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A differential scanning calorimeter study of the monoclinic ($P2_1/b$) ↔ hexagonal ($P6_3/m$) reversible phase transition in hydroxyapatite

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Abstract

The apparent transition temperature (T_c) and enthalpy (ΔH) of monoclinic ($P2_1/b$) ↔ hexagonal ($P6_3/m$) reversible phase transition in stoichiometric ($Ca/P = 5/3$) hydroxyapatite were investigated as a function of heating/cooling rate by means of a differential scanning calorimeter (DSC), in the heating/cooling rate range of 0.5–3.0 K/min. The apparent T_c value slightly increased and decreased with increasing heating and cooling rates, respectively, while the apparent ΔH value was almost same within the experimental error. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydroxyapatite; Reversible phase transition; DSC; Heating/cooling rate dependence; Hysteresis

1. Introduction

Hydroxyapatite (HAp) has a chemical formula of $Ca_{10}(PO_4)_6(OH)_2$ and is known as a biocompatible material, ion exchange reactor, laser host material, and so on [1–5]. This compound exhibits a reversible phase transition at about 480 K between monoclinic (abbreviated as M, space group $P2_1/b$) and hexagonal phases (abbreviated as H, space group $P6_3/m$) [7]. This phase transition was first investigated by optical microscopy [6]. Recently, Suda et al. in our laboratory [7] confirmed the reversible heat anomaly accompanying the phase transition by means of a differential scanning calorimeter (DSC) for the first time, and reported the phase transition temperature ($T_c = 480.0 \pm 0.3$ K) and enthalpy ($\Delta H = 630.0 \pm 25$ J/mol). It is important to investigate the dependence of the apparent phase transition temperature and enthalpy on heating/cooling rate from the point of view of thermochemistry [8–11]. Nevertheless, no studies have been carried out on the behavior of the M ↔ H phase transition in HAp. The purpose of the present work is to investigate the heating/cooling rate dependence of the apparent T_c and ΔH values.

2. Experimental

Stoichiometric HAp powder with $Ca/P = 5/3$ was synthesized via solid state reaction according to Fowler [12]. Calcium hydrogen phosphate dihydrate

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($CaHPO_4{\cdot}2H_2O$, 98.0%, Kanto Chemical Co. Inc., Tokyo, Japan) and calcium carbonate ($CaCO_3$, 99.0%, Kanto Chemical Co. Inc., Tokyo, Japan) were used as starting materials. They were thoroughly mixed in an agate mortar with $Ca/P = 5/3$ as ethanol slurries and dried powders for 3 h, and pressed into pellets of 20 mm in diameter and 2–3 mm in height. They were fired in an electric furnace (KDF70GLS, Denken Co. Ltd., Kyoto, Japan) at 1253 K for 10 h in vacuum and then at 1173 K for 30 h under flowing a pure argon gas which was passed bubbling thorough distilled water at a room temperature, with flow rate of 0.5–1.0 l/min. After crushing and grinding the pellet into powder for 3 h by the same method described above, the powder was pressed again into a pellet and fired at 1173 K for 10 h under the same flowing argon plus water atmosphere. After recrushing and regrinding the pellet into powder for 4 h by the same method described above, the powder was pressed again into pellet and fired at 1253 K for 7 h and then 1173 K for 7 h under the same flowing argon plus water atmosphere. The pellet was finally crushed into powder for 1 h. The HAp powder thus obtained was characterized by means of an X-ray diffractometer (MXP^{3VA}, Cu Kα, 40 kV–40 mA, MAC Science Co. Ltd., Tokyo, Japan) and Fourier transform infrared (IR) spectrometer (SYSTEM 2000, Perkin-Elmer, Beaconsfield, Norwalk, USA) to check the sample homogeneity. X-ray diffraction (XRD) profile was obtained by a step-scan technique (0.02° per step, 10 s per step) in a scanning range of 20–40° (2θ). Lattice parameters were obtained also by the step-scan technique (0.01° per step, 7 s per step) in a scanning range of 20–80° (2θ). The sample powder was mixed with pure silicon powder (High-Purity Chemical Co. Ltd., Sakado, Japan, 99.999% purity) as an internal standard for an angular calibration. The lattice parameters were calculated by a least-squares program using the peak positions of $\bar{1}\,6\,1, \bar{1}\,4\,2, \bar{2}\,2\,4, \bar{1}\,6\,2, 2\,4\,2, 2\,10\,1, 1\,8\,0, 5\,10\,1$ and $6\,10\,1$, reflection peaks of HAp and 1 1 1, 2 2 0, 3 1 1, 4 0 0 and 3 3 1 reflection peaks of silicon. IR spectrum was obtained from discs of the HAp and KBr, mixed in the ratio of 1:150 by weight with resolution of 4 cm^{-1}. DSC measurements (heat flux type, DSC 3200, MAC Science Co. Ltd., Tokyo, Japan) were carried out under following conditions, heating/cooling rates of 0.5, 1.0, 2.0 and 3.0 K/min, nitrogen atmosphere (flow rate 100 ml/min), sample size for HAp powder of 49.090 mg. Temperature and caloric calibrations were performed at all heating rates. Temperature was calibrated by the melting points of high purity In (99.999%, 5N), Sn (99.999%, 5N), and Pb (99.9999%, 6N). The enthalpy was calibrated by the heat of fusion of In (5N) and Pb (6N).

3. Results and discussion

Both XRD patterns (Fig. 1) and IR spectrum (Fig. 2) of the final product showed typical patterns for stoichiometric ($Ca/P = 5/3$) monoclinic HAp [13,14]. Impurities such as β-TCP and CaO were not observed. Since the sample heated at 900°C for 7 h forms no β-TCP and CaO, the final product is considered to have exactly stoichiometric composition of calcium and phosphorus [15]. XRD pattern also shows some weak reflection peaks (denoted as asterisk (∗)) forbidden for hexagonal symmetry ($P6_3/m$), which are identified as due to the monoclinic phase ($P2_1/b$) [13]. Lattice parameters were determined as $a = 9.4202(3)$ Å, $b = 18.8399(4)$ Å, $c = 6.8818(3)$ Å, $\gamma = 120.001(1)^\circ$ with monoclinic symmetry, which is close to that reported for stoichiometric HAp ($a = 9.4214(8)$ Å, $b = 2a$, $c = 6.8814(7)$ Å, $\gamma = 120^\circ$ [16]). This sample showed a typical IR spectrum of stoichiometric HAp (Fig. 2). IR bands at 3573 and 632 cm^{-1} were assigned to OH stretching and librational modes, respectively, and the bands at 1090 and 1048, 963, and 602 and

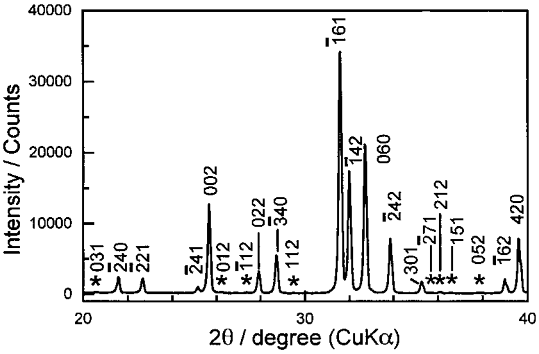

Fig. 1. XRD pattern of stoichiometric ($Ca/P = 5/3$) HAp powder. Monoclinic ($P2_1/b$) reflection peaks forbidden for hexagonal symmetry ($P6_3/m$) are marked by asterisk (∗). Indices are shown on the basis of the monoclinic cell.

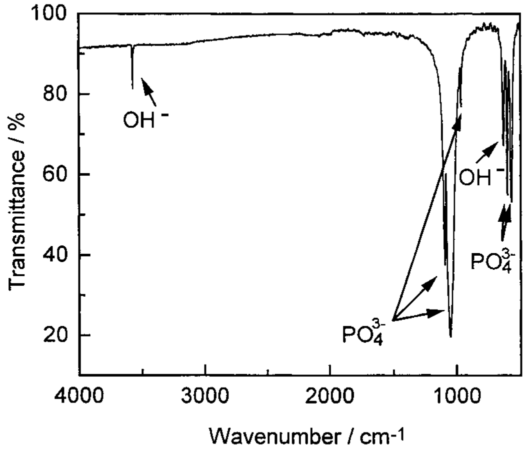

Fig. 2. IR spectrum of stoichiometric (Ca/P = 5/3) HAp powder.

572 cm^{-1} were assigned to ν_3, ν_1 and ν_4 PO_4 modes, respectively [14].

Fig. 3 shows the DSC curves of HAp measured at various heating/cooling rates. The peak area increases and peak top (T_c) shifts with increasing heating/cooling rate. In addition, the apparent transition temperature (T_c), which was the onset temperature determined as the cross point of the extrapolated base line and the extrapolated peak line, also shifted slightly with the heating/cooing rates. Apparent transition temperature (T_c) and enthalpy (ΔH) are plotted against (a) heating and (b) cooling rate in Fig. 4. The apparent T_c value slightly increases with increasing the heating rate from 478.1 K for 0.5 K/min to 478.8 K for 3 K/min, while it decreases with increasing the cooling rate from 479.2 K for 0.5 K/min to 478.8 K for 3 K/min. Apparent ΔH value was almost independent of the heating/cooling rate of 0.5–3.0 K/min within the experimental error. The mean value of apparent ΔH among four heating runs was 339 J/mol with the standard deviation of 7 J/mol.

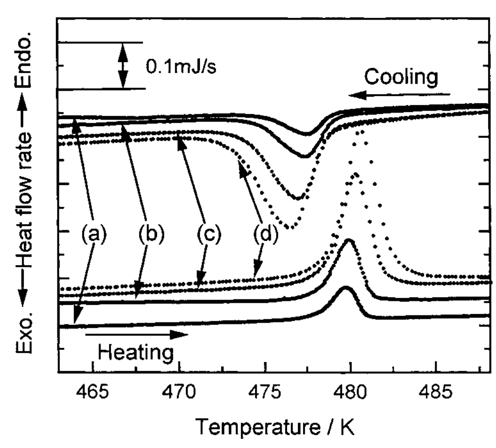

Fig. 3. The DSC curves of HAp at the heating/cooling rates of (a) 0.5 K/min, (b) 1.0 K/min, (c) 2.0 K/min and (d) 3.0 K/min.

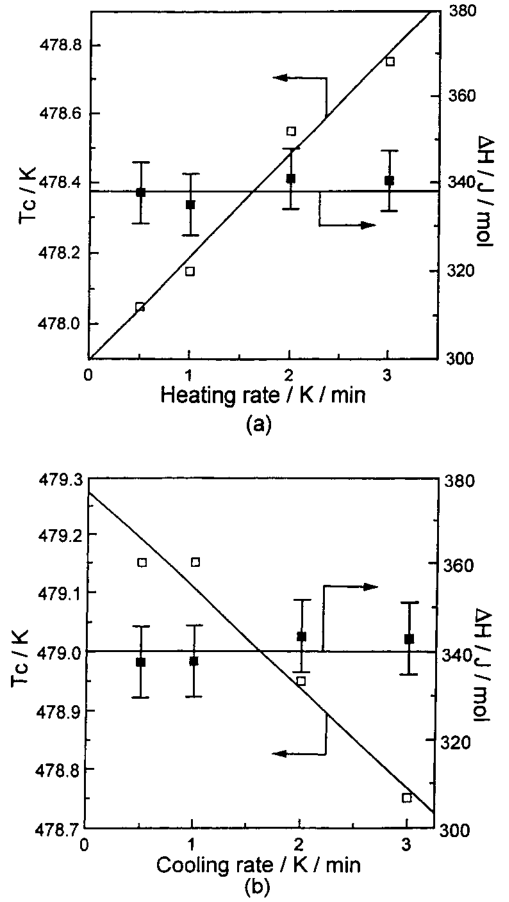

Fig. 4. The transition temperature (T_c) and enthalpy (ΔH) as a function of (a) heating and (b) cooling rate.

In the present work, we have demonstrated the heating/cooling rate dependence of the apparent phase transition temperature and enthalpy for HAp. This effect has been studied for other materials. For instance, trimethylammonium trichlorocadmium(II) [10], the dependence of apparent transition temperature on heating/cooling rate was small as well as that observed for HAp in this work, and in addition, judging from apparent phase transition temperature in Fig. 4, thermal hysteresis in HAp seems quite small compared with that observed, for example, ZrO_2 or HfO_2 [17,18]. This behavior is similar to that reported for potassium thiocyanate by Hamilton and House [9]. As reported previously, thermal hysteresis is related to the differences in cell volumes before and after the transformation, ΔV. [19]. From the result in this work, the phase transformation in HAp seems to have relatively small volume change accompanying phase transition. Actually, 3 0 1 reflection peak at around $2\theta \sim 35.5^\circ$ in XRD patterns did not show significant shift between 473 and 483 K, i.e. just before and after the phase transformation, as shown in [7]. On the other hand, in case of transition enthalpy, this sample prepared in this work showed rather small value compared with that described in [7]. Although the reason why we obtained small ΔH value is not clear, this difference may be brought by quite small amount of impurities, which cannot be detected by XRD and IR, during longer mixing procedures. The heating/cooling rate dependence of transition enthalpy is also studied for other substances. For instance, anhydrous potassium acetate [8], and potassium thiocyanate [9] have been reported to show large dependence on heating/cooling rate. On the contrary, Breuer and Eysel [11] showed that there is little dependence of ΔH on heating rate for CsCl within a heating rate less than 10 K/min. This result, i.e. no dependence of ΔH on heating/cooling rate, is same to that obtained in this work. DSC is not a static method for the evaluation of transition temperature or enthalpy, we could obtain stable value which does not depend on heating/cooling rate in the range of 0.5–3.0 K/min for HAp.

4. Conclusions

The apparent transition temperature and enthalpy of $M \leftrightarrow H$ reversible phase transition in stoichiometric ($Ca/P = 5/3$) HAp were investigated as a function of heating/cooling rate by means of DSC, in the heating/cooling rate range of 0.5–3.0 K/min. The apparent T_c value slightly increased with increasing the heating rate and decreased with increasing cooling rate, while the apparent ΔH value was almost same within the experimental error.

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References

[1] K. Aoyama, J. Chiba, J. Immunol. Methods 162 (1993) 201.
[2] Y. Matsumura, J.B. Moffat, J. Catal. 148 (1994) 323.
[3] W. Suchanek, H. Suda, M. Yashima, M. Kakihana, M. Yoshimura, J. Mater. Res. 10 (1995) 521.
[4] L.L. Hench, J. Am. Ceram. Soc. 74 (1991) 1487.
[5] R. Jagannathan, M. Kottaisamy, J. Phys.: Condens. Matter 7 (1995) 8453.
[6] H.B.V. Rees, M. Mengeot, E. Kostiner, Mater. Res. Bull. 8 (1973) 1307.
[7] H. Suda, M. Yashima, M. Kakihana, M. Yoshimura, J. Phys. Chem. 99 (1995) 6752.
[8] J.H. House Jr., K.A. Kemper, Thermochim. Acta 162 (1990) 325.
[9] C.D. Hamilton, J.E. House Jr., Thermochim. Acta 206 (1992) 91.
[10] J.E. House Jr., C.D. Dunbar, Thermochim. Acta 204 (1992) 213.
[11] K.-H. Breuer, W. Eysel, Thermochim. Acta 57 (1982) 317.
[12] B.O. Fowler, Inorg. Chem. 13 (1974) 207.
[13] J.C. Elliott, P.E. Mackie, Colloques internationaux C.N.R.S., No. 230, Physico-chimie et cristallographie des apatites d'intérêt biologique, 1975, p. 69.
[14] B.O. Fowler, Inorg. Chem. 13 (1974) 194.
[15] J.C. Elliott, Structure and chemistry of the apatites and other calcium orthophosphates, in: Studies in Inorganic Chemistry, Vol. 18, Elsevier, Amsterdam, 1994, p. 188.
[16] J.C. Elliott, Structure and chemistry of the apatites and other calcium orthophosphates, in: Studies in Inorganic Chemistry, Vol. 18, Elsevier, Amsterdam, 1994, p. 112.
[17] G.M. Wolten, J. Am. Ceram. Soc. 46 (1963) 418.
[18] A. Arias, J. Am. Ceram. Soc. 49 (1966) 334.
[19] K.J. Rao, C.N.R. Rao, J. Mater. Sci. 1 (1966) 238.