FORMATION OF PHASES IN COMPLEX OXIDES WITH A PYROCHLORE STRUCTURE CONTAINING LITHIUM IONS

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Abstract: Formation laws of potassium and lithium antimonate-tungstates during heating of complex oxide (y-x)K_2CO_3-xLi_2CO_3-ySb_2O_3-2(2-y)WO_3 mixture in air were studied. For a temperature of 1123 K in the $KSbO_3$-WO_3-$LiSbO_3$ concentration triangle, the formation zone of $Li_xK_{y-x}Sb_yW_{2-y}O_6$ containing phases with a pyrochlore-type structure was determined.

Keywords: ionic conductivity, pyrochlore-type structure, potassium antimonate tungstate, concentration triangle.

ОБРАЗОВАНИЕ ФАЗ В СЛОЖНЫХ ОКСИДАХ СО СТРУКТУРОЙ ПИРОХЛОРА, СОДЕРЖАЩИХ ИОНЫ ЛИТИЯ

Аннотация: Изучены закономерности образования антимонатов-вольфраматов калия и лития при нагревании смеси сложных оксидов (y-x)K2CO3-xLi2CO3-ySb2O3-2(2-y)WO3 на воздухе. Для температуры 1123 К в концентрационном треугольнике KSbO3-WO3-LiSbO3 определена зона образования LixKy-xSbyW2-yO6, содержащих фазы со структурой типа пирохлора.

Ключевые слова: ионная проводимость, структура типа пирохлора, вольфрамат антимоната калия, концентрационный треугольник.

INTRODUCTION

The studied solid electrolytes have ionic conductivity at the level of the world's best analogues, which allows them to be recommended for use in the following various electrochemical devices: chemical sources of electricity, thermoelectric generators; ion and ion-plasma engines for space objects; sensor devices for determining the activity of alkali metals in various liquid and gaseous media as diaphragms to separate the anode and cathode spaces during the electrolysis of molten salts [1-6]. A type of synthesized solid electrolytes with high conductivity for this type of ions, but different chemical composition; also differ in the type and concentration of modifying inputs, allowing to choose the electrolyte with the most appropriate performance indicators for working in certain conditions. Another area of application of the synthesized solid electrolytes is for research purposes, such as studying the thermodynamics of solid-phase reactions. The phase relations in the considered quasibinary systems can be used as information about the values of electrical conductivity depending on the temperature and composition of solid electrolytes, as well as the results of the study of the crystal structure of the main compounds [1- 8].

Compounds based on complex antimony oxides of the pyrochlore type are of great interest because they are good ion conductors and ion exchangers [1-2]. These compounds can be obtained by solid phase synthesis in the (y-x) K_2CO_3-xLi_2CO_3-ySb_2O_3-2 (2-y) WO_3 system [3-4]. Carriers involved in ion transfer and ion exchange are usually alkali metal ions. In this case, such ions can be potassium and lithium ions. The replacement of potassium ions with a large radius by lithium ions with a smaller ionic radius indicates that such compounds have large values of ionic conductivity, when changing the amount of antimony (V) and tungsten (VI) ions in the 16c positions of the pyrochlore-type structure, it is possible to obtain a wide range of compounds with an irregular cation sublattice [8-12].

However, until now, the issues of formation and stability of the phases obtained in this system have not been studied, and the concentration field of the synthesis of pyrochlore-type phases has not been determined.

In this regard, the purpose of this work was to establish the field of formation of potassium and lithium antimonate tungstate in the (y-x) K_2CO_3-xLi_2CO_3-ySb_2O_3-2 (2-y) WO_3 system, and to determine the composition and structure of the resulting phases.

EXPERIMENTAL

Powdered antimony Sb (III) oxide, W (VI) tungsten, "chemically pure" potassium and lithium carbonates were taken as initial reagents. Reagents were pre-ground, homogenized and dehydrated. The mixtures were prepared in the range of $0 <x <y$, $1.0 <y <2.0$ in the amount of (y-x) K_2CO_3-xLi_2CO_3-ySb_2O_3-2 (2-y) WO_3 moles. The samples were heated in air at a temperature of 1123 K for a long time until a constant mass was formed. As a result of solid-phase synthesis, it was assumed that complete decomposition of potassium and lithium carbonates and oxidation of trivalent antimony to the pentavalent state occurs.

The phase composition was investigated using X-ray analysis method performed on a D8 ADVANCE diffractometer (Bruker, Germany) under filtered CuKα_1 radiation. The parameter α of the elementary cell was determined by reflexion 8.4.4. The error in determining the a parameter was ± 0.005 Å [8-10].

X-ray data shows that at 1123 K, the single-phase zone of pyrochlore-type compounds is bounded by a pentagon, the ends of which correspond to points 1-5 on the $KSbO_3$-WO_3-$LiSbO_3$ diagram (Fig. 1). Outside this region, individual compounds with other types of symmetry can be formed during isothermal heating of mixtures, depending on the specific values of x and y.

RESULTS AND DISCUSSION

X-ray patterns of single-phase samples of potassium and lithium antimonate tungstates have the same set of diffraction maxima, the sum of which is described by the quadratic formula for cubic syngony crystals and satisfies the extinction laws of the spatial symmetry group *Fd-3m*. Let's move on to the analysis of the composition of potassium and lithium antimonate tungstates located at the boundaries of the defined concentration area (Fig. 1). In the segment connecting points 1, 2, there are potassium antimonate tungstates in $K_ySb_yW_{2-y}O_6$ ($1.0\leq y\leq 1.375$). Thus, the $KSbWO_6$ composition phase obtained by solid-phase synthesis is known in the literature and has a pyrochlore-type structure (point 1 in the diagram). With an increase in the concentration of potassium ions in the system, the composition of the phase changes, and at $y = 1.375$ it is described by the chemical formula $K_{1.375}W_{0.625}Sb_{1.375}O_6$ (point 2 in the diagram).

X-ray images of the obtained samples contain a certain set of diffraction maxima in the region $1.0\leq y\leq 1.375$, which are satisfactorily described for cubic syngonia crystals and the analysis of the extinction laws of reflexes shows that the composition of $K_ySb_yW_{2-y}O_6$ was formed in the area with the pyrochlore-type structure of the spatial symmetry group *Fd-3m* [10-12].

Redistribution of the intensity of reflexes with even and odd index is noted on the X – ray graphs of the samples placed in the field ($1.0\leq y\leq 1.375$) (Fig. 2 a,b,c,d). In particular, the intensity of the (311) reflex decreases monotonically with increasing y compared to the (222) reflex (Fig. 3, a). At the same time, the unit cell parameter a increases from 10.235 Å to 10.322 Å (Fig. 3b). It can be seen that the change of structural parameters in the phase of $K_ySb_yW_{2-y}O_6$ composition is related to the filling of appropriate positions of the pyrochlore-type structure with ions.

As the amount of Sb_2O_3 decreases, the x-concentration of lithium ions increases in the samples placed in the concentration interval ($0\leq x\leq 1.375$) between (points 2 and 3) va a sphere containing $Li_xK_{1.375-x}Sb_{1.375}W_{0.625}O_6$ is formed. The sample containing $Li_{1.375}W_{0.625}Sb_{1.375}O_6$ (point 3) contains the maximum concentration of lithium ions. An increase in the amount of WO_3 in the $Li_xK_{y-x}Sb_yW_{2-y}O_6$ system leads to a change in composition to $Li_{1.25}W_{0.75}Sb_{1.25}O_6$ (point 4). Phase 3-4 is stable (Fig. 1).

As the amount of WO_3 increases, the stability of the phase with sodium ions decreases in the range of 4-5 (Fig. 1) and until lithium ions are completely replaced by potassium ions (point 5), a $Li_{0.4}K_{0.6}SbWO_6$ compound with a stable pyrochlore-type structure is formed [13-15].

For samples with $Li_xK_{1.375-x}W_{0.625}Sb_{1.375}O_6$ and $Li_xK_{1.25-x}W_{0.75}Sb_{1.25}O_6$ contents, it was found that the dependence of the unit cell parameter on *a* (Fig. 4, a, b) is non-monotonic and is characterized by two concentration areas. As the amount of lithium ions increases in the first area, the value of α decreases monotonically, this is due to the fact that potassium ions have a smaller radius ($r(K^+)=0{,}133$ nm, $r(Li^+)=0{,}068$ nm) than lithium ions [16-22]. In this case, the relative intensity of reflexes located in this concentration area does not undergo significant changes (Fig. 5, a, b). In the second area ($0.6 \leq x \leq 1.2$), a monotonous increase of the parameter *a* of the elementary cell is observed, redistribution of reflex intensity with even and odd index is noted (Fig. 5, a, b). The decrease in the reflex intensity with odd indices and the increase in the unit cell parameter are apparently due to the filling of the appropriate positions of the pyrochlore-type structure with ions.

CONCLUSIONS

The properties of pyrochlore-type structural phases in the $(y-x)K_2CO_3-xLi_2CO_3-ySb_2O_3-2(2-y)WO_3$ system when heated at a temperature of 1123 K in the $KSbO_3-WO_3-LiSbO_3$ concentration triangle were studied.

When heated in air, a complex oxide $(y-x)K_2CO_3-xLi_2CO_3-ySb_2O_3-2(2-y)WO_3$ phase of potassium and lithium antimonate-tungstate is formed. In the $KSbO_3-WO_3-LiSbO_3$ concentration triangle, the $Li_xK_{y-x}Sb_yW_{2-y}O_6$ phase with a pyrochlore type structure was formed for a temperature of 1123 K.

The obtained results make an important contribution to the understanding of the mechanism of ion transport in complex oxide compounds with pyrochlore-type structure.

In our future work, we hope to expand the concentration ranges of potassium antimony tungstate, achieve high levels of ionic conductivity in them, and contribute to the creation of new alternative energy sources.

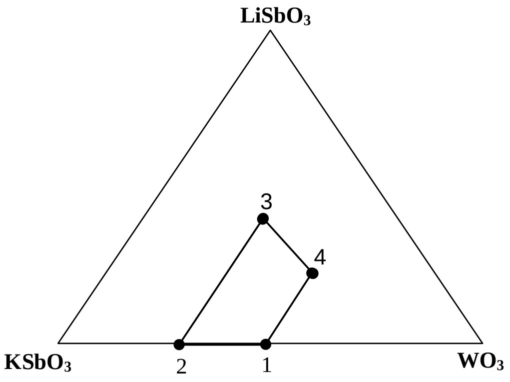

Fig. 1. In the $KSbO_3-WO_3-LiSbO_3$ composition diagram, the area where pyrochlore-type potassium and lithium antimonate tungstates are formed (T = 1123 K)

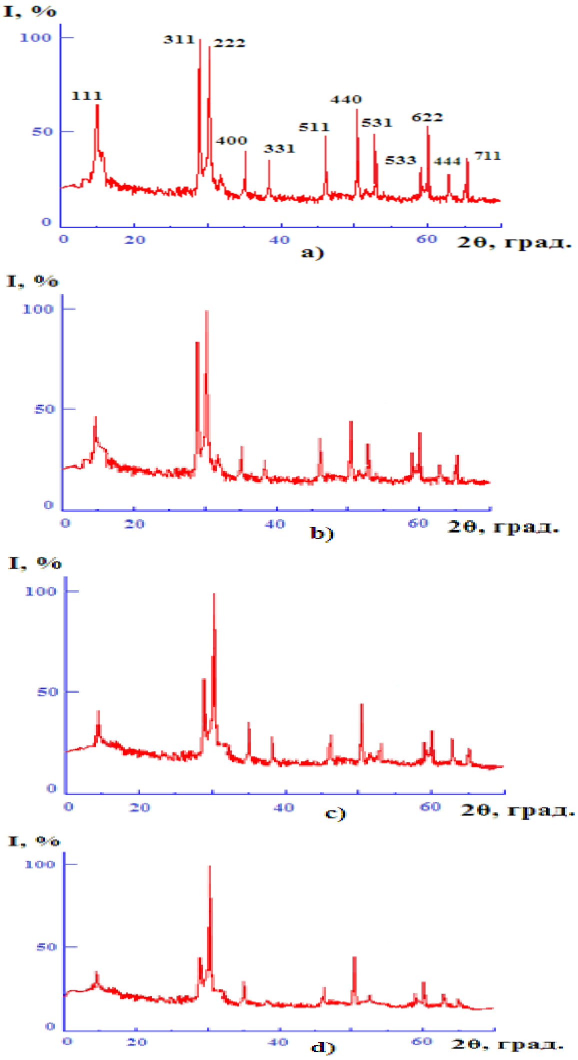

Fig.2. Diffractograms of samples obtained after heating at 1123 K and having gross compositions: $KWSbO_6$ (a), $K_{1.125}W_{0.875}Sb_{1.125}O_6$ (b), $K_{1.25}W_{0.75}Sb_{1.25}O_6$ (c), $K_{1.375}W_{0.625}Sb_{1.375}O_6$ (d).

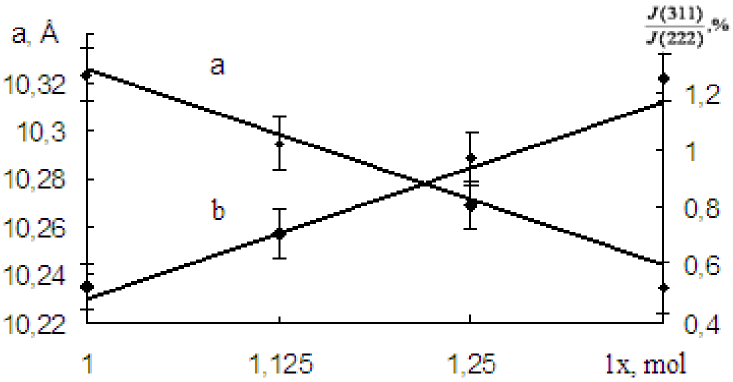

Fig.3. Variation of the relative intensity of the reflex J_{311}/J_{222} (a) and unit cell parametric a (b) as a function of the number of potassium ions in the $K_ySb_yW_{2-y}O_6$ $1.0 \leq y \leq 1.375$ phase.

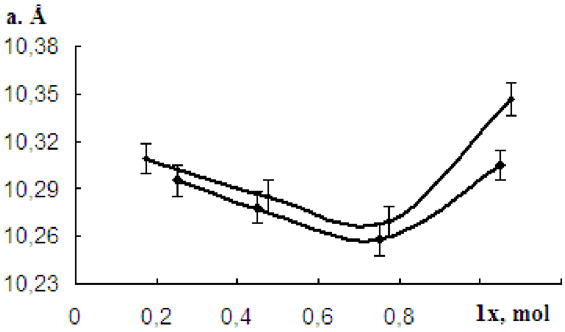

Fig.4. Dependence of the unit cell parameter a on the amount of lithium ions for $Li_xK_{1.375-x}W_{0.625}Sb_{1.375}O_6$ (a) and $Li_xK_{1.25-x}W_{0.75}Sb_{1.25}O_6$ (b) compositions.

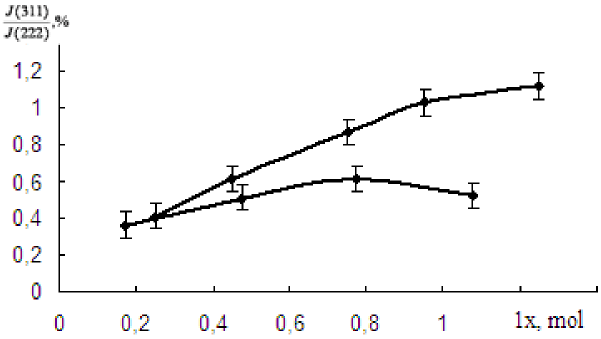

Fig.5. Variation of the relative intensity of the $J_{(311)}/J_{(222)}$ reflex for $Li_xK_{1.375-x}W_{0.625}Sb_{1.375}O_6$ (a) and $Li_xK_{1.25-x}W_{0.75}Sb_{1.25}O_6$ (b) compositions according to the number of lithium ions.

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