COMPOSITION AND STRUCTURE REFINEMENT OF SUPERCONDUCTING CRYSTALS

Y\(_{1-x}\)Tb\(_x\)Ba\(_2\)Cu\(_3\)O\(_{6+\delta}\) (\(x = 0.10\); \(\delta = 0.75\))


Crystals of Y\(_{0.90}\)Tb\(_{0.10}\)Ba\(_2\)Cu\(_3\)O\(_{6.75}\) have been prepared by spontaneous crystallization from slowly cooled non-stoichiometric melt of the system Y–Tb–Ba–Cu–O. Average size of platelet crystals having mirror surface is 2×2, the largest — 8×9 mm with thickness 0.1-0.2 mm. The crystals have been characterized by powder X-ray diffraction and electron microprobe analysis. Tetragonal symmetry of the crystals has been determined by X-ray diffraction. Magnetic susceptibility measurements have revealed that the crystals manifest transition to superconducting state without additional annealing (\(T_c = 60\) K). Structures and compositions — Y/Tb ratio (\(\sigma = 0.01\)) and oxygen content (\(\sigma = 0.04\)) — have been refined for two single crystals. Possibility of rhombic distortion of the tetragonal symmetry is discussed.

Keywords: superconducting crystals Ln123, (Y/Tb)123 crystals, crystallization, structure, solid solutions, superconductivity.

INTRODUCTION

Complete substitution of yttrium in HTSC compounds YBa\(_2\)Cu\(_3\)O\(_{6+\delta}\) (Y123) with majority of rare-earth elements yields isostructural series of compounds having similar superconducting and other properties. Terbium, like cerium and praseodymium, makes an exception in failing to afford 123 phases [1–6]. Its ability to exist in higher oxidation state [2, 7] and/or formation of the phase BaTbO\(_3\), more stable under experimental conditions, are considered as possible explanations [2, 4, 8]. However, partial substitution of terbium for yttrium yielding solid solution (Y\(_{1-x}\)Tb\(_x\)Ba\(_2\)Cu\(_3\)O\(_{6+\delta}\)) is possible, but extent of the substitution substantially varies in the studies undertaken by different workers. The data on terbium oxidation state are also ambiguous. The authors of [2] has demonstrated that single-phase samples comprising tri-valent Tb exist in the field with \(x \leq 0.17\), while at \(x > 0.17\) the increase in oxidation state of Tb is observed accompanied by appearance of admixture phase BaTbO\(_3\), its content rising with \(x\). Other authors note multiphase nature of samples obtained by solid state synthesis, like in [2], already at \(x > 0.1\) [8]. According to their data, terbium exists as Tb(III) and Tb(IV) at the whole range of \(x\). The authors of [9] also came to a conclusion about two oxidation states of Tb relying on the data of a structural study of a non-superconducting crystal Y\(_{0.8}\)Tb\(_{0.18}\)Ba\(_{1.11}\)Al\(_{0.1}\)Cu\(_{2.7}\)O\(_{6+\delta}\) (synthetic details were not reported). In thin films prepared by laser ablation [3], solubility limit \(x = 0.7\) was achieved, oxidation state of terbium was not commented by the authors.
The above data establish the goal of the present study: preparation, characterization and refinement of the crystal structure of single crystals having general formula \((Y_{1-x}Tb_x)Ba_2Cu_3O_{6+\delta}\) for examination of magnetic properties aimed at acquisition of information on crystal field and interaction parameters in layered perovskites [10].

**EXPERIMENTAL**

**Crystal preparation and characterization.** The crystals were prepared by spontaneous crystallization form slowly cooled non-stoichiometric melt of the system \(Y–Tb–Ba–Cu–O\) in a vertical electrical furnace equipped with a heating/cooling control unit. Oxides \(Y_2O_3\), \(Tb_2O_7\), \(BaO\), \(CuO\) were used as the starting components of the load (purity on the main component better than 99.99% for all the oxides). The ratio of the starting components provided the following composition of the mixture: \(Y_{0.9}Tb_{0.1}Ba_2Cu_3O_{6+\delta}\) — 10 wt.% + \((0.28BaO + 0.72CuO)\) — 90 wt.%. After thorough grinding in electrically powered agate mortar with addition of acetone, the starting mixture was placed in an alumina crucible and heated to 1020°C in the furnace. After isothermal annealing during 24 h the temperature was lowered to 930°C at the rate 0.3-0.5 deg/h.

The crystals were separated from remaining liquid by decantation and cooled at 12 deg/h. Thin (thickness 0.1-0.2 mm) mirror surface crystals have average size about 2×2, the largest — 8×9 mm (Fig. 1a). Powder diffraction patterns of the crystals were recorded on a diffractometer Philips PW-1700 (CuK\(_\alpha\) radiation). According to powder XRD, the crystals belong to the structural type Ln123, they are tetragonal, unit cell parameters are \(a = 3.865\) Å, \(c = 11.72\) Å (Fig. 2). A minor amount of mechanical admixture of \(BaCuO_2\) is observed. Determination of element composition of the crystals obtained was performed on a scanning electron microscope Jeol JSM6700F equipped with a field-emission cathode. It was found that terbium ion distribution is fairly homogeneous within a given crystal, and the composition is well reproduced between the crystals (Fig. 3). Without additional annealing, the crystal exhibited superconducting phase transition at 60 K (Fig. 4).

**Single crystal X-ray diffraction.** Two small black prismatic crystals having sizes 0.08×0.07×0.06 mm and 0.12×0.08×0.07 mm (hereafter I, II, Fig. 1b, c) were picked for the structural investigation. Intensity data were collected on an automated