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Synthesis of crystalline yttrium oxycarbonate in a single phase

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Abstract

Crystalline yttrium oxycarbonate, $Y_2O_2CO_3$, was synthesized by our original flux method using the $0.476Li_2CO_3$–$0.270Na_2CO_3$–$0.254K_2CO_3$ eutectic mixture at 450 °C. The oxycarbonate was characterized by X-ray powder diffraction (XRD), thermogravimetric analysis (TGA), and Fourier-transfer infrared spectroscopy (FT-IR). The $Y_2O_2CO_3$ prepared by the flux method was a crystalline single phase of hexagonal rare earth oxycarbonate (type-II). This is the first report on the single-phase synthesis of crystalline hexagonal type-II $Y_2O_2CO_3$.

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Keywords: Crystalline $Y_2O_2CO_3$; Flux method; FT-IR

1. Introduction

There are three types of crystal structures in rare earth oxycarbonates, $RE_2O_2CO_3$ (RE = rare earths), i.e., tetragonal type-I, monoclinic type-Ia, and hexagonal type-II [1,2]. Among these three structures, the type-II oxycarbonate is the most stable one and has a high durability against water and carbon dioxide [3]. Some studies on the preparation and characterization of the type-II rare earth oxycarbonates have been reported up to now. However, it is rather difficult to obtain the hexagonal type-II rare earth oxycarbonates in a single phase. For examples, $La_2O_2CO_3$-II was prepared by the carbonation of La_2O_3 under a stream of carbon dioxide at 850 °C for 5 days, and $Nd_2O_2CO_3$-II was synthesized by decomposition of neodymium acetate hydrate at 500 °C and the subsequent firing for 5 more days at 765 °C under flowing carbon dioxide [4].

In the case of middle and heavy rare earth oxycarbonates (RE = Y and Gd–Lu), it is more difficult to synthesize the type-II oxycarbonate as single phase. Dysprosium, holmium, erbium, and ytterbium oxycarbonates were prepared in a single phase form of the type-II phase by the hydrothermal treatment of their carbonates at considerably high pressures of 1400–3400 atm [5]. Although yttrium, gadolinium, and erbium oxycarbonates were also obtained by hydrothermal treatment of their carbonates in the presence of transport solutions (6 M K_2CO_3, 6 M NH_4Cl, or 5.5 M K_2CO_3 + 1 M KCl), only erbium oxycarbonate was synthesized in a single phase and the others were mixtures of hydroxycarbonate and potassium compounds [6]. $Gd_2O_2CO_3$-II can be obtained as single phase by annealing the carbonate for several weeks in a stream of CO_2 [1]. However, $Y_2O_2CO_3$-II has not been synthesized as single phase yet.

In our previous work, we have found a new simple flux method to synthesize well-crystallized rare earth oxycarbonates in a single phase, where alkaline metal carbonates were applied as the flux to promote the oxycarbonate formation [7–10]. This method has enabled us to synthesize single-phase $La_2O_2CO_3$-II [7–9] and $Gd_2O_2CO_3$-II [10] by heating the precursor in a flow of 10%CO_2-90%N_2 gas for only 12 h at atmospheric pressure.

The light and middle rare earth oxycarbonates (RE-La–Gd) are relatively stable up to at least 800 °C in CO_2,

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while the other heavier rare earth oxycarbonates (RE = Y and Tb–Lu) usually decompose below 650 °C because thermal stability of rare earth oxycarbonates decreases with decreasing ionic radius [1]. Therefore, the simple alkaline metal carbonates such as Li_2CO_3 (m.p. 726 °C), Na_2CO_3 (m.p. 851 °C), and K_2CO_3 (m.p. 891 °C) are not useful for the synthesis of the heavy rare earth oxycarbonates because their melting points are higher than the decomposition temperatures of the oxycarbonates. However, this problem can be solved by employing the $0.476Li_2CO_3$–$0.270Na_2CO_3$–$0.254K_2CO_3$ eutectic mixture as the flux. The melting point of this eutectic mixture is 390 °C, which is considerably lower than the decomposition temperatures of the heavy rare earths oxycarbonates. Accordingly, the flux treatment can be performed at lower temperatures. Furthermore, the low melting point of the flux is suitable for producing the type-II oxycarbonate of high crystallinity effectively.

Therefore, in the present study, the $0.476Li_2CO_3$–$0.270Na_2CO_3$–$0.254K_2CO_3$ eutectic mixture (m.p. 390 °C) has been employed as the flux, and, we have succeeded in synthesizing the hexagonal $Y_2O_2CO_3$-II of high crystallinity in a single phase for the first time.

2. Experimental

2.1. Synthesis

Yttrium acetate tetrahydrate, $Y(CH_3COO)_3 \cdot 4H_2O$, was calcined at 400 °C for 6 h in air. The precursor obtained was mixed with the $0.476Li_2CO_3$–$0.270Na_2CO_3$–$0.254K_2CO_3$ eutectic mixture in a ratio of 50 mol%, where the eutectic melting point is 390 °C. The mixture was heated at 450 °C for 12 h in a flow of 10% CO_2 diluted with N_2 gas, and then the sample was calcined again in air at 400 °C for 1 h. The oxycarbonate obtained was washed with deionized water three times and subsequently once with ethanol, and then was dried at room temperature.

2.2. Characterization

The crystalline structure of the sample was identified by X-ray powder diffraction (XRD, Rigaku Multiflex) using Cu*Kα* radiation. Silicon was used as an internal standard. Thermal analytical measurements were carried out on a thermogravimetric analyzer (TGA, Shimadzu DTG-60AH). Infrared spectra were obtained with Fourier-transfer infrared spectroscopy (FT-IR, Bruker TENSOR 27). The solid sample was prepared in the form of a pressed wafer (ca. 2 wt% sample in a KBr pellet).

3. Results and discussion

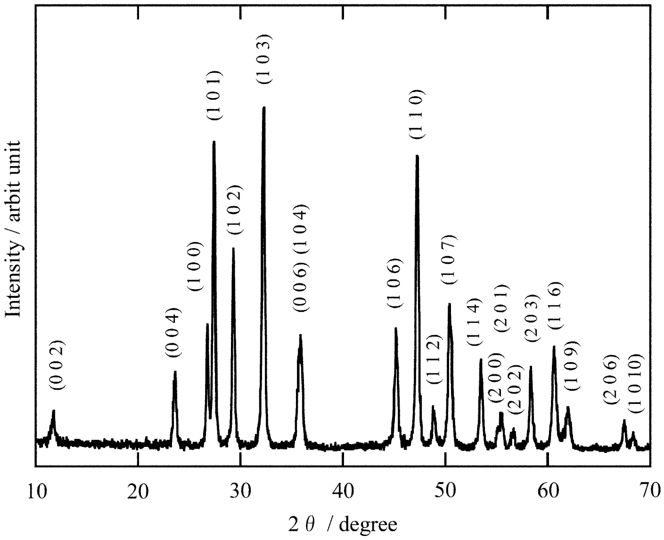

Fig. 1. XRD pattern of the $Y_2O_2CO_3$ powder prepared at 450 °C by the flux method using the $0.476Li_2CO_3$–$0.270Na_2CO_3$–$0.254K_2CO_3$ eutectic mixture.

Table 1
X-ray powder diffraction patterns of hexagonal $Y_2O_2CO_3$

hkl	d_{obs} (nm)	d_{calc} (nm)	I/I_0 (%)
0 0 2	0.7559	0.7539	9
0 0 4	0.3773	0.3770	22
1 0 0	0.3334	0.3333	36
1 0 1	0.3255	0.3254	88
1 0 2	0.3048	0.3048	57
1 0 3	0.2780	0.2778	100
0 0 6	0.2513	0.2513	33
1 0 6	0.2008	0.2007	34
1 1 0	0.1924	0.1924	85
1 1 2	0.1865	0.1864	10
1 0 7	0.1809	0.1809	42
1 1 4	0.1715	0.1714	26
2 0 0	0.1666	0.1666	6
2 0 1	0.1656	0.1656	10
2 0 2	0.1627	0.1627	5
2 0 3	0.1582	0.1582	24
1 1 6	0.1527	0.1528	29
1 0 9	0.1498	0.1497	12
2 0 6	0.1389	0.1389	7
1 0 10	0.1373	0.1374	4

$a = 0.3848_5$ nm, $c = 1.5078_6$ nm. Space group: $P6_3/mmc$.

Fig. 1 shows the XRD pattern of the $Y_2O_2CO_3$ sample prepared at 450 °C by the flux method using the $0.476Li_2CO_3$–$0.270Na_2CO_3$–$0.254K_2CO_3$ eutectic mixture. The sharp diffraction peaks observed in Fig. 1 demonstrate a high crystallinity of the sample, and the pattern is in good agreement with the reflections of the hexagonal type-II rare earth oxycarbonate (space group $P6_3/mmc$) [4–6]. No impurity peaks were observed in the diffraction pattern and the oxycarbonate was obtained in a single phase. Since single-phase synthesis of crystalline $Y_2O_2CO_3$ has been reported for the first time in the present study, the pattern has not been presented before and the detail information is summarized in Table 1. The unit cell parameters of the hexagonal $Y_2O_2CO_3$-II are $a = 0.3848_5$ nm and $c = 1.5078_6$ nm, respectively.

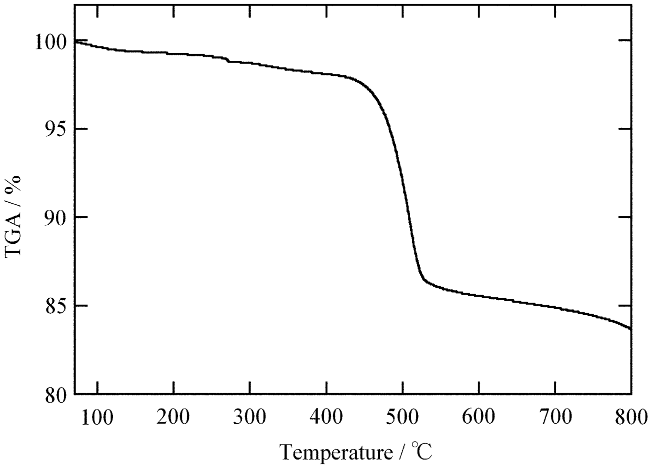

Fig. 2. TGA curve of the crystalline $Y_2O_2CO_3$.

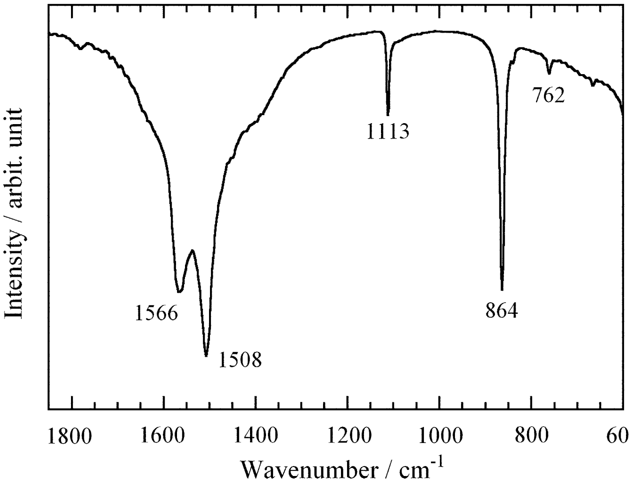

Fig. 3. FT-IR spectrum of the type-II $Y_2O_2CO_3$ sample.

As shown in Fig. 2, TGA measurement of the synthesized $Y_2O_2CO_3$ was conducted at a heating rate of 5 °C min^{-1} between room temperature and 800 °C. There is a steep weight loss at around 500 °C, which is ascribed to the decomposition of $Y_2O_2CO_3$ to form Y_2O_3. According to the TGA result, the weight loss ratio of 13 wt% from 400 to 600 °C is almost equivalent to the calculated value (16 wt%) corresponding to the release of carbon dioxide. The TGA result also indicates that $Y_2O_2CO_3$ is thermally stable up to 470 °C.

Fig. 3 displays the FT-IR spectrum for the hexagonal $Y_2O_2CO_3$. The spectrum shows five bands at 1566, 1508, 1113, 864, and 762 cm^{-1} similar to those reported for the single-phase samples of the hexagonal (type-II) light rare earth oxycarbonates [1,11]. The bands at 1556 and 1508 cm^{-1} are attributed to the antisymmetric vibration bands (ν_3) of CO_3^{2-}, and the 1113 cm^{-1} band corresponds to the symmetric vibration mode (ν_1). The other bands at 864 and 762 cm^{-1} are assigned to the ν_2 and the ν_4 bending modes, respectively.

As evidenced previously for the synthesis of lanthanum oxycarbonate [7], the phase and the crystallinity of the oxycarbonate produced are also strongly affected by the presence of the flux. The sample prepared without flux became yttrium oxide, while the one prepared using the flux consisted of a single phase of the type-II yttrium oxycarbonate. These results suggest that the precursor reacted with carbon dioxide, which was brought mainly by the flux and additionally by the flowing gas to form the crystalline $Y_2O_2CO_3$-II phase during the flux treatment at 450 °C. The effect of the flux is to accelerate the carbonation of the yttrium precursor by contacting the surface with a molten salt because the melting point of the $0.476Li_2CO_3$–$0.270Na_2CO_3$–$0.254K_2CO_3$ eutectic mixture is as low as 390 °C. Furthermore, the crystallinity of the sample was appreciably improved by the flux treatment. We conclude that the existence of the eutectic mixture flux of alkaline metal carbonates is essential for the single-phase synthesis of yttrium oxycarbonate.

4. Conclusions

In summary, it has been shown in the present study that hexagonal type-II $Y_2O_2CO_3$ can be synthesized for the first time by a simple flux method using the $0.476Li_2CO_3$–$0.270Na_2CO_3$–$0.254K_2CO_3$ eutectic mixture at 450 °C in a flow of 10% CO_2 diluted with N_2 gas. The structural and optical analyses of the sample elucidate that the type-II $Y_2O_2CO_3$ oxycarbonate phase has been obtained in a single phase.

Acknowledgment

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