Available online at www.sciencedirect.com

ELSEVIER

Journal of Solid State Chemistry 178 (2005) 2867–2872

JOURNAL OF SOLID STATE CHEMISTRY

www.elsevier.com/locate/jssc

# Space group and crystal structure of the Perovskite $CaTiO_3$ from 296 to 1720 K

Roushown Ali[1], Masatomo Yashima*

*Department of Materials Science and Engineering, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, 226-8502, Japan*

Received 3 November 2004; received in revised form 2 June 2005; accepted 14 June 2005

**Abstract**

The structural phase transitions of the calcium titanate perovskite $CaTiO_3$ were investigated by the Rietveld analysis of high-temperature neutron and X-ray powder diffraction data in the temperature range of 296–1720 K. The present work demonstrates that the compound exhibits two reversible phase transitions of orthorhombic *Pbnm*-tetragonal $I4/mcm$ and of $I4/mcm$-cubic $Pm\bar{3}m$ at $1498 \pm 25$ K and $1634 \pm 13$ K, respectively. No evidence of *Cmcm* phase is observed between the *Pbnm* and $I4/mcm$ structures. The lattice parameters discontinuously change at the *Pbnm*–$I4/mcm$ transition point, while a continuous change is observed for the $I4/mcm-Pm\bar{3}m$ transformation. These results indicate that the *Pbnm*–$I4/mcm$ transition is of first order and that the $I4/mcm-Pm\bar{3}m$ transformation is of either second or higher order.

*Keywords:* Crystal structure; Rietveld method; Phase transition; In situ measurements

## 1. Introduction

Perovskite-structured compounds are promising materials in current science and technology [1], and are of fundamental importance in solid-state science and geoscience [2]. The mineral perovskite $CaTiO_3$ is the parent compound of the perovskite-structured family. It is widely used in electronic ceramic materials and in immobilizing high-level radioactive waste [3–5]. The structural phase transition of $CaTiO_3$ has been studied extensively [6–18] and reported to undergo structural changes from orthorhombic *Pbnm* to cubic $Pm\bar{3}m$ symmetry as summarized in Table 1. Vogt and Schmahl [12] reported a direct phase transition from the *Pbnm* to $Pm\bar{3}m$ phase and observed no intermediate phase between them. On the contrary, some research groups [8–10] reported one intermediate phase between the *Pbnm* and $Pm\bar{3}m$ forms. Guyot et al. [11] and Kennedy et al. [13] suggested two intermediate phases including a *Cmcm* form between the *Pbnm* and $Pm\bar{3}m$ forms. However, the existence of the *Cmcm* phase has not been established yet. Therefore, the number of existing phases in the $CaTiO_3$ is an unresolved issue and it differs from 2 to 4, depending on the literature (Table 1).

The present work has been undertaken to examine the structural phase transitions of $CaTiO_3$. In particular we focus on the possibility of the *Cmcm* phase between the *Pbnm* and tetragonal $I4/mcm$ structures by using not only neutron but also X-ray powder diffraction data. With the help of higher angular resolution of the X-ray method, the present work reveals no possibility of the *Cmcm* phase. The crystal structures of all existing phases are refined by the Rietveld analyses of neutron powder diffraction data with the help of the relatively large scattering length of oxygen in neutron diffraction.

---

*Corresponding author. Fax: +81 45 924 5630.

*E-mail address:* yashima@materia.titech.ac.jp (M. Yashima).

[1] Present address: Department of Chemistry, University of Rajshahi, Rajshahi-6205, Bangladesh.

0022-4596/$ - see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2005.06.027

Table 1
Existing phases of $CaTiO_3$ in the literature and in the present work

| Reference and method | Space groups and temperature range of existing phases | | | |
|---|---|---|---|---|
| Kay and Bailey (1957)<br>In situ XRPD* [6] | Orthorhombic (*Pcmn*)<br>$T \le 1173$K | Not measured<br>$T > 1173$ | | |
| Liu and Liebermann (1993)<br>In situ XRPD* [7] | Orthorhombic (*Pbnm*)<br>$T \le 1373$K | Not measured<br>$T > 1373$K | | |
| Guyot et al. (1993)<br>Drop calorimetry [11] | *Pbnm*<br>$T < 1384$K | Orthorhombic (*Cmcm*)**<br>1384K$< T <$ 1520K | Tetragonal or Cubic**<br>1520K$< T <$ ? | Cubic**<br>?$< T$ |
| Wang and Liebermann (1993)<br>Ex situ TEM [10] | Orthorhombic (*Pbnm*)<br>$T < 1496$K | Tetragonal (*P*4/*mbm*)<br>1496K $< T <$ 1585K | Cubic<br>$T > 1673$K | |
| Vogt and Schmahl (1993)<br>In situ NPD* [12] | Orthorhombic (*Pbnm*)<br>$T \le 1550$K | Cubic ( $Pm\bar{3}m$ )<br>$T \ge 1600$K | | |
| Redfern (1996)<br>In situ XRPD* [8] | Orthorhombic (*Pbnm*)<br>$T \le 1373$K | Tetragonal (*I*4/*mcm*)<br>1423 $\le T \le$ 1523K | Cubic ( $Pm\bar{3}m$ )<br>$T > 1523$K | |
| Kennedy et al. (1999)<br>In situ NPD* [13] | Orthorhombic (*Pbnm*)<br>$T \le 1373$K | Orthorhombic (*Cmcm*)<br>1398K $\le T \le$ 1493K | Tetragonal (*I*4/*mcm*)<br>1513K $\le T \le$ 1573K | $Pm\bar{3}m$<br>1593K $\le T \le$ 1633K |
| Ali and Yashima, This work<br>In situ NPD and XRPD* | Orthorhombic (*Pbnm*)<br>$T \le 1486$K | Tetragonal (*I*4/*mcm*)<br>1523K $\le T \le$ 1622K | $Pm\bar{3}m$<br>$T \ge 1647$K | |

*XRPD and NPD denote X-ray powder diffraction and neutron powder diffraction, respectively.**No crystallographic evidence but speculation from analogy with $CaGeO_3$.

## 2. Experimental

### 2.1. Sample preparation

$CaTiO_3$ sample used in this experiment was prepared by solid-state reactions. High-purity powders of $CaCO_3$ (Purity 99.99%, High-Purity-Chemical Co., Saitama, Japan) and $TiO_2$ (Purity 98.5%, Kanto-Chemical Co., Tokyo, Japan) were mixed and ground using an agate mortar as dried powders and as ethanol slurries for 3 h. The mixture was pressed into pellets under the pressure of 200 MPa and then calcined in air at 1473 K for 12 h. The pellets were crushed by an alumina mortar, and then ground by the agate mortar as dried powders and as ethanol slurries for 2 h. The powders were pressed into a rod at 200 MPa and then sintered at 1673 K for 12 h. The sintered product with a cylindrical shape of 12 mm in diameter and of 70 mm in height was used to measure the neutron powder diffraction profiles. A part of the pellet was crushed and ground into powders for X-ray powder diffraction measurements.

### 2.2. High-temperature neutron powder diffraction

We performed neutron powder diffraction experiments on the Kinken powder diffractometer for high-efficiency and high-resolution measurements, HERMES [19]. Incident neutrons with a fixed wavelength of 1.8196 Å were obtained by a vertically focusing (331) Ge monochromator. Diffraction data were collected at step intervals of 0.1° over a $2\theta$ range from 20 to 152°, using 150 $^3$He counters set at 1° intervals. We have utilized a furnace [20] with $MoSi_2$ heaters to heat the $CaTiO_3$ rod in air under atmospheric pressure at 296, 453, 661, 868, 1069, 1173, 1270, 1322, 1373, 1423, 1473, 1523, 1548, 1572, 1598, 1622, 1674, 1671 and 1720 K. There are two thermocouples in the furnace. One thermocouple near the heater was used to control the temperature and the other contacting with the rod-sample, which monitored the sample temperature. The $CaTiO_3$ rod was heated at the rate of about 10 K/min, and then the sample temperature was kept constant during each measurement, within $\pm 1$ K above 1273 K and within $\pm 2$ K below 1273 K.

### 2.3. High-temperature X-ray powder diffraction

X-ray powder diffraction data were collected at the sample temperatures of 1431, 1486 and 1598 K by an X-ray powder diffractometer with a Rotaflex X-ray generator (RINT2550V/PC, Rigaku Co. Ltd., Tokyo, Japan) under the following experimental set up: Bragg–Brentano geometry, Cu$K\alpha$ radiation, voltage 40 kV, current 400 mA, divergence slit 0.5°, scattering slit 0.63 mm, receiving slit 0.15 mm. The measurement conditions were: Step-scanning mode with step interval