Preparation of Calcium-Strontium Apatite through Mechanochemical Method

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The formation of a calcium-strontium apatite solid solution precursor via mechanochemical method was described. The precursor is formed by a process of ball-milling of a slurry consisting of a mixture of the starting materials; $CaHPO_4 \cdot 2H_2O$, $CaCO_3$, $SrHPO_4$ and $Sr(OH)_4 \cdot 8H_2O$ in a zirconia pot mill for 24 h in the presence of water at room temperature over the entire Ca/(Ca+Sr) compositional range. Calcium-strontium apatite precursor obtained from ball-milling began to change to calcium-strontium apatite upon heating at temperature over 500 °C.

Hydroxyapatite has been of interest from the point of view of science and technology of functional ceramics such as biomaterials, fertilizers, conductors, sensors, etc.. Synthesis of hydroxyapatite has usually been carried out by means of wet or dry methods. The former involves preparation from solution, while the latter involves a solid state reaction. Powders prepared by the wet method generally give a product with a smaller particle size than powders prepared by the dry method. But accurate pH adjustment and reaction temperature control is necessary in case of the wet method. Mechanochemical synthetic method for preparing phosphates is simple in adjusting pH and reaction temperature with pure orthophosphate powders wih a fine size being resulted. The main aspects of this method are: 1) using starting materials that are insoluble or slightly soluble in water, and 2) mechanical agitation in a pot mill in the presence of a solvent. We have synthesized orthophosphate of the type $M_3(PO_4)_2 \cdot xH_2O$ (M = Ca, Mg, Sr)[1-3] through a mechanochemical synthesis. We have also extended this method to synthesize hydroxyapatite type orthophosphate. The preparation of a series of calcium-strontium hydroxyapatite solid solutions by wet method have been reported elsewhere.[4] This paper describes a method for the synthesis of a solid solution of calcium-strontium hydroxyapatite via ball-milling and reaction of a slurry of the starting materials.

Reagent grade calcium hydrogen phosphate 2-hydrate ($CaHPO_4 \cdot 2H_2O$), calcium carbonate ($CaCO_3$) and strontium hydroxide 8-hydrate ($Sr(OH)_2 \cdot 8H_2O$) from Wako Junyaku Chemicals were used for starting materials. Strontium hydrogen phosphate ($SrHPO_4$) was prepared using the method of Tartar and Lorah.[5] These starting materials are sparingly soluble or insoluble in water. Water was added in variable amounts to a mixture of the starting materials in order to make a slurry. The Sr/(Sr+Ca) molar ratio of the mixture varied from 0-1.0 in molar ratio increments of 0.2 for these materials while the molar ratio of $(Ca+Sr)/(PO_4)$ was kept constant at 3/2. The slurry thus prepared was subsequently ball-milled using 500 g zirconia balls in a zirconia pot mill (75 mm inner diameter, 90 mm depth) at 50 rpm and room temperature to effect reaction of the components. Ball-milling time was varied from 1 to 48 h. The reacted slurry was dried to produce a powder, followed by heating in air. Each sample prepared under the varying conditions was analyzed by X-ray powder diffraction (Mac Science, MXP^{3V}), scanning electron microscopy (HITACHI, SX-5300), thermal analysis (Shinku Riko, TA7000), and infrared absorption spectroscopy (JASCO, FT/IR-8000S). Transmission electron microscopy including the determination of elemental compositions by energy dispersion analysis (JEOL, JEM4000FZ) was also carried out.

Figure 1 shows the X-ray diffraction patterns of products obtained by magnetic stirring and ball-milling at 20 °C of a mixture of starting materials with a Ca/(Ca+Sr) molar ratio of 0.4. Figure 1(a) indicates that the product obtained using an ordinary magnetic stirrer method consists of starting materials along with a small amount of apatite precursor. On the other hand, Figure 1(b) indicats that a product, obtained from a ball-milled slurry in a zirconia pot mill at room temperature for 24 h, consists only of apatite precursor. A similar trend was observed when the product by magnetic stirring and zirconia ball pot milling was compared over the entire Ca/(Ca+Sr) compositional range. In the case of ordinary magnetic stirring in a flask, starting materials are sparingly soluble in water and thus only react with each other to a negligible extent at room temperature. However, when mechanically agitated in a potmill, the reaction in solution is accelerated by the ball-milling in the presence of water by mechnochemical effects. If warter was not included in the ball-milling process, the starting materials did not react and thus remained unchanged. Heating of products from a dry ball-milled mixture of staring materials at a molar ratio of Sr/(Ca+Sr) =1.0 was found not to produce apatite type orthophosphate but tristrontium phosphate as reported by Feenstra et al.[6] Only the peaks corresponding to apatite were observed in X-ray diffraction patterns of the products obtained by heating the ball-milled at 500 °C.

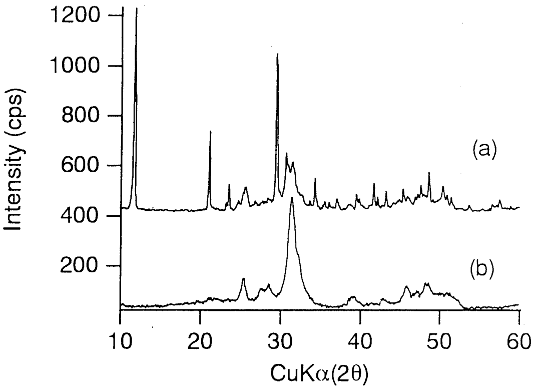

Figure 1. X-ray diffraction patterns of the products obtained by stirring for 24 h at 20 °C a mixture of starting materials whose Sr/(Ca+Sr) molar ratio is 0.4 in a zirconia potmill using zirconia ball (b), or in flask with a magnetic stirrer (a).

Figure 2 shows the lattice constants of the calcium-strontium hydroxyapatite over the entire compositional range for a Ca/(Ca+Sr) molar ratio of 0-1.0. The relationships between the

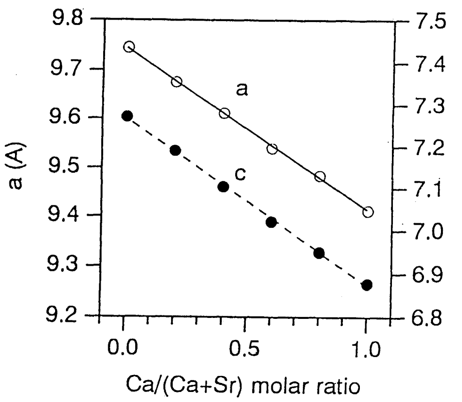

Figure 2. Lattice constants of calcium strontium hydroxyapatite obtained by heating the products ball-milled precursors with 0 - 1.0 Ca/(Ca+Sr) molar ratio at 500 °C.

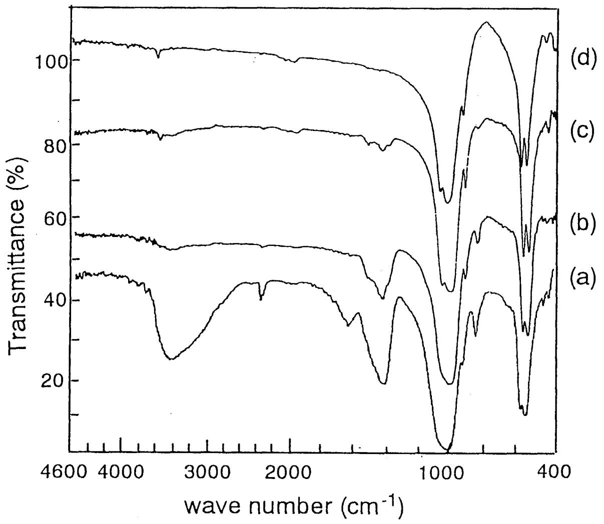

Figure 3. Infrared absorption spectra of the specimens obtained by heating the ball-milled precursors with at a Ca/(Ca+Sr) molar ratio of 0.4.(a) at 500 °C (b), 800 °C (c), and 1000 °C (d)

lattice constants and molar ratio are linear and governed by the Vegard's rule, which confirms the formation of calcium-strontium apatite solid solution over the entire compositional range for a Ca/(Ca+Sr) molar ratio of 0-1.0.

Figure 3 shows the infrared spectra of the products heated at various temperatures. The Spectrum of the specimen heated at 800 °C is identical to that of calcium-strontium hydroxyapatite reported by Fowler.[7] Sharp peaks, however, at 1430 cm^{-1} and 1580 cm^{-1} are observed in spectra of specimens. These were assigned to vibrational bands of carboxyl groups, indicating the formation of carbonate apatite. The intensities of these 1430 cm^{-1} and 1580 cm^{-1} bands became weaker with an increase in heating temperature and disappeared in the specimen heated at 1000 °C.

TEM micrographs of the specimen with a Ca/(Ca+Sr) molar ratio of 0.4 as a function of heating temperature reveal that the precursor is transformed into fine microcrystals with an increase of heating temperature but between 800 °C and 1000 °C calcium-strontium apatite crystal growth is observed with particles growing to 300 µm in diameter.

This study describes the formation of a calcium-strontium apatite solid solution precursor via mechanochemical method. In this method, the precursor is formed by a process of ball-milling of a slurry consisting of a mixture of the starting materials; $CaHPO_4 \cdot 2H_2O$, $CaCO_3$, $SrHPO_4$ and $Sr(OH)_4 \cdot 8H_2O$ in a zirconia pot mill for 24 h in the presence of water. Calcium-strontium apatite precursor obtained from ball-milling began to change to calcium-strontium apatite upon heating at temperature over 500°C.

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