Electric and ionic conductivity of potassium antimony tungstate with addition of alkali metals

Kh.N. Bozorov[1], O.O. Mamatkarimov[1], B.T. Abdulazizov[*,2]

[1]Namangan Institute of Engineering and Technology, Kasansay str. 7, 160115, Namangan, Uzbekistan
[2]Namangan State University, Uychi str. 316, 716019, Namangan, Uzbekistan

Received 07.05.2022

* Corresponding author: e-mail bt_abdulazizov@mail.ru, Phone: +998 91 186 06 05

Изучена электропроводность сложных оксидов $K_{1-x}Na_xSbWO_6$ ($0 \le x \le 0.6$) и $K_{1-x}Li_xSbWO_6$ ($0 \le x \le 0.4$), имеющих структуру типа пирохлора. Определены температурная зависимость ионной проводимости соединений и величина ионного радиуса. По мере уменьшения значения ионного радиуса щелочного металла значение энергии активации уменьшается, а ионная проницаемость увеличивается. Предложена модель транспорта ионов в этих соединениях. Установлено, что соединение, содержащее $Li_{0,4}K_{0,6}SbWO_6$, достигает максимальных значений электропроводности.

Ключевые слова: ионная проводимость, структура типа пирохлора, антимонат вольфрамата калия, введение ионов щелочных металлов, модель ионного транспорта.

The electrical conductivity of complex oxides $K_{1-x}Na_xSbWO_6$ ($0 \le x \le 0.6$) and $K_{1-x}Li_xSbWO_6$ ($0 \le x \le 0.4$), which have a pyrochlore-type structure, was studied. The temperature dependence of the ion permeability of the compounds and the value of the ion radius were determined. As the ion radius value of the alkali metal decreases, the value of the activation energy decreases, and the ion permeability increases. A model of ion transport has been proposed in these compounds. It was found that the compound containing $Li_{0.4}K_{0.6}SbWO_6$ reaches the maximum values of electrical conductivity..

Keywords: ion permeability, pyrochlore-type structure, potassium antimony tungstate, the introduction of alkali metal ions, ion transport model.

DOI: https//doi.org/10.52304/.v24i2 332

I. Introduction

In [1-7], the laws of formation of potassium antimony tungstate are considered, in which sodium ions are introduced during solid-phase synthesis. For the temperature of 1123 K, the area of phase formation with variable composition $K_{1-x}Na_xSbWO_6$ was determined at $0 \le x \le 0.6$ with a pyrochlore-type structure. In [2-6], the conductivity of potassium antimony tungstate is studied and showed that potassium ions are the main charge carriers.

It can be seen that the replacement of potassium ions with sodium and lithium ions with smaller ionic radii makes it possible to establish a relationship between the structural properties of the compounds and their ionic conductivity properties. However, such studies have not been adequately for potassium antimonate tungstates.

In this regard, this work aims to study the ionic conductivity of a complex oxide potassium antimony tungstate containing sodium and lithium ions, and to illuminate the relationship between the ion radius value of alkaline ions and the ionic conductivity properties of these compounds.

II. Experimental

Potassium antimony tungstate $K_{1-x}Me_xSbWO_6$ (Me = Na, Li) with different compositions were obtained in the concentration range $0 \le x \le 0.6$ and $0 \le x \le 0.4$, respectively, by step $\Delta x = 0.1$ according to

the method described in [1-9]. The X-ray diffraction patterns of the samples of potassium antimonate tungstate of the pyrochlore type doped with sodium and lithium ions ($K_{1-x}Na_xSbWO_6$ ($0 \le x \le 0.6$) and $K_{1-x}Na_xSbWO_6$ ($0 \le x \le 0.4$)) contain a certain set of diffraction maxima, which is satisfactorily described for cubic crystals. From the analysis of the laws of extinction of reflexes, it follows that in the specified concentration intervals the phases with a pyrochlore-type structure with a spatial group of symmetry Fd3m are formed [1-11].

The samples synthesized to measure electrical conductivity were pressed in the form of tablets with the diameter of 8.0×10^{-3} m and the thickness of $(1.0–2.0)\times10^{-3}$ m and heated for 11 hours at the temperature of 1173 K.

The electrical conductivity of alternating current is similar to that of [8-14] in the two-contact method using an alternating current bridge R 5030 (f = 1 kHz) with a step of 5 K in the temperature range 295–1000 K, also measured at 800 K in a muffle furnace under isothermal exposure according to thermogravimetric analysis data. Samples in the form of tablets were placed in measuring chamber, which was heated in a tubular electric furnace. Platinum plates with clamp contacts were used as electrodes. The temperature was measured with a chromium-aluminum thermocouple to the nearest 1 K.

III. Results and discussion

Investigation of electrical conductivity of potassium antimony tungstate $Me_xK_{1-x}SbWO_6$ with alkali

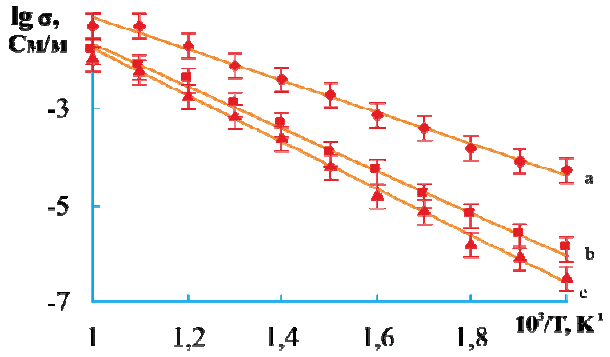


Figure 1. Temperature dependence of the electrical conductivity of $Li_{0.4}K_{0.6}SbWO_6$ (a), $Na_{0.4}K_{0.6}SbWO_6$ (b), $KSbWO_6$ (c) samples.

metal ions (Me = Na, Li) showed that increasing temperature in sample in the range of 500–1000 K leads to exponential growth of conductivity (Fig. 1).

So, the largest angle of inclination has a direct dependence of the electrical conductivity on the reciprocal temperature for potassium antimonate tungstate (Fig. 1c). When sodium ions are introduced into the $Me_xK_{1-x}SbWO_6$ phase, the slope of the straight-line decreases (Fig. 1b). Potassium antimony tungstate with lithium ions has the smallest angle of inclination (Fig. 1a). This indicates that potassium antimony tungstate has the highest activation energy (see Table). When sodium and lithium ions are introduced into this $Me_xK_{1-x}SbWO_6$ phase, the activation energy E_σ decreases up to 79 and 57 kJ/mol (see Table). A study of the electrical conductivity of the phases obtained during isothermal holding at a temperature of 800 K shows that potassium antimony tungstate has the lowest conductivity. As sodium and lithium ions are introduced in $Me_xK_{1-x}SbWO_6$ phase, the electrical conductivity σ of the compounds $Na_{0.4}K_{0.6}SbWO_6$ and $Li_{0.4}K_{0.6}SbWO_6$ increases up to 1.26×10^{-3} and 2.51×10^{-3} Sm/m, respectively.

Comparing the values of activation energy and ionic conductivity ion with the ionic radii of alkali metals, we can conclude that these values depend on the size of the ions. Thus, for phases containing the same amount of sodium and lithium ions, the permeability of the samples decreases, and the activation energy increases with increasing ionic radius (see Table).

Table. The specific electrical conductivity of the samples at 800 K and the activation energy values of the antimony tungstate containing $Me_xK_{1-x}SbWO_6$ (Me = Na, Li) with the same amount of sodium and lithium ions (x = 0.4).

Phase composition	r_{Me}, Å	σ, Sm/m	E_σ, кJ/mol
$KSbWO_6$	1.33	3.15×10^{-4}	88± 4
$Na_{0.4}K_{0.6}SbWO_6$	0.98	1.26×10^{-3}	79±4
$Li_{0.4}K_{0.6}SbWO_6$	0.68	2.51×10^{-3}	57±4

The value of the ion radius (given from [15-24]) and the activation energy calculated from the data on the temperature dependence of the electrical conductivity are shown in Fig. 1.

The X-ray diffraction patterns of the compounds obtained contain a certain set of diffraction maxima, which are satisfactorily described for cubic syngonal crystals, and it follows from the analysis of the laws of extinction of reflections that, in a given certain range of concentrations, a group of spatial symmetry

©Academy of Sciences of Republic of Uzbekistan, 2022

Fd3m with a variable composition of phases is formed. (Fig. 2).

According to [2-8], the degree of defectiveness of compounds with a pyrochlore-type structure can be increased by heterovalent exchange of Sb(V) ions for W(VI) ions at position 16*c*, based on the mechanisms of the formation of Frenkel and Schottky defects. Thus, the partial substitution of Sb^{5+} for W^{6+} in the $KSbWO_6$ phase composition results in the filling of positions 8*b* with potassium ions [1-11]. In this case, the 16*d* positions in the pyrochlore-type structure remain completely empty, which allows potassium ions to migrate over the defects in the cationic lower lattice, leading to charge transfer in this phase. However, due to the large ionic radius, it prevents the propagation of potassium ions through these channels (positions 16*d* and 8*b*), which is confirmed by high values of conductivity activation energy (Table).

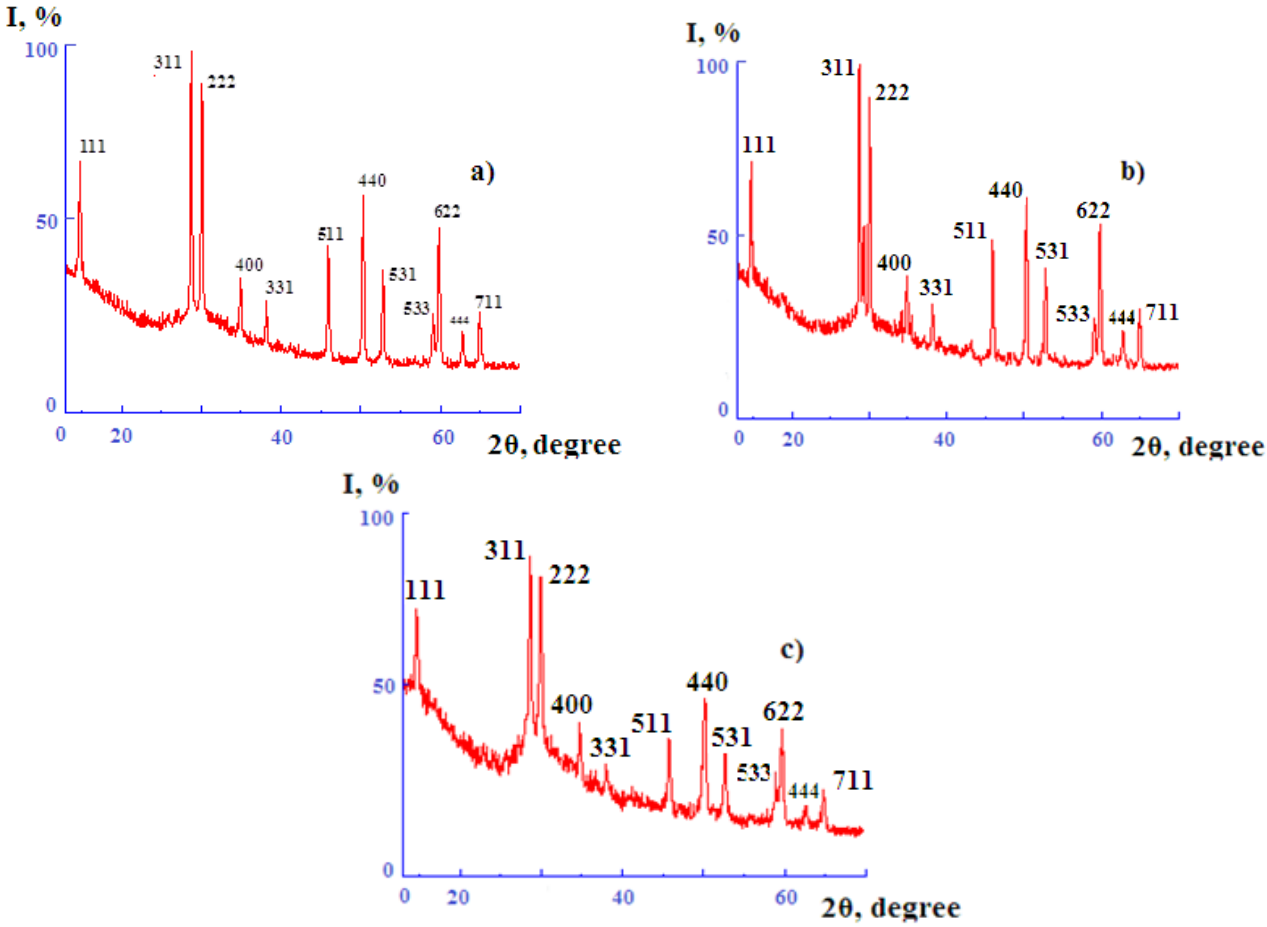


Figure 2. X-ray graphs of samples taken after heating of the mixture and having the following composition: $KWSbO_6$ (a), $Na_{0,4}K_{0,6}WSbO_6$ (b), $Li_{0,4}K_{0,6}WSbO_6$ (c).

Apparently, the ionic conductivity of lithium antimony in tungsten-containing $Li_xK_{1-x}SbWO_6$ is achieved by transporting lithium ions, which are characterized by a relatively small ionic radius from the 16*d* position, which results in high ionic conductivity in these compounds.

IV. Conclusions

The temperature dependence of the electrical conductivity of potassium antimonate tungstate $K_{1-x}Me_xSbWO_6$ of a pyrochlore-type structure with the addition of sodium and lithium ions in the concentration range $0 \le x \le 0.6$ and $0 \le x \le 0.4$ has been studied.

A correlation was established between the value of the ionic radius and the ionic conductivity of the compounds of potassium antimony tungstate $K_{1-x}Me_xSbWO_6$, with a pyrochlore-type structure in which sodium and lithium ions were included.

©Academy of Sciences of Republic of Uzbekistan, 2022

In potassium antimony tungstates containing sodium and lithium ions, ion permeability is achieved by transporting alkaline ions along positions 16*d* of the pyrochlore-type crystal structure. As the ion radius value of the alkali metal decreases, the value of the activation energy decreases and the ion conductivity increases.

Maximum values of electrical conductivity are obtained in compound $Li_{0.4}K_{0.6}SbWO_6$.

Ion permeability in sodium and lithium antimony tungstate is achieved by transporting alkaline ions along with positions 16*d* of the pyrochlore-type crystal structure.

References

[1] E.I. Burmakin. Solid electrolytes with conductivity in alkali metal cations (Moskva, Nauka 1992).

[2] V.N. Chebotin, M.V. Perfiliev. Electrochemistry of solid electrolytes (Moskva, Chemistry 1978).

[3] A.K. Ivanov-Shits, I.V. Ionics of a solid state. (St. Petersburg, Publishing House of St. Petersburg University, 2000).

[4] M. Avdeev, V.B. Nalbandyan, I.L. Shukaev. Solid State Electrochemistry (Wiley-VCH, Weinheim) **7**, 227-278 (2009).

[5] P.J. Baymatov, A.G. Gulyamov, B.T. Abdulazizov, Kh.Yu. Mavlyanov, M.S. Tokhirjonov. International Journal of Modern Physics B 2150070, 1-13 (2021).

[6] A.R. West. Solid State Electrochemistry **5**, 7-43 (1995).

[7] C. Hu, Y. Shen, and L. Chen. Current Opinion in Electrochemistry **22**, 51-57 (2020).

[8] Yu.A. Lupitskaya, V.A. Burmistrov. Vestnik Chelyabinskogo. Gosudarstvennogo Universiteta No.3, 39-43 (2008).

[9] V.A. Burmistrov, D.A. Zakharyevich. Inorg. Materials **39**, No.1, 77-81 (2003).

[10] X.N. Bozorov, Yu.A. Lupitskaya, VD Buchelnikov, H.O. Abdullaev. Phase formation in a complex oxide xK_2CO_3-xSb_2O_3-2(2-x)WO_3 ($0<x<2.0$) system and their filling with ions. Republican scientific-practical conference on "Actual problems of physics of semiconductors and polymers" (Tashkent, 2022), pp. 268-270.

[11] Yu.A. Lupitskaya, A.G. Fazlitdinova, V.V. Khovailo. Diagnostics of the structure and properties of materials: textbook-method (Chelyabinsk, Publishing house Chelyabinsk State University, 2017), p 34.

[12] Kh.N. Bozorov, Yu.A. Lupitskaya, N.Yu. Sharibaev, G.U. Abdullaeva. Scientific Bulletin of Namangan State University No.12, 98-101 (2021).

[13] Yu.A. Lupitskaya. Investigation of a phase with a pyrochlore-type structure formed in the (x-y)K_2CO_3-xLi_2CO_3-ySb_2O_3-2(2-y)WO_3 ($0\le x\le y$, $1.0\le y\le 1.375$) system during heating to create ion-conducting ceramics. Abstracts VII All-Russian Scientific Conference, (Syktyvkar, 2010), p. 57.

[14] A.L. Podkorytov, S.R. Kudakaeva, E.V. Sokolova, S.A. Shtin, D.N. Ashikhmin. Inorganic Chemistry **51**, No.1, 52-57 (2006).

[15] S.S. Stroev, E.I. Burmakin, G.Sh. Shekhtman. Inorg. Materials **44**, No.8, 989-994 (2008).

[16] B.T. Abdulazizov. Eurasian Journal of Physics and Functional Materials **6**, No.1, 32-37 (2022).

[17] B.T. Abdulazizov, G. Gulyamov, P.J. Baymatov, Sh.T. Inoyatov, M.S. Tokhirjonov and Kh.N. Juraev. World Scientific Publishing Company **12**, No.1, 2250002 (2022).

[18] E.I. Burmakin, G.Sh. Shekhtman, B.D. Antonov. Electrochemistry **47**. 48-483 (2011).

[19] E.I. Burmakin, G.Sh. Shekhtman, G.V. Nechaev. Electrochemistry **48**. 1079-1083 (2012).

[20] E.I. Burmakin, G.V. Nechaev, and S.V. Plaksin. Electrochem. Energy **11**, No.1, 26-30 (2011).

[21] A.I. Efimov. Properties of inorganic compounds: a reference book (Leningrad, Chemistry. 1983), p. 142-172.

[22] G.Gulyamov, B.T. Abdulazizov, P.J. Baymatov. Journal of Nanomaterials Article ID 5542559 (2021). https://doi.org/10.1155/2021/5542559

[23] Z. Li, H.X. Xie, X.Y. Zhang, and X. Guo. J. Mater. Chem. A **8**, No.7 (2020).

[24] C. Hu, Y. Shen, and L. Chen. Current Opinion in Electrochemistry **22**, 106-107 (2020).

Натрий ва литий киритилганда калийли антимонат вольфраматнинг электр ва ион ўтказувчанлиги

Х.Н. Бозоров[1], О.О. Маматкаримов[1], Б.Т. Абдулазизов[2]

[1]Наманган муҳандислик-технология институти, Касансай кўч. 7, 160115, Наманган, Ўзбекистон

[2]Наманган Давлат Университети, Уйчи кўч. 316, 716019, Наманган, Ўзбекистон

Пирохлор типидаги тузилишга эга бўлган $K_{1-x}Na_xSbWO_6$ ($0\le x\le 0.6$) ва $K_{1-x}Li_xSbWO_6$ ($0\le x\le 0.4$) таркибли оксидларининг электр ўтказувчанлиги ўрганилди. Бирикмаларнинг ион ўтказувчанлигининг ҳароратга боғлиқлиги ва ион радиусининг қиймати аниқланди. Ишқорий металлнинг ион радиуси қиймати камайиши билан активланиш энергиясининг қиймати камаяди ва ион ўтказувчанлиги ортади. Бу бирикмаларда ионларни ташиш модели таклиф қилинган. $Li_{0.4}K_{0.6}SbWO_6$ ни ўз ичига олган бирикма электр ўтказувчанлигининг максимал қийматларига этиб бориши аниқланди.

Калит сўзлар: ион ўтказувчанлиги, пирохлор типидаги структура, калийли антимонат вольфрамат, ишқорий метал ионларининг киритилиши, ион ташиш модели.

©Academy of Sciences of Republic of Uzbekistan, 2022