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Growth and Characterization of Photorefractive $Bi_{12}TiO_{20}$ Single Crystals

Photorefractive $Bi_{12}TiO_{20}$ single crystals of high optical quality were grown in a resistive heating furnace from high temperature nonstoichiometric (10:1) solutions of Bi_2O_3 and TiO_2 at pulling rates 0.3–0.8 mm/h at rotation 20–30 rpm along the ⟨001⟩ and ⟨011⟩ axis. Powder X-ray analysis, Laue method, and electron-probe microanalysis were used for characterization. BTO crystals have the bcc structure of sillenite type with $a_0 = 10.178(8)$ Å. The chemical composition of the crystals can be written down as $Bi_{12.1\pm0.2}Ti_{0.96\pm0.09}O_{20.1}$. Natural optical activity ϱ of BTO crystals is 6.3 ± 0.2 deg/mm at $\lambda = 0.633$ µm and 11.9 ± 0.2 deg/mm at $\lambda = 0.5145$ µm, optical absorption coefficient $\alpha = 0.42 \pm 0.04\ \mathrm{cm}^{-1}$ at $\lambda = 0.633$ µm and linear electro-optic coefficient $r_{41} = r_{52} = r_{63} = 5.3$ pm/V. Fanning effect in the "fiber-like" BTO sample was studied and double phase conjugation with conversion efficiency up to 8% was observed in a wide range of incidence angles of the pump at $\lambda = 0.633$ µm for 2×3 mW input light power.

1. Introduction

Photorefractive crystals of the sillenites ($Bi_{12}GeO_{20}$, $Bi_{12}SiO_{20}$, $Bi_{12}TiO_{20}$ etc.) have an interesting combination of electro-optic, acoustooptic, and piezoelectric properties, which allows to use them in optical information processing, including spatial light modulators, optical memories, phase conjugation, image inversion and optical interconnects (GÜNTER, HUIGNARD). In comparison to other sillenites, bismuth titanium oxide ($Bi_{12}TiO_{20}$, BTO) exhibits a higher sensitivity for red light that permits to use a cheap HeNe laser. In addition, BTO crystals have a lower optical activity ϱ, which is favourable for many applications. However, some technological problems (the incongruent melting of $Bi_{12}TiO_{20}$, the high tendency of Bi_2O_3-containing melts to the supercooling etc.) did not allow to produce large single crystals of high optical quality.

There are two main methods to grow single crystals with sillenite structure: hydrothermal synthesis (BARSUKOVA et al.) and the crystal pulling from the melts. The most rapid technique of crystal growth is the Czochralski method. Congruently melting $Bi_{12}GeO_{20}$ and $Bi_{12}SiO_{20}$ single crystals were first grown by this method in Bell Telephones Laboratories (BALLMAN). $Bi_{12}TiO_{20}$ single crystals can be grown from high temperature solutions containing some excess of Bi_2O_3 (BRUTON et al. 1974). The RF inductive heating and the resistance furnaces are usually used for growing crystals with sillenite structure. However, the better conditions for crystal growth can be created in the resistance furnace. Moreover, in this case all necessary equipment is simple and very cheap.

In this report we present the technology for growing high optical quality photorefractive BTO single crystals from high temperature solutions in the resistive heating furnace and the results of X-ray and scanning electron-probe microanalyses. Description of a fanning effect in a "fiber-like" BTO sample and some optical parameters of the as-grown BTO crystals are also reported here.

2. Experimental

Bismuth titanium oxide single crystals have been pulled by using an equipment that was especially built for the growth of sillenite structure materials. A resistive heating furnace has been used with the stabilization and regulation unit (Eurotherm) with accuracy not less than ± 1 °C. A Pt-PtRh thermocouple has been used to control the heater temperature. The vertical (axial) temperature gradient has been selected to get a smooth front of crystallization. The crystals were pulled from cylindrical crucibles 50 mm in diameter and 60 mm in height made from pure platinum and surrounded by an alumina ceramic shield to minimize the temperature oscillations inside the crucible during the growing process and to optimize the radial and axial temperature gradients in the hot part of the furnace.

Single crystals of $Bi_{12}TiO_{20}$ have been grown from high temperature nonstoichiometric (10:1) solutions of Bi_2O_3 and TiO_2 because according to the phase diagram of the binary system $Bi_2O_3-TiO_2$ (BRUTON 1974) (Fig. 1), bismuth titanium oxide melts incongruently at 873 °C. The starting melt has been prepared by thoroughly mixing appropriate amounts of bismuth carbonate $(BiO)_2CO_3$ (99.5%) and titanium oxide TiO_2 (99.9%) followed by melting at 900–950 °C in 48 h. All runs have been carried out in air. The single crystal's growth was initiated on the seeds of $Bi_{12}GeO_{20}$ oriented along the ⟨001⟩ and ⟨011⟩ axis, held in a pure platinum seed holder. The pulling rates were in the range 0.3–0.8 mm/h at the rotation rates of 20–30 rpm. These values are within the range of critical growth conditions established by BRICE et al. (1974). The crucible has not been rotated during the growth run. At the end of the pulling the crystal was withdrawn from the melt to a position about 10–15 mm above the melt surface, where it was annealed at temperature 845 °C. Then the crystal was cooled down to room temperature at a rate of 5–25 °C/h.

The structure of the as-grown crystals has been studied by powder X-ray diffraction using an automatic diffractometer RIGAKU-ROTAFLEX RO-200B with CuKα radiation. The external faces of the as-grown BTO single crystals have been indexed using the Laue method. The concentrations of bismuth and titanium have been determined by the electron-probe microanalysis on a Digital Scanning Electron Microscope DSM960 (Zeiss). They have been measured at least in 3 points of a crystal, at that the composition was checked in each point 3 times with an accuracy not less than 1%. We could not detect the oxygen concentration in the studied samples by available technique, therefore, the quantity of oxygen was calculated theoretically.

Two types of elements for further optical experiments were cut from the as-grown BTO crystals: "bulk" samples with dimensions 8 × 8 × 8 mm and "fiber-like" ones of 1 × 1 × 15 mm. End-faces of elements were polished with 1 µm alumina paste.

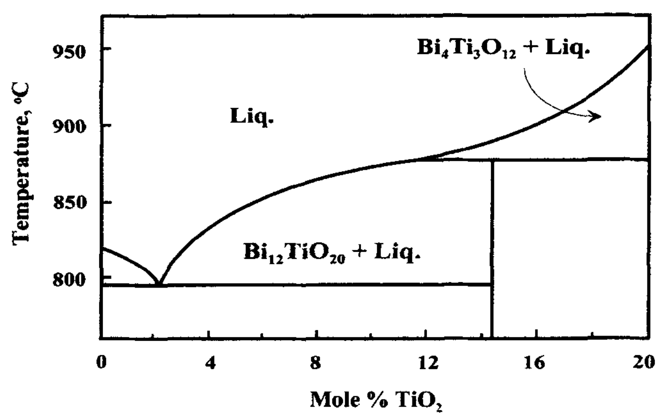

Fig. 1. Part of phase diagram of $Bi_2O_3-TiO_2$ binary system

Optical activity was determined on the "bulk" BTO sample by direct measurement of the angle of rotation of the polarization plane of the transmitted light at $\lambda = 0.633\ \mu m$ (He-Ne laser) and at $\lambda = 0.5145\ \mu m$ (Ar laser). Optical absorption was measured with a nonpolarized He-Ne laser beam. The linear electro-optic coefficient r_{41} was computed from a direct diffraction efficiency measurement in a self-stabilized holographic recording as described by DOS SANTOS et al.

Fanning effect has been studied in the "fiber-like" BTO sample cut along the ⟨110⟩ axis and glued between two electrodes so that the plane (111) was perpendicular to the electric field vector. The ac electric field of a square-wave form with pulse duration of 14 ms and with front duration of 2.5 ms was applied to the sample. Experiments were carried out at pump beam ($\lambda = 0.633\ \mu m$) incidence angles from $-56°$ to $+56°$ with respect to the element axis. The angular distribution of the fanning light has ben measured as a function of the incidence angle (KAMSHILIN et al.)

3. Results and discussion

High optical quality BTO single crystals up to 80 mm in length with diameters of 20 – 25 mm were grown by the proposed technique (Fig. 2). Single crystals were pale yellow in colour. All crystals have body-centered cubic structure characteristic of sillenite family with the unit cell parameter $\alpha_0 = 10.178 \pm 0.008$ Å. These data are in good agreement with earlier data published for $Bi_{12}TiO_{20}$ (SWINDELLS, GONZALEZ).

The crystals grown along both ⟨001⟩ and ⟨011⟩ crystallographic axes have clearly distinguished external faces. Crystals grown along the ⟨001⟩ axis have the most developed facets (100) and (010). Crystals grown along the ⟨011⟩ axis have the most developed facets (100) and $(01\bar{1})$ as shown in Figure 3. When a single crystal grows from the melt in an RF heating furnace, a cylindrical rod is usually produced. The crystal grown in high temperature solution has a cubic form with the planes (100), (010) and (001) as faces (BRICE et al. 1977). Sometimes the edges of the crystal are "chamfered" (110) planes. This form is also characteristic of the crystals pulled along the ⟨001⟩ axis from the melt in a resistive heating furnace. Such form is closer to the "equilibrium" shape. By our opinion, it means that the crystal growth process in a resistive heating furnace is carried out in conditions closer to "equilibrium" ones. The crystals grown in these conditions usually have higher optical quality, first of all, due to less steep axial and radial temperature gradients in this furnace compared with an RF heating one. However, striations perpendicular to the growth direction

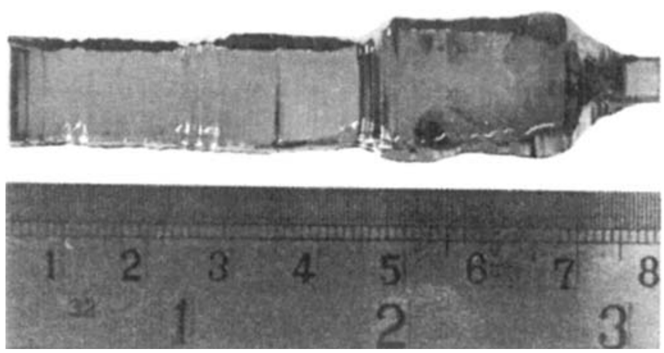

Fig. 2. $Bi_{12}TiO_{20}$ single crystal grown at IFQSC/USP

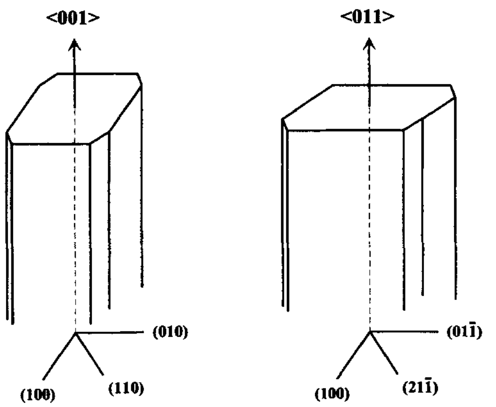

Fig. 3. Morphology of $Bi_{12}TiO_{20}$ single crystals with plane indices

was found to be the main defect in the grown crystals. Some crystals have a dark central core associated with a convex growth interface. These defects commonly occur in sillenite-type crystals. More detailed studied of the influence of the growth parameters on the structural perfection of the sillenite crystals are in progress.

The availability of highly homogeneous crystals is very important for the optical applications because of a significant effect of variations in the composition of grown sillenite crystals on its optical properties (ARRETT). The problem of obtaining homogeneous crystals is especially important for BTO crystals. Due to its incongruent melting, $Bi_{12}TiO_{20}$ single crystals cannot be grown directly from stoichiometric starting mixtures. One of possible techniques of producing these crystals is the growth from high temperature solutions containing some excess of Bi_2O_3, e.g. from 8 to 10 mol Bi_2O_3 per 1 mol TiO_2 (Fig. 1). The melt with a starting composition 10 $Bi_2O_3:TiO_2$ has been used for the growth of BTO crystals. According to the results of electron-probe microanalysis, the summary chemical composition of the grown BTO crystals in defect-free regions is close to the theoretical one and can be written down as $Bi_{12.1\pm0.2}Ti_{0.96\pm0.09}O_{20.1}$. These data are in good agreement with results obtained on single-crystal BTO fibers pulled by the LHPG method (PROKOFIEV et al.).

Natual optical actitivity ϱ of BTO crystals is 6.3 $\pm$ 0.2 deg/mm at $\lambda = 0.633$ μm and 11.9 $\pm$ 0.2 deg/mm at $\lambda = 0.5145$ μm, optical absorption coefficient $\alpha = 0.42 \pm 0.04\ cm^{-1}$ at $\lambda = 0.633$ μm and linear electro-optic coefficient $r_{41} = r_{52} = r_{63} = 5.3$ pm/V. The obtained results are in good accordance with data for bulk BTO crystals (FELDMAN et al.; FOX, BRUTON). The "bulk" BTO optical element has been used in an adaptive holographic interferometry system (BARBOSA et al.).

The angular distribution of the fanning light in the "fiber-like" BTO sample has been observed to differ significantly from that one in the "bulk" sample. In the latter case, the position of the gain factor maximum depends on the material parameters and is independent of the incident angle (STEPANOV, PETROV). In the "fiber-like" sample however, owing to the influence of internal reflections there are few maxima of gain factor marked A, B, C (Fig. 4). Two-wave mixing and double phase conjugation experiments were also carried out. Double phase conjugation mirror with conversion efficiency of 2–8% has been recorded in this sample in a wide range ($-12° - +18°$) of incidence angles of the pump at $\lambda = 0.633$ μm for 2×3 mW input light power. "Fiber-like" samples can be successfully

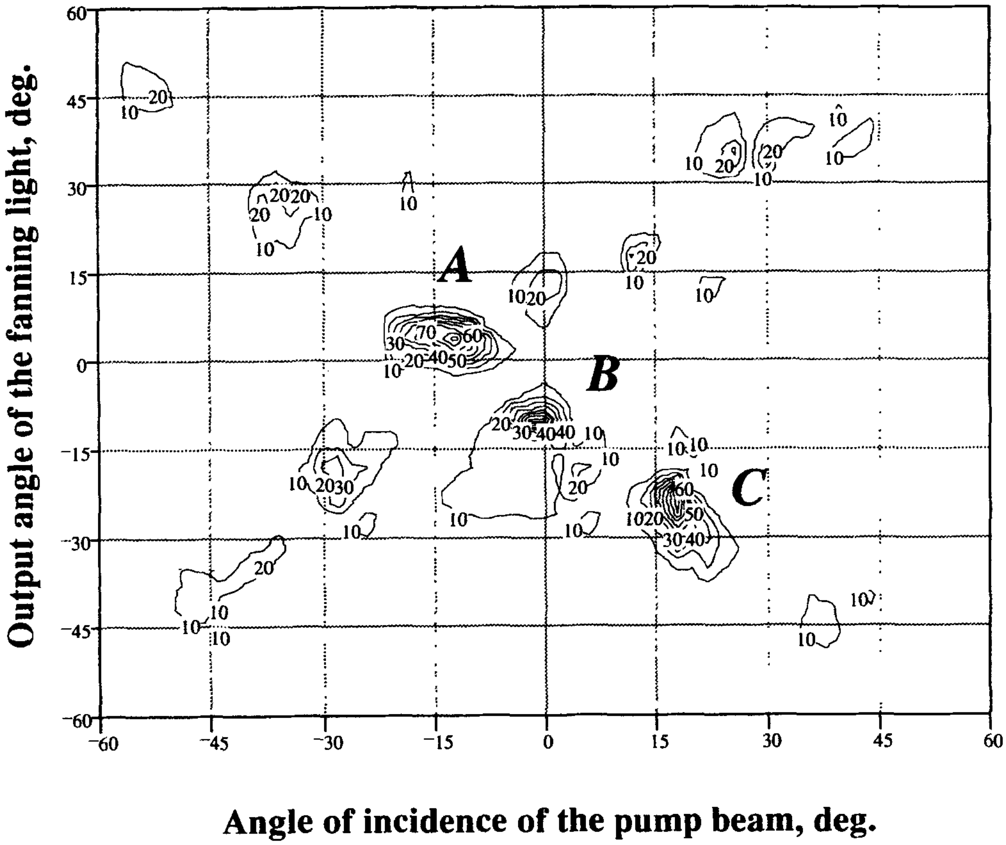

Fig. 4. Angular distribution of fanning light in a "fiber-like" BTO sample as a function of the incidence angle

used as a basic element for the experimental study of dynamic optical interconnections, associative memories, and optical implementation of neural networks.

More detailed optical and technological experiments are in progress and will be published elsewhere.

4. Conclusions

Large $Bi_{12}TiO_{20}$ single crystals of high optical quality were successfully grown from high temperature nonstoichiometric (10:1) solutions containing some excess of Bi_2O_3. The powder X-ray analysis, Laue method, and electron-probe microanalysis were used for characterization of the as-grown BTO crystals. The summary chemical composition of crystals in defect-free regions can be written down as $Bi_{12.1\pm0.2}Ti_{0.96\pm0.09}O_{20.1}$.

Natural optical activity ϱ of BTO crystals is 6.3 ± 0.2 deg/mm at $\lambda = 0.633$ µm and 11.9 ± 0.2 deg/mm at $\lambda = 0.5145$ µm, optical absorption coefficient $\alpha = 0.42 \pm 0.04$ cm^{-1} at $\lambda = 0.633$ µm, linear electro-optic coefficient $r_{41} = r_{52} = r_{63} = 5.3$ pm/V.

Fanning effect in the "fiber-like" BTO sample significantly differs from the "bulk" one. Double phase conjugation with conversion efficiency up to 8% has been observed in this sample in a wide range of incidence angles of the pump at $\lambda = 0.633$ µm for 2×3 mW input light power.

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