

PEROVSKITE-TYPE MN-BASED OXYGEN STORAGE MATERIALS SYNTHESIZED BY MECHANICAL MILLING

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ABSTRACT

In this paper, we report on oxygen storage-related properties of selected Ba and Pr containing double perovskite-type Mn-based A-site ordered BaPrMn₂O_{5+δ} system.

Samples were synthesized by solid state reaction (SSR) method. BaO, Pr₂O₃ and Mn₂O₃ were used as starting materials. The oxide powders, whose compositions were stoichiometric to BaPrMn₂O_{5+δ}, were mechanically milled for 1 hour at 500 min⁻¹. The powders were then presintered at 1150°C, and pressed into pellets. The pellets were also mechanically milled for 20 hours or 40 hours, and sintered at 1150°C for 12 hours.

Oxygen storage-related properties, including oxidation and reduction behaviors, were evaluated using a thermo gravimeter. For reduction at 500°C, 2% H₂ in N₂ gas mixture was used, while the oxidation process was measured under air flow. Crystal structural studies were performed with a CuKα radiation using an X-ray diffractometer.

Although formation of a double perovskite structure was reported from a route of soft chemical (sol-gel) method, a single perovskite structure was formed by SSR method. Furthermore it was considered that ZrO₂ (material used for the vial) was mixed together with the powders after mechanical milling (MM). When MM time became longer, oxidation kinetics decreased while reduction kinetics increased.

1. INTRODUCTION

Oxygen storage materials (OSM) are materials capable of storage and release of oxygen. These were started to be used from 1980s as support catalysts, when transportation industry implemented them as reservoirs of oxygen, which were needed for an efficient work for three-way catalytic (TWC) converter.

TWC converter is installed behind of car muffler. The converter is needed for cleaning harmful gases (CO, HC, and NO_x). To clean these gases, main catalysts and support catalysts are required. Main catalysts are noble metals which are Pt, Pd, and Rh, and support catalysts are support the main catalysts. Since noble metals are expensive, it has been demanded to create support catalysts not using noble metals. Although the current mainstream of support catalyst is CeO₂-ZrO₂, we have proposed double-perovskite structure in this study.

In this paper, we report on oxygen storage-related properties of selected Ba and Pr containing double perovskite-type which is two-stored single perovskite Mn-based A-site ordered BaPrMn₂O_{5+δ} system.

2. EXPERIMENTAL

The considered oxides were synthesized using a solid state reaction (SSR) method. BaO, Pr₂O₃ and Mn₂O₃ were used as starting oxides. The oxide powders, whose compositions were stoichiometric to BaPrMn₂O_{5+δ}, were mechanically milled for 1 hour at 500 min⁻¹. The powders were then presintered at 1150°C, and pressed into pellets. The pellets were also mechanically milled for 20 hours (MM for 20h) or 40 hours (MM for 40h), and sintered at 1150°C for 12 hours.

Oxygen storage-related properties, including oxidation and reduction behaviors, were evaluated using a thermo gravimeter. The measurements were performed in the powdered samples. For reduction at 500°C, 2% H₂ in N₂ gas mixture was used, while the oxidation process was measured under air flow. The maximum cycle of oxidation and reduction number was 5.

Crystal structural studies were performed with a CuKα radiation using an X-ray diffractometer in the 10-110° range. After measurement, GSAS/EXPGUI software was used to refine XRD data.

3. RESULTS AND DISCUSSION

3.1 Thermogravimetric measurement

The obtained materials of TG data were shown in Fig.1. The beginning of 2 cycle in 5 cycle was shown in Fig 1, but after 3 cycle stability collapsed.

Compared to the similar sample made by soft chemical (sol-gel) method, it was found that oxidation kinetics decreased while reduction kinetics increased. Quantitatively, in Fig.1, at the first cycle, the sample after MM for 20h, oxidation kinetic was 0.9 times smaller than sol-gel one, but reduction was 1.3 times larger than sol-gel one. For the sample after MM for 40h, the oxidation was 0.8 times smaller than sol-gel one, but reduction was 2 times larger than sol-gel one. It was considered that ZrO_2 (material used for the vial) was mixed together with the powders after mechanical milling (MM).

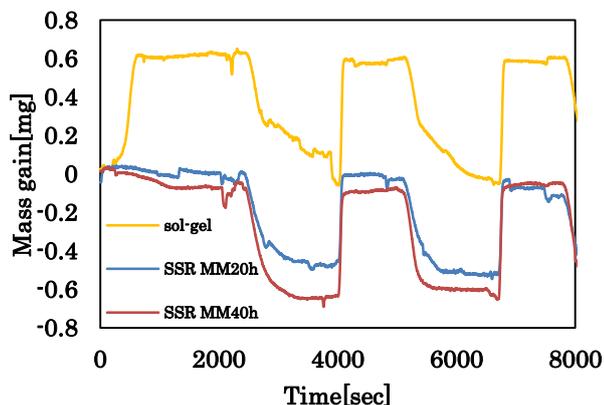


Fig.1 TG results

3.2 X-ray diffraction measurement

The XRD pattern obtained materials of were shown in Fig.2. Double perovskite structure could almost make two peaks around 32° , but it was found that peak was single. It is considered that double perovskite structure could not be made by MM. On the other hand, after MM for 40h each peak was smaller than MM for 20h, so it was revealed that perovskite structure appeared less when MM time became longer.

Both after MM for 20h and 40h, space group of the product was found to be Pnma ($Ba_{0.3}Pr_{0.7}MnO_3$) or I4/m ($Ba_{0.35}Pr_{0.65}MnO_3$). Incidentally, it was reported that space group of double perovskite of Mn-based was P4/mmm.¹⁾ According to crystallographic information file (CIF), these were be expected to be Pnma. Since double perovskite structure could not be confirmed, it was considered that ZrO_2 (material used for the vial) was mixed together with the powders after mechanical milling (MM) as mentioned before.

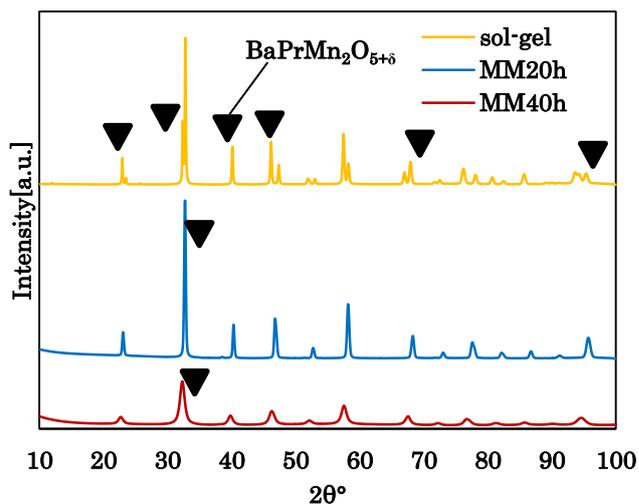


Fig.2 XRD results

CONCLUSION

Ba and Pr containing double perovskite-type Mn-based A-site ordered $BaPrMn_2O_{5+\delta}$ system was reported in this report. Although a formation of a double perovskite structure was reported from a route of soft chemical (sol-gel) method¹⁾, a single perovskite structure formed by SSR method. Furthermore, it was considered that ZrO_2 (material used for the vial) was mixed together with the oxide powders after MM. When MM time became longer, the oxidation kinetics decreased while reduction kinetics increased.

REFERENCES

- 1) Klimkowicz, A., Świerczek, K., Zheng, K., Takasaki, A., Dabrowski, B., Evaluation of $BaY_{1-x}Pr_xMn_2O_{5+\delta}$ oxides for oxygen storage technology, Solid State Ionics, Volume 262, 1 September 2014, pp659-663, 2014