Composite materials based on hydroxyapatite (HAP) are of much interest for biology and medicine owing to their bioactivity. The advanced strength properties of HAP can be achieved by its reinforcement with dispersed titanium and titanium oxide particles. This makes it possible to combine biocompatibility with high mechanical strength and fracture toughness.

The XRD patterns of TiO$_{y}$/HAp nanocomposites at room temperature (a), after annealing at 400 (b) and 600 °C (c) (black, blue and red line respectively).

Annealing of nanocomposites gives rise to forming of different phases depending on the stoichiometry of additives the composition of the initial mixture: ordered Ti$_{4.5}$O$_3$, TiO$_2$ (anatase), TiO$_2$ (rutile).

The Raman spectra of TiO0.92 (a) and TiO1.23 (b) nanopowders after high-energy milling for 8 h.

HRTEM images of the TiO$_2$ nanoparticles formed during annealing of nanocomposites TiO$_{y}$/HAp at 600 °C.

SEM images: (a) cylinder nanoparticles in initial HAp; (b) TiO$_{0.92}$/HAp powders after high energy milling.

**Results**

- The dependence on the stoichiometry of additives manifests itself in the presence of a phase with variable titanium valence (Ti$_{4.5}$O$_3$) and anatase in TiO$_{0.92}$/HAp and of TiO$_2$ (anatase and rutile).
- in TiO$_{1.23}$/HAp after annealing, as well as in the possibility of partial substitution of titanium ion of different valence (Ti$^{3+}$ and Ti$^{4+}$) for Ca$^{2+}$ positions.
- This causes different positions of the bands related to Ti-O vibrations and different distortion of positional symmetry of PO$_{4}^{3-}$ ion resulting in different broadening of its vibration bands.

**Conclusion**

1. Initial HAp and HAp after milling during 8 h contained cylinder nanoparticles, which were not observed in the mixes of TiO$_{y}$/HAp.
2. The shift and value of the relative intensity of the band in the region of 144-151 cm$^{-1}$ in the Raman spectrum indicated changes in the relative concentration of vacancies and bond length in the TiO system.
3. In the process of annealing of TiO$_{y}$/HAp nanocomposites from room temperature to 600 °C, new phases Ti$_{4.5}$O$_5$ and TiO$_2$ were formed (depending on the stoichiometry of additives). At the first stage (400 °C), the surface groups [Ti(OH)$_3$]$_{2}^{2+}$ and [TiHPO$_4$]$_{2}^{2-}$ were formed, and partial cation heterovalent substitution of Ti$^{3+}$ and Ti$^{4+}$ for Ca$^{2+}$ took place, which was accompanied by vacancy formation and anion substitution. Terminal carbonyls were formed. As the annealing temperature raised to 600 °C, the surface groups disappeared.