Crystal structural change of Ba-doped-tricalcium phosphate

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Abstract

Crystal structural change of barium-doped-tricalcium phosphate (TCP) has been investigated using high-temperature neutron powder diffraction and Rietveld method. The alpha-alpha' phase transition temperature decreased with an increase of Ba composition x in Ca3(1-x)Ba3x(PO4)2. Structural refinement of Ba-doped-TCP was successfully performed by P21/a. Temperature dependence of unit cell parameters was determined around the alpha-alpha' phase transition point. Unit-cell parameter a discontinuously changed at the alpha-alpha' transition temperature, indicating that the transition is of first order.

(1) Introduction

Tricalcium phosphate [TCP: Ca3(PO4)2] has increasingly been used as a biocompatible material for bone replacement or for the coating of bone prostheses. There are many studies to investigate doped TCPs. Although many researches for crystal structure of doped-TCP have been reported for ?-phase, crystal structure of alpha-type doped-TCP has been insufficiently understood and studied, probably due to their complicated crystal structures. In this study, we investigated the crystal structural change of Ba-doped-TCP using high-temperature powder neutron diffraction analysis.

(2) Experiments and Data Processing

High-purity alpha TCP was prepared by solid-state reactions from beta Ca3(PO4)2 and Ba3(PO4)2. Stoichiometric amounts of high-purity CaHPO4 (99.6% purity, Kyowa Chemical Industry, Takamatsu, Japan) and CaCO3 (99.99% purity, Kojundo Chemical Lab. Co., Ltd., Sakado, Japan) powders were mixed for about 3.0 h in an agate mortar. The mixture was pressed into pellets under a uniaxial pressure of 150 MPa. The pellets were sintered for 12 h at 1000?C to obtain single phase beta TCP. Ba3(PO4)2 was obtained after sintering BaCO3 and NH 4 H2PO4 mixture at 1000 C deg. for 12 hours. The sintered pellets of beta Ca3(PO4)2 and Ba3(PO4)2 were ground and mixed (Ca/Ba atomic ratio= 95/5). And the mixtures were sintered at 1400 C deg. for 6 h. The resultant products were used for neutron powder diffraction study.

To investigate the temperature dependence of the crystal structure of Ba-doped-TCP, neutron powder diffraction experiments were carried out at high temperatures in air with a 150-detector system, HERMES, installed in the JRR-3M reactor at the Japan Atomic Energy Agency, Tokai, Japan. Neutrons with a wavelength of 0.182 nm were obtained by the (3 1 1) reflection of a Ge monochromator. The diffraction data were collected in the 2 theta range from 3 deg. to 153.9 deg. in a step interval of 0.1 deg. in the temperature range from 24 to 1533 C deg. A furnace with MoSi2 heaters was placed on the sample table, and used for the neutron diffraction measurements at the high temperature. The unit-cell and structural parameters of the Ba-doped-TCP were refined by Rietveld analysis using the RIETAN-2000 computer program. The diffraction patterns were fitted with a Pearson VII type function.

(3) Results and Discussion

Figure 1 shows the temperature depen-

dence of the neutron diffraction pattern for 5 mol% Ba doped TCP. Closed and open circles in Fig. 1 denote neutron diffraction peaks of high-temperature alpha ’- and low-temperature alpha-phases, respectively. At 1449.9 C deg., the pattern exhibited both peaks of the alpha (closed circles in Fig. 1) and alpha’ (open circles in Fig. 1) phases, indicating the alpha and alpha ’ phases co-existed at this temperature. The characteristic peaks of the alpha phase (closed circles in Fig. 1) disappeared between 1425.9 and 1474.8 C deg. Therefore, the alpha-TCP transforms into alpha’-phase between 1425.9 and 1474.8 C deg.

Structural refinement was successfully performed by a monoclinic structure, space group P21/a. The reliability factors were Rwp = 5.32%, S = 2.05, RI = 0.40%, RF = 0.19%. The unit-cell parameters obtained from the Rietveld analysis were a = 1.2936(3), b = 2.7540(3), c = 1.5252(4)nm, alpha = beta = 90 deg., gamma = 126.66(1) deg.

We successfully determined the temperature dependence of the unit-cell parameters a for TCP around the alpha? alpha ’ phase transition point. Thus we were able to clearly indicate that the alpha? alpha ’ phase transition is of first order.

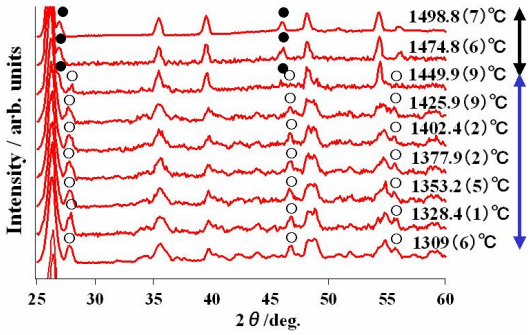

Fig. 1. Neutron powder diffraction patterns of 5mol% Ba-doped-TCP at different temperatures. Closed and open circles denote neutron diffraction peaks of high-temperature alpha’- and low-temperature alpha-phases, respectively.