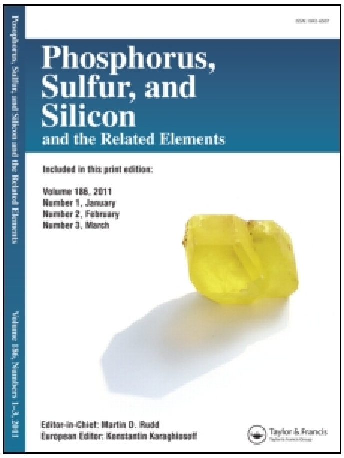

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Esca Spectra for Carbonate-Containing Apatites

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ESCA Spectra for Carbonate-Containing Apatites

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Abstract Powder samples and sintered bodies of carbonated apatites were examined by ESCA and IR in order to study on thermal change.

INTRODUCTION

Incorporation of carbonate in apatites was often found in phosphorus ores, hard tissues of animals and sintered bodies. However, no detailed study was done on thermal change of carbonate-containing apatite. Moreover, nonstoichiometry of the Ca/P ratio in hydroxyapatite was often explained in terms of the phosphate adsorption.

Carbon 1s, Ca 2p, P 2p and O 1s spectra for carbonate-incorporated apatites were measured in order to know the composition change in apatite surface. Carbonate apatites substituted for OH and PO_4 sites were sintered and examined by means of X-ray diffraction, IR and ESCA.

This paper deals with thermal change of carbonate-containing apatite during sintering process.

EXPERIMENTAL

Materials

Three types of carbonate-substituted hydroxyapatites and the stoichiometric apatite were prepared by the methods reported previously[1,2,3]. Substitution of carbonate for phosphate were carried out by the precipitation produre[1] similar to those of pure hydroxyapatite without N_2 bubbling and carbonation proceeded by carbon dioxide in the air during the aging. Carbonate exchange for OH was done in dry carbon dioxide from liquid CO_2.

Analyses

The spectra of ESCA for powder samples and sintered bodies were measured using ESCA-750(Shimazu Co.Ltd.) with Mg $K\alpha$. Graphite podwer was mixed into the sample as the standard.

Substitution sites of carbonate in the apatite lattice were determined by measuring the shifts of IR absorption for carbonates[4,5,6]. The lattice constants of carbonate-containing apatites were calculated from the X-ray diffraction patterns.

RESULTS

Nonstoichimetry of apatite

The ratios of Ca/P of the surface layers of precipitated apatites were often less than 1.67, which had suggested the presence of absorbed phosphate ion. However, these P-rich layers were easily removed by Ar^+ etching under the conditions of 2kV, 25mA and 2-3 mininutes and at the same time the elements of impurities also disappeared. Therefore, nonstoichiometry of apatite cannot be explained in terms of absorption of phosphates or other components. Precipitated apatites often absorbed water vapor and carbon dioxide probably from the air and most part of these absorbed molecules were removed by thermal treatment above

300℃.

Carbon 1s spectra for apatite

FIGURES 1 and 2 shows the C 1s spectra for the apatite powder prepared by the solid-state reactions[2)] and the precipitated carbonate-bearing apatite. Even on the top surface of the apatite obtained by the dry process, C 1s for carbonate probably from absorbed carbon dioxide in the air was detected. The peaks of 285eV in FIGURES 1 and 2 were assigned to the C 1s's from the contaminants in the spectrometer and from the graphite of the standard, respectively. Substitution sites were recognized from IR spectra in FIGURE 3.

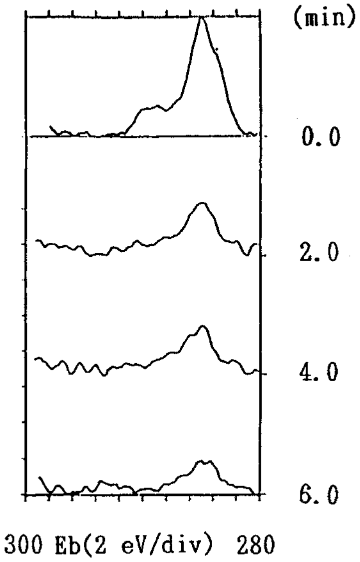

Fig. 1 C 1s spectra of HAp by the thermal method.

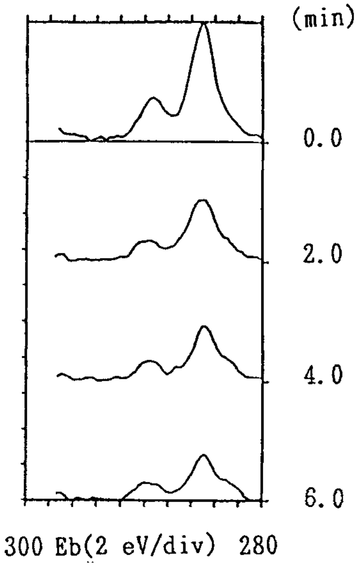

Fig. 2 C 1s spectra of carbonate-bearing HAp.

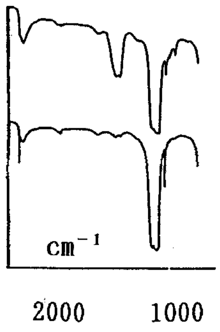

Fig. 3 IR a)carbonate-bearing HAp, b)precipitated and calcined HAp.

The carbonate incorporated for PO_4 was known from the aborption bands of 1455 and 1415 cm^{-1}, and 872 cm^{-1}. The peak near 290 eV appeared in the spectra of C 1s in FIGURE 2 for the carbonate at the phosphate sites of the apatitelattice. Although no apparent C 1s peak for the carbonate at the OH site of the apatite was observed, the peak near 286 eV was found and assigned to be the binding energy for the carbon of carbonate at the OH site from the results of curve-fitting analyses for C 1s profile.

Thermal decomposition of sintered carbonate-containing apatites

Phosphorus 2p for the apatite containing carbonate at the PO_4 site disappeared near the surface of the sintered bodies and the peaks for Ca 2p and O 1s were detected. After 20-60 minute-Ar^+ etching under the conditions of 2kV and 25mA, phosphate-containing layers appeared and the stoichiometric composition of apatite was found. On the other hand, surface layers of the powdered samples of sintered body of the above apatite and the top surface of the sintered apatite polished by emery paper were recognized to possess stiochiometric Ca/P.

The carbonate substituted for phosphate might be easily removed from the apatite lattice, which induced vaporization of phosphate near the surface of the sintered apatite. Then, successively, decomposition of the apatite structure near the surface might occur during sintering process.

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