Crystal growth of carbonate apatite using a $CaCO_3$ flux

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Single crystals of carbonate apatite were grown using a $CaCO_3$ flux under an Ar gas pressure of 55 MPa. The crystals obtained were observed by scanning electron microscopy, optical microscopy and X-ray diffraction. Electron probe microanalyses and thermal analyses were performed. CO_3 ions in planar triangle form replaced both OH sites and PO_4 tetrahedral sites in the apatite structure: in particular, the OH sites were perfectly substituted by CO_3 ions using this method.

1. Introduction

There has been considerable interest in the growth of synthetic single crystals of carbonate apatite (abbreviated as CAp hereafter), since this material is the main mineral constituent of bones and teeth. However, its structural properties and functional behavior in hard tissue are not sufficiently elucidated.

Artificial materials have been prepared by a coprecipitation method [1] under normal pressure below 100 °C or by an ion-exchange method from hydroxyapatite (abbreviated as HAp hereafter) near 1000 °C [2]. The problem of the substitutional site of CO_3 ions has not yet been solved by direct measurement, but Montel [2] indirectly indicated that CO_3 ions can replace both OH (A-site) and PO_4 (B-site) in the HAp structure.

As regards single crystals, there are a few reports in which single crystals are successfully prepared by a hydrothermal technique [3, 4]. In the present paper we describe single crystal growth of CAp using a $CaCO_3$ flux without water, in order to eliminate hydroxide ions from the crystals. The crystals obtained were analyzed by scanning electron microscopy (SEM), optical microscopy, X-ray diffraction (XRD), electron probe microanalysis (EPMA) and thermal analysis.

2. Materials and methods

Brushite ($CaHPO_4 \cdot 2H_2O$) powder was synthesized by reaction of pure $CaCO_3$ (Calseed, $> 99.99\%$) with phosphoric acid, and heated at 800 °C in air for 2 h to make β-calcium pyrophosphate ($Ca_2P_2O_7$). Then α-TCP ($Ca_3(PO_4)_2$) powder was obtained by heating the mixture of β-calcium pyrophosphate and $CaCO_3$ at 1300 °C for 1 h.

A dry mixture of the α-TCP and $CaCO_3$ powder was sealed in a Pt tube (10 mm in diameter and 50 mm in length) and apatite crystals were grown with Ar gas pressure. The conditions for several runs are listed in Table I. The pressure could not be very accurately controlled as the temperature was varied.

In order to grow large crystals, both temperature oscillation and slow cooling were tried. The temperature of run No. 5 was oscillated in 11 cycles between 1200 and 1300 °C after having been kept at 1400 °C for 1 h. The rate of temperature change was $10\,^\circ C\,min^{-1}$ (1200 → 1300 °C) and $1\,^\circ C\,min^{-1}$ (1300 → 1200 °C). Experiment No. 6 was performed at a cooling rate of $1\,^\circ C\,min^{-1}$ and the cooling rate of run No. 7 was $2\,^\circ C\,h^{-1}$ (1500 → 1400 °C) and $4\,^\circ C\,h^{-1}$ (1400 → 1100 °C).

After growth at high temperature, specimens were quenched by turning off the heater and releasing the heat. The cooling rate of this quenching process was about $30\,^\circ C\,min^{-1}$. The residual $CaCO_3$ was removed using ethylenediaminetereacetic acid (EDTA)–Na_2 aqueous solution.

The structure of the crystals obtained was identified with an X-ray powder diffractometer (XRD, Philips PW1820) and a Fourier transform infrared (FTIR) spectrometer (BIORAD FTS-45A). XRD measurements were carried out with CuK_α radiation. The voltage and current of the X-ray tube were 40 kV and 50 mA, respectively. FTIR spectra were measured for pulverized specimens using the diffuse reflectance method. Lattice symmetry and cell parameters were investigated with a precession camera (Rigaku 1531B1) and a four-circle diffractometer (Rigaku AFC-5R). The X-ray source for the precession photography was MoK_α at 40 kV and 20 mA. Lattice parameter measurement by the four-circle diffractometer was performed using AgK_α generation at 40 kV and 120 mA.

Chemical analyses of Ca and P were performed by an electron probe X-ray microanalyzer (EPMA, Jeol JXA-8600MX) using a stoichiometric HAp standard. Total carbon contents were determined using a carbon analyzer (Horiba EMIA 511). The specimens were pulverized and heated with Sn powder as a combustion improver at

TABLE I Preparation conditions

Run no.	Starting mixture (TCP wt %)	Maximum temperature (°C)	Pressure (MPa)	Time at maximum temperature (h)	Temperature change rate
1	60	1300	190	80	-
2	60	1300	65	60	-
3	60	1300	55	70	-
4	30	1400	55	12	-
5	50	1400	55	1	Oscillated 11 cycles $+10\,^{\circ}\mathrm{C\,min^{-1}}$ (1200 → 1300 °C) $-1\,^{\circ}\mathrm{C\,min^{-1}}$ (1300 → 1200 °C)
6	60	1300	55	18	$-1\,^{\circ}\mathrm{C\,min^{-1}}$ (1300 → 1100 °C)
7	60	1500	50	1	$-2\,^{\circ}\mathrm{C\,h^{-1}}$ (1500 → 1400 °C) $-4\,^{\circ}\mathrm{C\,h^{-1}}$ (1400 → 1100 °C)

1400 °C, and then desorbed CO_2 gas was quantitatively measured by an infrared (i.r.) detector. The temperature dependence of desorption of CO_2 gas from the specimens was measured by a Leco RC-412. The specimen was heated up to 1200 °C at $1\,^{\circ}\mathrm{C\,s^{-1}}$ and kept at 1200 °C for 10 min in O_2 gas. Thermogravimetric analyses (TGA) were carried out with a Rigaku TG 8101C. The weight of the specimen was 9.76 mg. The temperature was raised up to 1400 °C at $10\,^{\circ}\mathrm{C\,min^{-1}}$.

3. Results and discussion

3.1. Phase under high pressure

A phase diagram for the $CaCO_3$–TCP system under a pressure of about 10 MPa appeared in [5]. In this diagram, shown in Fig. 1, no CAp phase is found, but a spodiosite phase ($Ca_4CO_3(PO_4)_2$) is found. The experimental conditions of the present study were thus located near the spodiosite phase line. According to the XRD analyses (Fig. 2), however, the specimens under high pressure did not have spodiosite structure but apatite structure. The XRD pattern of the specimens was very similar to that of HAp. These results suggest that the spodiosite phase in this diagram corresponds to the CAp phase under high pressure.

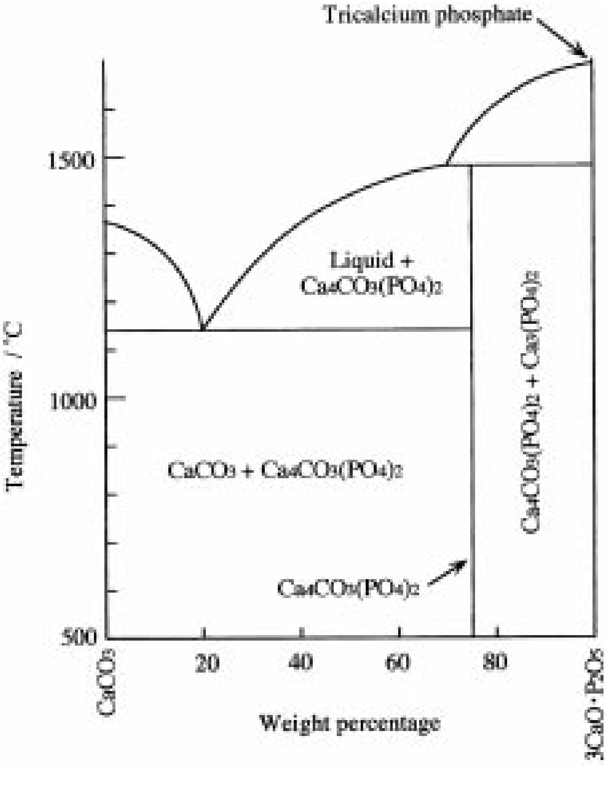


Figure 1 Phase diagram of the system $CaCO_3 - 3CaO \cdot P_2O_5$ reproduced from [5].

The equilibrium CO_2 pressure for the reaction $CaCO_3 \leftarrow\rightarrow CaO + CO_2$ is about 10 MPa at the melting point of $CaCO_3$, i.e. 1339 °C [6]. This means that an experiment on the crystal growth of CAp should be performed at pressures over 10 MPa. This phase diagram was determined at about 10 MPa, but higher pressure up to about 55 MPa was required in order to grow large crystals at higher temperature. The purpose of runs No. 1, 2 and 3 was to find out the pressure under which the melting point of a mixture of 60 wt % TCP is 1300 °C. Experiment No. 3 yielded apatite single crystals, while specimens from experiments No. 1 and 2 did not melt, although their phases were CAp and $CaCO_3$. This result indicates that the solidus of this system coincides with the 1300 °C line under a pressure of between 55 and 65 MPa. $CaCO_3$ cannot act as flux above 65 MPa at 1300 °C.

3.2. Crystal growth of CAp

Fig. 3 shows photographs of the crystals obtained. The crystals from run No. 4 (Fig. 3a) are acicular, of about 100 μm in length, and are assumed to grow during the rapid cooling process from 1400 °C. Further, this result indicates that the whole content of No. 4 melted while being held at 1400 °C, as is approximately consistent with the liquidus line in this diagram (Fig. 1) though the pressure applied was 55 MPa.

Fig. 3b shows one of the crystals from run No. 5. The shape of the crystal was hexagonal prismatic and elongated along the *c*-axis. Its length was 700 μm. Fig. 3c and d shows the polished thin sections of specimens No. 6 and 7, respectively. The crystals obtained from No. 6 were short prisms about 100 μm in length. The crystals from No. 7 were over 5 mm in length and about 500 μm in thickness, the largest of all the seven runs, but cracked into fragments, probably during the quenching process. These crystals were almost perfectly transparent.

3.3. Analyses of CO_3 ions

Fig. 4 indicates the FTIR spectrum of the No. 5 specimen. By comparison with HAp, it is clear that the

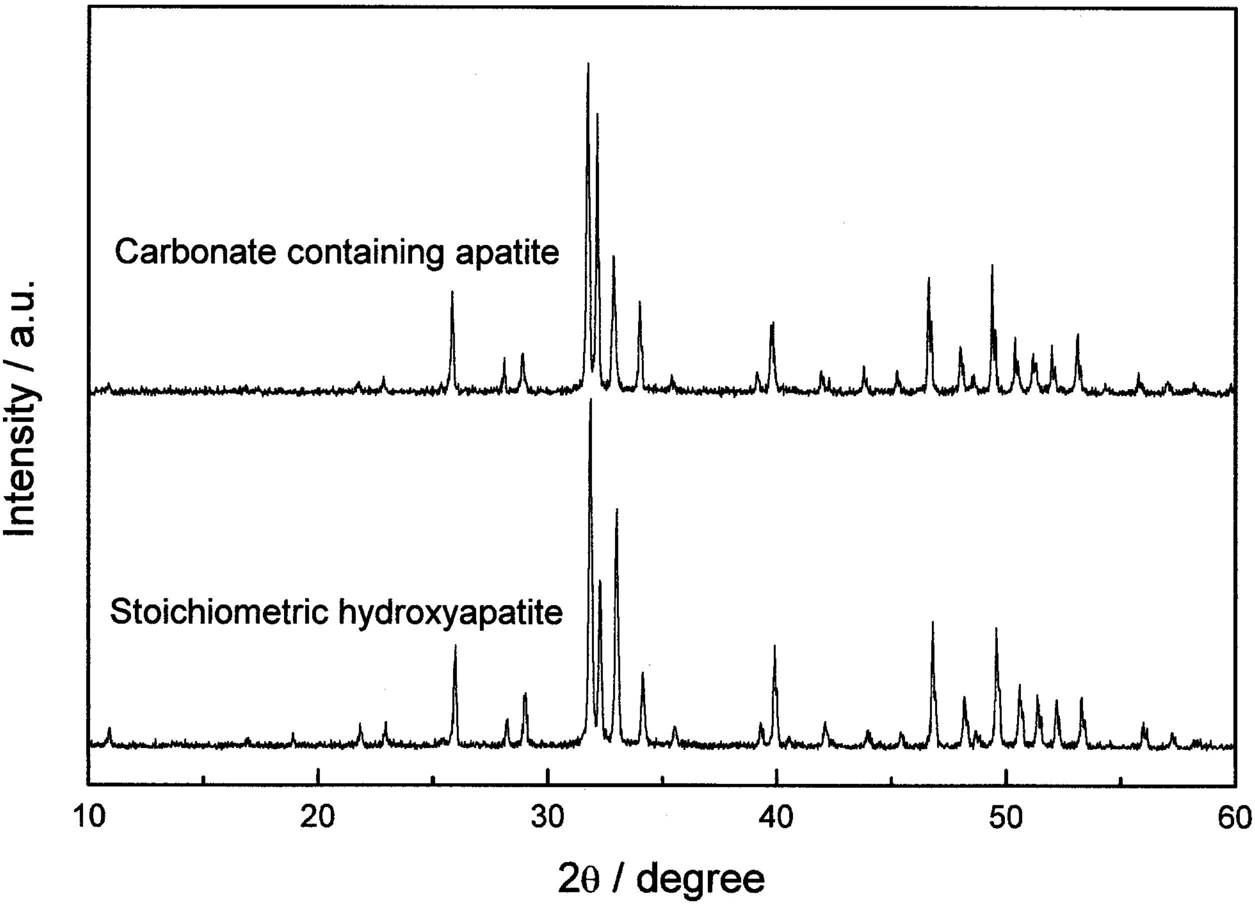


Figure 2 X-ray powder diffraction pattern of CAp and stoichiometric HAp.

OH band (3600 cm^{-1}) disappears and the CO_3 bands (800, 1300–1500 cm^{-1}) appear. The CO_3 bands are assigned to the A- and B-sites [7] as indicated in Fig. 4. Thus, in the crystals grown using the $CaCO_3$ flux, the CO_3 ions replace both the A- and B-sites. On the basis of chemical analysis by EPMA and carbon analysis, the chemical formula for sample No. 5 was determined as $Ca_{9.8}(PO_4)_{5.6}(CO_3)_{0.4}(CO_3)$, i.e. the A- and B-sites were replaced by 6.5 and 2.5 wt % CO_3 ions, respectively. CO_3 contents did not change significantly over the variety of preparation conditions.

Fig. 5 shows the temperature dependence of desorption of CO_2 gas for specimen No. 5. Two peaks are observed. The peak near 1200 °C is assigned to CO_3 ions at the A-sites [2]. Since the peak near 350 °C is very small for the amount of total B-site CO_3, desorption due to B-site CO_3 probably occurs above 1200 °C, which is the maximum operational temperature of the Leco RC-412. In fact, when the specimen was heated up to 1400 °C, gas desorption was detected by the carbon analyzer. TGA, however, indicated only one differential thermogravimetric (DTG) or differential thermal

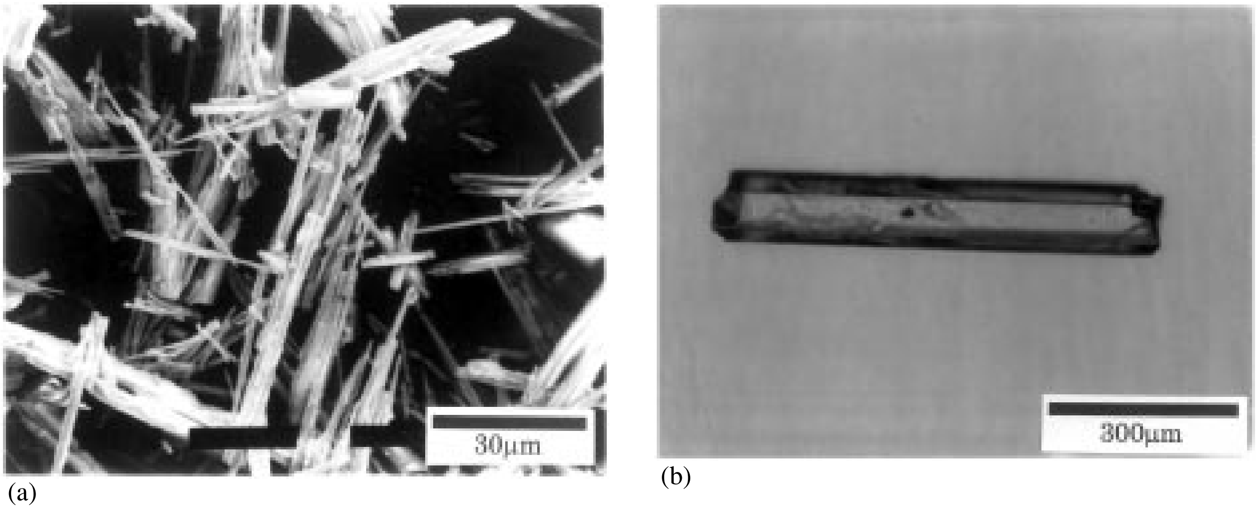
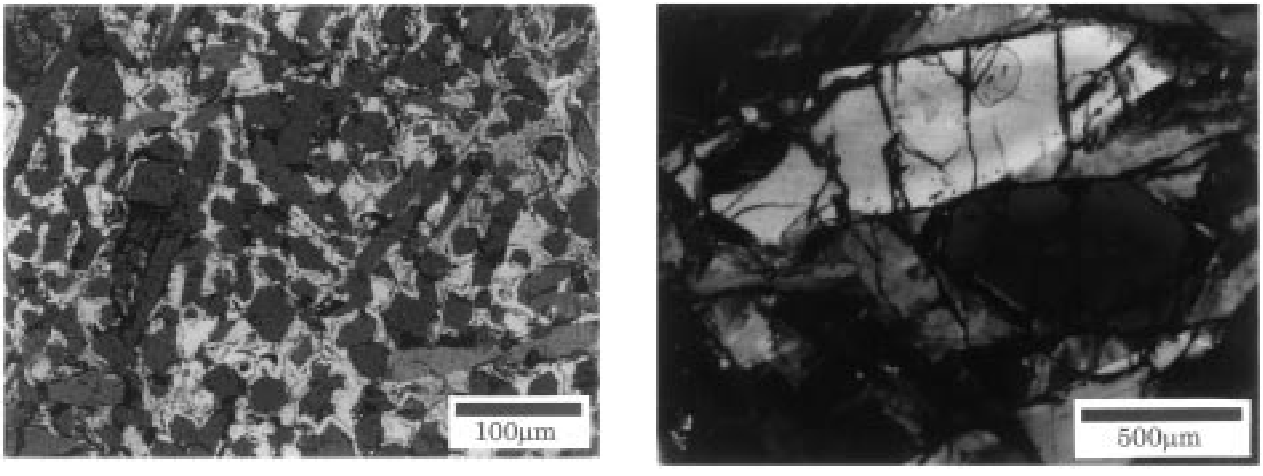


Figure 3 CAp single-crystals grown by $CaCO_3$ flux method. (a) 1400 °C constant, (b) oscillation (1200–1300 °C), (c) cooled by 1 °C, (d) cooled by 2 °C h^{-1}.



(c) (d)

Figure 3 (Continued)

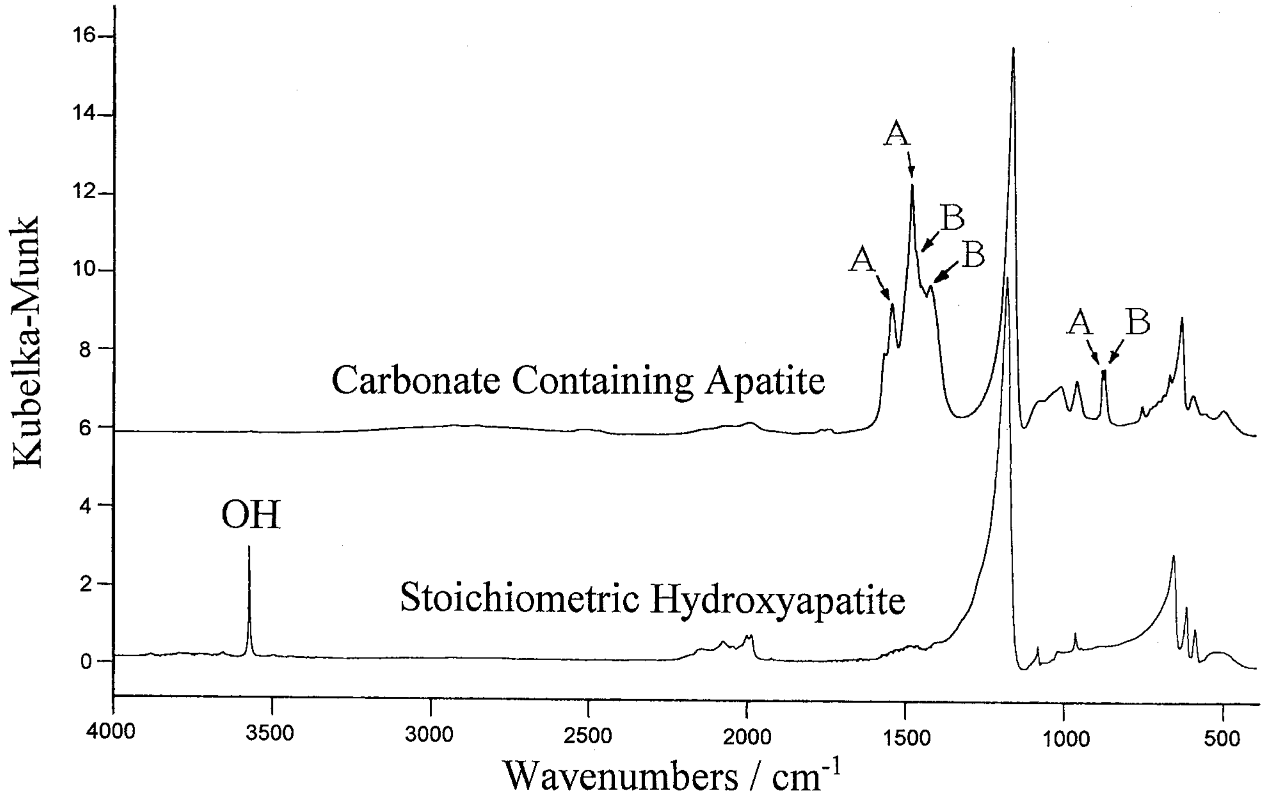


Figure 4 Diffuse reflectance FTIR spectra of CAp and stoichiometric HAp: (A) A-site CO_3, (B) B-site CO_3.

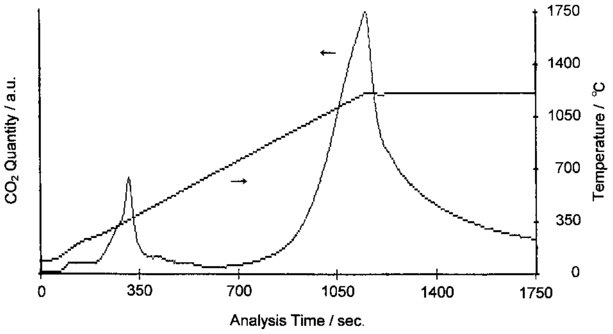


Figure 5 Temperature-programmed decomposition of CAp: CO_2 gas detected by i.r. absorption.

analysis (DTA) peak near 1300 °C (Fig. 6). It is concluded that the desorption temperatures for the two CO_3 sites in apatite are so close that they are not able to be separated by TGA measurement. The peak at 350 °C in Figs 5 and 6 can probably be ascribed to a relatively unstable CO_3 site, for example, near the surface.

3.4. Lattice parameters of CAp

According to [8], CAp does not have hexagonal symmetry but probably belongs to a monoclinic system. Fig. 7 shows the precession photographs

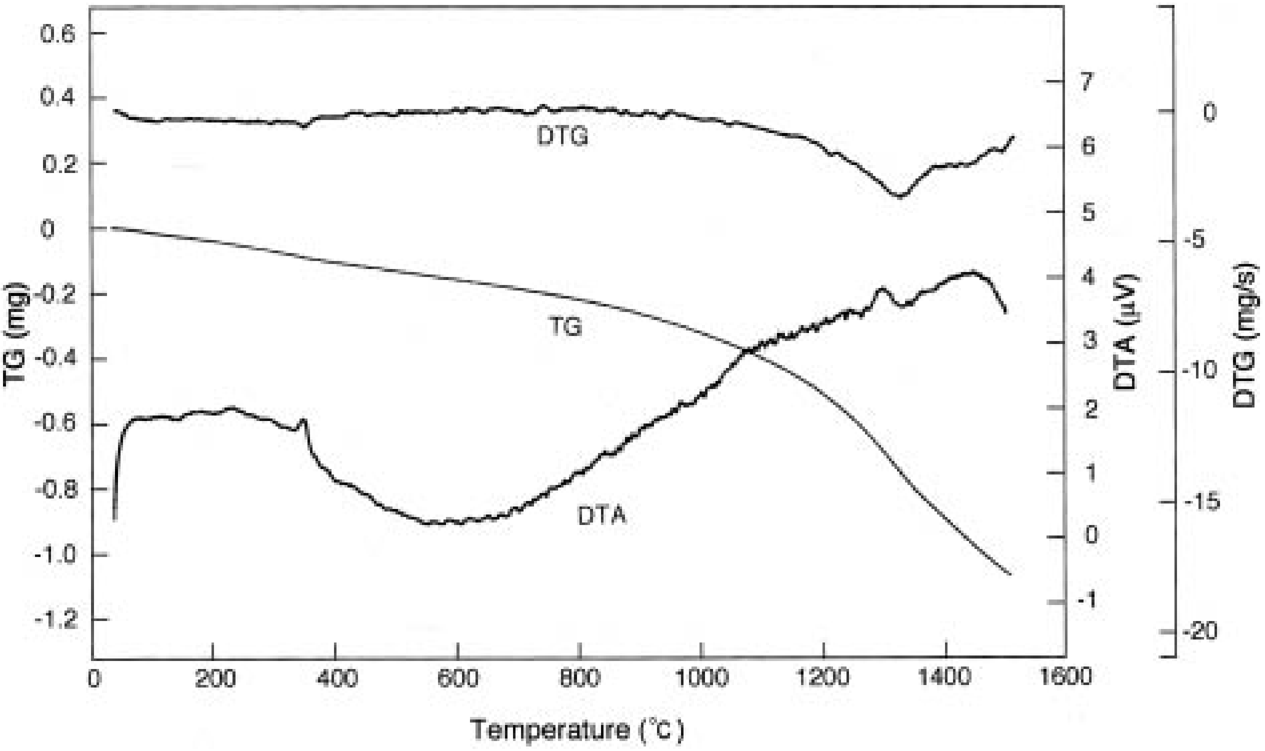


Figure 6 TGA, DTG and DTA diagram for CAp (initial weight of the specimen was 9.76 mg).

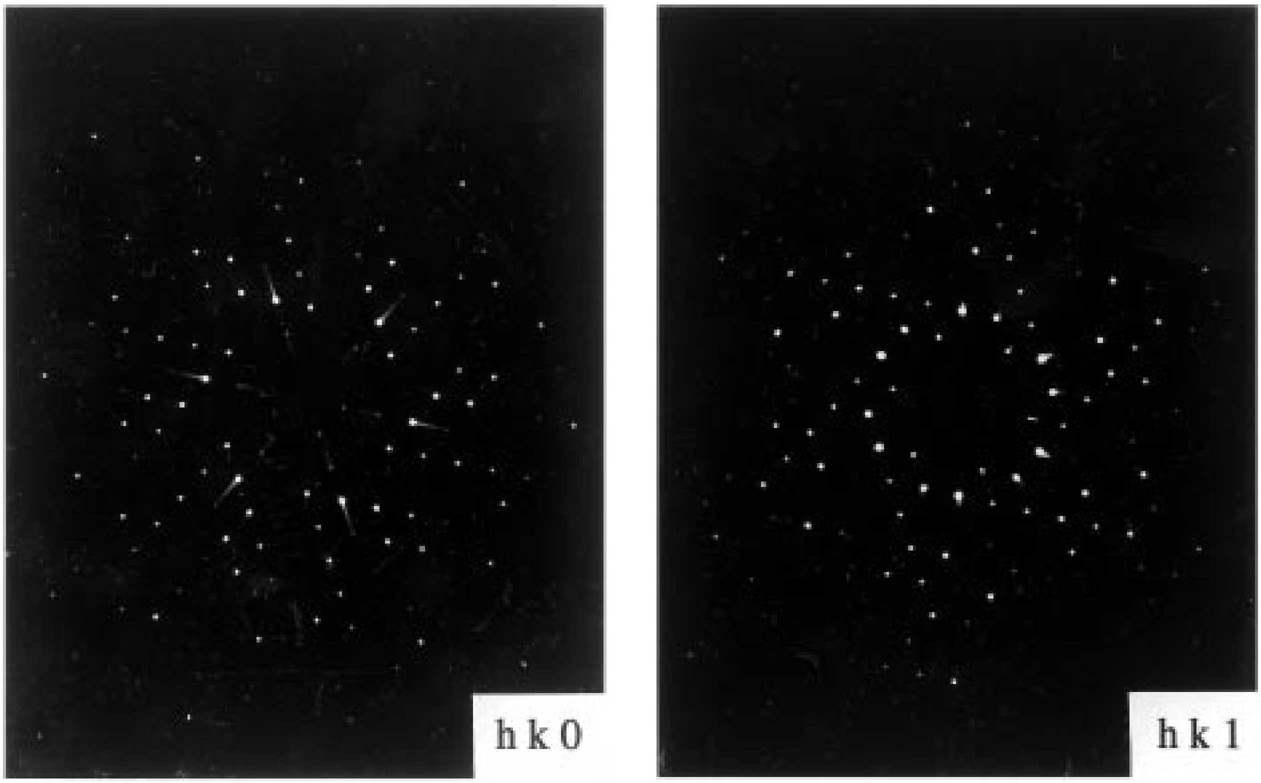


Figure 7 Precession photographs of CAp. Left: *hk*0 diffraction; right: *hk*1 diffraction.

obtained from one of the No. 5 crystals. Both photographs show the existence of a six-fold symmetry axis. In addition, in the $h\,k\,1$ photograph, there are no diffraction spots at intermediate points between the $h\,k\,1$ and $h\,k + 1\,1$ spots, which would have to exist if the crystal belonged to a monoclinic system and had a *b*-axis whose cell parameter was twice the *a*-value as shown in [8]. Fig. 7 thus indicates that the crystal used in the present work belongs to a hexagonal system. This inconsistency might be ascribed to the difference in the amount of Ca-deficiency and/or carbonate ions in the specimens used.

Lattice constants were determined by a four-circle diffractometer in the hexagonal system, i.e. $a = 0.9475$ nm, $c = 0.6895$ nm. Both *a*- and *c*-values are larger than those of HAp ($a = 0.9418$ nm, $c = 0.6880$ nm, respectively [9]), reflecting the fact that both A- and B-sites have been replaced by CO_3 ions.

4. Conclusions

Single crystals of CAp were grown using a $CaCO_3$ flux under an Ar gas pressure of 55 MPa. CO_3 ions replaced both A- and B-sites giving a chemical formula of $Ca_{9.8}[(PO_4)_{5.6}(CO_3)_{0.4}](CO_3)$. The crystals had hexagonal symmetry and the lattice constants were $a = 0.9475$ nm, $c = 0.6895$ nm.

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