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STRUCTURE CHANGES OF SINGLE- AND DOUBLE-PHASE Bi–Sr–Ca–Cu–O FILMS UNDER THE THERMOCYCLING

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Structure and texture of Bi–2212 single-phase and double-phase (Bi-2201+Bi–2212) films and their changes under the thermocycling in the temperature range 77–300 K were studied by X-ray diffraction analysis. Under the thermocycling double-phase film revealed a more perfect texture and stability than the single phase one. It is explained by the fact that simple and perfect Bi–2201 phase is as the "reinforcement" for the Bi–2212 phase, being rigidly connected to the latter one by means of crystalline intergrowth.

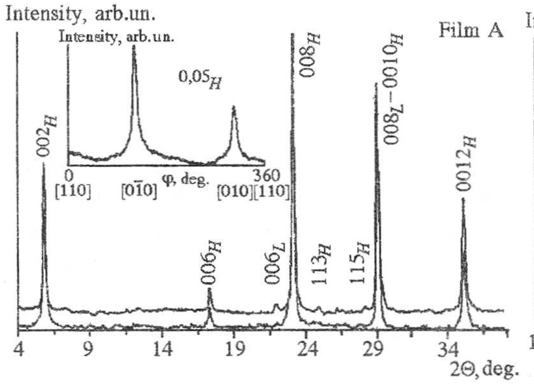
1. Since the discovery of high temperature superconductivity (HTSC) the problem of development of equipment and electronic devices based on filmy HTSC-materials is the pressing question. The inclination of these materials to degradation is one of the serious obstacles. $YBa_2Cu_3O_y$ [1,2] and Bi-based [3] ceramics deteriorate the superconducting properties interacting with water and aqueous vapor. The interaction of high-T_c superconductors with inert [4] and reactive [5] atmosphere also leads to a change of the properties of these compounds. The decrease of grain superconducting transition temperature of $Bi_2Sr_2Ca_2Cu_3O_y$ (Bi–2223) ceramics after low temperature thermocycling has been revealed and studied in [6,7]. The results show that the multi-phase (Bi–2223 + Bi–2212) ceramics degrade more rapidly and considerably than single-phase ones. The reducing of critical current density of Bi–2212 superconducting tapes has been observed at the 320–77 K thermal cycling [8]. Degradation of $YBa_2Cu_3O_y$ films was observed in [9]. At that time the influence of thermocycling on the stability of Bi-based films has not been studied yet.

Study of this problem is of practical interest because the obtaining of structurally stable Bi-based films is connected with the solution of the problem of predicted growth of coexisting phases in the homologous series $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ [10]. In the present work structure and texture changes of single-phase and double-phase films under the low temperature thermocycling are studied by means of the X-ray diffraction.

2. Thin films $Bi_2Sr_2CaCu_2O_y$ (Bi–2212) and $Bi_2Sr_2CuO_y$ (Bi–2201) were prepared by molecular beam epytaxy (MBE) technique on the monocrystalline MgO substrates (001). The substrate temperature during the deposition was 350°C. After the deposition the films were subjected to annealing under air at 1–1.5 hours at temperature of 820–830°C. Heating and cooling rates were 5°C/min and 7°C/min, respectively. Thermocycling was performed in the

vacuum mounting filled with helium that was turned down into the transport dewar with liquid nitrogen. The X–ray analysis was performed using Cu–Kα radiation. The heating up to room temperature was performed inside the insertion for the elimination of possible effect of degradation due to the water vapor condensation on film surface. The X-ray analysis was performed before and after thermocycling. Rocking curves of reflections (00l) were measured to reveal *c*-axis misorientation of crystallites by means of rotation of sample holder at fixed counter position (ω-scans, 2Θ = const). Misorientation in (*a*,*b*) plane was measured by the rotation of film in it's own plane (φ-scan) in the reflecting position (115) for Bi–2212 phase (2Θ = 27.5°; tilting angle χ = 58.1°) and position (113) for Bi–2201 phase (2Θ = = 25.8°; χ = 64.9°).

3. Single-phase film (film A) was found to be strongly textured after annealing (axial texture [*00l*], see Fig. 1). However, rocking curves of (0010) Bi–2212 reflection were splitted in two peaks (Fig. 2). The broad peak has a maximum at Θ = 14.5° that coincides with position of reflection in Θ–2Θ scan. The sharp peak coincides with the tilting of c-axis of crystallines at the angle of 1.3° relatively to the normal to the substrate ([100] direction). The direction of c-axis of crystallines relatively to the substrate was determined from the φ-scan of texture reflection (008) (see insert in Fig. 1). The chaotic distribution of crystallines in the (*a*,*b*) plane was revealed for film A by the φ-scan of (115) reflection.



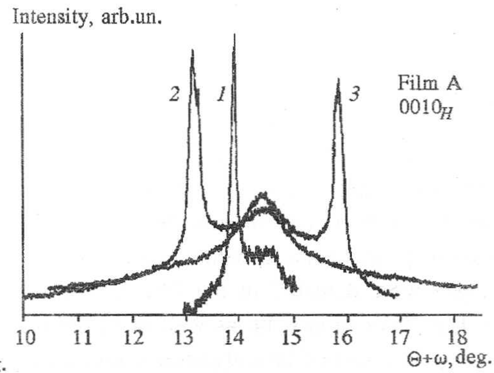
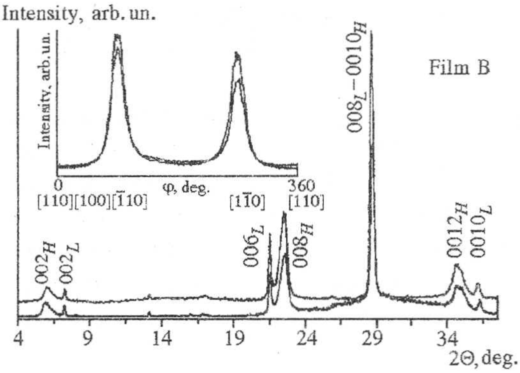


Fig. 1. X-ray pattern of film A (lower curve – before; upper – after the first cycle). Reflections of Bi–2201 phase are marked by index *L*; reflections of Bi–2212 phase are marked as *H*. In the insert – φ-scan of (008) reflection of Bi–2212 phase

Fig. 2. Rocking curves (ω- scans) of (0010) Bi–2212 reflection of film A before cooling (*1*), after the first (*2*) and third (*3*) cooling

Double-phase film (20% Bi–2201 + 80% Bi–2212, film B) was strongly textured too ([*00l*], see Fig. 3). A strong interaction existed between the phases; such an interaction was described in detail in [11]. The interaction is in the arising of the phase intergrowths and manifests itself in the "forcing" by the Bi–2201 phase it's structure to the Bi–2212 one. Position of (008) Bi–2201–, (0010) Bi–2212–, and (0012) Bi–2223 phases reflection coincides for all of these three phases in the homologous series Bi–2201 – Bi–2212 – Bi–2223, and crystal intergrowths are revealed in the corresponding planes (see [11]). The interaction appears on the X-ray pattern (Fig. 3) as an asymmetric broadening of Bi–2212 phase reflections and their shifting in the direction of the most close Bi–2201 reflections.

Film B was grown on a tapered substrate too. The φ-scans of (006) and (008) reflections show the presence of the selected direction in the film plane (see inset in Fig. 3). However, the rocking curves reveal the presence of only one type of crystallites with a *c*-axis misorientation less than 0.2° to the substrate normal. There is a selected direction [1 $\bar{1}$ 0] in the (*a*,*b*) plane (see φ-scan, Fig. 4). Note that (113) reflection of Bi–2201 phase is more intense and sharp than the (115) one of Bi–2212 phase, in spite of the considerably lower (20%) amount of B–2201 phase in the film. This fact illustrates the leading role of Bi–2201 phase in the process of film growth.



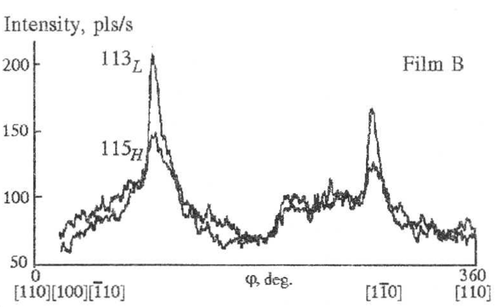


Fig. 3. X-ray pattern of film B (lower curve – before, upper – after five cycles). In the insert – φ-scans of Bi–2201 (006) and Bi –2212 (008) reflections

Fig. 4. φ-scans of Bi–2201 (113) and Bi–2212 (115) reflections

Structural changes in the film A appeared just after the first thermocycle. It was revealed in the appearance of small amount of Bi–2201 phase, nontextured component of Bi–2212 phase (see Fig. 1) and in wide broadening of rocking curves in ω-scan (see Fig. 2). A small broadening was also detected under further thermocycling. On the contrary, no structure changes were detected in the film B even after five cycles of cooling either in the pattern (see Fig. 3) or in ω-scan, as well as in the (*a*,*b*) plane orientation.

4. As a result of investigation it was observed that

– double-phase film with phase intergrowths is more perfect than the single-phase one. The coherent growth of the film relatively to the substrate plane with an absence of intermediate zone of misoriented crystallites as well as ordering in (*a*,*b*) plane usually nontypical for films on the MgO substrates are revealed of this film;

– double-phase film is considerably more stable to the thermocycling then the single phase one. It holds out the perfect *c*-orientation even after a few thermocycles;

– more simple and perfect Bi–2201 phase being rigidly connected with the Bi–2212 one plays the role of "reinforcement" for the last one and in small amounts (5–20%) influences usefully the film structure.

The last conclusion is confirmed by the temperature dependence of resistance obtained in [11], the superconducting transition of double-phase films was sharper than that of the single-phase ones and critical temperature of double phase films was not less than critical temperature of single-phase ones.

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