

Synthesis of the solid solutions $\text{H}_2\text{Sb}_{2-x}\text{V}_x\text{O}_6 \cdot n\text{H}_2\text{O}$ with the pyrochlore-type structure

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Abstract

In this paper, the possibility of isovalent doping with vanadium ions of the polyantimonic acid $\text{H}_2\text{Sb}_2\text{O}_6 \cdot n\text{H}_2\text{O}$ crystallizes within the defect pyrochlore-type structure (sp. gr. Fd3m) is shown. In the introduction advantages of this method of modifying solid electrolytes with a pyrochlore-type structure were noted: preservation the charge of the framework $[\text{BO}_3]$; a constant number of mobile protons; a change in the interaction energy of protons with an anionic framework.

Solid substitution solutions of $\text{H}_2\text{Sb}_{2-x}\text{V}_x\text{O}_6 \cdot n\text{H}_2\text{O}$ were synthesized by the method of coprecipitation. The elemental composition of the synthesized samples was found by two independent methods: the remains of vanadium ions in mother solutions and by energy-dispersive spectrometry. Amounts of vanadium ions in the solid phase coincided within the limits of the errors this methods. X-ray studies have shown that solid solutions with the pyrochlore-type structure (sp. gr. Fd3m) are formed in a wide range of variation of the vanadium amount, the parameter x can take values $0 < x < 0.48$. For samples in which $x > 0.48$, broad background line and redistribution of the intensities of the reflexes were observed on X-ray diffraction patterns.

In paper, the structural parameters and morphology of the particles extreme solid solution of the composition $\text{H}_2\text{Sb}_{1.52}\text{V}_{0.48}\text{O}_6 \cdot n\text{H}_2\text{O}$ were investigated. On micrographs of this sample there are no bright or dark areas, particles have spherical shape smaller than $0.5 \mu\text{m}$. The unit cell parameter $\text{H}_2\text{Sb}_{1.52}\text{V}_{0.48}\text{O}_6 \cdot n\text{H}_2\text{O}$ was 10.314 \AA , which is less than for polyantimonic acid (10.360 \AA). It is shown that this difference is related to the dimensions of the ions of antimony and vanadium. A smaller value of the pycnometric density of the solid solution $\text{H}_2\text{Sb}_{1.52}\text{V}_{0.48}\text{O}_6 \cdot n\text{H}_2\text{O}$ (3.60 g/cm^3) as compared to the polyantimonic acid (3.85 g/cm^3) is due to filling of 16c-positions of the pyrochlore-type structure with vanadium ions.

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