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Mechanism of Formation of $Bi_4Ti_3O_{12}$

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Abstract—The mechanism of solid-phase reaction of $Bi_4Ti_3O_{12}$ formation was studied. Formation of the layered perovskite-like bismuth titanate occurs via intermediates with sequential changes in the coordination polyhedron of bismuth. A correlation is analyzed between the temperature of the onset of activation of the solid-phase reaction and the melting point of the surface (intergrain) phase based on bismuth oxide.

Bismuth titanate $Bi_4Ti_3O_{12}$ belongs to the class of ferroelectrics $A_{m-1}Bi_2M_mO_{3m+3}$ having a layered perovskite-like structure [1]. The lattice of such compounds consists of alternating bismuth–oxygen layers and perovskite-like layers of various thicknesses. In bismuth titanate, the perovskite-like stack consists of three layers ($m = 3$). A kinetic study of formation of bismuth titanate as a representative of the class of structurally related compounds will furnish information on the structural and chemical origin of ferroelectric properties of layered perovskite-like compounds.

We studied the formation of $Bi_4Ti_3O_{12}$ in the Bi_2O_3–TiO_2 system at various reactant ratios and under various conditions of heat treatment. Figure 1 shows the diffraction patterns of the samples, illustrating the phase transformations in the system in the course of heat treatment. It is seen that, in reaction of $Bi(NO_3)_3 \cdot 5H_2O$ with TiO_2, an intermediate phase, $Bi_{12}TiO_{20}$, starts to form at ~500°C. Along with reflections of this product, the diffraction pattern contains peaks corresponding to TiO_2-rutile and to α-Bi_2O_3 as a product of thermal decomposition of the initial bismuth nitrate pentahydrate. Even traces of the final product, $Bi_4Ti_3O_{12}$, are not detected at this temperature. As the temperature is increased above 600°C, the content of $Bi_{12}TiO_{20}$ gradually decreases with the formation of $Bi_4Ti_3O_{12}$. The synthesis of layered perovskite-like bismuth titanate is complete at 900°C. Formation of the reaction products in the Bi_2O_3–TiO_2 system (2 : 3) in the stepwise heating mode is illustrated in Fig. 2.

The kinetics of $Bi_4Ti_3O_{12}$ formation at various temperatures are shown in Fig. 3. Formation of $Bi_4Ti_3O_{12}$ becomes noticeable starting from approximately 600°C. Activation of the solid-phase chemical reaction at this temperature may be due to sharp acceleration of mass transfer as a result of melting of the surface phase based on $Bi_{12}TiO_{20}$, since, for this compound, transition of the surface phase to the quasi-liquid state occurs in the range 550–580°C [2]. As the temperature is increased further, the reaction rate grows, reaching a maximum at 875°C, i.e., at a temperature close to the melting point of $Bi_{12}TiO_{20}$ [3].

The intermediate $Bi_{12}TiO_{20}$ is formed in the temperature range insufficient for the transfer of the surface phase based on the lowest-melting component of the system, Bi_2O_3, to the quasi-liquid state (at 520–550°C, according to calculations), as suggested by the fact that the content of $Bi_{12}TiO_{20}$ formed in the multicomponent system becomes appreciable even at 500°C (Figs. 1, 2). Thus, when considering the mechanism of the solid-phase reaction in the system, the crystallochemical aspect should be taken into account.

A solid-phase chemical reaction in a heterogeneous system consists of three steps [2]: (1) transport of reactants to the reaction zone, with their contact becoming more active; (2) nucleation of the new phase; and (3) growth of the new phase. In the light of this concept, the reaction acceleration is apparently due to a decrease in the relaxation times of the above transformation and transport processes. Bismuth titanate Bi_1TiO_{20} is crystallochemically related to γ-Bi_2O_3; these compounds have similar structural frameworks and almost identical cubic cell parameters [4]. In view of this fact, formation of $Bi_{12}TiO_{20}$ in the Bi_2O_3–TiO_2 system can be considered as a phase transition α-$Bi_2O_3 \rightarrow \gamma$-$Bi_2O_3$ initiated by incorporation of a titanium dioxide admixture into the Bi_2O_3 structure. According to Buerger's classification [5], if the formation of a new phase does not require changes in the type of chemical bonds, the phase transition occurs the faster, the less significant are the rearrangements in the first and second coordination spheres. Since the formation of $Bi_{12}TiO_{20}$ does not involve significant mass transfer (only 1 mol of TiO_2 should be incorporated per 12 mol of $BiO_{1.5}$ units), the reactant transport

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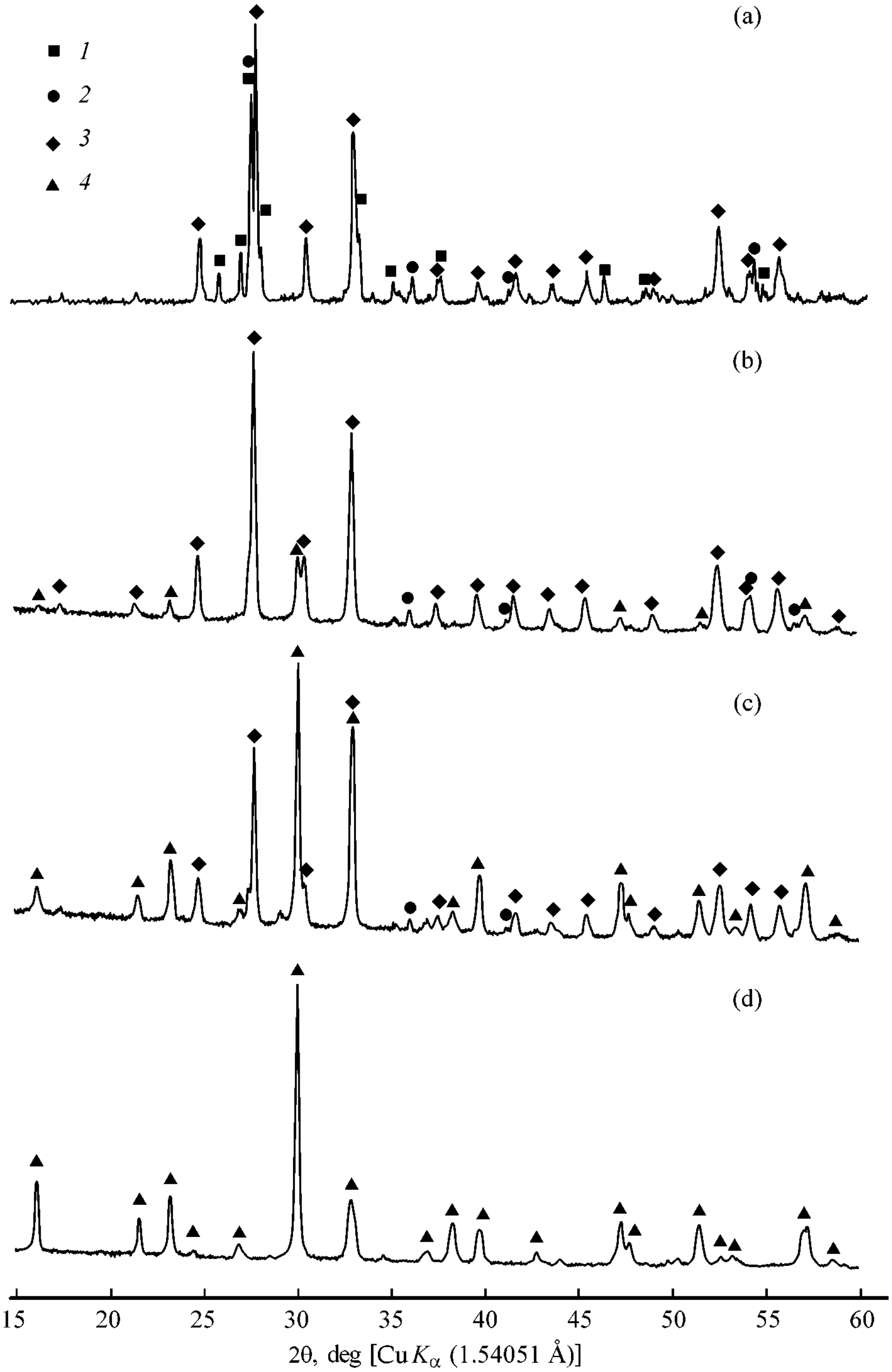

Fig. 1. X-ray diffraction patterns illustrating formation of $Bi_4Ti_3O_{12}$ in the Bi_2O_3–TiO_2 system. Heat treatment temperature, °C: (a) 500, (b) 600, (c) 700, and (d) 900. Peaks: (*1*) α-Bi_2O_3, (*2*) TiO_2, (*3*) $Bi_{12}TiO_{20}$, and (*4*) $Bi_4Ti_3O_{12}$.

cannot be the limiting stage of this solid-phase reaction. This is confirmed by the fact that $Bi_{12}TiO_{20}$ starts to form at temperatures insufficient for melting of the nonautonomous phases in the system (Figs. 1, 2), i.e., formation of $Bi_{12}TiO_{20}$ does not require significant activation of the mass transfer. The solid-phase synthesis of $Bi_4Ti_3O_{12}$ involves occurrence of both rearrangement and transport processes; as already noted, such a reaction is initiated on reaching the melting point of the surface phase. Thus, formation of $Bi_4Ti_3O_{12}$ occurs by the mechanism of successive rearrangements:

$$\alpha\text{-}Bi_2O_3 \rightarrow Bi_{12}TiO_{20} \rightarrow Bi_4Ti_3O_{12}.$$

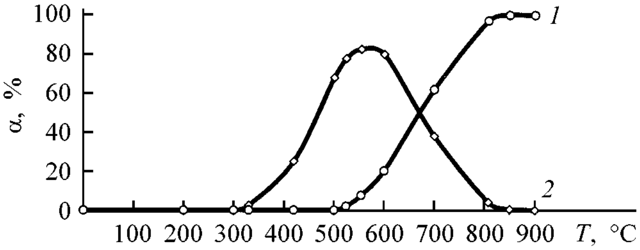

Fig. 2. Phase formation in the course of $Bi_4Ti_3O_{12}$ synthesis in the Bi_2O_3–TiO_2 system at stepwise increase in the heat treatment temperature *T*. (α) Degree of formation. (*1*) $BiTi_{3/4}O_3$ and (*2*) $BiTi_{1/12}O_{5/3}$.

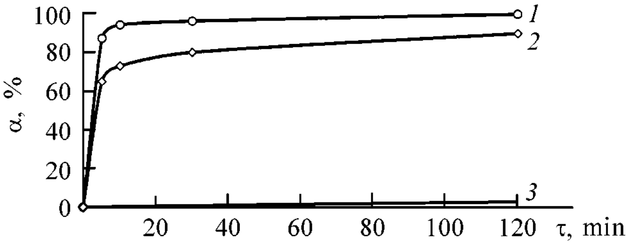

Fig. 3. Degree of formation, α, of $BiTi_{3/4}O_3$ as a function of the time τ of heat treatment at various temperatures, °C: (*1*) 900, (*2*) 800, and (*3*) 600.

α-Bi_2O_3. Monoclinic system. The structure contains two sorts of nonequivalent bismuth atoms with distorted octahedral coordination: five neighbors at distances of 2.13–2.6 Å and one neighbor at a distance of more than 2.8 Å or two neighbors at distances of 3.3 and 3.4 Å [6].

$Bi_{12}TiO_{20}$. Cubic system. The structure is built of BiO_5E octahedra with the basis composition $Bi_{24}O_{40}^{8-}$. In the voids of this structure, there are two tetrahedral positions occupied by $(Ti^{4+}Ti^{4+})$ ions. Bismuth is coordinated by seven oxygen atoms, of which five form an incomplete octahedron and the two most remote oxygen atoms are located on opposite sides of the inert $6s^2$ orbital of Bi, which completes the coordination octahedron [7, 8].

$Bi_4Ti_3O_{12}$. Rhombic system. Perovskite-like $Bi_2Ti_3O_{10}^{2-}$ layers alternate in the structure with $(Bi_2O_2)^{2+}$ bismuth–oxygen layers. In the perovskite-like layers, the coordination number of Bi with respect to oxygen is 12 [1].

This transformation pattern reflects the crystallochemical genesis of the structure in the course of the solid-phase reaction. The structure formation involves a successive increase in the number of the nearest atoms adjacent to Bi, with the last, high-temperature stage being accompanied by a considerably larger change in the bismuth coordination number than the first, low-temperature stage.

EXPERIMENTAL

The mechanism and kinetics of phase formation in the Bi_2O_3–TiO_2 system were studied by two procedures. In the first procedure, a mixture of the initial components corresponding to the $Bi_4Ti_3O_{12}$ stoichiometry was subjected to stepwise heat treatment at temperatures increasing from 200 to 900°C with a 100°C step. The mixture was kept at each temperature for 18 h. After each step, the mixture was reground. The starting compounds were ultrapure grade bismuth nitrate pentahydrate $Bi(NO_3)_3 \cdot 5H_2O$ and analytically pure grade titanium dioxide (rutile modification). In the second procedure, heat treatment was performed in the isothermal annealing–quenching mode at various temperatures and anealing times. The initial stock corresponded to the $Bi_4Ti_3O_{12}$ stoichiometry. Bismuth and titanium oxides were of ultrapure grade. In all cases, samples were pressed in pellets at 100 MPa. Homogenization and high dispersity of the stock were ensured by vibrational milling for 1 h before heat treatment.

Qualitative and quantitative X-ray phase analysis was performed with DRON-3 and Siemens D-500HS diffractometers according to [9].

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