ELSEVIER

Journal of Nuclear Materials 247 (1997) 72–75

journal of nuclear materials

High temperature phase transitions of $CaTiO_3$ and $(Ca_{0.85}Nd_{0.15})TiO_3$ by X-ray diffractometry and differential thermal analysis

Tsuneo Matsui *, Hirotake Shigematsu, Yuji Arita, Yutaka Hanajiri, Norihiko Nakamitsu, Takanori Nagasaki

Department of Quantum Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

Abstract

The two phase transitions of $CaTiO_3$ and $(Ca_{0.85}Nd_{0.15})TiO_3$ were studied by high temperature X-ray diffraction and differential thermal analysis in the temperature range 300–1723 K. The presence of the two kinds of phase transitions in $CaTiO_3$ and $(Ca_{0.85}Nd_{0.15})TiO_3$ at about 1390 K and about 1530 K recently found by the heat capacity measurement in our laboratory was confirmed. From the X-ray diffraction patterns of $CaTiO_3$ and $(Ca_{0.85}Nd_{0.15})TiO_3$, the first phase transition at lower temperature was due to the change from the orthorhombic Pbnm to the orthorhombic Cmcm structure, and the second one at higher temperature was due to change from Cmcm to the cubic Pm3m structure, originating from the sequential rotations of the TiO_6 octahedra about one of the axes. Since no clear peak was seen at the phase transition around 1390 K in the DTA curve in contrast with the presence of the endothermic peak at the transition around 1530 K, it is thermodynamically considered that the former and the latter transition were second- and first-order phase transition, respectively. © 1997 Elsevier Science B.V.

1. Introduction

Perovskite oxides such as $CaTiO_3$ have been thought to be an important constituent of the waste forms that are being developed for the disposal of high level radioactive wastes since these ceramic oxides are capable of immobilizing lanthanides and actinides by forming solid solutions with them.

Previous studies on high temperature phase transition in undoped $CaTiO_3$ are limited [1–6], and there has been considerable difference in the number of phase transitions, transition temperature and structural changes as shown in Fig. 1. Naylor and Cook [1] have reported the presence of only one transition whereas Guyot et al. [2] observed two phase transitions, even though these two groups used the same drop method for the heat capacity measurements. Vogt and Schmahl [3] and Liu et al. [4,5] reported the presence of only one phase transition up to 1800 K by differential thermal analysis and high temperature X-ray diffraction, respectively. Although Wang and Liebermann [6] proposed the presence of two phase transitions by high temperature X-ray diffraction and transmission electron microscopy, the transition temperature for the second one at high temperature has not been definitely determined. It is noted that the Cmcm structure proposed by Guyot et al. [2] as the intermediate phase for $CaTiO_3$ was simply estimated without the experimental data by X-ray diffraction by the analogy with the known phase transition observed for $CaGeO_3$ [4,5]. Considering these results given in Fig. 1 and other crystallographic studies by Sasaki et al. [7] and Buttner and Maslen [8], it is concluded that the crystal structure of the low temperature phase around room temperature and the one above 1530 K are the orthorhombic Pbnm structure and the cubic Pm3m structure, respectively. However the crystal structure of undoped $CaTiO_3$ at the intermediate temperature still remains unclear. Concerning doped $CaTiO_3$, the heat capacity measurement on $CaTiO_3$ doped with Nd has been recently carried out in our

* Corresponding author. Tel.: +81-52 789 4682; fax: +81-52 789 4691; e-mail: t-matsui@mail.nucl.nagoya-u.ac.jp.

PII S0022-3115(97)00030-5

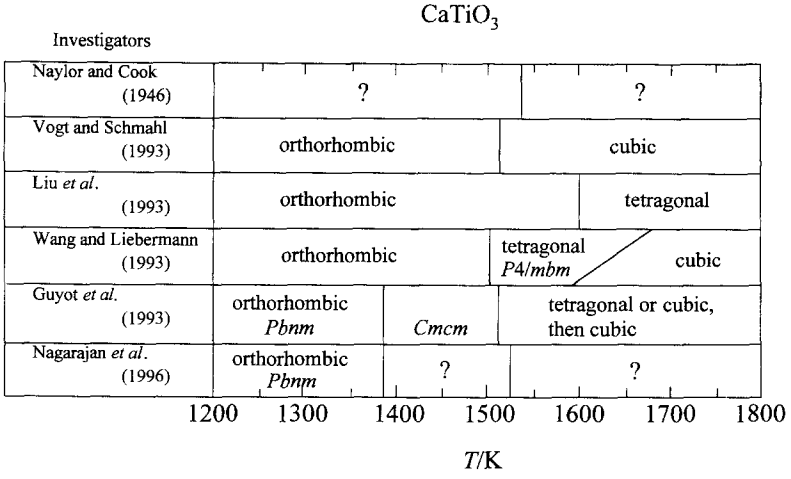

Fig. 1. Summary of the literature data on the transition temperatures and the crystal structures for three (or two) phase transitions of undoped and those of Nd-doped $CaTiO_3$.

laboratory [9] and the result is shown in Fig. 2. In this figure the presence of two phase transitions, one at 1386 K and another at 1528 K is seen similarly to the case of undoped $CaTiO_3$. However the information on the crystal structure of Nd-doped $CaTiO_3$ has not been obtained in relation to the phase transition.

In this study, the phase transitions of $CaTiO_3$ and $(Ca_{0.85}Nd_{0.15})TiO_3$, where Nd was selected as a stand-in of TRU, were investigated by high temperature X-ray diffraction and differential thermal analysis in the temperature range of 300–1723 K to confirm the presence of two phase transitions recently found by the heat capacity measurement in our laboratory and to clarify the crystal structure for three phases, especially the intermediate phase.

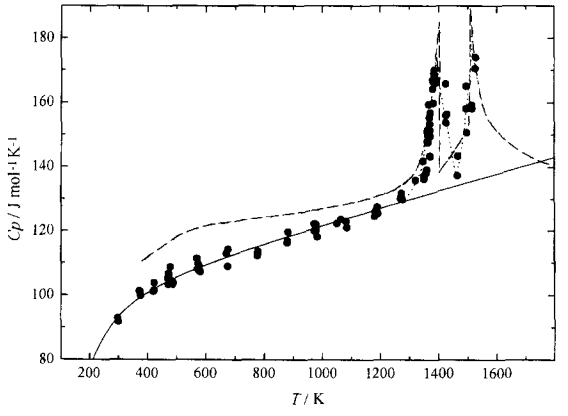

Fig. 2. Heat capacity of $(Ca_{0.85}Nd_{0.15})TiO_3$ recently obtained by the present authors [9]. ●, measured values; ————, least squared fitting curve based on the values below 1200 K; ---, estimated curve for the peak of phase transitions from 1300 to 1500 K; — — —, Guyot et al. [2] for undoped $CaTiO_3$.

2. Experimental

Powder samples of $CaTiO_3$ and $(Ca_{0.85}Nd_{0.15})TiO_3$ were prepared by mixing 99.99% pure $CaCO_3$ and TiO_2 (and Nd_2O_3) powders, pressing to pellets, and then heating in air at 1573 K for 7 days. High-temperature X-ray diffraction patterns were obtained from the powder sample on a platinum strip as the heating element using Rigaku high-temperature diffractometer and the position sensitive proportional counter with Cu–Kα radiation. X-ray diffraction patterns were measured in the range from $2\theta = 10°$ to 90° with a step size 0.02°. Differential thermal analysis was conducted with platinum pans in air at the heating rate 10 K/min with a DTA 92 device made by Setaram.

3. Results and discussion

The X-ray diffraction patterns of $CaTiO_3$ and $(Ca_{0.85}Nd_{0.15})TiO_3$ were very similar to each other, and, therefore, the X-ray patterns of $CaTiO_3$ at temperatures from 448 to 1723 K are only shown in Fig. 3. The X-ray diffraction pattern at low temperature (448 K) can be fit reasonably well by the Pbnm space group as is expected in the literature [2–6]. Based on the group-theoretical arguments [10,11], five kinds of crystal structures such as P4/mbm, Cmcm, I4/mcm, Imam and R3c have been proposed to exist as a possible intermediate crystal structure between Pm3m structure (high temperature cubic phase) and Pbnm structure (low temperature orthorhombic phase). According to the recent results given in Fig. 1, two crystal structures, i.e., tetragonal one with the space group P4/mbm [6] and orthorhombic one with Cmcm [2], are considered to be possible as an intermediate phase. To make clear the crystal structure at the intermediate temper-

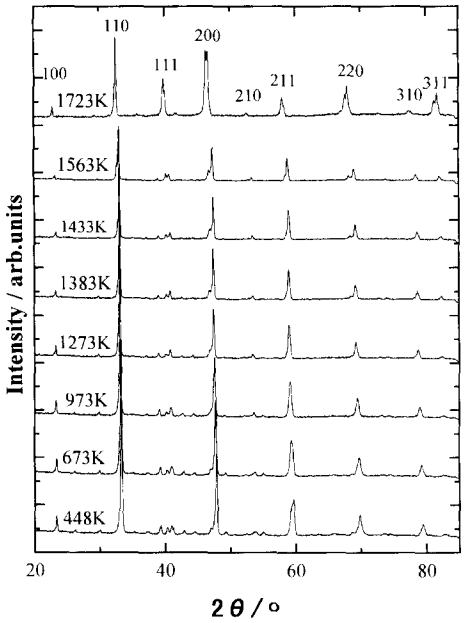

Fig. 3. X-ray diffraction patterns of undoped $CaTiO_3$.

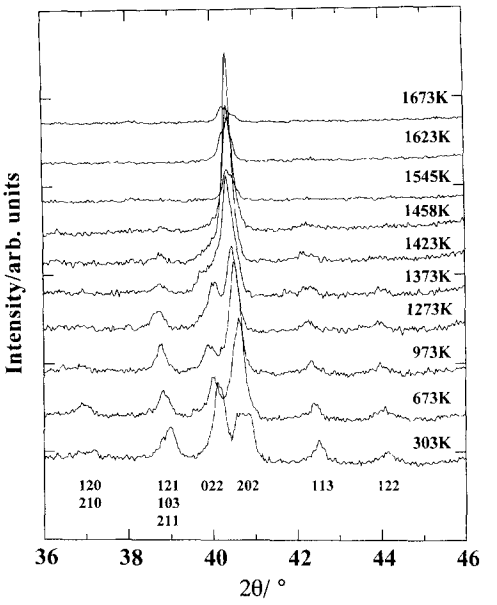

Fig. 4. X-ray diffraction patterns of $(Ca_{0.85}Nd_{0.15})TiO_3$ near the angles from 36° to 46°.

ature, the orthorhombic distortions of $CaTiO_3$ and $(Ca_{0.85}Nd_{0.15})TiO_3$ with Pbnm space group at room temperature were examined by monitoring the characteristic diffraction lines from $2\theta = 36$ to 46° as a function of temperature. The very similar change in the intensities of the diffraction lines was observed both for undoped $CaTiO_3$ and $(Ca_{0.85}Nd_{0.15})TiO_3$. The intensity change for $(Ca_{0.85}Nd_{0.15})TiO_3$ is shown in Fig. 4 as a function of temperature. As seen in this figure, two diffraction lines near $2\theta = 39°$ and 42° corresponding to those from the lattice planes {121}, {103} and {211}, and from the plane {113}, respectively remain even at temperatures above 1423 K, that is higher than the transition temperature 1386 K recently determined by the heat capacity measurement in our laboratory [9]. The presence of these two lines characterized by odd l values in Miller indices $\{hkl\}$ leads to the conclusion that the intermediate phase is the orthorhombic structure with the space group Cmcm, since these lines should disappear in the case of tetragonal P4/mbm structure from the crystallographic symmetry element. In Fig. 3 the phase transition from the intermediate structure to the high temperature cubic phase with Pm3m is also seen at 1723 K above the transition temperature 1528 K determined by the heat capacity measurement in our laboratory [9], although the occurrence of the transition to cubic Pm3m is not so clear at 1563 K since the intensity of the diffraction line near $2\theta = 40°$ is not enough strong and the intensity of the line near $2\theta = 48°$ is not larger than that near $2\theta = 32°$. This incompleteness of the transition at 1563 K is thought to be due to the inaccuracy of the measured temperature of (and/or temperature gradient in) the sample on the platinum strip in the high temperature X-ray furnace. The structural relation among the three modifications Pm3m, Cmcm and Pbnm with decreasing temperature is shown in Fig. 5. As seen in this figure, the Cmcm structure can be obtained from the Pm3m structure by rotating the TiO_6 octahedra about

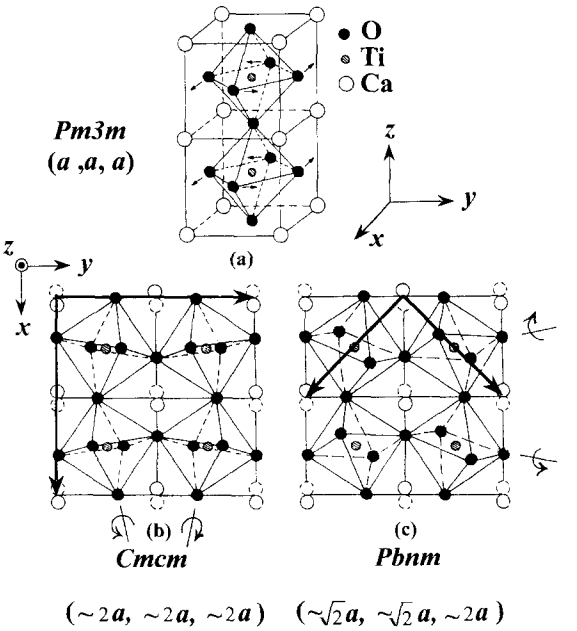

Fig. 5. Structural relation among the three modifications of undoped $CaTiO_3$ and $(Ca_{0.85}Nd_{0.15})TiO_3$.

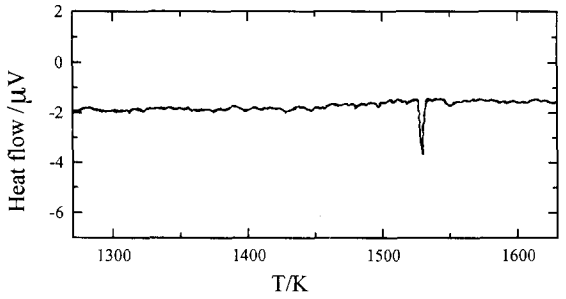

Fig. 6. DTA curve of $(Ca_{0.85}Nd_{0.15})TiO_3$.

z-axis of the Pm3m structure and sequentially (or simultaneously) about x-axis (i.e., about one of the axes of the tilted TiO_6 octahedra in the xy plane). Then the Cmcm structure finally changes to the Pbnm structure by the single rotation about y-axis (the remained axis of the tilted TiO_6 octahedra in the xy plane). The present result first proposed for $CaTiO_3$ and $(Ca_{0.85}Nd_{0.15})TiO_3$ shown in Fig. 5 is in good agreement with the structural change previously proposed for the same perovskite $CaGeO_3$ [4,5]. The Cmcm structure proposed by Guyot et al. [2] as the intermediate structure for $CaTiO_3$ was not determined based on the experimental data by X-ray diffraction, but simply estimated by analogy with the known phase transition observed for $GaGeO_3$.

The DTA result on $(Ca_{0.85}Nd_{0.15})TiO_3$ at the heating rate 10 K/min in air is shown in Fig. 6. The similar DTA curve was obtained for undoped $CaTiO_3$. Although an endothermic peak corresponding to the phase transition at higher temperature ($\sim$ 1530 K) is seen, no clear peak is observed for the phase transition at lower temperature ($\sim$ 1390 K), suggesting that the former is the 1st order-transition (or the 2nd order-transition with large enthalpy change) and the latter is the 2nd-order transition. The larger values for the enthalpy and entropy of the transition around 1530 K than those around 1390 K have been reported for Nd-doped $CaTiO_3$ [9]. The order and the magnitude of the enthalpy and entropy of transition of these phase transitions are in good accordance with the structural change in the crystal structure at two phase transitions determined by X-ray diffraction in this study, since the transition at low temperature involves only one rotation of TiO_6 octahedra in contrast with that at high temperature originating from two sequential (or simultaneous) rotations. The more detailed study on the structural change at these transitions by X-ray diffraction is under way in our laboratory.

Acknowledgements

The authors wish to express their gratitude to Dr S. Kitaoka of Japan Fine Ceramic Center for his assistance and advice in performing X-ray studies. This work was partly supported by a Grant-in-Aid for Scientific Research No. 08458122 from the Ministry of Education, Science and Culture.

References

[1] H.F. Naylor, O.A. Cook, J. Am. Chem. Soc. 68 (1946) 1003.
[2] F. Guyot, P. Richet, Ph. Courtial, Ph. Gillet, Phys. Chem. Miner. 20 (1993) 141.
[3] T. Vogt, W.W. Schmahl, Europhys. Lett. 24 (1993) 281.
[4] X. Liu, Y. Wang, R.C. Liebermann, P.D. Maniar, A. Navrotsky, Phys. Chem. Miner. 18 (1991) 224.
[5] X. Liu, Y. Wang, R.C. Liebermann, P.D. Maniar, A. Navrotsky, Phys. Chem. Miner. 20 (1993) 171.
[6] Y. Wang, R.C. Liebermann, Phys. Chem. Miner. 20 (1993) 147.
[7] S. Sasaki, C.T. Prewitt, J.D. Bass, Acta Crystallogr. C43 (1987) 1668.
[8] R.H. Buttner, E.N. Maslen, Acta Crystallogr. B48 (1992) 644.
[9] K. Nagarajan, Y. Arita, N. Nakamitsu, Y. Hanajiri, T. Matsui, J. Nucl. Mater. 230 (1996) 124.
[10] A.M. Glazer, Acta Crystallogr. B28 (1972) 3384.
[11] K.S. Aleksandrov, Ferroelectrics 14 (1976) 801.