Paper

Properties and Characterization of Perovskite Related Oxides for Rapid CO₂ Solidification

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SYNOPSIS

Perovskite related oxides such as (Ba,Ca)(Fe,Co)O_{3-δ}, (Sr,Ca)(Fe,Co)O_{3-δ} and (Ba,Ca)(Fe,Mg)O_{3-δ} have been developed as safety materials for quick solidification of CO₂ at high temperatures. The CO₂ solidification properties and microstructures were investigated. Perovskite oxides (ABO₃) become active for CO₂ accommodation due to the lattice distortion produced by mixing different alkaline earth ions in site A and the mixed valence states by substitution of Fe ions by Co and Mg ions in site B. The mechanism of rapid CO₂ accommodation was taken into consideration.

KEY WORDS

Carbon dioxide gas solidification, mixed perovskite, brownmillerite, Mössbauer spectroscopy

1 Introduction

The accumulation of CO₂ gas in the atmosphere causes the global warming as a green house effect. In Japan, the total amount of exhausted CO₂ was 3.43×10^2 Mt a year in 1994. The amount of CO₂ emitted from industry was 1.36×10^2 Mt, i.e. about 40 % of the total emission¹⁾. It is important to reduce the amount of exhausted CO₂ before it diffuses into the air. So materials for direct and rapid solidification of CO₂ emitted from industrial furnaces should be developed.

In the beginning of 1990s²⁾, we found that the mixed perovskite, (Ba,Ca)(Fe,Co)O_{3-δ}, absorbs CO₂ rapidly at high temperatures between 600 and 950 °C^{3,4)}. The decomposition temperatures of MgCO₃, CaCO₃, SrCO₃, and BaCO₃ are 540 °C, 898 °C, 1150 °C, and 1350 °C, respectively. The control of the solidification and decomposition temperatures may be realized by substitutions in the perovskite lattice. From the tolerance factor of ionic radii for formation of cubic perovskite (ABO₃), it is expected that Mg²⁺ ions can substitute for Fe⁴⁺ ions at site B of the perovskite structure, whereas Ba²⁺, Sr²⁺, and/or Ca²⁺ ions occupy site A.

In this paper, the microenvironments of Fe in (Ba,Ca)(Fe,Co)O_{3-δ}, (Sr,Ca)(Fe,Co)O_{3-δ} and (Ba,Ca)(Fe,Mg)O_{3-δ} mixed oxides were characterized from the view points of rapid CO₂ accommodation mechanism at high temperature.

2 Experimental

The mixed oxides of (Ba,Ca)(Fe,Co)O_{3-δ}, (Sr,Ca)(Fe,Co)O_{3-δ}, and (Ba,Ca)(Fe,Mg)O_{3-δ} were prepared by simply mixing metal nitrates and carbonates with a shaker ball-mill for 30 min, and heated at higher than 850 °C for more than 10 hours in air. Alternatively, the mixed oxides were prepared by a sol-gel method using an ethylene glycol solution including metal nitrates and citric acid. The mixed solutions were stirred at 80 °C and the solvent was evaporated at around 200 °C. The solid residue was preheated at 500 °C for 2 hours and annealed at 850 °C for 10 hours.

The CO₂ solidification properties were measured at a heating rate of 20 °C /min by thermogravimetric analysis (TGA). The structures of mixed oxides were analyzed by X-ray powder diffraction (XRD). The microenvironment of Fe species at site B was characterized by ⁵⁷Fe Mössbauer spectroscopy.

3 Results

3.1 Absorption Properties

BaFeO_{3-δ} and CaFeO_{2.5} have no potential to absorb CO₂ rapidly. However, (Ba,Ca)(Fe,Co)O_{3-δ} absorbs CO₂ at temperatures higher than 700 °C in air + 10% CO₂ atmosphere, and shows 46 mol% absorption at 850 °C³⁾. In the case of (Ba_{0.95}Ca_{0.05})(Fe_{1-y}Co_y)O_{3-δ} with y=0.2, the weight increased in the temperature range between 600 °C and 950 °C and the maximum of CO₂ absorption was 35 mol%, whereas

with $y=0.8$, the weight increased quickly from 550 °C and reached 51 mol% at 800 °C. Co rich oxides were more active for CO₂ absorption than Fe rich oxides.

The mixed oxides (Sr_{1-x}Ca_x)(Fe_{1-y}Co_y)O_{3-δ} showed rapid absorption of CO₂ in the temperature range from 550 °C to 850 °C. The substitution of Sr by a half mole of Ca and of Fe by a half mole of Co provided rapid absorption of CO₂, whereas the temperature of maximum CO₂ absorption decreased from 850 °C to 780 °C with the increase of Ca contents. Comparing Ba(Fe,Co)O_{3-δ} and Sr(Fe,Co)O_{3-δ} with the same substitution level of Ca, one finds that Ba mixed oxides were more active than Sr mixed oxides. Moreover, the decomposition temperature was higher for the Ba-compounds by about 100 °C.

(Ba_{1-x}Ca_x)(Fe_{1-y}Mg_y)O_{3-δ} ($x=0.5, 0.95$, and $y=0.2, 0.5, 0.8$) showed high activity for CO₂ absorption, namely, from 32 mol% to 55 mol% at 850 °C⁵⁾. The Mg mixed oxides with equal Ba and Ca contents started to absorb CO₂ gas at around 350 °C, and released above the 890 °C. The starting and releasing temperatures of CO₂ absorption were determined by the Mg/Fe ratio, and by the Ba/Ca ratio, respectively. The decomposition of Ca-rich perovskite absorbed with CO₂ started at around 900 °C, which corresponds to the decomposition temperature of CaCO₃, whereas all oxides with Ba/Ca = 1 released CO₂ rapidly around 1070 °C. The Mg ions were not isolated as MgCO₃ in the CO₂-treated materials since the decomposition temperature of MgCO₃ is 540 °C. The lattice oxygen of these oxides was easily released by endothermic reaction in air around 420 °C, while the CO₂ absorption began at the same temperature as shown in Fig. 1. It is considered that good oxygen permeability is necessary for quick absorption or solidification of CO₂.

A mechanical treatment by ball milling were studied for CO₂ absorption using (Sr_{1-x}Ca_x)(Fe_{0.5}Co_{0.5})O_{3-δ} with $x=0.05$

(not so active for CO₂ absorption) and $x=0.5$ (active for CO₂ absorption)⁶⁾. The ball milling of (Sr_{0.95}Ca_{0.05})(Fe_{0.5}Co_{0.5})O_{3-δ} for 5 minutes increased the absorption capacity of CO₂ from 10 mol% to 39 mol% and the starting temperature of CO₂ absorption decreased from 650 °C to 510 °C. A ball milling for 5 min improved the absorption properties, but a ball milling for a long time decreased the potential for CO₂ absorption. It is considered that necks between the grains appeared at the beginning of the ball milling, and that the surface area increased. The milling for a long time was considered to affect the structure of crystals such as deformation, defects and grain size. These suggest that not only the surface of the oxide grains but also the bulk structure is crucial for the CO₂ absorption.

(Ba_{0.5}Ca_{0.5})(Fe_{0.8}Mg_{0.2})O_{3-δ} was measured by TGA in CO₂ atmosphere. The weight gains due to CO₂ absorption before and after ball milling for 5 min were 34 mol%, and 38 mol%, respectively, and the starting temperature decreased from 600 °C to 410 °C after ball milling.

3.2 Characterizations of oxides

(Ba_{0.95}Ca_{0.05})(Fe_{1-y}Co_y)O_{3-δ} with $y < 0.6$ showed cubic structures ($a = 0.4030 - 0.4083$ nm), and became orthorhombic like BaCoO_{2.93} with increasing Co contents.

(Sr_{1-x}Ca_x)(Fe_{0.5}Co_{0.5})O_{3-δ} ($x = 0.05$ and $x = 0.5$) showed cubic structure ($a = 0.3862$ nm) and orthorhombic structure ($a = 0.5576$, $b = 1.536$, $c = 0.5419$ nm), respectively. The oxygen deficiencies increased with Ca contents.

The lattice parameters of the cubic (Ba,Ca)(Fe,Mg)O_{3-δ} increased with temperature, whereas, in the orthorhombic structure with more oxygen defects, the lattice parameter of b increased with temperature drastically as compared with the behavior of a and c .

In ABO_{3-δ}, one tetrahedron and two octahedra are produced at site B in a random or ordered distribution when $\delta = 1/n$ and $n = 3$, and layered structures of tetrahedra and octahedra are produced when $n = 2$. The latter corresponds to the brownmillerite structure. When one oxygen atom releases from the cubic perovskite, two octahedral Fe^{IV} species become two Fe^{III} species; one with tetrahedral, the other with octahedral coordination. If the tetrahedra and octahedra are ordered, two sextets due to ferrimagnetism appear in the Mössbauer spectrum, whereas Fe^{IV} species in octahedron show a singlet or a doublet due to paramagnetic behavior, depending on the electron configuration around the Fe nucleus⁷⁾. It is found from Mössbauer analysis that the line widths of the mixed oxides are broad, and that Fe atoms prefer octahedral sites ($B_{in} = 48.5$ T), whereas Co atoms prefer tetrahedral sites ($B_{in} = 40.1$ T).

3.3 Characterization of the mixed oxides absorbed with CO₂

Fig.1 Typical TGA curves of (Ba_{1-x}Ca_x)(Fe_{1-y}Mg_y) oxides in CO₂ and in air.

In $(\text{Ba}_{0.95}\text{Ca}_{0.05})(\text{Fe}_{0.9}\text{Co}_{0.1})\text{O}_{3-\delta}$ ⁴⁾, the paramagnetic peaks changed into two magnetic sextets ($B_{in} = 41.4$ T, and 50.4 T) upon CO₂ accommodation, and an additional new sextet with $B_{in} = 47.5$ T appeared on further CO₂ absorption. The formers were similar to those due to oxygen defect structures. The latter could correspond to a spinel like BaFe_2O_4 .

In the case of $(\text{Sr}_{0.5}\text{Ca}_{0.5})(\text{Fe}_{0.5}\text{Co}_{0.5})\text{O}_{3-\delta}$ after CO₂ absorption, the doublets disappeared and a new sextet of magnetic Fe^{III} species was also observed together with a pair of sextets of the tetrahedral and octahedral sites⁸⁾. The intensity of the new sextet due to spinel increased with the CO₂ solidification.

In the case of $(\text{Ba}_{0.5}\text{Ca}_{0.5})(\text{Fe}_{0.5}\text{Mg}_{0.5})\text{O}_{3-\delta}$, paramagnetic Fe^{III} ($\delta = 0.29$ mm/s, $\Delta = 0.85$ mm/s, Area Int. = 62%) and Fe^{IV} ($\delta = -0.09$ mm/s, $\Delta = 0.84$ mm/s, Area Int. = 38%) were produced after CO₂ absorption. The valence state of Mg²⁺ ions is stable, and, from the population ratio of Fe^{III} and Fe^{IV} doublets, we conclude that only a part of the Mg ions is built in the perovskite lattice, and that the rest is present as MgO-CaO. Distorted structures are produced around Fe^{III} atoms by CO₂ accommodation, and Mg ions are removed from the perovskite lattice. When the sample absorbed 41 mol% CO₂, a pair of sextet due to octahedral ($H_{in} = 48.0$ T, $\delta = 0.21$ mm/s, $\Delta = -0.24$ mm/s) and tetrahedral ($H_{in} = 43.7$ T, $\delta = 0.21$ mm/s, $\Delta = -0.31$ mm/s) Fe^{III} species appeared in the Mössbauer spectra. B_{in} for the octahedral coordinated species was affected by large amounts of accommodated CO₂. However, when the sample was heated at 1000 °C, the pair of sextets had more distinct parameters between octahedral sites ($B_{in} = 51$ T, $\delta = 0.36$ mm/s, $2\epsilon = 0.57$ mm/s), and tetrahedral sites ($B_{in} = 43.2$ T, $\delta = 0.19$ mm/s, and $2\epsilon = -0.73$ mm/s). In addition, a new sextet with $B_{in} = 48$ T was observed, due to a spinel type compound such as MgFe_2O_4 and/or $(\text{Ba,Ca})\text{Fe}_2\text{O}_4$.

The hyperfine fields of the Mg mixed oxides were larger than those of Co mixed perovskites. The peak intensity corresponding to tetrahedral Fe^{III} species was a little larger than that of octahedral sites. It shows that Mg ions favor to occupy the octahedral site. In the case of Fe and Co mixed perovskite, Fe and Co ions prefer the octahedral and tetrahedral sites, respectively.

The oxygen permeability in $(\text{La}_{0.6}\text{A}'_{0.4})(\text{Fe,Co})\text{O}_{3-\delta}$ ⁹⁾ became large in the order of $\text{A}' = \text{Ba}$, Ca , and Sr . It is considered to be due to the lattice distortion on the basis of difference of ionic radii between La^{3+} (ionic radius: 0.118 nm) and alkaline earth metals (ionic radius: $\text{Ba}^{2+} = 0.136$ nm, $\text{Sr}^{2+} = 0.116$ nm, $\text{Ca}^{2+} = 0.099$ nm). The oxygen permeability may be the important precondition for CO₂ uptake in the mixed oxides. The excess oxygen and alkaline earth ions in the brown-

millerite thus play an important role in CO₂ solidification.

4 Conclusions

The Co ions in $(\text{Sr,Ca})(\text{Fe,Co})\text{O}_{3-\delta}$ prefer to occupy the tetrahedral site as +3 valence state. A small portion of Mg ions occupy the octahedral site of $(\text{Ba,Ca})(\text{Fe,Mg})\text{O}_{3-\delta}$ oxides although the excess Mg ions are present as CaO-MgO mixed oxides in the perovskite structure. The mixed perovskites with distortion at site A and different valence states of metal ions at site B are active for CO₂ solidification at high temperatures. CO₂ is quickly accommodated as carbonate in the microstructure of $(\text{AA}')(\text{BB}')\text{O}_{2.5}$ due to good oxygen permeability. The maximum amount of quickly accommodated CO₂ is at largest half mole of the original perovskite, and the mixed perovskite oxides are decomposed into brownmillerite as bone structure, spinel compounds, and Ba, Sr, Ca or Mg carbonates.

The mixed oxides for CO₂ solidification should be selected on the basis of the various purposes of reuse, storage, disposal, and conversion to another materials. The perovskite oxides aged can simply be activated by ball milling for several minutes. The modified perovskites are useful for direct and rapid CO₂ solidifications at high temperatures.

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