THE CRYSTAL CHEMISTRY OF NEW SYNTHETIC COMPOUNDS $CsNaCu(P_2O_7)$ AND $Rb_2Cu(P_2O_7)$

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In this work we describe preliminary results of the synthesis and of a crystal-chemical study of synthetic phosphates with transition metals. Due to the increasing requirements for environmental safety specialists from various industries, we are searching for sustainable forms of immobilization of hazardous waste during storage. We are also developing a component-based waste for new materials. In our continued exploratory synthesis of compounds containing transition-metals, we were able to produce the new phosphate phases $CsNaCu(P_2O_7)$ and $Rb_2Cu(P_2O_7)$.

A crystal chemical study has allowed us to identify the new phosphates. Crystals of $CsNaCu(P_2O_7)$ (Phase 1) and $Rb_2Cu(P_2O_7)$ (Phase 2) have been obtained by high-temperature reaction of $CsNO_3$, $Cu(NO_3)_2$, NaOH and $(NH_4)_4P_2O_7$. The reagents were mixed in an agate mortar in ratios of Cs:Na:Cu:P 1:1:3:4 (1) and Rb:Cu:P 1:3:3 (2). The mixtures were heated up to 650°C and kept at this temperature for 8 hours in air, followed by cooling down to 25°C at a cooling rate of 25°C/h. The product consisted of blue platy crystals of compounds (1) and (2). Synthetic crystals of the phosphate of copper and rubidium were studied in detail by us on the structures of $Rb_2Cu(P_2O_7)$ and $Rb_2Cu_3(P_2O_7)_2$ – new alkali metal copper diphosphates (CHERNYATIEVA *et al.,* 2008).

The structures of these synthetic compounds were solved using single-crystal X-ray diffraction and a computer program from SHELDRICK (1997). $CsNaCu(P_2O_7)$ (1) is orthorhombic, crystallizes in space group $Pmn2_1$, with a = 5.147(8), b = 15.126(2), c = 9.717(2) Å, V = 756.20 Å^3, $R1$ = 0.066 for 1221 unique reflections [$I > 2\sigma(I)$]. The structure is based upon 2-D layers of Cu square pyramids and P_2O_7 groups. Additional distortion occurs in the [6]-coordinated Cu pyramids due to JAHN & TELLER (1937). $Rb_2Cu(P_2O_7)$ (2) is orthorhombic as well, crystallizes in space group $Pmcn$, with a = 5.183(8), b = 10.096(1), c = 15.146(3) Å, V = 793.55 Å^3, $R1$ = 0.063 for 1326 unique reflections [$I > 2\sigma(I)$]. The structure is based upon 2-D layers of Cu square pyramids and groups of P_2O_7, similar to the structure of compound (1). However, the latter structure consists of different layers, with the scheme ABAB. A qualitative chemical analysis was performed with an electron microscope Quanta200 3D (FEI, Galanda), a microprobe analysis was performed on the microprobe EDAX (USA) at an accelerating voltage of ~20 kV.

Here we report the synthesis, the structure and the properties of the title compounds and we compare these phases with the previously discovered $K_2CuP_2O_7$ (ELMAADI *et al.,* 1995) and $CsNaMnP_2O_7$ (HUANG *et al.,* 1998). These structures crystallize in other space groups, although their structures are also based on 2-D layers, formed by P_2O_7 groups combined with polyhedra of the transition metals.

This work was supported by the Russian Ministry of Science and Education 3.37.84.2011.

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