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THE SYNTHESIS AND CRYSTAL STRUCTURES OF NEW CONDENSED PHOSPHATES OF MANGANESE

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This work deals with the synthesis of condensed phosphates of Mn(II), Mn(III), and also their combinations with Na, Cs. The reaction of MnO₂ with molten polyphosphoric acids, partially neutralized with carbonates of Na and Cs is used. In the course of reaction of MnO₂ with molten polyphosphoric acids, Mn(IV) is reduced to Mn(III) or/and Mn(II). The ratio Mn(III)/Mn(II) depends on the conditions of synthesis (temperature, time, presence of oxidants or reductants etc.). By varying these parameters we obtained 7 new manganese phosphates and determined their structures.

Mn(II) Products: MnP₄O₁₁ (a=9.306, b=9.271, c=10.758 Å, α=71.43, β=71.07, γ=90.34°, *P* $\bar{1}$) - an ultraphosphate with a new type of anion. NaMn(PO₃)₃ (a=14.429, b=14.429, c=14.431 Å, *Pbca*) - polyphosphate.

Mn(III) Products: Na₃MnP₈O₂₃ (a=11.914 Å, *P*₄132) - an ultraphosphate, which contains an isolated "cage" anion, isostructural to Na₃FeP₈O₂₃. CsMnHP₃O₁₀ (a=8.994, b=8.629, c=6.511 Å, β=113.39°, *C*2) - a new type of triphosphate with a framework structure.

Mn(II)+Mn(III) Products: CsMn(II)Mn(III)P₆O₁₈-I (a=10.329, b=13.356, c=6.277 Å, β=113.05°, *C*2/m), CsMn(II)Mn(III)P₆O₁₈-II (a=12.942, b=12.505, c=5.061 Å, β=110.59°, *C*2/m) - cyclohexaphosphates with a statistical distribution of Mn(II) and Mn(III) atoms. First of two cyclohexaphosphates has 10 isostructural analogs: CsM¹M²P₆O₁₈ (M¹=Zn, Mg, Mn, Co, M²=V, Fe, Al, Ga). Cs₃Mn(II)₃Mn(III)(P₆O₁₈)₂ (a=16.166, b=9.953, c=12.435 Å, β=127.23°, *C*2/m) - a cyclohexaphosphate, where Mn(II) completely occupies one crystallographic position, while the other position is shared with Mn(III). We synthesized one more isostructural analog of similar composition - Cs₃Mg₃In(P₆O₁₈)₂.

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