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Physical and chemical transormations in $(Na_{0.5}Bi_{0.5})TiO_3$ based solid solutions in solid solution synthesis process

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Physical and chemical transformations under solid-state synthesis of sodium-bismuth titanate $(Na_{0.5}Bi_{0.5})TiO_3$ and based on it solid solutions have been studied. It has been found that the processes are multi-stage and involve the formation of a number of intermediate phases. Their identification was carried out by the method of X-ray structural analysis. The optimal conditions for the synthesis of the studied materials and electrophysical characteristics of piezoelectric ceramic elements have been defined.

Исследованы физико-химические превращения при твердофазном синтезе титаната натрия-висмута $(Na_{0,5}Bi_{0,5})TiO_3$ и твердых растворов на его основе. Показано, что процессы синтеза являются многостадийными и проходят через образование целого ряда промежуточных фаз. Методом рентгеноструктурного анализа проведена их идентификация. Определены оптимальные условия синтеза исследуемых материалов и электрофизические характеристики пьезокерамических элементов на их основе.

1. Introduction

Piezoelectric ceramics is widely used in various areas of technology. At the present time the lead zirconate-titanate (PZT — $Pb(Zr_{1-x}Ti_x)O_3$) based solid solutions are the leaders in production of piezoelectric ceramic materials. They have the high level of properties, their production technology is very simple and the cost of final product is low. But as a result of restrictions on the use of materials containing lead in electronics adopted by a number of countries, (July 1, 2006; the European directive RoHS — Restriction of Hazardous Substances, 2002/95/CE), the investigations related to the substitution of PZT for lead-free materials in a production of piezoelectric ceramics are carried out intensively.

The most perspective for practical use are lead-free materials based on sodium-bismuth titanate $(Na_{0.5}Bi_{0.5})TiO_3$ — NBT. NBT shows a strong ferroelectricity (Pr = 38 μC/cm^2) and high Cure temperature (T_c = 320°C) [1, 2]. The technology of these ceramic elements production is almost similar to the one of materials based on PZT. The cost of the required equipment and starting materials is very low.

However, the based on no alloyed NBT ceramics have some disadvantages such as high conductivity and high values of coercive field (Ec reaches the value of 70 kV/cm) which cause problems in the polarization of working elements. As a result the level of the piezoelectric properties is low. That is why very intensive search and studying of new systems of $(Na_{0.5}Bi_{0.5})TiO_3$ based solid solutions with improved piezoelectric properties have been carried out [3–6]. We have chosen the approach which until the present time has not been used by other researchers — the search of solid solutions of the system $(Na_{0.5}Bi_{0.5})TiO_3$ — $(Na_{0.5}Bi_{0.5})ZrO_3$ (NBTZr), which is a structural analog of PZT. It is expected that in this system of solid solutions the level of piezoelectric properties will be exceed the properties level of PZT.

We have solved the problems of solid state synthesis of NBTZr. This paper considers the results of the investigation of physical and chemical processes of synthesis of sodium-bismuth titanate and based on it solid solutions.

The main tasks of the work were following:

— to study the phase formation during solid state synthesis of the sodium-bismuth titanate and based on it solid solutions;

— to identify the optimal conditions for the synthesis of the studied materials and their electro-chemical characteristics.

In the next paper the results of the investigation of sodium-bismuth zirconate synthesis will be considered. The results of the research of the phase transformation in the system of solid solutions $(Na_{0.5}Bi_{0.5})TiO_3$ — $(Na_{0.5}Bi_{0.5})ZrO_3$, providing the high properties level, will be represented in the subsequent papers.

2. Experimental

For obtaining the sodium-bismuth titanate $(Na_{0.5}Bi_{0.5})TiO_3$ and solid solutions on it base we have used the traditional method of solid state synthesis. Reagent grade oxides and carbonates of corresponding metals were used as starting materials. All the starting materials were mixed in the appropriate stoichiometry by ball milling. The mixture was calcined at 700–1100°C. The synthesized powders were uniaxially pressed into disks and sintered at 950–1150°C. X-ray analysis was carried out on diffractometer DRON-3 using filtered CuK_α radiation. The piezoceramics elements were controlled according to the standard technique, the piezoelectric modulus d_{33} was measured by the static method [7].

3. Results and discussion

As a result of X-ray phase analysis in the powder mixture $0.25Na_2CO_3 + 0.25Bi_2O_3 + TiO_2$ sodium-bismuth titanate $(Na_{0.5}Bi_{0.5})TiO_3$ with cubic perovskite structure (a = 3.884 Å) is found after calcination at a temperature of 700°C. Intermediate phases in the form of sodium titanates $Na_2Ti_6O_{13}$ and $Na_2Ti_3O_7$, and also bismuth titanate $Bi_{12}TiO_{20}$ (which is on the phase diagram [8]) are also presented among the reaction products. The temperature increase leads to decreasing the share of the sodium titanates and $Bi_{12}TiO_{20}$ compound disappear from reaction mixture at T = 800°C. For T > 800°C the new intermediate phase $2Bi_2O_3{\cdot}3TiO_2$ — bismuth titanate $Bi_4Ti_3O_{12}$ appears existing in the reaction products up to 850°C. Single-phase $(Na_{0.5}Bi_{0.5})TiO_3$ only with pseudo-cubic perovskite structure (a = 3.884 Å) is formed as a result of calcinations process at the temperature 850°C during long time (Fig. 1). The time of NBT formation is decreased with temperature increasing.

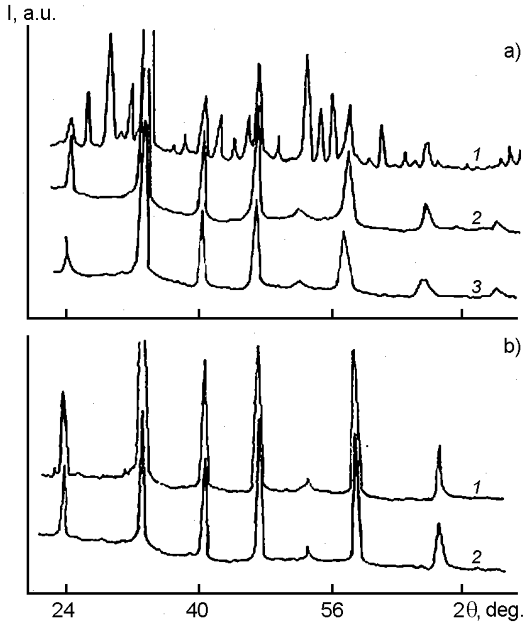

Fig. 1. X-ray patterns after different calcination temperatures. At the top: T_{cal}, °C: *1* — 700 (6 h), *2* — 700 + 850 (16 h), *3* — 700 + 850 (23 h). At the down: T_{cal}, °C: *1* — 850 (5 h), *2* — 850 (15 h).

X-ray patterns in the Fig. 1 indicate peculiarity of the solid-state reactions in the oxides system. At the top of the Fig. 1 diffraction patterns are presented which have been obtained using less temperature (700°C) primary calcinations of the initial mixture of the components. The second diffraction pattern has been obtained using usual primary calcination at 850°C. The X-ray patterns for the cases synthesis at 700°C and at 850°C only show less time of the process in the second case. It is determined by the formation of the stable low temperature phases at the low temperatures. Its transformation into high temperature phases demands addition energy and occurs under more long time aging under 850°C.

At quick crossing the temperature interval of (600–800)°C (in particular such temperature regime corresponds to second diffraction pattern) low temperature phases are not able to form because ionic diffusion at these temperatures is very low.

700°C is starting temperature for formation of $(K_{0.5}Bi_{0.5})TiO_3$ with pseudocubic structure (a = 3.94 Å). The process take place during the calcinations under this temperature in appropriate stoichiometric mixture of oxides (carbonates). The only intermediate compound at this temperature is bismuth titanate with formula $Bi_{12}TiO_{20}$. In the temperature interval from 800 to 850°C titanate with formula $Bi_4Ti_3O_{12}$ is formed. Single-phase potassium-bismuth titanate (a = 3.946 Å) is formed at 850°C during more long time (Fig. 2) of exposure in comparison to $(Na_{0.5}Bi_{0.5})TiO_3$. As well as in the case of $(Na_{0.5}Bi_{0.5})TiO_3$ for $(K_{0.5}Bi_{0.5})TiO_3$ there are particularities which are the results of primary exposure under 700°C.

Now let us consider the synthesis of $[(Na_{0.5}K_{0.5})_{0.5}Bi_{0.5}]TiO_3$.

In the case of substitution some sodium ions to potassium ones in the structure of sodium-bismuth titanate (substitution in sublattice A) with formation of solid solution $[(Na_{0.5}K_{0.5})_{0.5}Bi_{0.5}]TiO_3$, the nature of phase transformations differs in relation to pure $(Na_{0.5}Bi_{0.5})TiO_3$. In starting powder's mixture sodium-potassium-bismuth titanate $[(Na_{0.5}K_{0.5})_{0.5}Bi_{0.5}]TiO_3$ with the parameter of pseudo-cubic lattice 3.901 Å also is formed after calcining at 700°C. Intermediate titanates $Na_2Ti_6O_{13}$ and $Na_2Ti_3O_7$ are not formed unlike the pure $(Na_{0.5}Bi_{0.5})TiO_3$. The only intermediate compound at this temperature, like in case with $(Na_{0.5}Bi_{0.5})TiO_3$, is bismuth titanate $Bi_{12}TiO_{20}$, which can be found in reactive mixture in large quantity together with of TiO_2 (rutile). After increase of the calcining temperature up to 800°C, bismuth titanate with formula $Bi_4Ti_3O_{12}$ is formed and exists in the reaction products up to 850°C as well as in previous to cases. Formation of single-phase solid solution $[(Na_{0.25}K_{0.25})_{0.5}Bi_{0.5}]TiO_3$ comes to an end after calcining at 850°C.

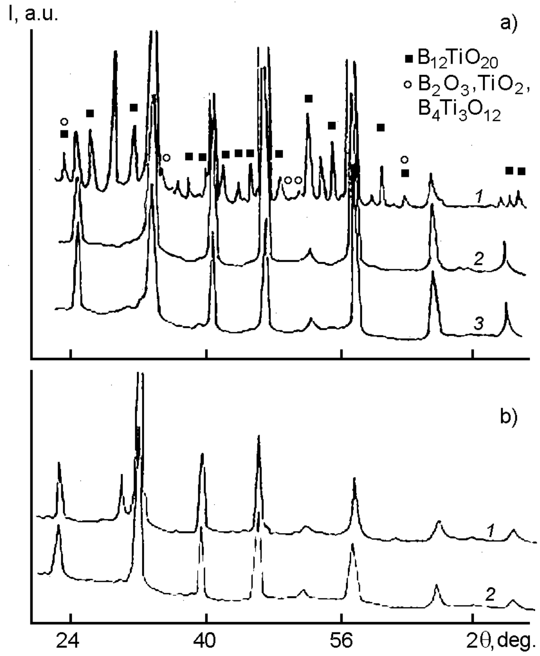

Fig. 2. X-ray patterns after different calcination temperatures. At the top: T_{cal}, °C: *1* — 700 (6), *2* — 700 + 850 (16 h), *3* — 700 + 850 (30 h). At the down: T_{cal}, °C: *1* — 850 (5 h), *2* — 850 (20 h).

The main predominate phase in the mixture of the initial components with the composition $[(Na_{0.5}Bi_{0.5})_{0.95}Ba_{0.05}]TiO_3$ after calcining at 900°C is solid solution with tetragonal distorted structure of perovskite type with the lattice parameters a = 3.89 Å and c = 3.96 Å. In small quantity the solid solution on the base of $Bi_2Ti_2O_7$ with perovskite structure (a = 3.97 Å) is found also. Single-phase product with pervoskite structure is formed at 1100°C.

As it has been noticed before, the aim of a great number of works on piezoelectric materials is replacement of PZT based ceramics by lead free materials. At present the level of piezoelectric properties lead-free materials is lower then PZT parameters. Relying on the results obtained in this work by alloying the solid solu tions we produced piezoelectric ceramics with the level of characteristics, presented in the Table.

As you can see, on this stage the obtained lead-free piezoelectric ceramics have the piezosensitivity g_{33} — one of the main characteristics of piezoelectric materials — comparable with one of PZT ceramics. We

Table. Parameters of NBT-based piezoelectric ceramics

Composition	$\varepsilon_{33}{}^T/\varepsilon_0$	tgδ, %	T_c, °C	P_r, μC/cm^2	E_c, kV/cm	$d_{33}\cdot10^{12}$, C/N	$g_{33}\cdot10^3$, V·m/N
$(Na_{0.5}Bi_{0.5})TiO_3$	624	3.10	324	10.99	25.5	80	14.5
$[(Na_{0.5}Bi_{0.5})_{0.95}Ba_{0.05}]TiO_3$	723	2.65	273	42.90	23.0	160	25.0

reached such results in this work on the samples of solid solutions of the system (Na,Bi)TiO$_3$ (substitution of ions is made in A-sublattice of perovskite structure) by means of suppression of intermediate phase formation in the process of solid state synthesis. As a result of sintering we have obtained ceramics with good quality and parameters. Further improvement of the piezoelectric characteristics level will be reached in solid solutions, which will be obtained in the way of substitution of titanium by zirconium.

4. Conclusion

Thus, solid state synthesis of sodium-bismuth titanate $(Na_{0.5}Bi_{0.5})TiO_3$ and solid solutions on its base is of multi-stage process. Reaction starts with the formation of sodium-bismuth titanate (or corresponding solid solution on its base) and is accompanied by formation of a number of intermediate titanates: $Na_2Ti_6O_{13}$; $Na_2Ti_3O_7$; $Bi_{12}TiO_{20}$; $Bi_4Ti_3O_{12}$; $Bi_2Ti_2O_7$. Titanates $Bi_{12}TiO_{20}$; $Bi_4Ti_3O_{12}$ are the most stable of them. Two intermediate stages are formed the most intensively under the process of solid phases interaction: $Bi_{12}TiO_{20}$ in the temperature range 700–800°C and phase $Bi_4Ti_3O_{12}$ in the temperature range 800–850°C. The stability of intermediate substances depends on the interval of temperatures they were formed at. The lead-free piezoelectric ceramics with piezosensitivity g_{33} (which is similar to one of PZT materials) were obtained.

References

1. B.Jaffe, W.R.Cook, H.Jaffe, Piezoelectric Ceramik, Academic Press, London (1971).
2. G.Smolensky, V.Isupov, A.Agranovskaya, N.Kraynik, *Fiz. Tv. Tela*, **2**, 2982 (1960).
3. H.Nagata, T.Takenaka, *J. Korean Phys. Soc.*, **32**, 1298 (1998).
4. Z.Yang, B.Liu, L.Wei, Y.Hou, *Mater. Res. Bull.*, **43**, 81 (2008).
5. S.H.Choy, X.X.Wang, H.L.W.Chan, S.L.Choy, *Appl. Phys.*, **A 89**, 775 (2007).
6. Chune Peng, Jing-Feng Li, Wen Gong, *Mater. Lett.*, **59**, 1576 (2005)
7. OST 110444-87, Piezoceramic Materials: Specifications.
8. N.A.Toropov, V.P.Barzakovskiy, V.V.Lapin, N.N.Kurtseva, Silicate Systems Diagrams, Nauka, Moscow and Leningrad (1965) [in Russian].

Фізико-хімічні перетворення при твердофазному синтезі титанату натрію-вісмуту і твердих розчинів на його основі

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Досліджено фізико-хімічні перетворення при твердофазному синтезі титанату натрію-вісмуту $(Na_{0,5}Bi_{0,5})TiO_3$ і твердих розчинів на його основі. Показано, що процеси синтезу є багатостадійними і проходять через утворення низки проміжних фаз. Методом рентгеноструктурного аналізу проведено їх ідентифікацію. Визначено оптимальні умови синтезу досліджених матеріалів і електрофізичні характеристики п'єзокерамічних елементів на їх основі.