

On the Incorporation of Li(I) into the Fluoroapatite Lattice

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In attempts to incorporate the Li(I) cation into the Ca(II) positions of the fluoroapatite lattice it has been shown that the unit cell becomes increasingly distorted with the increase of lithium concentration. Crystallographic data have been obtained from X-ray powder data. The infrared spectra of these substituted apatites show that the Li(I) incorporation has a negligible effect on the strength of the P-O bonds.

Introduction

The use of lithium salts in the treatment of affective disorders and manic depressive psychoses is well known [1–4]. Some recent investigations also point out the possible essentiality of this element [4,5].

It has been shown that lithium is accumulated in bones to a higher concentration than in most other tissues, probably because of its chemical similarity to calcium and magnesium [1,3,6,7]. It was suggested that such accumulation might affect the structure and function of bone in long-term treated patients [8]. An extensive series of studies with lithium-treated patients and with laboratory animals suggest that special caution should be observed in the treatment of children and persons with immature bone structure or mineralization defects [1,3].

In order to attain a wider insight into the characteristics of the incorporation of lithium in bone, we have investigated the substitution of Ca(II) by Li(I) in the fluoroapatite-lattice, $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$,

which is considered a good model for the inorganic phase of hard tissues of vertebrates [9,10].

Results

A series of phases of composition $\text{Li}_x\text{Ca}_{10-0.5x}(\text{PO}_4)_6\text{F}_2$ were prepared by standard solid state reactions, as described in the Experimental Part. They were characterized by X-ray powder diffractometry and IR spectroscopy.

The crystallographic study shows that only the phases containing one or two lithium ions present the typical fluoroapatite pattern. The material of composition $\text{Li}_3\text{Ca}_{8.5}(\text{PO}_4)_6\text{F}_2$ and all others, with a higher degree of calcium substitution, show significant distortions of the apatite structure and the presence of other phases. The crystallographic data of the first three members of the investigated series, compared with those of the pure fluoroapatite, obtained and measured in the same conditions, are shown in Table I.

Table I. Lattice constants of the investigated apatites*.

Phase	<i>a</i> [Å]	<i>c</i> [Å]	Vol.[Å ³]
$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	9.378(3)	6.883(4)	524.28
$\text{Ca}_{9.5}\text{Li}(\text{PO}_4)_6\text{F}_2$	9.368(2)	6.880(2)	522.96
$\text{Ca}_9\text{Li}_2(\text{PO}_4)_6\text{F}_2$	9.345(4)	6.881(4)	520.40
$\text{Ca}_{8.5}\text{Li}_3(\text{PO}_4)_6\text{F}_2$	9.334(4)	6.868(4)	518.20

* Hexagonal, space group $P6_3/m$.

As can be seen, a slight overall volume diminution occurs with increasing calcium substitution, in agreement with the smaller ionic radius of lithium ($\text{Ca(II)} = 1.14 \text{ \AA}$, $\text{Li(I)} = 0.90 \text{ \AA}$ in octahedral coordination [11]), confirming the effective incorporation of this cation in the lattice.

In order to analyze the influence of the substitutional process on the phosphate groups, we have recorded the infrared spectra of all the obtained samples and compared them with that of pure calcium fluoroapatite. As stated earlier, during the study of other similar substitutional processes in the same lattice, the P-O symmetric stretching mode (ν_1) is especially adequate to investigate any type of influence of the calcium substitution on the phosphate moieties [12–16]. In the present case, a slight shift of the order of 3 cm^{-1} is observed in this frequency value, on passing from the pure fluoroapatite to the materials containing one or two lithium ions. This result implies a weak decrease of the strength of the P-O bonds as a consequence of the substitutional process.

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Table II. Phosphate vibrations in the investigated apatites*.

Apatite	ν_1	ν_3	ν_4	ν_2
$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	964 w	1094s, 1045vs 1027sh	603vs, 576vs	473w
$\text{Ca}_{9.5}\text{Li}(\text{PO}_4)_6\text{F}_2$	961 w	1093sh, 1045vs	604vs, 574vs	472w
$\text{Ca}_9\text{Li}_2(\text{PO}_4)_6\text{F}_2$	961 w	1102sh, 1042vs	604vs, 574vs	472w
$\text{Ca}_{8.5}\text{Li}_3(\text{PO}_4)_6\text{F}_2$	967sh	1105sh, 1044vs	616sh, 601s, 577s, 547sh	472w

* From IR spectra (values in cm^{-1}). vs = very strong; s = strong; w = weak; sh = shoulder.

As can be seen from Table II, the process practically does not affect the values of the antisymmetric stretching mode (ν_3), and also the bending modes (ν_2 and ν_4) remain largely unaffected.

To conclude, this model study has shown that only the incorporation of macroscopic quantities of Li(I) in the fluoroapatite lattice (three or more Li(I) ions) produces important structural distortions and suggests that the incorporation of small quantities of Li(I) in the lattice does not affect its

structural characteristics and has a negligible effect on the strength of the P-O bonds of the phosphate groups.

Experimental Part

The investigated apatites were prepared by solid state reactions of stoichiometric mixtures of CaHPO_4 , CaCO_3 , CaF_2 and $\text{Li}(\text{CH}_3\text{COO})$. The ground and well homogenized mixtures were heated at 1000°C during 20 h in platinum crucibles in air with several intermediate grindings to ensure the reaction progress.

The X-ray powder diagrams were obtained with a Siemens D-5000 diffractometer, using $\text{Cu-K}\alpha$ radiation (Ni filter). The analysis of the obtained diagrams and the refinement of the unit cell constants was performed with a locally modified version of the program PIRUM of Werner [17].

The infrared spectra were recorded on KBr pellets of the microcrystalline powders using a Perkin Elmer model 1600 FTIR spectrophotometer.

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