

International conference

Functional Inorganic Materials



FIM 2022

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Synthesis and Optical Properties of Mn-Doped Calcium Pyrophosphate Polymorphs

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Calcium phosphates (CPs) are the family of materials, widely used in different areas such as medicine and bone regeneration [1], sensors [2], removal of heavy metals from water [3], etc. Whereas in medicine, mainly calcium orthophosphates such as hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), tricalcium phosphate (TCP, $\text{Ca}_3(\text{PO}_4)_2$), or amorphous calcium phosphate (ACP) are used, some recent studies on biomaterials showed the potential of the use of calcium pyrophosphate (CPP, $\text{Ca}_2\text{P}_2\text{O}_7$) for biomedical applications.

One of the strategies for modifying CPs considers partial substitution of Ca^{2+} by other biocompatible ions with specific properties [4]. Modification of CPs with magnetic or optically active ions can be used for bio-imaging purposes [5] or monitoring phase transitions in CPs *in situ* [6]. This approach was also employed to tune the properties of CPP.

Manganese is an essential element in the human body that plays a vital role in many biological processes, including bone development. Previously biological properties of different Mn-substituted CPs were investigated, and it was shown that the presence of Mn^{2+} ions in the CP matrix provides superior biological performance [7]. However, high concentrations of Mn^{2+} result in toxicity of the materials; therefore, Mn content should be limited to a relatively low level [8].

Although CPP has three different polymorphs, most of the works focus exclusively on β -CPP, whereas two others are quite poorly investigated. Studies on α -CPP are most often related to the preparation of optical materials by substitution of Ca^{2+} ions by lanthanides [9]; nevertheless, β -CPP besides of the use in medicine also finds an application in the preparation of phosphors [10]. The least studied polymorph is γ -CPP. This work demonstrates a simple and time-efficient way of preparing Mn^{2+} -substituted brushite with subsequent conversion to γ -, β -, and α -CPP. Structural, optical, and morphological properties of synthesized materials were investigated in detail.

Acknowledgements

Vilnius University is highly acknowledged for financial support from the Science Promotion Foundation (MSF-JM-5/2021).

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