THE STRUCTURE AND FERROELECTRIC PROPERTIES IN THE SOLID SOLUTIONS WITH THE STRUCTURE OF TETRAGONAL TUNGSTEN BRONZE

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The investigation results of solid solution systems $K_2Ba_4Nb_{10}O_{30}$-$K_6Li_4Nb_6O_{30}$ (KBN-KLN) $K_2Sr_4Nb_{10}O_{30}$-$K_6Sr_4Nb_{10}O_{30}$ (KSN-KLN) with the structure of tetragonal tungsten bronze with the aim of revealing of influence of tetragonal position filling on the system structural parameters and electrophysical properties, in which the morphotropic phase transitions with the storage of the similar cell symmetry in whole interval of solid solution existence of tetragonal-tetragonal type (*T-T`*), accompanying by the clear anomalies on the concentration dependencies of structural and electrophysical parameters are given in the given work.

Introduction

The study of oxide solid solutions with the structure of tetragonal tungsten bronze (TTB), ,having the essential electrophysical properties (ferro-, antiferro-, ferroelastic and others) is presented actual both from scientific point of view, that is the order establishments, caused by their complex hierarchical construction and practical one, that is the use of accompanying structural instabilities of extreme material properties.

The aim of the given work is the revealing influence of filling of triangular positions on the system structural parameters and electrophysical properties, in which the morphotropic phases transitions (MPhT) with the storage of similar cell symmetry in the whole interval of solid solution existence (SS) of tetragonal-tetragonal type (*T-T`*), accompanying by clear anomalies on the concentration dependence of structural and electrophysical parameters in double systems of solid solutions with TTB structure [5].

Experimental part

The samples of TR systems $K_2Sr_4Nb_{10}O_{30}$-$K_6Li_4Nb_{10}O_{30}$ (KSN-KLN) and $K_2Ba_4Nb_{10}O_{30}$-$K_6Li_4Nb_{10}O_{30}$ (KBN-KLN) are obtained by the solid-phase synthesis from the stoichiometric oxide mixtures or carbonates of corresponding elements in two stages (with intermediate grinding) at annealing temperature in the interval from 1150 up to 1475K and duration from 2 up to 6 hours. The disk samples of high-density ceramics for the measurement of dielectric and piezoelectric parameters ($\varepsilon_{33}/\varepsilon_0$, $tg\sigma$, d_{31}, K_p and Q_M) on the techniques, described in [6] are prepared by the method of hot pressing.

The symmetry and parameters of elementary cell of the samples are defined on the powder roentgenograms (diffractometer DRON-3.0, CuK_α is filtered radiation).

The results and their discussion

The compounds of solid solutions with TTB structure with the limited solubility $K_6Li_4Nb_{10}O_{30}$ (80 mol%) [4,5] are obtained by addition introductions. The ceramic properties of solid solution compounds, which are close to *KBN* and *KSN*, which aren't baked in the pure form are investigated.

The morphotropic phase transitions (MPhT) with the storage of the similar cell symmetry in the whole interval of TR existence of tetragonal-tetragonal (*T-T`*) type, accompanying by the clear anomalies on the concentration dependencies of structural and electrophysical parameters are observed in the systems of solid solutions (TR) $K_2Ba_4Nb_{10}O_{30}$-$K_6Li_4Nb_{10}O_{30}$ (KBN-KLN) $K_2Sr_4Nb_{10}O_{30}$-$K_6Li_4Nb_{10}O_{30}$ (KSN-KLN) with the structure of tetragonal tungsten bronze (TTB), also as in the system of solid solutions $K_2Pb_4Nb_{10}O_{30}$ – $Na_2Pb_4Nb_{10}O_{30}$ (KPN-NPN) with TTB structure and rhombic symmetry of extreme component (*Pl – P`l*).

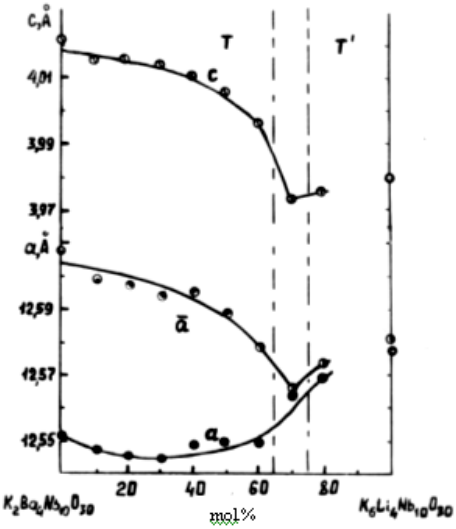

Fig.1. The concentration dependencies of structural parameters in the system of solid solutions $K_2Ba_4Nb_{10}O_{30}$-$K_6Li_4Nb_{10}O_{30}$.

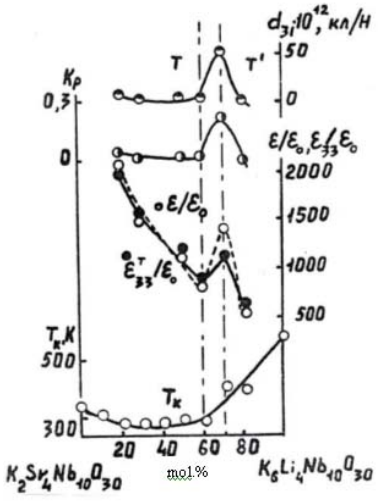

Fig.2. The concentration dependencies of electrophysical parameters in the system of solid solutions $K_2Sr_4Nb_{10}O_{30}$-$K_6Li_4Nb_{10}O_{30}$.

MPhT *T-T`* in these systems reveals in the anomalous behavior of elementary cell parameters: bend in the going of

average parameter $\overline{\alpha}$ ($\overline{\alpha} = c^3\sqrt{10a^2c}$, average cell parameter, is equivalent one on the volume with "ideal" [1,2]) in KSN-KLN system (table), minimum on the curves of parameter changes $\overline{\alpha}$, c (KBN-KLN system, fig.1); the bend in *KSN-KLN* system in the going of average parameter $\overline{\alpha}$ is accompanied by the clear maximums of dielectric and piezoelectric parameters at 70% KLN (fig.2).

The solid solutions with the structure, which is similar to the KLN*(T`)* structure [7] form in *KBN-KLN* system (fig.1) in the interval $0,7 \le \chi \le 0,8$ (χ-KLN), i.e. at the content of three and more *Li* ions on the elementary cell, and at solid solutions on KBN*(T)* basis form at $0 \le \chi \le 0,7$. As it is seen, the *a* parameter in the tetragonal phase *T* almost doesn't change. This can be explained by the fact, that the ion average radius in A-position in KBN and KLN almost doesn't differ ($R(K^{1+})$ – 1,64Å (c.c. 12) and 1,70Å (c.c. 15); $R(Ba^{2+})$ – 1,6Å (c.c. 12) 1,72Å (c.c. 15)) [5,7].

In KSN-KLN system the parameters of elementary cell increase with the increase of KLN content (table), as ion average radius in A-position in KSN is smaller, than in KLN $R(Sr^{2+})$ – 1,44Å (c.c. 12)) [4,7].

Table

Structural parameters of double system of solid solutions $K_2Sr_4Nb_{10}O_{30}$-$K_6Li_4Nb_{10}O_{30}$.

KSN(%)	KLN(%)	Lattice parameters				
		a, Å	*C*, Å	$\overline{a}$, Å	$\sqrt[3]{a^2c}$	$c\sqrt{10}/a$
90	10	12,4864	3,944	12,483	8,505	0,999
80	20	12,513	3,942	12,494	8,513	0,996
70	30	12,527	3,943	12,507	8,523	0,995
60	40	12,5460	3,9531	12,542	8,544	0,995
50	50	12,553	3,958	12,539	8,543	0,997
40	60	12,566	3,966	12,557	8,554	0,998
30	70	12,568	3,965	12,558	8,556	0,998
20	80	12,569	3,989	12,583	8,574	1,004
0	100	12,5784	3,9796	12,5803	8,572	1,001

The bent changes of piezomodule d_{31} and coefficient of electromechanical bond K_p go through the maximum on the area boundary MPhT; are accompanied by the increase of Curie temperature values (530K). The permittivity has the maximum on MPhT boundary, to which the compound with minimum value of mechanical quality Q_m is equal (fig.2).

In these systems the compound change is accompanied by the gradual filling of positions by *Li* ions in triangular canals and observable MPhT, probably, is connected with different filling character of these positions: with ordering or shifting from polyhedron center with coordination number 9 in the one from two incorrect octahedrons, consisting it.

[1] *V.A. Isupov.* FTT, 1980, t.22, v.1, s.25-28. (in Russian)

[2] *L.A. Rezniçenko, R.Z. Mextieva, L.A. Şilkina, A.İ. Mamedov.* AMEA-nın Xəbərləri, fiz.-riyaz. və t.e. bül., 2003, 5(1), S.53-57.

[3] *R.Z. Mekhtieva, V.G. Krishtop, E.N. Sidorenko, R.U. Devlikanova.* Izv. AN SSSR. Ser. fiz. – 1990, t.54, № 6, s.1167-1170. (in Russian)

[4] *R.Z. Mekhtieva, R.U. Devlikanova, G.I. Stepovoy i dr.*

[5] Neorgan. materiali. 1991, t.27, №.7, c.1483-1487. (in Russian)

[6] *V.Q. Krishtop, R.U. Devlikanova, O.A. Bunina, V.S. Filipev.* Izv. AN SSSR. Neorgan. materiali. 1988. T.24. №9. S.1513–1515. (in Russian).

[7] QOST 12370-80. Materiali pyezokeramicheskie. Metodi ispitaniy. M.: Izd-vo standartov; 1982. 30 s.

[8] *V.A. Isupov, A.B. Lutsevich, A.U. Sheleg, T.N. Urban.* Izv. AN SSSR. Ser. fiz. 1983, t.47, №4, S.813-815. (in Russian)

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TETRAQONAL-VOLFRAM TUNC STRUKTURLU BƏRK MƏHLULLARIN STRUKTURU VƏ SEQNETOELEKTRİK XASSƏLƏRİ

Bu işdə üçbucaq kanalların doldurulmasının tetraqonal-tetraqonal (*T-T'*) tipli bərk məhlulların bütün mövcud intervalında özəyin vahid simmetriyasının saxlanılması ilə morfotrop faza keçidləri müşahidə olunan sistemlərin elektrofiziki xüsusiyyətlərinə və struktur parametrlərinə təsirinin öyrənilməsi məqsədilə tetraqonal volfram tunc strukturlu $K_2Ba_4Nb_{10}O_{30}$- $K_6Li_4Nb_{10}O_{30}$ (KBN-KLN) $K_2Sr_4Nb_{10}O_{30}$-$K_6Li_4Nb_{10}O_{30}$ (KSN-KLN) bərk məhlulların tədqiqat sistemlərinin nəticələri göstərilmişdir.

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СТРУКТУРА И СЕГНЕТОЭЛЕКТРИЧЕСКИЕ СВОЙСТВА В ТВЕРДЫХ РАСТВОРАХ СО СТРУКТУРОЙ ТЕТРАГОНАЛЬНОЙ ВОЛЬФРАМОВОЙ БРОНЗЫ

В данной работе приводятся результаты исследований систем твердых растворов *$K_2Ba_4Nb_{10}O_{30}$-$K_6Li_4Nb_{10}O_{30}$ (KBN-KLN)* *$K_2Sr_4Nb_{10}O_{30}$-$K_6Li_4Nb_{10}O_{30}$ (KSN-KLN)* со структурой тетрагональной вольфрамовой бронзы с целью выяснения влияния заполнения треугольных позиций на структурные параметры и электрофизические свойства систем, в которых наблюдаются морфотропные фазовые переходы с сохранением одинаковой симметрии ячейки во всем интервале существования твердых растворов, типа тетрагональная-тетрагональная (*T-T'*), сопровождающиеся четкими аномалиями на концентрационных зависимостях структурных и электрофизических параметров.

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