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Synthesis of the solid solutions $H_2Sb_{2-x}V_xO_6 \cdot nH_2O$ 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 $H_2Sb_2O_6 \cdot nH_2O$ 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 [BO_3]; a constant number of mobile protons; a change in the interaction energy of protons with an anionic framework.

Solid substitution solutions of $H_2Sb_{2-x}V_xO_6 \cdot nH_2O$ 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 $H_2Sb_{1.52}V_{0.48}O_6 \cdot nH_2O$ were investigated. On micrographs of this sample there are no bright or dark areas, particles have spherical shape smaller than 0.5 μm. The unit cell parameter $H_2Sb_{1.52}V_{0.48}O_6 \cdot nH_2O$ was 10.314 Å, which is less than for polyantimonic acid (10.360 Å). 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 $H_2Sb_{1.52}V_{0.48}O_6 \cdot nH_2O$ (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.

References

[1] A.V. Egorysheva, O.M. Gaitko, T.I. Milenov, P.M. Rafailov, G.V. Avdeev, T.D. Dudkina. Optical and vibrational spectra of $Bi_{1.8}Fe_{1.2(1-x)}Ga_{1.2x}SbO_7$ solid solutions with pyrochlore-type structure. *Russian Journal of Inorganic Chemistry*. **2017**. Vol.62. No.7. P.960-963. (russian)

[2] A.G. Krasnov, I.V. Piir, N.A. Sekushin, Y.V. Baklanova, T.A. Denisova. Electrophysical properties of bismuth titanates with the pyrochlore structure $Bi_{1.6}M_xTi_2O_{7-\delta}$ (M = In, Li). *Russian Journal of Electrochemistry*. **2017**. Vol.53. No.8. P.866-872. (russian)

[3] T.B. Kuvshinova, A.V. Egorysheva, O.M. Gaitko, P.O. Rudnev, A.E. Baranchikov, T.D. Dudkina. Synthesis of nanocrystalline ternary bismuth iron antimony oxide with pyrochlore structure. *Russian Journal of Inorganic Chemistry*. **2015**. Vol.60. No.10. P.1179-1183. (russian)

[4] S.V. Yudintsev, T.S. Livshits, J. Zhang, R.C. Ewing. The behavior of rare-earth pyrochlores and perovskites under ion irradiation. *Doklady Earth Sciences*. **2015**. Vol.461. No.1. P.247-253. (russian)

[5] D. Klestchov, V. Burmistrov, A. Sheinkman, R. Pletnev. Composition and structured phases formed in the process of hydrated antimony pentoxide thermolysis. *Journal of Solid State Chemistry.* **1991**. Vol.94. No.2. P.220-226. (russian)
[6] F.A. Yaroshenko, V.A. Burmistrov. Proton conductivity of polyantimonic acid studied by impedance spectroscopy in the temperature range 370-480 K. *Inorganic Materials.* **2015**. Vol.51. No.8. P.783-787. (russian)
[7] F.A. Yaroshenko, V.A. Burmistrov, and K.S. Makarov. Dielectric relaxation of polymer composits based on a MF-4SK membrane and polyantimonic acid. *Butlerov Communications.* **2017**. Vol.49. No.2. P.88-95. DOI: 10.37952/ROI-jbc-01/17-49-2-88
[8] A.B. Yaroslavtsev. The main directions of development and research of solid electrolytes. *Russ. Chem. Rev.* **2016**. Vol.85. No.11. P.1255-1276. (russian)
[9] I.A. Stenina, A.B. Yaroslavtsev. Low- and intermediate-temperature proton-conducting electrolytes. *Inorganic Materials.* **2017**. Vol.53. No.3. P.253-262. (russian)
[10] M.S. Shchelkanova, M.I. Pantyukhina, B.D. Antonov, and A.V. Kalashnova. Produce new solid electrolytes based on the $Li_{8-x}Zr_{1-x}V_xO_6$ system. *Butlerov Communications.* **2014**. Vol.38. No.5. P.96-102. ROI: jbc-02/14-38-5-96
[11] Y.A. Lupitskaya, V.A. Burmistrov. Ionic conductivity of potassium antimonate tungstates with partial Na^+ or Li^+ substitution for K^+. *Inorganic Materials.* **2013**. Vol.49. No.9. P.930-934. (russian)
[12] V.N. Muzgin, L.B. Khamzina, V.L. Zolotavin, I.Ya. Bezrukov. Analytical chemistry of vanadium. *Moscow: Science.* **1981**. 215p. (russian)