Features of growth of non-cubic bicrystals from the melt (example of leucosapphire and neodymium gallate)

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Abstract. Neodymium gallate (NdGaO₃) and sapphire (Al₂O₃) are most suitable materials to produce bicrystal substrates for high-temperature superconducting (HTSC) films’ microwaves Josephson junctions. Perfect bicrystal border is important for the devices, and it can be obtained in bicrystals grown directly from the melt. Unfortunately both materials have non-cubic symmetry and anisotropic thermophysical properties what complicates the bicrystal growth process. The experimental results of NdGaO₃ bicrystals growth by Czochralski method using compound bicrystal seeds with different symmetries in the plane perpendicular to the growth axis are presented. The results proved to be very unstable and depended critically upon growth conditions and on bicrystal border orientation. The bicrystals with misorientation angle 180° which correspond to the natural (110) twins are grown. When bicrystal angles are within 22-28° range which is optimum for bicrystal Josephson junctions it is very difficult to grow the long bicrystals: the bicrystal border goes out of the crystal quickly. It is supposed that in the last case the symmetry of compound bicrystal seed in the plane perpendicular to the growth direction can differ from the heat field symmetry in the growth system. Requirements for growth of anisotropic crystals by Czochralski method are formulated. It is shown that the requirements of seed and heat field symmetry correspondence can be satisfied more easily in Stepanov’s growth method (EFG). The sapphire bicrystal ribbons suitable for manufacturing of high quality substrates for HTSC film Josephson junctions using Stepanov’s method are grown.

1. Introduction.
Results of researches of practical realization of possibility to produce bicrystal substrates for HTSC films’ microwaves Josephson junctions using bicrystals growth directly from the melt offered by the authors earlier [1] are presented. This should allow the fabrication of the perfect bicrystal border. Bicrystals of various metals and semiconductors only with cubic symmetry having isotropic thermophysical properties were grown by Czochralski method to the beginning of these researches [2]. Unfortunately, the single crystals most suitable for manufacturing of the microwave devices on the films with high-temperature superconductivity (HTSC), - NdGaO₃ and Al₂O₃ [3,4] - have lower symmetry and do not have such important property for growth of bicrystals by Czochralski method. The analysis of possibilities of known methods of melt growth has shown that Stepanov’s method (EFG) is the most suitable one to grow bicrystals of anisotropic materials. The compound bicrystal seed having mm or m symmetry can be oriented in such a way that its mirror symmetry plane going through the growth axis will coincide with mirror symmetry plane of metal shaper used in this method. The temperature gradients in the shaper’s plane are small owing to good heat conductivity of shaper’s metal and free convection in the narrow gap of the shaper is suppressed in this method. In this case small temperature fluctuations aside of growth axis will not be followed by deviation in growth velocity and growth directions of single crystal blocks of the seed, in contrast to the situation in Czochralski growth method. The possibility to grow the sapphire bicrystals, suitable for manufacturing of high quality substrates for HTSC film Josephson junctions using Stepanov’s method is shown. Unfortunately, NdGaO₃ melt reacts with molybdenum containers, usual for growth of sapphire by Stepanov’s method, so this technology is not acceptable to grow NdGaO₃ bicrystals. We describe here
some results of our efforts to grow NdGaO$_3$ bicrystals by Czochralski method (some preliminary data were given in [5]) and Al$_2$O$_3$ bicrystals by Stepanov’s method.

2. Experimental.

2.1. Czochralski growth.
Czochralski growth system is shown in fig. 1. The system has comparatively low temperature gradients and was successfully used previously to grow dislocation-free Gd$_3$Ga$_5$O$_{12}$ crystals [6].

![Czochralski system for NdGaO$_3$ bicrystals growth.](image)

Ir crucible having diameter 50 mm and height 50 mm was placed in the furnace with RF coil heater. The growth system gave the possibility to change vertical and radial temperature gradients in the broad ranges owing to the displacement of heat shields and to the change of crucible position in relation to RF coil. The special attention was paid to creation of axially symmetrical heat field in the crucible and to coincidence of heat field center of the crucible with the crystal rotation axis. Growth procedure was identical to that one used by us to grow NdGaO$_3$ single crystals [7]. Pulling rates were 2.5 – 3 mm/hour, crystal rotation rate 0 – 50 rpm, vertical temperature gradients 1 - 50 $^\circ$/mm. NdGaO$_3$ single crystals having no twins, cracks and inclusions were successfully grown at these conditions. [100] and [110] were the main growth directions. The crystals were symmetrical and had external faceting. The crystals with seeds’ directions inclined by 11-14$^\circ$ to [100] and [110] axes were also grown because it was planned to obtain bicrystals with growth axes inclined in relation to the basic orientations. In that case the crystals were unsymmetrical but did not have any additional defects as compared to the crystals of the basic orientations. Plates were cut from the crystals and were studied under microscope after polishing and subsequent etching in phosphoric acid.

Compound seeds of two types were used for bicrystal growth (fig. 2). In one case [110] directions of two blocks in the seed were inclined symmetrically in relation to the growth axis by the angle equal to the half of the bicrystal angle (fig. 2a), and in the second case [110] directions were also turned each to other on the bicrystal angle but were situated in the plane perpendicular to the growth axis (fig. 2b). Both blocks have the same size and the pulling axis goes through the center of the seed. Bicrystal angles were chosen in 22-28$^\circ$ range.
2.2 Stepanov’s method
Details of the experiments are described in [8,9]. The industrial Stepanov’s method growth system developed by VNIIETO with resistive graphite heater and Ar atmosphere was used. Molybdenum crucible was used for Al₂O₃ melt. NdGaO₃ melt was found to react with the crucible so the growth experiments were carried out only with sapphire. Two orientations of sapphire ribbons’ planes which can be obtained by this method are suitable for HTSC films growth: (0112) and (1010). The seeds orientations used to grow Al₂O₃ bicrystals are shown in fig. 3.

Pulling direction was [1120] in both cases. Pulling rate was 0.6-0.8 mm/min. Ribbons with 35x4.5 mm cross-section and lengths up to 100-110 mm were obtained. They had small ridges (width and height 0.1-0.5 mm) on both side surfaces and bicrystal border along the whole length.
3. Results and discussion

Results of experiments for NdGaO$_3$ Czochralski growth proved to be very unstable and depended critically upon growth conditions and on bicrystal border orientation. We succeeded to obtain the bicrystal border going along the whole length of the crystal only by using the seed with natural twin border. The border itself looks under microscope as clear straight line, with no change in the density of etch pits near the border and far from it after etching in phosphoric acid. It means, existence of such border does not cause additional stresses in the crystal, and the border itself does not contain visible defects. Unfortunately bicrystals grown on seeds with natural twin border are not suitable for preparation of Josephson junctions on the substrates made from them because the Josephson effect is practically absent at values of bicrystal angles 90° and 180°.

One of bicrystal blocks disappeared (outwent) as a rule already during crystal shoulder growth for compound seeds of both types (fig. 2) with misorientation angles in the range 22° -28°, and only the single crystal grew further. By that additional multiple twins and defects appeared often on crystal shoulder near the blocks’ border. Growth instability can be connected with a number of reasons: heat field asymmetry, border defectiveness in the compound seed, small variations in orientation of adjacent blocks in relation to the growth axis, anisotropy of thermophysical properties of NdGaO$_3$ when small temperature nonuniformities are followed by the change in growth velocity of one block of the seed and its fast disappearance after that. The similar bicrystal border instability was discovered in SrTiO$_3$ bicrystals grown by optical floating zone method [10]. It was asserted in [2] that it was necessary to control vertical and radial temperature gradients with precision 0.1°C to grow silicon bicrystals by Czochralski method.

Constant temperature control with such precision around NdGaO$_3$ melting temperature (near 1700 °C) with RF heating is an extremely complicated problem, therefore till now we succeeded in growing the bicrystals with the bicrystal border length not more than 20 mm before its outgo. Further progress in bicrystal growth requires even more careful control of all experimental conditions. NdGaO$_3$ anisotropy which causes additional stresses in compound seeds and outgo of one block is very substantial. Analysis shows that some additional requirements for stable bicrystal growth connected with anisotropy of rhomcic NdGaO$_3$ properties appear besides the ones formulated previously in [2] and necessary for cubic semiconductors’ bicrystals Czochralski growth which correspond to conditions of dislocation-free crystal growth. We formulated the following additional basic requirements for Czochralski growth of non-cubic bicrystals:

1. Bicrystal pulling direction should coincide with one of the basic axes of crystal elementary cell.
2. Crystallographic orientations of adjacent blocks’ surfaces of compound seed should be fully identical.
3. Seed axis should coincide with its rotation axis and with the center of heat field.

Realization of all these requirements is a rather complicated problem. The situation with bicrystal growth by Stepanov’s method is much simpler. The “longitudinal” temperature gradient along the shaper’s plane is equalized in this method owing to good heat conductivity of shaper’s metal and to convection damping in the narrow shaper’s gap. Results of calculations of temperature distribution in sapphire ribbon grown by Stepanov’s method [11] are shown in fig. 4 and 5.
Temperature gradients in the ribbon’s plane are equal only to some degrees per cm, and the temperature distribution has usually mm symmetry. If we use the compound seed with the same symmetry and symmetry planes of the heat field and of the seed coincide small temperature fluctuations aside of growth axis will not be followed by deviation in growth velocity and growth directions of single crystal blocks of the seed, in contrast to the situation in Czochralski growth method. Owing to this we succeeded in growing bicrystal Al₂O₃ ribbons of two orientations (fig. 3) suitable for HTSC Josephson junctions fabrication, with bicrystal border length up to 110 mm. Bicrystal substrate prepared out of such ribbon is shown in fig. 6.

Unfortunately it is difficult to use this method for NdGaO₃ bicrystal growth because its melt reacts with Mo containers, Pt containers and shapers have too low working temperature, and Ir is too brittle for fabrication of the shaper which has rather complex design.
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