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Application News

No. X268

X-Ray Diffraction

Quantitative Analysis of Calcium Compounds by Rietveld Method

– Phase Identification by Match!3 and Rietveld Analysis by FullProf –

The Rietveld method (Rietveld refinement) is a crystal structure analysis technique that enables analysis of the crystal structures of both single-component and multi-component samples from their powder X-ray diffraction patterns. Because quantitative analysis is possible without using a calibration curve, various types of analytical software applying the Rietveld method are employed in research and development, and manufacturing processes.

Match!3 software (Crystal Impact GbR) is a phase identification program that specifies the components of a sample by comparing the X-ray diffraction pattern of the sample and patterns in a database. Use of Match!3 in combination with the Rietveld analysis program FullProf (Juan Rodríguez-Carvajal, Laboratoire Léon Brillouin) enables crystal structure analysis and quantitative analysis.

This article introduces a case of phase identification by Match!3 and crystal structure analysis and quantitative analysis by FullProf using a multi-component sample of a calcium compound prepared by adding calcium carbonate to hydroxyapatite, which is known as the main component of teeth and bones.

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Sample Material

(1) Hydroxyapatite 95 wt%
Apatite HAP (FUJIFILM Wako Pure Chemical Corp.), monoclinic phase

(2) Calcium carbonate 5 wt%
Calcium carbonate (FUJIFILM Wako Pure Chemical Corp.)

Hydroxyapatite is one type of calcium phosphate and is well-known as the main component of teeth and bones. In addition to hydroxyapatite, calcium phosphate is also known to have various crystal phases with different ratios of phosphoric acid and calcium. On the other hand, calcium carbonate is known to have different crystal structures with the same chemical formula, or polymorphs.

X-Ray Diffraction Profile

XRD-6100 was used in this measurement. The OneSight™ wide-range high-speed detector was used as the detector. Fig. 1 shows the X-ray diffraction pattern of the measured sample.

Phase Identification

Table 1 shows the results of phase identification by Match!3. The table shows the chemical formulas of the components corresponding to the X-ray diffraction peaks in Fig. 1. The database used here was COD (Crystallography Open Database), an accessory database of Match!3.

Two components, hydroxyapatite and calcite, can be confirmed from the phase identification results. Although the sample consisted of two components with overlapping diffraction peaks, it can be understood that the main component was identified as hydroxyapatite and the low-concentration calcium carbonate was identified as calcite.

Table 1 Phase Identification Results

Chemical Formula		Component
$Ca_{10}(PO_4)_6(OH)_2$	: HAp	Hydroxyapatite
$CaCO_3$	: Ca	Calcite

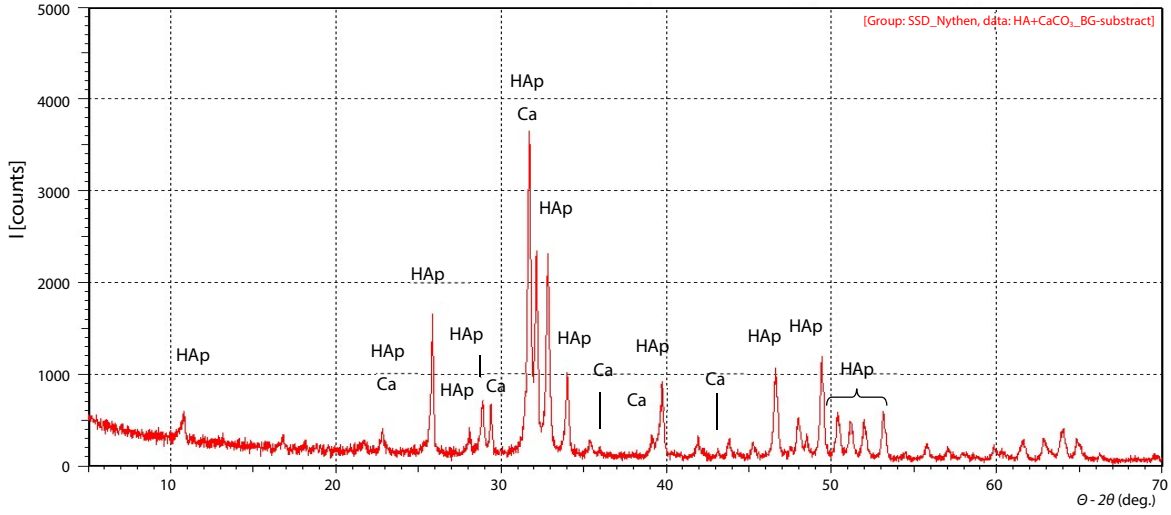

Fig. 1 X-Ray Diffraction Pattern of Calcium Compound

Rietveld Analysis Results

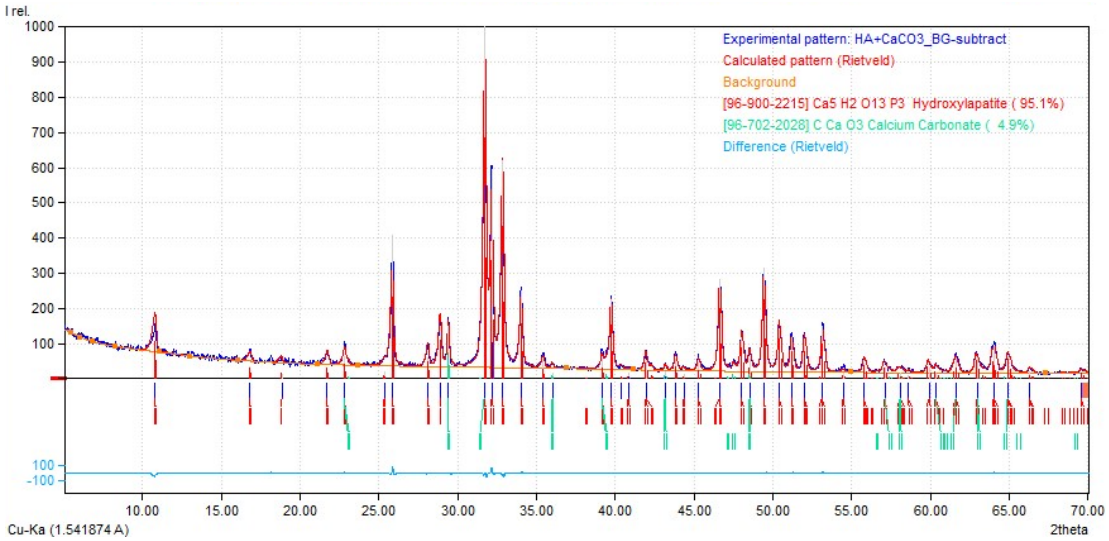

Fig. 2 Rietveld Analysis Result Screen for Calcium Compounds

Next, the Rietveld analysis results using FullProf will be presented. FullProf enables crystal structure analysis and quantitative analysis using the peak shape and the lattice constants of the crystal phase that was obtained with Match!3 as parameters. Fig. 2 shows the result of the FullProf analysis. Blue shows the measurement pattern, red shows the calculated pattern, and the light blue at the bottom shows the difference between the measured and calculated patterns. Satisfactory fitting was confirmed.

Fig. 3 shows the crystal structure model diagram obtained by analysis, and Tables 2 and 3 show the crystal structure analysis results and quantitative analysis results, respectively. The values of the factors Chi^2 and R_{wp} which show the degree of agreement between the measured pattern and the calculated pattern are small, indicating a high degree of coincidence. The quantitative analysis values were also satisfactory, being 4.9 wt% for calcium carbonate in comparison with the preparation value of 5 wt%.

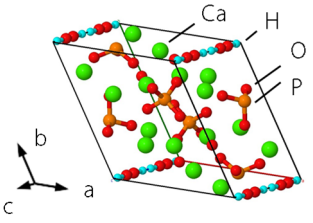

Fig. 3 Crystal Structure Model of Hydroxyapatite

Table 2 Results of Crystal Structure Analysis of Hydroxyapatite

R_{wp}	15.3
Chi^2	1.8
Crystal system	Hexagonal
Space group	P63/m (176)
a, b	9.4382 Å
c	6.88803 Å

Table 3 Results of Quantitative Analysis Unit: wt%

Hydroxyapatite	95.1
Calcite	4.9

Match!3 Software

Match!3 is a software program that identifies the components of powder samples by comparison of the X-ray diffraction pattern and peak data of the sample and reference patterns in a database. Phase identification is possible even with samples having multi-component systems including multiple crystal phases with overlapping diffraction peaks.

The applicable reference databases are not limited to the accessory COD and cement compound database, but also include the PDF-2 and PDF-4 databases of the International Centre for Diffraction Data (ICDD).

In addition to crystal structure analyses such as lattice constant refinement, quantitative analysis is also possible by using Match!3 in combination with the Rietveld analysis program FullProf.

Measurement Conditions

Table 4 Measurement Conditions

Instrument	:	XRD-6100
Detector	:	OneSight
X-ray tube	:	Cu target
X-ray condition	:	40 kV – 30 mA
Monochromatization	:	Ni filter
Divergence slits	:	0.5 deg.
Scan mode	:	Step scan - Standard
Scan range	:	5 – 70 deg.
Step	:	0.0155 deg.
Scan speed	:	10 deg./min
Integration time	:	23.228 s

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