Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2023, **33**, 531–533

Mendeleev Communications

Ceramics based on double magnesium–sodium phosphates for bone regeneration

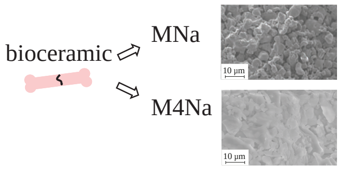
Ilya I. Preobrazhenskiy*[a] and Valery I. Putlyaev[a,b]

[a] *Department of Materials Science, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. E-mail: preo.ilya@yandex.ru*

[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*

DOI: 10.1016/j.mencom.2023.06.029

The fabrication of ceramics based on double phosphates $MgNaPO_4$ and $Mg_4Na(PO_4)_3$ is considered. Volume changes in phase transformations of $MgNaPO_4$ and $Mg_4Na(PO_4)_3$ upon thermal treatment in a range of 800–1100 °C and their effect on the microstructure of ceramics are studied.



Keywords: magnesium–sodium phosphates, bioceramics, bone implants, microstructure, regenerative medicine, biomaterials.

Restoration of large bone areas while healing injuries or bone defects still remains a challenge for regenerative medicine.[1,2] Polymers[3–7] and bioceramics[8,9] are used for the regeneration of damaged bone tissues, but attention is focused on materials containing calcium phosphates because they are similar in composition to natural bone and biocompatible.[10–13] However, bioceramics based on calcium phosphates do not meet basic requirements for the materials aimed at bone healing. Ceramics and composites based on hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ are characterized by poor solubility and a low resorption rate of ceramics during *in vivo* implantation.[14–16] From this viewpoint, magnesium phosphates can be a useful alternative to calcium phosphates due to the ability of magnesium to replace calcium in the bone mineral and bioceramics.[17] Enhanced *in vitro* and *in vivo* biodegradation of the materials based on magnesium phosphates was reported.[18,19] Thus, Ostrowski *et al*.[18] noted that amorphous magnesium phosphate pellets released up to 9 mM magnesium ions after immersion in cell culture media for 125 h, whereas the concentration of magnesium ions in a control experiment with β-tricalcium phosphate $Ca_3(PO_4)_2$ remained unchanged. The phases containing Mg^{2+} ions are promising due to their biological properties and the possibility of the formation of natural bone tissue. Magnesium is found in bone tissue, and it can replace calcium in body minerals due to their chemical similarity. Magnesium phosphates, such as newberite ($MgHPO_4 \cdot 3H_2O$) and struvite ($NH_4MgPO_4 \cdot 6H_2O$), can be used as precursors for bone implants.[20,21] The addition of 0.01 M Mg^{2+} to a cell culture medium enhanced the mineralization of an extracellular matrix.[22] Due to a greater enthalpy contribution to the hydration of cations in the course of dissolution, magnesium phosphates are characterized by a higher rate of resorption in the body environment, and they are promising biomaterials for the treatment of bone tissue defects. However, fabrication of bioceramics based on magnesium phosphates received little attention.[23,24] To tune the resorption of bioceramics, sodium cations[25,26] can be introduced into the crystal lattice of phosphates. Thus, the aim of this work was to study a relationship between phase transformations in the test double magnesium–sodium phosphates and the microstructure of corresponding ceramics.

The double magnesium–sodium phosphates were prepared using $Mg_2P_2O_7$, $Mg_3(PO_4)_2$, MgO, and Na_2CO_3 as starting materials (see Online Supplementary Materials).

The double phosphate $MgNaPO_4$ (MNa) was obtained under reported conditions[27] according to reaction (1). A mixture of magnesium pyrophosphate $Mg_2P_2O_7$ and sodium carbonate was ball-milled and then calcined in two stages at 900 and 600 °C for 10 h:

$$Mg_2P_2O_7 + Na_2CO_3 \rightarrow 2MgNaPO_4 + CO_2\uparrow. \qquad (1)$$

The double orthophosphate $Mg_4Na(PO_4)_3$ (M4Na) was synthesized by solid-phase reaction (2) from the phosphate $MgNaPO_4$ and magnesium orthophosphate $Mg_3(PO_4)_2$ heated at 1100 °C for 10 h:

$$Mg_3(PO_4)_2 + MgNaPO_4 \rightarrow Mg_4Na(PO_4)_3\,. \qquad (2)$$

The powder samples for dilatometric analysis were shaped by uniaxial pressing with a Carver C hydraulic manual press (see Online Supplementary Materials). Here, we report the preparation and properties of ceramics based on the double magnesium–sodium phosphates. Sintering temperatures were 800, 900, and 1000 °C. Sintering temperatures higher than 900 °C for the $MgNaPO_4$ phase caused cracks due to polymorphic transformations.[27] The crystal lattice volumes determined from powder XRD data were 916.37(4) and 950.04(2) Å^3 for MNa and M4Na powders, respectively. The powder XRD analysis of ceramic samples after calcination (Online Supplementary Materials, Figures S1 and S2) showed that a sample based on $MgNaPO_4$ sintered at 800 °C did not contain impurities of other polymorphic modifications, while the sintering temperature of 900 °C led to the appearance of impurity polymorphic modifications. It can be assumed that the high-temperature modification was a $MgNaPO_4$ phase (ICDD card 32-1121) because the intensity of its reflexes increased with temperature. At 1000 °C, $MgNaPO_4$ decomposed with the formation of $Mg_4Na(PO_4)_3$ and Na_3PO_4. Ceramic samples based on