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FTIR STUDY OF BIOLOGICAL HYDROXYAPATITE

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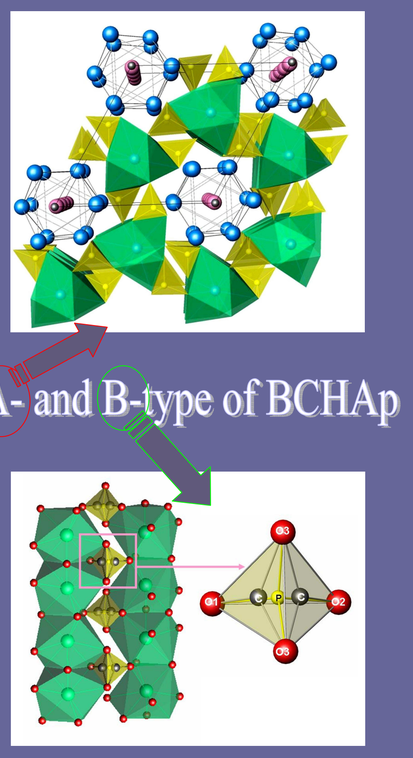
ABSTRACT

Here, Fourier transform infrared (FTIR) spectroscopy was used to resolve setting of carbonate ions in biological hydroxyapatite (BHAp). Even though preliminary XRPD results indicate that BHAp is B-type carbonated hydroxyapatite, the detailed FTIR spectroscopy analysis show that carbonate ions substitute both phosphate and hydroxyl ions in the crystal structure of BHAp, representing a mixed AB-type.



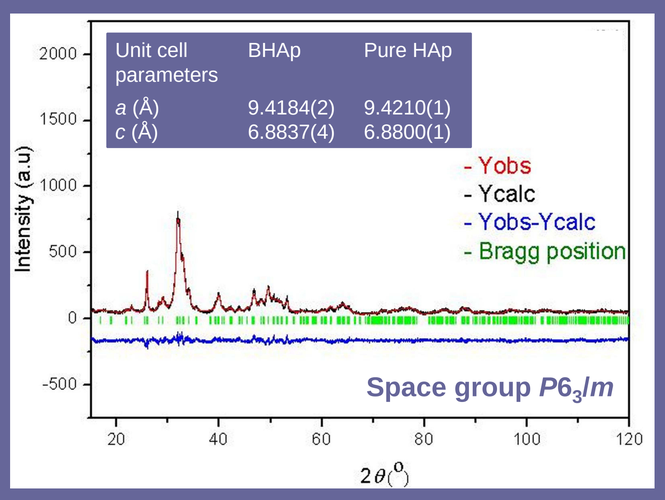
EXPERIMENTAL

The biological apatite (BHAp) was derived from human alveolar bone. To remove organic part, the bone was deproteinated, after that, the sample was dried at room temperature and grinded in an agate mortar.
The crystal phase of BHAp was identified by XRPD analysis obtained on Philips PW-1050 automatic diffractometer. The diffraction measurement was done over scattering angle from 8 to 120 $^{o}2\theta$ with a step of 0.02^{o} and a counting time of 12s. The FTIR measurement was performed on MIDAC M 2000 Series Research Laboratory FTIR Spectrometer using the KBr pellet technique, in the spectral range of 400–4000 cm^{-1}, with spectral resolution of 4 cm^{-1}. The deconvolution of recorded FTIR spectrum was done using PeakFite™ (version 4.05, demo) software.

RESULTS

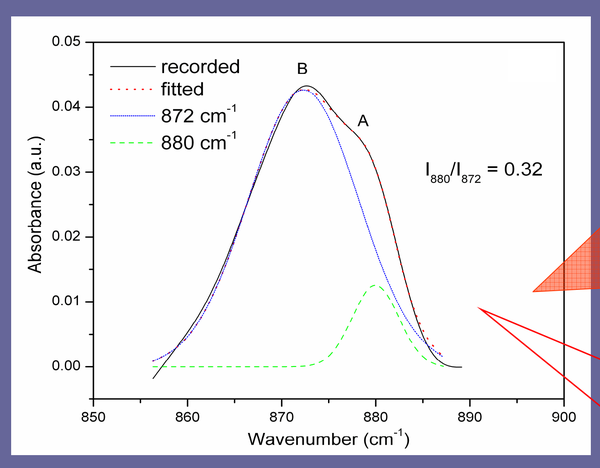
XRPD

Results of XRPD analysis show that the BHAp has a poorly crystalline hydroxyapatite phase of B-type.



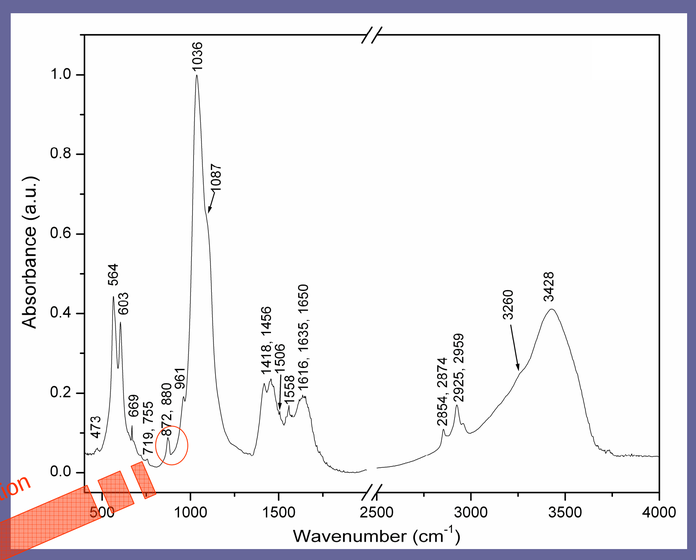
Rietveld refinement of BHAp

FTIR



Recorded, deconvoluted and fitted 860-890 cm^{-1} spectral region

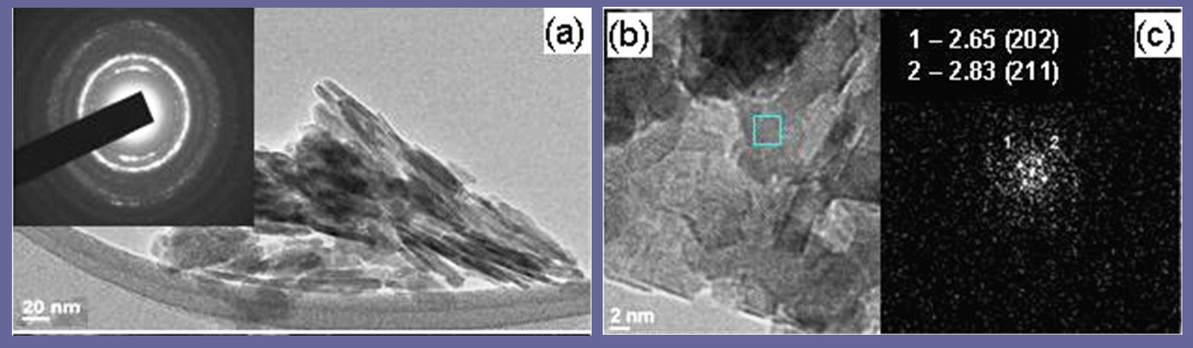
deconvolution



FTIR spectrum of BHAp

The ratio of the intensities of the peaks at 880 and 873 cm^{-1} corresponds to the ratio of A-type:B-type carbonated apatite.
After a deconvolution it is found that I_{880}/I_{872} = 0.32, indicating that much more carbonate ions are placed on the phosphate (B) site than on the hydroxyl (A) site in the crystal structure of BHAp.

TEM



(a) TEM and SAED; (b) HRTEM, and (c) FFT of BHAp

The **TEM** image of the BHAp powder shows needle-like directional oriented and agglomerated crystallites. The orientation of BHAp crystallites is a consequence of the orientation and arrangement of collagen fibers in the bone.
The concentric circles of the **SAED** patterns reveal the polycrystalline nature of the BHAp.
The **HRTEM** analysis of the BHAp confirmed hexagonal symmetry. The corresponding fast Fourier transform (FFT) calculated inter-planar distances (*d*) of the BHAp powder represents two sets of lattice fringes corresponding to the planes (202) and (211), with the inter-planar distance of 2.6 and 2.8 Å, respectively, which is in agreement with those in the JCPDS card (09-0432).

Assignment and vibrational modes	Bands positions
ν_2 bending O-P-O, double degenerate	473_{vw}
ν_4 bending O-P-O, triply degenerate	564_{m}, 603_{m}
O-H libration	669_{m}
ν_4 C-O	719_{vw}, 755_{vw}
ν_2 C-O B	872_{w}
ν_2 C-O A	880_{sh}
ν_1 symmetric stretching P-O	961_{w}
ν_3 assym. stretching P-O, triply degenerate	1036_{vs}, 1087_{sh}
ν_3 C-O	1418_{m}, 1456_{m}, 1506_{m}, 1558_{m}
bending O-H-O	1616_{m}, 1635_{m}
bending C=O (Amide I)	1650_{m}
stretching C-H	2854_{w}, 2874_{vw}, 2925_{m}, 2959_{w}
adsorbed H_2O	3260_{sh}, $3428_{m,b}$

CONCLUSION

- A biological carbonated hydroxyapatite (BHAp) extracted from human alveolar bone is chosen as a model system to resolve the problem of crystal structure and carbonate ions placing.
- Rietveld refinement of XRPD data confirmed that BHAp has a crystal structure of the B-type of carbonated hydroxyapatite.
- FTIR analysis resolved the nature of carbonated apatite. According to the results carbonate ions are placed in both A and B positions, which indicates mixed AB-type of carbonated apatite. After the deconvolution of FTIR band at 860-880 cm^{-1} it is calculated that I_{880}/I_{872} = 0.32, meaning that only a small amount of carbonate ions occupy the OH^- sites while a large amount is at PO_4^{3-} positions. Hence, the BHAp from human alveolar bone is mixed AB-type of carbonated hydroxyapatite but with dominant B-type.