Structural evolution of $FeCO_3$ through decarbonation at elevated temperatures

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Abstract. The structural evolution of siderite (s), $FeCO_3$, through decarbonation at elevated temperatures has been investigated by the *in-situ* single-crystal X-ray diffraction technique using an area detector. When the crystal was heated above 255 ºC, the transparent crystal turned colour in faint black from surface, indicating that the decarbonation commenced. The spinel-type magnetite (m), Fe_3O_4, first appeared in coexistence with the $FeCO_3$ parent crystal. The orientation relationship between the rhombohedral $FeCO_3$ and the cubic Fe_3O_4 can be described as $[111]_m$ // $[001]_s$, and $[2\text{-}1\text{-}1]_m$ // $[120]_s$. On further heating, additional diffraction spots appeared at 411 ºC. They were indexed on the basis of the corundum-type hematite (h), (α-Fe_2O_3). The rhombohedral α-Fe_2O_3 unit cell had the same orientation relationship with the parent rhombohedral $FeCO_3$ one, i.e., $[001]_h$ // $[001]_s$, and $[100]_h$ // $[100]_s$. On further heating the parent $FeCO_3$ phase disappeared completely at 464 ºC. The formation of iron oxides in $FeCO_3$ depended on not only temperature but also the holding time. The structural relationships among $FeCO_3$, Fe_3O_4, and α-Fe_2O_3 are discussed.

1. Introduction

The $FeCO_3$, siderite (s), is commonly found in hydrothermal veins, and considered as potential CO_2 mineral trapping[1]. A use of Fe/CO_2 fuel cells for CO_2 mitigation has been examined [2]. The decarbonation of the $FeCO_3$ product is important in a view point of carbon monoxide retrieval as a carbon resource. The thermal decomposition of $FeCO_3$ has been reviewed [3-5]. Decarbonation of carbonate salt has been considered to occur topotaxially [6-8]. Studies on iron carbonate, however, are quite few [9-10] in spite of its importance in an environmental point of view. The present study was thus undertaken to unveil the evolution of siderite structure associated with the decarbonation.

2. Experimental

Single-crystals of $FeCO_3$ were grown by the hydrothermal method. A preliminary check about the extinction rules of reflections of the rhombohedral $FeCO_3$ at the room temperature was carried out at the beamline 14A, Photon Factory, KEK, using a horizontal-type four-circle diffractometer [11]. The *in-situ* X-ray diffraction experiments were carried out at elevated temperatures using a single-crystal CCD diffractometer (Smart Apex II, Bruker) with Mo Kα laboratory source [12]. A crystal was

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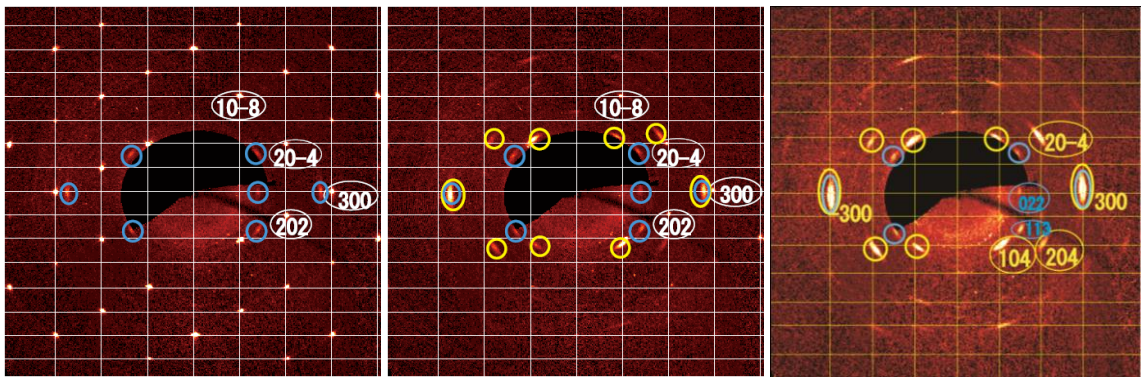
mounted on a silica glass capillary by Sauereisen cement (#970000, Niraco Co.), and soaked in a preheated nitrogen gas stream. The temperature at the crystal position was calibrated by the K-type fine gauge thermocouple (KFC-50-200-100, Anbe SMT Co.).

Intensity distribution in reciprocal space was investigated through the sets of contiguous frame data so that more than 99% of crystallographically-independent reflections within $2\theta < 60^{\circ}$ can be measured. Each of the frame data was taken by either ω or φ scan techniques in the range of 0.3º with each exposure time of 5 s. It took 4-12 hours to collect a set of data at one temperature. The experimental temperatures span from room temperature to 825 °C. Integrated intensities were extracted from the frame data. The cell parameters were refined from all the observed reflections in the integration process. The SHELXL least-squares program [12] with WinGX crystallographic program package [13] was used for the structure refinement and the other calculations.

3. Results and discussion

Crystals of $FeCO_3$ have the rhombohedral *R*-3*c* structure at room temperature. When the crystal was heated above 255 ºC, the transparent crystal turned color in faint black from surface, indicating that the decarbonation commenced. The reciprocal sections of the diffraction pattern at 359, 411 and 464 ºC are shown in figure 1. On heating, the spinel-type Fe_3O_4, magnetite (m), appeared first. The orientation relationship between the rhombohedral $FeCO_3$ (s) and cubic Fe_3O_4 (m) can be described as $[111]_m$ // $[001]_s$, $[2\text{-}1\text{-}1]_m$ // $[120]_s$, as shown in figure 2.



(a) (b) (c)

Figure 1 The (h0l)* sections of the reciprocal space of the $FeCO_3$ parent phase at 359 (a), 411 (b) and (c) 464 ºC. Encircled diffraction spots in blue and yellow are spinel-type iron oxide (Fe_3O_4 or *r*-Fe_2O_3) and corundum-type α-Fe_2O_3. The $FeCO_3$ parent lattice is drawn in white with some indexed spots.

On further heating, additional diffraction spots encircled by yellow color in figure 1(b) appeared at 411 ºC. They were indexed on the basis of the corundum-type α-Fe_2O_3, hematite (h). The rhombohedral α-Fe_2O_3 unit cell had the same orientation relationship with the parent rhombohedral $FeCO_3$, i.e., $[001]_h$ // $[001]_s$, $[100]_h$ // $[100]_s$. On further heating the parent $FeCO_3$ phase disappeared completely at 464 °C, as shown in figure 1(c). The diffraction spots of the remaining iron oxides were slightly diffuse, but still showed a topotaxial relationship with the parent siderite lattice. This experiment suggested that the carbon oxide detached from the siderite single crystal, leaving iron oxide components. The formation of iron oxide in $FeCO_3$ depended on not only temperature but also the holding time. When samples were heated longer than 30 h at some low temperatures like 255 ºC, for example, the spinel-type Fe_3O_4 was able to form.

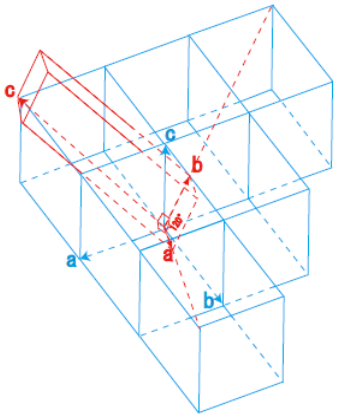


Figure 2. Orientation relationship between $FeCO_3$ (red) and Fe_3O_4 (blue) unit cells.

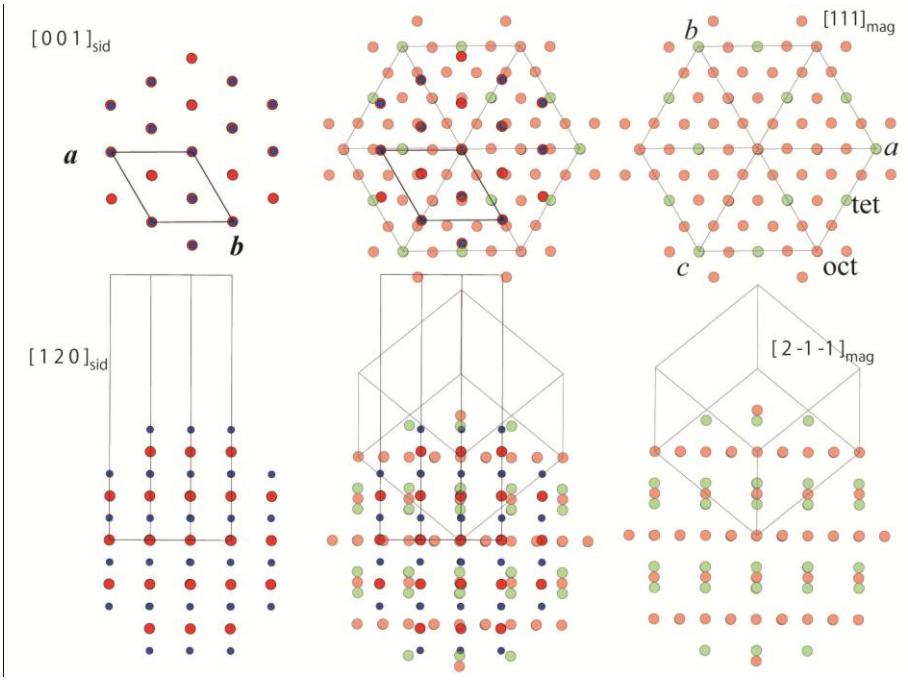


Figure 3. Structures of $FeCO_3$ viewed along [001] (top-left), Fe_3O_4 along [111] (top-right), and their superposition (top-middle), and structures of $FeCO_3$ viewed along [120] (bottom-left), Fe_3O_4 along [2-1-1] (bottom-right), and their superposition (bottom-middle),

The orientation relationship between $FeCO_3$ and spinel-type Fe_3O_4, as show in figure 2, can be explained from the structural point of view. The structures of $FeCO_3$ along [001] and [120] , and those of Fe_3O_4 along [111] and [2-1-1] are shown in figure 3. The superpositions of the corresponding pairs drawn in the middle of figure 3 indicated the rationality of the orientation relationships, and accordingly, justified the origin of topotaxy of Fe_3O_4 in the $FeCO_3$ parent crystal.

The orientation relationship between $FeCO_3$ and α-Fe_2O_3 can also be understood from the superposition of the structures along [001], as shown in figure 4. The oxygen packing of $FeCO_3$ and α-Fe_2O_3 are essentially the same, whereas the C atoms in $FeCO_3$ in are replaced with Fe in α-Fe_2O_3.

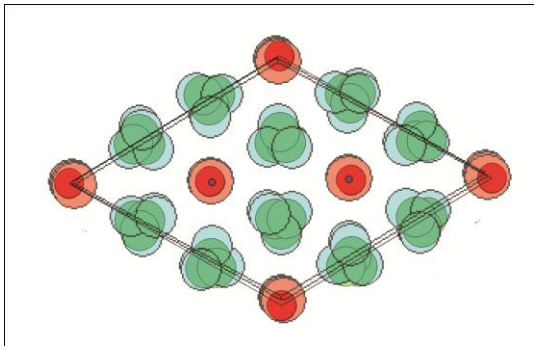


Figure 4. Superposition of $FeCO_3$ and α-Fe_2O_3 structures along [001]: O (light blue), Fe (orange), and C (blue dot) in $FeCO_3$; O(green), and Fe(red) in α-Fe_2O_3

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