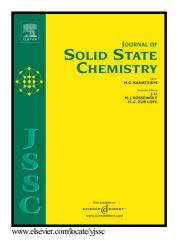
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Solid state solubility of copper oxides in hydroxyapatite

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Abstract.

Samples containing copper oxide doped hydroxyapatite with the composition $Ca_{10}(PO_4)_6(Cu_xOH_{1-x-\delta})_2$, x = 0.054 - 0.582, in the mixture with CuO/Cu₂O were prepared by a solid-state high-temperature treatment at varying annealing temperatures and at different partial water vapor and oxygen pressures. The crystal structures of the apatite compounds were refined using powder X-ray diffraction patterns and the content of copper ions *x* in the apatite was determined. Copper ions enter exclusively into the apatite trigonal channels formally substituting protons of OH-groups and the hexagonal cell parameters grow approximately linearly with *x*, the channel volume mostly expanding while the remaining volume of the crystal lattice changing only slightly. The equilibrium copper content in the apatite increases drastically, by almost a factor of 10 with the annealing temperature rising from 800 to 1200 °C. The reduction of the water partial pressure leads to a further increase of *x*, while the dependence of *x* on the oxygen partial pressure exhibits a maximum. The observed relations are consistent with the proposed chemical reactions implying the copper introduction is followed by the release of a considerable quantity of gaseous products – water and oxygen. The analysis of interatomic distances suggests that the maximum content of copper ions in the channel cannot exceed 2/3.

1. Introduction.

A considerable number of inorganic compounds adopts apatite structure with a general formula $M_{10}(AO_4)_6X_2$ [1,2]. M is a relatively large metal ion normally in a low oxidation state of +2 (e.g. alkaline-earth metal) or/and +3 (rare-earth metals), which can be partially replaced by alkaline metal ion. A is an atom in an oxidation state of +4 - +7 (e.g. P, As, Si, Mn^V, V^V), which forms a tetrahedral oxo-anion. X is a small anion (e.g. F⁻, Cl⁻, OH⁻, $\frac{1}{2}O_2^{2^-}$) located in the trigonal channel of the structure formed by M-cations. A well known father of the family is hydroxyapatite Ca₁₀(PO₄)₆(OH)₂. In the beginning of 2000th, a new subfamily with a modified

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