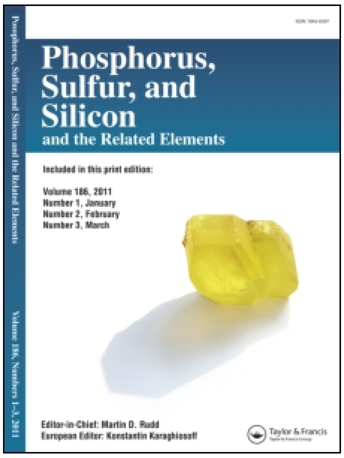

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SYNTHESIS AND CHARACTERIZATION OF NIOBIUM-BEARING MEMBERS OF THE NZP AND $NbOPO_4$ STRUCTURAL FAMILIES

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Theoretically predicted by us, $M_{1/3}Nb_{5/3}(PO_4)_3$ (M = Mg, Mn, Co, Ni, Cu or Zn) compounds with the sodium zirconium phosphate (NZP) framework structure having no interstitial ions were synthesized. The rising of temperature above 900°C causes the change of chemical composition of NZP compounds and formation $NbOPO_4$-like products. The phase formation regularities stated gave a possibility to choose optimal conditions for preparation of these phosphates.

Keywords: Divalent metals; $NbOPO_4$-like products; niobium; NZP structure; phosphates

NZP ($NaZr_2(PO_4)_3$) family materials are characterized by a three-dimensional framework of strongly bonded $[Zr_2(PO_4)_3]$ units made up of corner-linked PO_4 tetrahedra and ZrO_6 octahedra.[1] Sodium cations fill certain holes within this framework. The general crystal chemical formula is $(M1)(M2)_3\{[L_2(TO_4)_3]^{p-}\}_{3\infty}$, where M1 and M2 are positions in the framework holes partly occupied by Na; L and T are positions of the framework occupied by Zr and P, respectively. The role of Na^+ cations in the holes is only to balance the charge, *p*, of the anionic framework. If M-sites have no interstitial ions the charge on the framework $[L_2(TO_4)_3]$ will be zero, and it will be possible to prepare the NZP materials with the electrically neutral empty frameworks. We have calculated theoretically acceptable formula types of the empty orthophosphate frameworks. We have limited ourselves to the cases when two cations, having

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valences ranging from 1+ to 5+, enter into the L-positions of the framework. The framework formula for these sets of cations may be written as $[L_r^{a+}L_z^{b+}(PO_4)_3]^0$. Variables $r, s, a,$ and b are interconnected by relations: $r + s = 2$ and $a \cdot r + b \cdot s = 9$. The first expression is based on the fact that the frameworks $L_2(PO_4)_3$ are realized under stoichiometry of $L/P = 2/3$. The last equation is derived from the electrical neutrality principle. Mutual solving of the equations determines possible compositions of empty NZP frameworks.

Up to date, the NZP family phosphates of two formula types—$E^{5+}C^{4+}(PO_4)_3$ and $E_{3/2}^{5+}R_{1/2}^{3+}(PO_4)_3$—from the four possible ones have been synthesized. Substitution at two L sites by combination of Nb (V) and divalent M cation gives a possibility to prepare new compounds having formula type of $M_{1/3}Nb_{5/3}(PO_4)_3$.

Very little is known about compounds of the $NbOPO_4$ family. The tetragonal crystal structure of α-$NbOPO_4$ may be described as consisting of chains formed by NbO_6 octahedra linked together by sharing corners. Tetrahedra of PO_4 link the chains together to give a three-dimensional framework.[2]

This investigation reports about the synthesis, structural characterization and thermal stability of new niobium-bearing NZP- and $NbOPO_4$-type phosphates in MO—Nb_2O_5—P_2O_5 systems with M = Be, Mg, Ca, Mn, Co, Ni, Cu, Zn, Sr, Cd, Ba, Hg, and Pb. In addition, we have examined the ability of the empty NZP frameworks to accommodate divalent cations and Nb in the octahedrally coordinated L-sites, and the effect of temperature on the chemical stability of $M_{1/3}Nb_{5/3}(PO_4)_3$.

The syntheses have been carried out by the solid-state powder method in air. Required amounts of precursors were thoroughly mixed and calcined at different temperatures in the range from 600 to 1100°C and held at those temperatures for time intervals ranging from 1 to 100 h. Thermal treatment stages were alternated with careful grinding. The weight loss at various temperatures was determined. The samples were analyzed by X-ray diffraction (XRD) to determine the presence of any new phases in powders heated to various temperatures. The chemical composition and homogeneity of the single-phase materials were confirmed by microprobe analysis.

XRD showed the principal structural types of the synthesized materials are NZP, ε-, and α-$NbOPO_4$. We could obtain single phase NZP compounds of the formula $M_{1/3}Nb_{5/3}(PO_4)_3$ for M = Co, Mn, Ni, and Mg, free from detectable impurities. Our attempts to prepare the same phases for M = Cu and Zn resulted in ones containing both ε-$NbOPO_4$ and NZP structures due to competing reactions occurring. The solids with a $(M_{1/3}Nb_{5/3})/P$ ratio of 1/1 were structurally analogous to $NbOPO_4$. The powder XRD pattern of both Be-Nb and Cd-Nb containing products were found to be materials of only the ε-(the low temperature form) and α-(the high temperature form) NbOPO$_4$ type. Therefore, $M_{1/3}Nb_{5/3}(PO_4)_3$ with the NZP structure will be formed when the ion radii of divalent cation has ionic size larger than Be^{2+} and smaller than Cd^{2+}. The magnitude of the cell parameters for NZP compounds is similar to that of $Nb^{4+}Nb^{5+}(PO_4)_3$.[3]

IR spectra of NZP compounds of the formula $M_{1/3}Nb_{5/3}(PO_4)_3$ (M = Mg, Mn, Co, or Ni) show characteristic PO$_4$ vibrations of the NZP framework. The PO$_4$ distorted geometry in the NZP crystal structure (the characteristic absorption at around 950 cm^{-1}) is the manifestation of the combined effect of the framework ions (niobium and divalent cations).

DTA-TG and XRD experiments show that heating above 800°C of NZP phases of composition $M_{1/3}Nb_{5/3}(PO_4)_3$ predetermines their structural rearrangement into α-NbOPO$_4$-like product. This transformation is assigned to loss of phosphorus and confirmed by microprobe analyses.

It has been shown that the expansibility of charge-neutral framework is close to zero.[4] It may be expected that investigated compounds are low or negative thermal expansion materials.

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