Study of Aurivillius phases in $Bi_4Ti_3O_{12}$–$BiFeO_3$ system

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In the $Bi_4Ti_3O_{12}$–$BiFeO_3$ system, new compounds of general formula $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ with different m values have been synthesized having the structure of Aurivillius phases. The phase transition and decomposition temperatures of the obtained compounds have been determined. Thermomechanical properties of the materials based on those compounds have been studied, the linear thermal expansion coefficients and the sintering onset temperatures have been determined.

В системе $Bi_4Ti_3O_{12}$–$BiFeO_3$ получен ряд новых соединений состава $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ с различным значением m, имеющих структуру фаз Ауривиллиуса. Определены температуры фазовых переходов и температуры разложения полученных соединений. Исследованы термомеханические свойства материалов на основе этих соединений — определены коэффициент линейного термического расширения и температуры начала спекания.

In the $Bi_4Ti_3O_{12}$–$BiFeO_3$ system, a series of compounds is realizable having the layered perovskite-like structure similar to the Aurivillius phases and corresponding to the general formula $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ [1]. In those compounds, ferroelectric, semiconductor and ferromagnetic properties are combined [2, 3], thus, those are of good prospects for various technical applications and, first of all, in development of composite systems for data storage and processing devices. Within the unit cells of those compounds, the fluorite-like bismuth- oxygen layers of the $\{(Bi_2O_2)^{2+}\}_\infty$ composition are interchanged with perovskite-like $\{(Bi_{m+1}Fe_{m-3}Ti_3O_{3m+1})^{2-}\}_\infty$ layers of different thickness, m, separated out of the perovskite lattice by (001) planes.

The compounds were synthesized from bismuth oxide (pure grade), iron (III) oxide (analytical purity grade) and titanium (IV) oxide (special purity grade), the amounts used corresponding to the $(0.5n + 2)Bi_2O_3 + 0.5nFe_2O_3 + 3TiO_2$ stoichiometry with $n = 0$, 0.14, 0.17, 0.25, 0.67, 1, 1.5, 1.75, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5 and 6. The compositions mentioned answer to the ratio of 1 mole $Bi_4Ti_3O_{12}$ per n moles $BiFeO_3$ and to $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ compounds with the perovskite-like layer numbers in the structure $m = n + 3$.

After each synthetic stage, the samples were subjected to X-ray phase analysis (XPA) using D-500HS (Siemens) and DRON-3 diffractometers (Cu Kα emission). The structure and XPA studies were based on powder diffractographs. The microstructure diagnostics and chemical analysis of the revealed phases were carried out by scanning electron microscopy and electron probe microanalysis using a CamScan MV2300 scanning electron microscope with an Oxford Link microprobe extension. The sample thermal behavior was examined by differential thermal analysis (DTA) and differential scanning calorimetry (DSC) using a Q-1500D derivatograph (Paulik-Paulik-Erdey) and a STA 429 (NETZSCH) calorimeter, respectively. To determine the sintering onset temperatures and the linear thermal expansion coefficients, a DIL 402 ED dilatometer (NETZSCH) was also used.

The synthesis and XPA of the layered perovskite-like compounds of the $Bi_4Ti_3O_{12}$–$BiFeO_3$ system has demonstrated a high homological capacity of the $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ series expressed as realizability of numer-

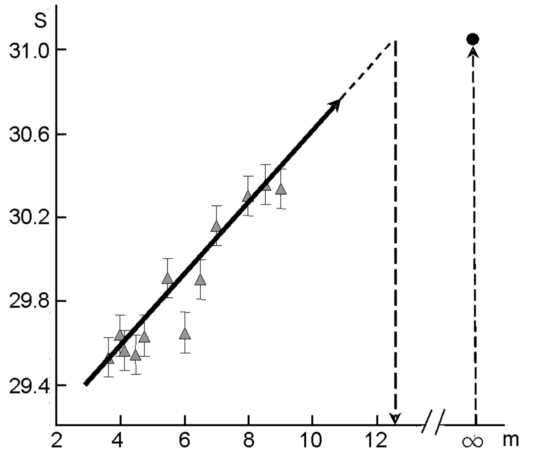

Fig. 1. Dependence of the face area perpendicular to the c axis, $S = ab$ ($\AA^2$), on the number of the perovskite-like layers in the structure of $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ compounds (*1* – Aurivillius phases; *2* – $BiFeO_3$).

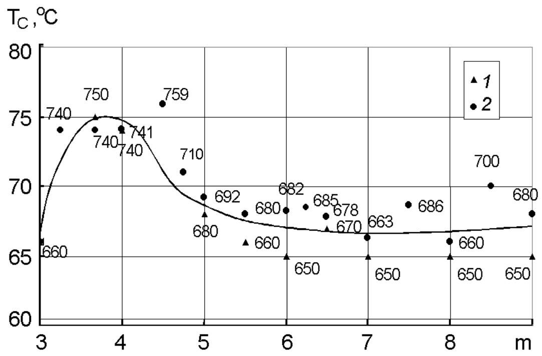

Fig. 2. Dependence of the Curie temperature on the number m (*1– DTA data; 2* – DSC ones).

ous structurally similar compounds corresponding to both integer and fractional m values. Thus, in the $Bi_4Ti_3O_{12}$–$BiFeO_3$ system, compounds with complex interchange of the perovskite-like layers in the crystal structure may exist along with those having integer m values. For example, the compound $Bi_{13}FeTi_9O_{38}$ ($m = 3.25$) contains in its structure interchanging perovskite-like layers having thickness values $m_1 = 3$, $m_2 = 3$, $m_3 = 3$, and $m_4 = 4$.

Consideration of the unit cell parameters of Aurivillius phases has shown that the c parameter changes essentially linearly as the number of the perovskite-like layers in the structure increases, i.e., the distortion extent of the perovskite-like lattice fragment built-in into the layered compound structure varies only slightly along the c axis. At the same time, as the number of the perovskite-like layers increases, the basal face area ($S = ab$) approaches the corresponding value for $BiFeO_3$ unit cell attaining that value at $m = 12$ or 13 (Fig. 1). So, the structure parameters (and thus the formation energy of perovskite-like layered compounds) can be believed to approach similar characteristics of non-layered perovskite-like $BiFeO_3$ as m increases. It follows therefrom that the stability of multilayered Aurivillius phases in the $Bi_4Ti_3O_{12}$–$BiFeO_3$ system decreases as the layer number increases.

According to TEM and electron probe microanalysis, all the samples studied show a good agreement of the elemental composition with the stoichiometry that, being combined with the X-ray examination data, evidences reliably that the compounds belong to the Aurivillius phase family. The DTA and DSC results evidence a progressive thermal stability decrease for the $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ compounds as m increases, thus confirming the above suggestions. The thermal analysis data make it possible to consider the thermal decomposition mechanism of the perovskite-like $Bi_4Ti_3O_{12}$–$BiFeO_3$ system compounds as a successive peritectic decomposition into compounds of the same homological series but containing a smaller number of the perovskite-like layers in the structure.

Fig. 2 presents the Curie temperature (T_C) dependence on the number m. The T_C value seems to be defined by the iron ion content in the perovskite-like layers ($BiFeO_3$ molar content).

The data on thermal expansion of the $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ compounds show that the linear thermal expansion coefficient is essentially independent on the number of the perovskite-like layers in the structure and its average value is about $(11\pm2)\cdot10^{-6}$ K^{-1}. The sintering onset temperature T_S of the samples synthesized is within limits of 500 to 850°C and decreases progressively as m increases, thus evidencing indirectly the above-mentioned decrease in thermal stability.

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Дослідження фаз Аурівілліса у системі $Bi_4Ti_3O_{12}$–$BiFeO_3$

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У системі $Bi_4Ti_3O_{12}$–$BiFeO_3$ одержано ряд нових сполук $Bi_{m+1}Fe_{m-3}Ti_3O_{3m+3}$ з різними значеннями m, які мають структуру фаз Аурівілліса. Визначено температури фазових переходів та температури розкладу одержаних сполук. Досліджено термомеханічні властивості матеріалів на основі цих сполук — визначено коефіцієнт лінійного термічного розширення та температури початку спікання.