

## ***In situ* observation of hydroxyapatite at high temperatures by Ultraviolet Laser Raman spectroscopy**

**Hiroyuki Toya, Hirotaka Fujimori, Koji Ioku, Seishi Goto  
and Masahiro Yoshimura\***

Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University,  
2-16-1 Tokiwadai, Ube, Yamaguchi, Japan 755-8611

Fax: 81-836-35-9965, e-mail: ioku@po.cc.yamaguchi-u.ac.jp

\*Materials and Structures Laboratory, Tokyo Institute of Technology  
4259 Nagatsuda-cho, Midori-ku, Yokohama, Kanagawa, Japan 226-8503  
Fax: 81-45-924-5358 e-mail: yoshimul@rlem.titech.ac.jp

Hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  : HA) is one of the most interesting materials with biomaterials, adsorbent, electrical devices and so on. It has been already suggested that the stability of OH ion is closely related to the ability for bone formation and the ionic conductivity. Thus, it is of vital importance to have reliable methods for measuring quantity of OH ion at wide range of temperature. However, the information can not be easily obtained by XRD, IR, NMR and TEM. In this study, Raman spectra of HA have been successfully obtained at temperatures up to 1200°C for the first time by using a new system of ultraviolet (UV) Raman spectroscopy. With increasing temperature the intensity of a band ascribed to the stretching vibration of the OH ion continuously decreased, moreover additional bands appeared in the vicinity of the original band. The total intensity of these bands did not change significantly up to about 800°C, whereas they decreased at temperatures higher than about 800°C. The total intensity at room temperature after cooling did not recovered to that of starting material. These results indicate that oxyhydroxyapatite is produced by dehydration of hydroxyapatite over 800°C in air and the dehydration is irreversible. This study can provide important information for designing new advanced materials in the near future.

Key words: UV Raman, *in situ* observation, hydroxyapatite, dehydration

### 1. INTRODUCTION

Hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  : HA) is one of the most interesting materials such as biomaterials, column materials for chromatography, electrical devices and so on. Their physical and chemical properties relating to such utility strongly depend on the crystal structure. Especially, it has been suggested that the stability of OH ion in the structure of HA is closely related to the temperature of decomposition, the solubility and the ionic conductivity. In a lower partial pressure of water at high temperature, oxyhydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-x}\text{O}_x\text{□}_x$ , □=vacancies : OHA), tricalcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ) and tetracalcium phosphate ( $\text{Ca}_4\text{P}_2\text{O}_9$ ) can be produced by dehydration

and decomposition of HA<sup>1)-3)</sup>. It has been reported that OHA has higher solubility than HA<sup>4), 5)</sup> and that the OH lattice sites are the conduction path of HA<sup>6), 7)</sup>. Thus, it is of vital importance to have reliable methods for measuring quantity of OH ion at wide range of temperature. The information with the characteristic spectral features of the OH group leads to the identification of important structural characteristics that can not be made by XRD. Degree of dehydration has been measured by FT-IR<sup>8), 9)</sup>, NMR<sup>10)</sup> and TG<sup>11)</sup>. However, the weight losses by TG contains the evaporation of different components such as P<sub>2</sub>O<sub>5</sub> and adsorbed water. FT-IR and NMR are also not appropriate for measurements at high temperatures. Ultraviolet (UV)

Raman spectroscopy, however, is more suitable for measurements at high temperatures, because the UV excitation shifts the wavelengths of Raman scattering away from the peak intensity of the thermal emission to lower wavelength positions<sup>12</sup>. Therefore, in this study, Raman measurements for HA at various high temperatures have been performed by using a new CW (continuous-wave) UV Raman spectroscopic system designed to measure the Raman scattering from materials at high temperatures.

## 2. EXPERIMENTS

The crystalline pure HA employed for Raman measurements was prepared by hydrothermally treatment from a low crystalline HA (by Mitsubishi Material Co. Ltd., Japan) at 200 °C for 10h. *In situ* Raman measurements for HA compacted specimen at various temperatures have been performed by using a system (Atago-Jobin Yvon, Japan-France) that is based on a UV argon-ion laser (363.8nm), a spatial filter, a single monochromator coupled to a double-grating rejection filter and a two-dimensional charge-coupled device (CCD) detector. The system was described in the past paper<sup>12</sup> in detail. The sample was mounted in a furnace with Pt-Rh heater where the sample was placed and then fixed on a PR-13 thermocouple with alumina cement. The specimen was heated with a rate of 10 °C · min<sup>-1</sup>, and then temperature was kept constant during the measurements (within ±1 °C). Each measurement was done in air after a constant temperature was maintained for 10min. The laser power at the tube level was set at 100mW.

## 3. RESULTS and DISCUSSION

In this study, particular attention was given to bands around 3570cm<sup>-1</sup>; this band is attributed to hydroxyl groups in structure of HA. At room temperature, a typical Raman spectrum of HA was observed in the wavenumber range of 3300-3800cm<sup>-1</sup>(Fig.1). The intensity and frequency of a band ascribed to the stretching vibration of the OH ion around 3570cm<sup>-1</sup> decreased continuously with increasing temperature. Moreover, additional bands appeared in the vicinity of the original band as indicated by ◆ (around 3540cm<sup>-1</sup>) and ▲ (around 3650cm<sup>-1</sup>)

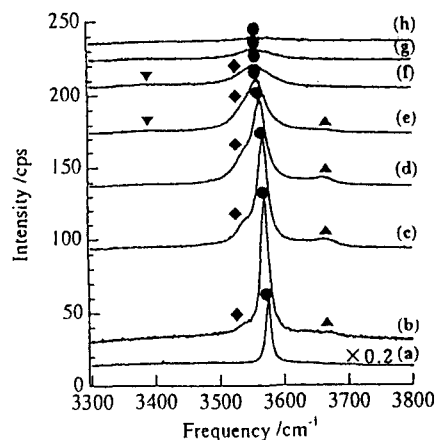


Fig. 1 Temperature dependence of Raman bands assigned to OH stretching vibration with increasing temperature. (a)R.T. (b)200°C (c)400°C (d)600°C (e)800°C (f)1000°C (g)1100°C (h)1200°C

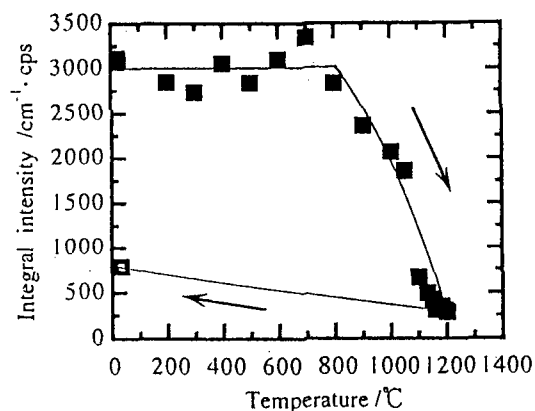


Fig. 2 Variation of the total intensity in the wavenumber range of 3300-3800cm<sup>-1</sup> with increasing temperature(■). The symbol (□) represents the total intensity after cooling.

in Fig.1. The intensity of additional band indicated by ◆ increased up to 800 °C, and then decreased over 800 °C. On the other hand, the intensity of additional band indicated by ▲ (around 3650cm<sup>-1</sup>) decreased with increasing temperature. A similar behavior has been found in the temperature dependence of IR spectra up to 500 °C for a band indicated by ◆ in Fig.1<sup>9</sup>. Another additional band indicated by ▼ became better resolved at temperatures in the range of 700° to 1050 °C. In this study, it was assumed that these additional bands are attributed to a disordering of OH ion in the hydroxy columns of the apatite and total intensity of these bands is proportional to the total number of OH ion. The total

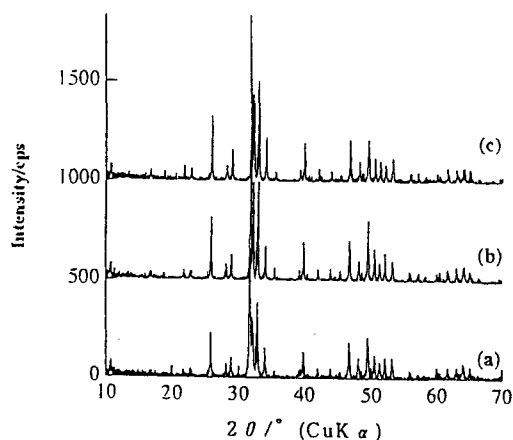


Fig. 3 XRD patterns of HA heated at (a) 800°C (b) 1000°C and (c) 1200°C for 15h.

All measurement has been done at room temperature.

intensity of these bands scarcely changed up to about 800°C, whereas the intensity decreased at temperatures higher than about 800°C (Fig.2). This result indicates that oxyhydroxyapatite was produced due to the dehydration of HA over 800°C without decomposition. Actually, XRD patterns did not change during dehydration up to 1200°C. That is, XRD could not determine the decomposition products formed during the heat treatment (Fig. 3). The total intensity of the Raman peak after cooling was smaller than that of the starting sample and the hysteresis was observed (□ in Fig.2). Therefore there is an irreversible eliminative reaction of OH ion from HA in air. This consideration was supported by the results of thermogravimetry<sup>11)</sup>. The weight loss due to elimination of OH ion from HA was observed over about 800°C. By cooling from these temperatures, the weight of sample scarcely recovered and the hysteresis was shown in TG curves.

#### 4. CONCLUSION

We have proposed that UV Raman system is available to observe the structural changes in hydroxyapatite at high temperatures. In this study, Raman spectra of hydroxyapatite have been successfully obtained at temperatures up to 1200°C for the first time by using a new system of UV Raman spectroscopy. It has been clearly shown that the loss of OH on by dehydration arise at higher temperatures than about 800°C without destruction of the HA structure. These facts imply that

changes in the composition during heat treatment should bring about the variation of the structure, the physical properties and chemical properties. This study will be able to provide important information for designing new advanced materials in the future.

#### ACKNOWLEDGMENT

The authors are thankful to Profs. M. Kakihana and M. Yashima for their help in UV Raman system. The present work has been supported partly with cooperative programs in Materials and Structures Laboratory of Tokyo Institute of Technology.

#### REFERENCES

- 1) A. M. J. H. Seuter, *Reactivity of solids: proceedings of the Seventh International Symposium on the Reactivity of Solids*, Ed. by J. S. Anderson, M. W. Roberts and P. S. Stone, Chapman and Hall, London, (1972), pp. 806-812
- 2) K. Ciesla and R. Rudnicki, *Polish J. Chem.*, **67**, 2103-2111 (1993)
- 3) J. Zhou, X. Zhang, J. Chen, S. Zeng and K. de Groot, *J. Mater. Sci.: Mater. Med.*, **4**, 83-85 (1993)
- 4) E. C. Moreno, T. M. Gregory and W. E. Brown, *J. Res. Natl. Bur. Stand.*, **72A**, 773-782 (1968)
- 5) P. Ducheyne, S. Radin and L. King, *J. Biomed. Mater. Res.*, **27**, 25-34 (1993)
- 6) T. Takahashi, S. Tanase and O. Yamamoto, *Electrochimica Acta*, **23**, 369-373 (1978)
- 7) K. Yamashita, K. Kitagaki and T. Umegaki, *J. Am. Ceram. Soc.*, **78** [5], 1191-1197 (1995)
- 8) T. Kijima and M. Tsutsumi, *J. Am. Ceram. Soc.*, **62**, 455-460 (1979).
- 9) I. Reisner and W. E. Klee, *Spectrochimica Acta*, **38A**, 899-902 (1982).
- 10) J. P. Yesinowski and H. Eckert, *J. Am. Chem. Soc.*, **109**, 6274-6282 (1987).
- 11) H. Owada, K. Yamashita and T. Kanazawa, *J. Mater. Sci. Lett*, **9**, 26-28 (1990)
- 12) M. Yashima, M. Kakihana, R. Shimidzu, H. Fujimori and M. Yoshimura, *Appl. spectrosc.*, **51**[8], 1224-1228 (1997)

(Received December 25, 1999; Accepted May 6, 2000)