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## ACCEPTED MANUSCRIPT

### Lanthanum–silicate–substituted apatite synthesized by fast mechanochemical method: characterization of powders and biocoatings produced by micro–arc oxidation

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#### Abstract

Lanthanum–silicate substituted apatite with equal concentrations of the substituents in the range of 0.2 - 6.0 mol were produced by a fast method – mechanochemical synthesis. This method makes it possible to synthesize a nanosized single–phase product by activating reaction mixtures containing CaHPO<sub>4</sub>, CaO, La(OH)<sub>3</sub> and SiO<sub>2</sub>·H<sub>2</sub>O for 25–30 min in AGO–2 and AGO–3 planetary mills. The structure of the apatites was investigated by the FTIR and XRD methods. It was found that the synthesized samples with substituent concentrations up to 2 mol are substituted oxy–hydroxyapatites, at higher concentrations, they are substituted oxyapatites. The mechanochemically synthesized apatite with a substituent concentration of 0.5 mol was used for depositing biocoatings on titanium substrates by the micro-arc oxidation method. The structure of the coatings is mainly amorphous. *In vitro* biological tests demonstrated high biocompatibility of the coatings and the absence of cytotoxic action on mesenchymal stem cells.

**Keywords:** lanthanum–silicate–substituted apatite, mechanochemical synthesis, micro-arc oxidation, calcium phosphate, biocompatibility

#### **1. Introduction**

Materials based on calcium phosphates (CaP) and hydroxyapatite (HA) have been studied for several decades due to their high potential for the field of traumatology and orthopaedics. A positive effect of  $\beta$ -tricalcium phosphate ( $\beta$ -TCP) on the stimulation of osteogenesis *in vivo* was demonstrated by Albee and Morrison back in 1920 [1]. Injecting a  $\beta$ -TCP suspension into the gap between the bone ends initiated a more rapid bone growth and joining [1]. Later, various CaP and especially HA as an analogue of the mineral component of the bone and tooth tissues were studied more extensively. In the early 1950s, HA ceramic granules were studied for the first time as a filler material for healing defects in the bone tissue and as a material for resorbable medical ceramics [2]. Numerous data on the successful application of various CaP as materials for medical ceramics, coatings and cements were published [3–8]. While studying physicochemical, biochemical and mechanical properties of ceramics based on apatite, Geesink et al. [5] demonstrated that implants made from sintered HA ceramics form tight bonds with the living bone, but are sensitive to fatigue. The authors proposed to solve this problem with the help of plasma–sprayed HA coatings on titanium implants. Mechanical tests and histological evaluation of canine femur containing these implants revealed a high shear strength of the "implant–bone" interface after 6 months. These results indicated that the HA coating can form a strong

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