Thermal behaviour of the system H_3BO_3–NH_4PO_3

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It was shown earlier that ammonium polyphosphate NH_4PO_3 (APP) was a convenient reagent for preparation of normal and double ammonium-containing condensed phosphates [1]. The use of APP as phosphate-containing reagent allows to synthesize well-known compounds as well as new condensed phosphates which cannot be prepared by other techniques. In this way more than 20 well-known double ammonium-containing phosphates were synthesized in the systems MO–NH_4PO_3 and MO_2–NH_4PO_3: polyphosphates $M^{II}NH_4(PO_3)_3$ (M^{II} = Mg, Co, Ni, Cu, Zn, Pb), cyclotriphosphates $M^{II}NH_4P_3O_9$ (M^{II} = Mg, Ca, Mn, Cd), polyphosphates $M^{II}(NH_4)_2(PO_3)_4$ (M^{II} = Mn, Co, Zn, Cd), cyclotetraphosphates $M^{II}(NH_4)_2P_4O_{12}$ (M^{II} = Sr, Pb), cyclooctaphosphate $Cu_3(NH_4)_2P_8O_{24}$, tetraphosphates $M^{IV}(NH_4)_2P_4O_{13}$ (M^{IV} = Si, Ge). Furthermore, 10 new compounds were also obtained in these systems. They are orthorhombic cyclotriphosphate $MnNH_4P_3O_9$, polyphosphates $M^{II}(NH_4)_2(PO_3)_4$ (M^{II} = Mg, Ca, Ni) and $Ni(NH_4)_2(PO_3)_4{\cdot}2H_2O$, polyphosphates $Ba_2NH_4(PO_3)_5$ and $Ba(NH_4)_4(PO_3)_6$, tetraphosphates $M^{IV}(NH_4)_2P_4O_{13}$ (M^{IV} = Sn, Ti) [2, 3].

Double metal-ammonium condensed phosphates are of practical interest because they reveal flame retardant properties in polyamides [4, 5]. An advantage of these compounds for this application is their high thermal stability. In fact, polyamides are processed at high temperatures limiting the use of flame-retardants having low thermal stability. Unfortunately, the fire retardant properties of the majority of well-known double ammonium-containing phosphates are still deficient for real applications. Therefore, a search for new compounds of this family demonstrating higher efficiency is topical.

This work continues our systematic investigation of synthesis of trivalent metal phosphates in the systems M_2O_3–NH_4PO_3 in a wide range of temperatures and reactant ratios covering the crystallization fields of phosphates of various condensation of the anion [6–8]. The aim of this study was to establish regularities of formation of boron phosphates in the APP flux, to develop a convenient technique for synthesis of detected compounds.

Thermal behavior of the H_3BO_3–NH_4PO_3 system within the temperature range of 30–800 ºC at the molar ratio $H_3BO_3 : NH_4PO_3 = 1 : (1{\div}10)$ using STA was studied. As a result, formation of only one boron phosphate BPO_4 was determined. It was shown by XRD that this compound was a tetragonal polymorph of BPO_4 [9]. No double ammonium-containing boron phosphates were detected. Finally, the “poorness” of boron phosphate chemistry is considered.

References

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