3)_{0.75}(Y_2O_3)_{0.25}$ (Fig. 1) and indicated that $(Bi_2O_3)_{0.70}(La_2O_3)_{0.30}$ is also a material that absorbs and desorbs CO_2. Here, we noticed that a typical exothermic peak was observed around 300 °C only in air, which meant combustion of alcohol in air but would not denote the phase change from amorphous to crystalline state to diminish the surface area; control of the CO_2-desorbing temperature may make the repeated CO_2 absorption and desorption possible.

Fig. 3 shows the result of weight variation (TG) when the 72 h MA'ed sample was kept at 440 °C in CO_2 for 100 min, then the atmosphere was changed to air along with the temperature increase to 500 °C. The first small weight decrease accompanied by temperature increase would be due to vaporization of residual ethyl alcohol used during milling. Before reaching 440 °C, the sample weight began to increase, which would correspond to the CO_2-absorption. Although the sample weight was still increasing at 440 °C, a big weight loss was observed with increasing the temperature to 500 °C and

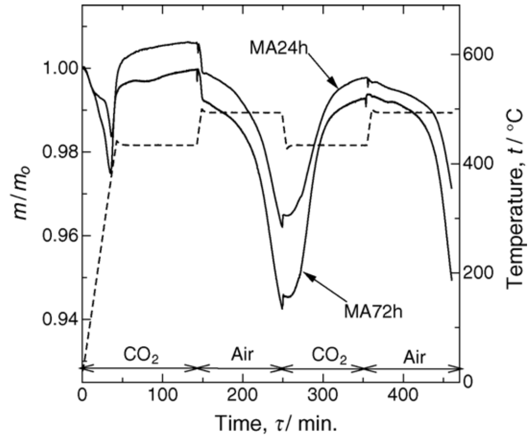


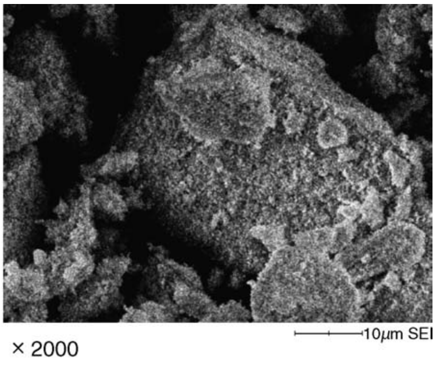
Fig. 3. Weight change curves for $(Bi_2O_3)_{0.70}(La_2O_3)_{0.30}$ MA'ed for 24 and 72 h. Dashed line shows the temperature variation.

changing the atmosphere to air. As a result, the weight loss could be calculated to about 6% against the top weight at 440 °C in CO_2. This weight loss, of course, depended on the keeping time at 440 °C in CO_2; when it was 140 min, about 9% weight loss was observed. The subsequent weight increase and decrease were observed in the next operation. These phenomena denoted that the $(Bi_2O_3)_{0.70}(La_2O_3)_{0.30}$ powder can absorb and desorb CO_2 repeatedly. After this experiment, the crystal phase of the sample powder was found to change from α-Bi_2O_3-type (monoclinic) to rhombohedral: the most stable crystal phase in sintered sample of $(Bi_2O_3)_{0.70}(La_2O_3)_{0.30}$ [5]. Therefore, this phase change phenomenon was considered not to affect the repeated operation in this system. The cyclic behavior of CO_2 absorption and desorption for $(Bi_2O_3)_{0.70}(La_2O_3)_{0.30}$ sample was further investigated. At least, cyclic repetition was found to be possible with about 4% weight change in five times.

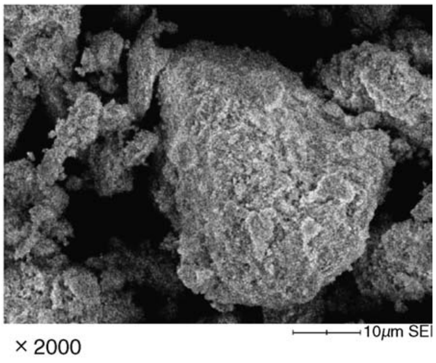
Similar results were obtained in the samples MA'ed for different periods. Fig. 3 mentioned above also shows a comparison of CO_2 absorption and desorption between the 72 and 24 h MA'ed samples; the former showed a bigger weight change than the latter, which showed that CO_2 absorbing and desorbing performance would depend on the particle morphology. Fig. 4 shows the SEM images of $(Bi_2O_3)_{0.70}(La_2O_3)_{0.30}$ obtained with different MA period. An obvious surface morphological difference could not be observed among the samples. However, the specific surface area increased from 22.0 $m^2 g^{-1}$ for 24 h MA to 42.8 $m^2 g^{-1}$ for 72 h MA.

Furthermore, as to the samples with different compositions in the system Bi_2O_3–La_2O_3, the same experiments have done. A representative result was shown in Fig. 5, where the performance was compared between $(Bi_2O_3)_{0.80}(La_2O_3)_{0.20}$, $(Bi_2O_3)_{0.70}(La_2O_3)_{0.30}$ and $(Bi_2O_3)_{0.50}(La_2O_3)_{0.50}$. Obviously, CO_2-absorbing performance of $(Bi_2O_3)_{0.70}(La_2O_3)_{0.30}$ was the highest. When MA'ed Bi_2O_3 and La_2O_3 themselves were tested as to their CO_2 absorbing properties in the same conditions, Bi_2O_3 es-

(a) MA24h



(b) MA48h



(c) MA72h

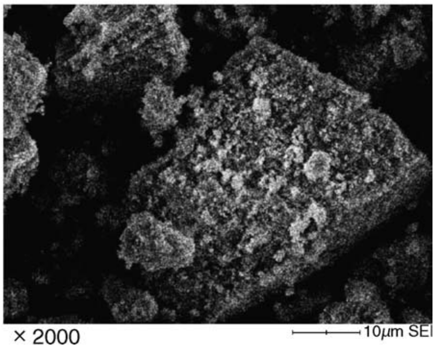


Fig. 4. SEM images for $(Bi_2O_3)_{0.70}(La_2O_3)_{0.30}$ obtained with different MA period.

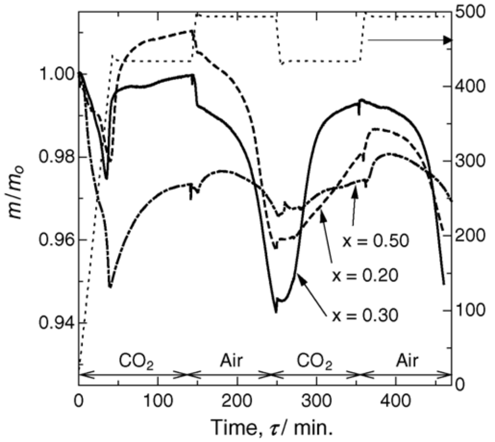


Fig. 5. Weight variation curves for $(Bi_2O_3)_{0.80}(La_2O_3)_{0.20}$, $(Bi_2O_3)_{0.70}(La_2O_3)_{0.30}$ and $(Bi_2O_3)_{0.50}(La_2O_3)_{0.50}$. MA'ed for 72 h. Dashed line shows the temperature variation.

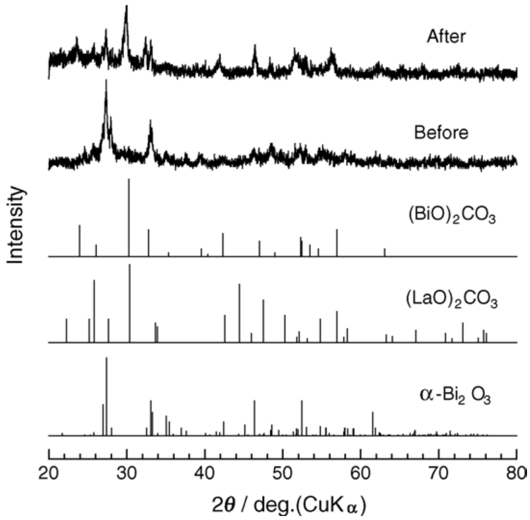


Fig. 6. XRD patterns of $(Bi_2O_3)_{0.70}(La_2O_3)_{0.30}$ before and after CO_2 absorption.

sentially absorbed very little CO_2 compared with the solid solution mentioned. La_2O_3 began to rapidly absorb CO_2 over 400 °C, but never desorbed CO_2 near the temperature from 400 to 500 °C. These results indicated that the present CO_2-absorbing property was performed by making the solid solution of $(Bi_2O_3)_{1-x}(La_2O_3)_x$ and by adjusting the best composition in that experimental condition.

In order to check the CO_2-absorbing mechanism, XRD analysis was carried out for the sample of $(Bi_2O_3)_{0.70}$ $(La_2O_3)_{0.30}$ before and after CO_2-absorption. As shown in Fig. 6, α-Bi_2O_3-type structure changed to that of $(BiO)_2CO_3$-type and/or $(LaO)_2CO_3$-type phase, both of which are very similar. Considering the weight increase in CO_2, if only La_2O_3 or Bi_2O_3 reacted with CO_2, then 3.1% or 7.1% weight gain should be observed respectively, and if $(Bi_2O_3)_{0.70}(La_2O_3)_{0.30}$, then 10.3%. Experimentally the weight increase was more than 9%, which denoted that CO_2 must be absorbed in the Bi_2O_3–La_2O_3 solid solution. Furthermore, if the numbers of CO_2 were calculated assuming adsorption on the sample powder surface, they exceeded 30 for 1 nm^{-1}. Considering the general size of CO_2 molecule, it was impossible. Totally, CO_2 was concluded to be absorbed chemically.

We stopped the MA experiments at 72 h, because the specific surface area did not increase so much (almost saturated) as compared with 48 h. From the present experiments, the 100 or 150 h MA would not give a marvelous result. If CO_2 was physically absorbed (adsorped) in addition to the chemical absorption, the performance would largely depend on the surface morphology, which means that the MA time could be more important factor for CO_2 absorption. In future, if the powder morphology could be controlled in nanosize, a physical absorption and desorption property would be also expected to manage much more CO_2 gas at lower temperatures.

4. Conclusions

CO_2-absorption and desorption properties were investigated in rare earth oxide-doped Bi_2O_3 powders prepared by mechanical alloying method. The sample powders were found to absorb CO_2 gas around 400–500 °C. However, the CO_2-absorption and desorption performance changed depending on the kind of doped rare earth oxide and the sample composition; the Y_2O_3-doped Bi_2O_3 did not show absorption and desorption repetition at all. Absorbed and desorbed CO_2 contents also varied with MA time. In the La_2O_3-doped Bi_2O_3, the 72 h MA'ed $(Bi_2O_3)_{0.70}(La_2O_3)_{0.30}$ was found to be the material with highest performance as for CO_2 content and cycleability. CO_2-absorption was considered to be due to formation of $(BiO)_2CO_3$-type phase in the oxide powder.

Acknowledgment

This study was partly supported by the JFE 21st Century Foundation.

References

[1] K. Nakagawa, T. Ohashi, J. Electrochem. Soc. 145 (1998) 1344.
[2] K. Nakagawa, T. Ohashi, Electrochemistry 67 (1999) 618.
[3] M. Kato, K. Nakagawa, J. Ceram. Soc. Jpn. 109 (2001) 911.
[4] T. Esaka, S. Takai, N. Nisimura, Denki Kagaku 64 (1996) 1012.
[5] H. Iwahara, T. Esaka, T. Sato, T. Takahashi, J. Solid State Chem. 39 (1981) 173.