Thermal changes in synthetic deuterioxyapatite

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Abstract

Deuterioxyapatite (Ca_{10}(PO_4)_{6}(OD)_{2}, DAp) was prepared from CaO, P_2O_5, and D_2O in H_2O and CO_2 free air at 298K. The obtained DAp was identified as apatite single phase by a powder XRD technique. The deuterioxy group was found by IR and MAS-NMR techniques, but hydroxyl group was not. Further, MAS-NMR measurement suggested the DAp had no tightly-bonded OD group. The deuterioxy group was not substituted with hydroxyl group at 298K by stirring in distilled water for 7 days. From TG-MS measurement, dried DAp powder released deuterium in two rapid steps and in a slow step up to 873K. High-temperature XRD measurement showed large thermal expansion for DAp due to lattice defect led by heating. High-temperature IR spectra showed release of deuterioxy group without substitution by hydroxyl group above 333K. Deuterioxy group in DAp was easily released by heating, and DAp changed into oxyapatite.

Introduction

Heavy water, deuterium dioxide, was reported as a cell growth inhibitor by inhibition of DNA synthesis due to the change in the strength of hydrogen bonding (Ohgaki et al., 1993). Some studies have reported substitution of deuterium for hydrogen in hydroxyapatite (Ca_{10}(PO_4)_{6}(OH)_{2}, HAp). Monoclinic-to-hexagonal transition of hydroxyapatite and deuteriohydroxyapatite was reported by Rees et al. (1973). Fowler (1973) reported that shifts of infrared absorption bands of three kinds of hydroxyapatite substituted by isotopes. He determined the OD stretching band of deuterium-substituted HAp, prepared by heating of HAp in D_2O air, as 2636 cm^{-1} from observed and calculated values. However, thermal change in deuterioxyapatite (Ca_{10}(PO_4)_{6}(OH)_{2}, DAp) was not reported. The present paper describes the synthesis of deuterioxyapatite by a wet method and a thermal change observed especially in OD group.

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Experimental

Four-nine grade CaCO₃ (Calceco Co., Ltd.), reagent grade P₂O₅ (Kanto Chemical, Co., Inc.), and 99% D₂O (Aldrich Chemical Co., Inc.) were used as starting materials. Suspension of Ca(OD)₂ in D₂O was prepared by adding D₂O into CaO, which was prepared by heating of CaCO₃ at 1323K for 3 hours. Solution of D₃PO₄, prepared by adding D₂O into P₂O₅, was added in drops into Ca(OD)₂ suspension with vigorous stirring. All procedure, described above, was carried out in a closed system. The reaction mixture was stirred for 3 days. The obtained suspension was stored at 277K in a refrigerator, and a necessary amount of the sample was taken out of the storage in each experiment. Hydroxyapatite synthesized by a similar method was used as a control.

The synthesized material, dried in vacuum at 293K, was analyzed by X-ray powder diffraction method. Existence of deuterioxyl groups was confirmed by infrared spectroscopy. Crystal shape was observed with transmission electron microscope (H-600A, Hitachi Co.) at an accelerating voltage of 100kV. Chemical composition of DAp was determined by back EDTA titration for Ca and molybdenum-blue photometry for P. Existence of D and H in DAp was examined by a MAS-NMR technique (GX270 system, JEOL Co., Ltd.) using undried DAp sample. Stability of OD group at room temperature was investigated by infrared spectroscopy using KBr tablet method using DAp stirred in distilled water for 7 days as a sample.

Thermal lattice expansion of DAp were studied by an X-ray powder diffractometry (PW-3050, Philips Japan, Ltd.) equipped with a heating unit (Anton Paar, Co.) using Graphite-monochromatized CuKα radiation at 40kV and 40mÅ. Deuterioxylapatite was pasted on a 99.99% pure Pt holder and heated to 1273K at a heating rate of 20K/min. After being held at the temperature for 10 minutes, diffraction patterns were measured at a scanning speed of 0.04°/s. The sample was cooled to 873, 393, and 298K at 20K/min. At each temperature, diffraction data were collected with the same condition. Lattice constants of DAp at 298, 393, 873, and 1273K were calculated from 15 diffraction angles using the program RLC-3 (Sakurai, 1967). The diffraction angles were corrected by those of Pt used as an internal standard. Thermal expansion coefficients of DAp were calculated from the variation of lattice constants with temperature.

Thermal changes in deuterioxyl group was examined by high-temperature infrared spectroscopy (I-2000, Hitachi Co.) using a KBr tablet technique. Infrared spectra were measured at 293, 313, 333, 353, 373, 393, 423, 453, and 473K; heating rate was 10K/min, and holding time was 30 min. Release of D₂O was measured by the TG-MS method by heating rate of 30K/min.

Results and Discussion

Fig. 1 shows X-ray powder diffraction pattern of DAp dried in vacuum at 293K, indicating only apatite phase. Transmission electron microphotograph of DAp is shown in Fig. 2. The selected area electron diffraction pattern showed 002, 210, and 211 diffractions of apatite. The
Fig. 1. X-ray powder diffraction patterns of DAp and HAp.

Fig. 2. Transmission electron micrograph of DAp crystals.
maximum size of crystals was 100 nm. In the infrared spectrum of the DAp shown in Fig. 3, the OH stretching band around 3570 cm\(^{-1}\) cannot be detected, but the OD stretching band around 2635 cm\(^{-1}\) was detected. The wave number of the OD stretching band was well-agreed with that of Fowler's data (1973), 2636 cm\(^{-1}\) (Fig. 3). Further, CO\(_3\) bands of 865, 1430, and 1455 cm\(^{-1}\), substituted for PO\(_4\) (Montel, 1968) were detected. Chemical composition of DAp is shown in Table 1. Values of D\(_2\)O (H\(_2\)O) in the table are summations of OD group and adsorbed water, therefore, the values are greater than theoretical value because it does not include adsorbed water. The Ca/P atomic ratio, 1.69, is slightly greater than theoretical value, 1.67. This is considered due to CO\(_3\) group substitution for PO\(_4\), as was detected by IR spectroscopy. Infrared spectra of DAp after stirring in H\(_2\)O is shown in Fig. 3. Sharp OD stretching bands at 2636 cm\(^{-1}\) and weak OH stretching band at 3572 cm\(^{-1}\) were observed, moreover weak v\(_5\)(PO\(_4\)) band of HAp was detected at 474 cm\(^{-1}\). The most OD group was not substituted by OH group even

**TABLE 1. Chemical composition of DAp.**

<table>
<thead>
<tr>
<th></th>
<th>DAp</th>
<th>HAp</th>
<th>Theoretical DAp</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO / wt%</td>
<td>52.46</td>
<td>51.24</td>
<td>55.71</td>
</tr>
<tr>
<td>P(_2)O(_5) / wt%</td>
<td>39.27</td>
<td>38.67</td>
<td>42.30</td>
</tr>
<tr>
<td>D(_2)O (H(_2)O) / wt%</td>
<td>8.24</td>
<td>8.9</td>
<td>51.99</td>
</tr>
<tr>
<td>Total / wt%</td>
<td>99.97</td>
<td>98.86</td>
<td>100.00</td>
</tr>
<tr>
<td>Ca / P</td>
<td>1.69</td>
<td>1.68</td>
<td>1.67</td>
</tr>
</tbody>
</table>
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**Table 2.** Lattice constants of DAp and HAp at each temperature.

<table>
<thead>
<tr>
<th>T/K</th>
<th>DAp</th>
<th>HAp</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a / Å</td>
<td>c / Å</td>
</tr>
<tr>
<td>298</td>
<td>9.4090(7)</td>
<td>6.875(1)</td>
</tr>
<tr>
<td>393</td>
<td>9.419(1)</td>
<td>6.880(2)</td>
</tr>
<tr>
<td>873</td>
<td>9.478(2)</td>
<td>6.918(3)</td>
</tr>
<tr>
<td>1273</td>
<td>9.564(5)</td>
<td>6.991(5)</td>
</tr>
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</table>

**Table 3.** Thermal expansion coefficient of DAp and HAp.

<table>
<thead>
<tr>
<th>range/K</th>
<th>DAp 298-873</th>
<th>DAp 873-1273</th>
<th>HAp 298-873</th>
<th>HAp 873-1273</th>
</tr>
</thead>
<tbody>
<tr>
<td>βa / 10⁶ K⁻¹</td>
<td>12.8</td>
<td>22.9</td>
<td>13.3</td>
<td>15.1</td>
</tr>
<tr>
<td>βc / 10⁶ K⁻¹</td>
<td>10.9</td>
<td>26.5</td>
<td>11.1</td>
<td>16.0</td>
</tr>
<tr>
<td>α / 10⁶ K⁻¹</td>
<td>36.3</td>
<td>74.5</td>
<td>38.3</td>
<td>46.9</td>
</tr>
</tbody>
</table>

**Fig. 4.** Thermal lattice expansions (Da/a, De/c, and DV/V) of DAp.

...dispersed in large amount of water at room temperature.

From proton MAS-NMR spectrum, no peaks originated from proton were detected, and a peak originated from deuterium of adsorbed D₂O was detected at 7.99 ppm. The result suggests that undried DAp did not have tightly-bonded OD groups in the crystal structure, nor protons. Peaks originated from the OD group in DAp structure was not detected in the spectrum.

Lattice constants at each temperature and thermal expansion coefficients of DAp are summarized in Tables 2 and 3, respectively. Lattice constants at 273K (l₀ and V₀) were calculated from lattice expansion from 298K to 393K. Figs. 4 a-c show thermal expansions of...
DAP and HAp calculated from lattice constants. Inclination of thermal expansions of HAp was slightly changed at 873K, being in agreement with previous data (Nakamura et al., 1990). However, thermal expansions of DAP above 873K were quite different from those of HAp values. Lattice defect due to release of deuterioxyxl group was suggested and was compatible with the observation of high-temperature infrared spectra shown in Figs. 5 and 6. From these results, DAP was confirmed to change into oxyapatite at 1273K. Lattice constants and thermal expansion of DAP below 873K were very similar to those of HAp. Slight difference of lattice constants between DAP and HAp was explained by Trombe et al. (1977) who showed lattice constants of oxyapatite were slightly smaller for the a-axis and slightly larger for the c-axis than those of hydroxyapatite at 1123K, which can be considered as the lowest temperature at which oxyapatite can exist stably. Dehydration and hydration rate of DAP was considered not to high from IR studies (Figs. 5 and 6). The oxyapatite obtained by heating of DAP was not completely hydrated at the conditions, therefore, lattice constants of DAP showed slightly small values compared with HAp.

The TG-MS measurements of DAP powder dried in vacuum showed two-stage rapid release of D$_2$O and slow release of D$_2$O and carbonate group. Since this, slow D$_2$O release continued up to 873K, it was considered to indicate decomposition of deuterioxyxl group, which was also supported by the high-temperature infrared spectra. It also suggests that the heated DAP contains vacancy in the OD site, that is, so-called oxyapatite, and is compatible with the large thermal lattice expansion of DAP.
Infrared spectra of DApS dried in the various temperatures are shown in Fig. 5. The OD stretching band was detected around 2635cm\(^{-1}\) in 298-413K dried samples. Upper 333K of drying temperature, the OD group was substituted by OH group with increasing in drying temperature, and the OD group was not detected by 453K drying. The intensities of OD and/or OH band was not so strong compared with CO\(_3\) band. Imperfection of crystal structure of DAp around the OD group may caused this phenomenon.

The release of OD group in DAp by heating, detected with high-temperature infrared spectroscopy, is shown in Fig. 6. As higher the temperature, the OD group was released from the crystal, however, the OH group was not substituted for the vacancy. After being cooled to room temperature, the OH group gradually compensated for the vacant site, and oxyapatite changed into HAp. From the above results, the release of the OD group in DAp was considered as follows: The OD group was gradually released from low temperature, i.e. 333K, however, the adsorbed water desorbed from high temperature of 373K but rapidly occurred compared with the OD group release. Although infrared spectra showed release of the OD group up to 333K, the release of the OD group was not detected at low temperature by the TG-MS method. These phenomena were not reported by Fowler (1973), because his infrared spectra of DAp was measured at 90 and 321K, and the OD group was not released at those temperatures. Fowler’s DAp was prepared by deuteration of HAp powder at 2.03-3.04 MPa D\(_2\)O pressure at 1173K for 12 hours, and contained small amount of hydroxyl group detected by IR spectroscopy. Fowler’s IR data suggests the OH group in HAp structure was exchanged for H\(_2\)O and D\(_2\)O in air at 1173K; therefore, Fowler’s DAp was considered to be changed into oxyapatite due to the release of OD group by heating without H\(_2\)O or D\(_2\)O air.

**Conclusion**

1) Deuterioxyl group was released slowly from DAp structure from a temperature of 333K, and the OD site became vacant.
2) With release of OD group, DAp slowly changed into oxyapatite. Partially OH-substituted DAp was formed when it was cooled before complete release of OD group.
3) At 1273K, the crystals changed into well-crystallized oxyapatite, and the lattice constants became greater than those of HAp because of defect created by OD release.
4) After cooling down to 873K, large lattice expansion of oxyapatite was not detected which was in agreement with the previous data (Trombe *et al.*, 1978).
5) After cooling down to 298K, oxyapatite gradually changed into HAp with hydration.

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References


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