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Crystal Growth Of Mixed Titanium Sillenites

Top Seeded Solution Growth (TSSG) technique has been used to produce Bi₁₂TiO₂₀ (BTO) and some mixed Bi₁₂Ti_{0.8}M_{0.2}O₂₀ single crystals in which Ti was substituted with M=V, Pb or Ga. Pure Bi₄₀Ga₂O₆₃ (BGaO) single crystals have been grown, too. Thermal conditions enabling growth of uniform [110] sillenite single crystals with totally flat (110) interface have been found. Influence of composition on spectral characteristics of the BTO mixed crystals has been investigated.

Keywords: sillenites, BTO, top seeded solution growth, optical absorption

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1. Introduction

Sillenites, which have the structure of metastable cubic γ -Bi₂O₃, are formed during solid state reaction of Bi₂O₃ and many metallic and non-metallic oxides (of Ge, Si, Ti, Pb, Ga, B, etc.) mainly in 6:1 molar ratio. Sillenites have very good photorefractive, electro-optic, piezoelectric and photochromic (when doped) properties, what enable to use them in signal processing and optical memories (GÜNTER). Different techniques (Czochralski (BALLMAN), flux (BRUTON, MIYAZAWA), hydrothermal (BARSUKOVA)) were used to grow bulk sillenite single crystals.

The main objective of this work was the investigation of composition influence on spectral characteristics of pure and vanadium, lead or gallium substituted bismuth titanium oxide Bi₁₂TiO₂₀ (BTO). The best known sillenites, Bi₁₂SiO₂₀ (BSO) and Bi₁₂GeO₂₀ (BGO), melt congruently and can be grown by Czochralski technique. However BTO, like most of the sillenites, melts incongruently, what imposes the necessity of using high temperature solution growth technique. The main problem, which has to be overcome during crystallisation of typical oxide materials, is a non-uniform distribution of components and dopants inside the growing crystal. To obtain good quality BTO single crystals proper thermal and mechanical conditions, which guarantee stable crystal-melt interface, had to be found.

2. Experimental procedure

2.1 Crystal growth

Two-zone resistance furnace was used in these investigation. The lower heating zone was used to set proper temperature of the molten raw material while the upper zone enabled to

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influence axial and radial temperature gradients in the furnace. Additionally, changes of the position of the platinum crucibles in relation to the heating zones also influenced the thermal conditions near the interface. Two independent Eurotherm 906S regulators controlled the temperature of the heating zones. Large heat capacity of the resistance furnace made the temperature stabilisation relatively easy. The temperature stabilisation below the bottom of the crucible was equal to $\pm 0.1^\circ\text{C}$.

Pure BTO, mixed $\text{Bi}_{12}\text{Ti}_{0.8}\text{M}_{0.2}\text{O}_{20}$ ($\text{M}=\text{V}, \text{Pb}, \text{Ga}$), and $\text{Bi}_{40}\text{Ga}_2\text{O}_{63}$ (BGaO) single crystals were grown from high temperature solutions. Top Seeded Solution Growth (TSSG) on [110] BSO seeds was used. An excess of Bi_2O_3 has been used as a solvent. The starting composition of the melt (molar ratio of Bi_2O_3 and stabilising oxides) was equal to 9:1. In case of mixed crystals growth the molar ratio of titanium oxide and added vanadium, lead or gallium oxides was 4:1. The upper heating zone was placed above the growing crystals and acted as an afterheater. As a result temperature gradients were small and all crystals growing in the [110] direction had rectangular cross-sections and their bottoms were confined with crystallographic planes. The growing crystals were pulled up and rotated at the rates of 0.3mm/h and 45 rpm, respectively.

2.2 Optical investigations

The optical absorption measurements were performed in a broad spectral range by phase-sensitive method (choppered light, phase to reference signal) with use of the PAR Lock-in Amplifier Model 5209. Halogen and mercury 150W lamps were used as sources of light. The former lamp was used for probing, the latter one for samples coloration. For temperature measurements the Oxford Instruments Cryostat CF1104 (3.5-500 K) was used. The thermally bleached state was reached after 2 hours annealing at 200°C in the darkness.

3. Results and discussion

During a typical Czochralski growth of sillenites there are two possible modes of crystallisation: growth under conditions of natural or forced convection in the melt (MAJCHROWSKI). The former mode, in which hot melt flows from crucible walls towards growing crystal, results in circular cross-section and convex bottom of the crystal, strong tendency to form a core in the central part of the crystal, and non-uniform distribution of dopants. Owing to properly chosen temperature conditions (diminishing of the temperature gradients) and high enough rotation rate of the crystal, inversion of convection from natural to forced one happens when the growing crystal reaches some critical diameter, which dimension depends on such parameters as crucible diameter, radial temperature gradient, rotation rate, and viscosity of the melt. Owing to this inversion of flows the shape of the interface changes from convex towards the melt to flat or slightly concave. The melt flows up in the central part of the crucible, then it is cooled by the growing crystal. In this way the growing crystal is surrounded by relatively cool melt, what results in a change of the circular cross-section to one confined with flat faces, more uniform distribution of dopants and vanishing of the core. The inversion of flows can cause some instabilities of the diameter of the growing crystal, but benefits resulting from uniform composition of as grown crystals surpass the troubles connected with the temporary disturbance of growth.

In our investigations of mixed BTO single crystals the choice of growth conditions was evident – incongruently melting multi-oxide crystals have to be grown under conditions securing as uniform composition of crystals as possible. Only growth under conditions of forced convection in the melt, caused by relatively low temperature gradients, could result in proper homogeneity. The two-zone construction of the furnace enabled us to change thermal conditions in a broad range. Moreover, the use of high temperature solution growth considerably lowered the temperature of crystallisation, comparing to BGO and BSO growth. As a result the interface not only could be formed by one crystallographic plane, but even grow into the melt, still being confined with several flat planes. We found that the most advantageous, when homogeneity was sought, was the one-plane interface. Fig. 1 presents three BTO single crystals grown under different thermal conditions. The crystal marked as A was grown under lower axial temperature gradient, comparing with crystals B and C. One can see nine $\{100\}$ and $\{110\}$ planes, which form the interface. By increasing the temperature gradients we were able to influence the shape of the interface. In crystal B (110) plane forms nearly 30% of the interface, while in crystal C, grown under the highest temperature gradient, over 95% of the interface was totally flat (110) plane.

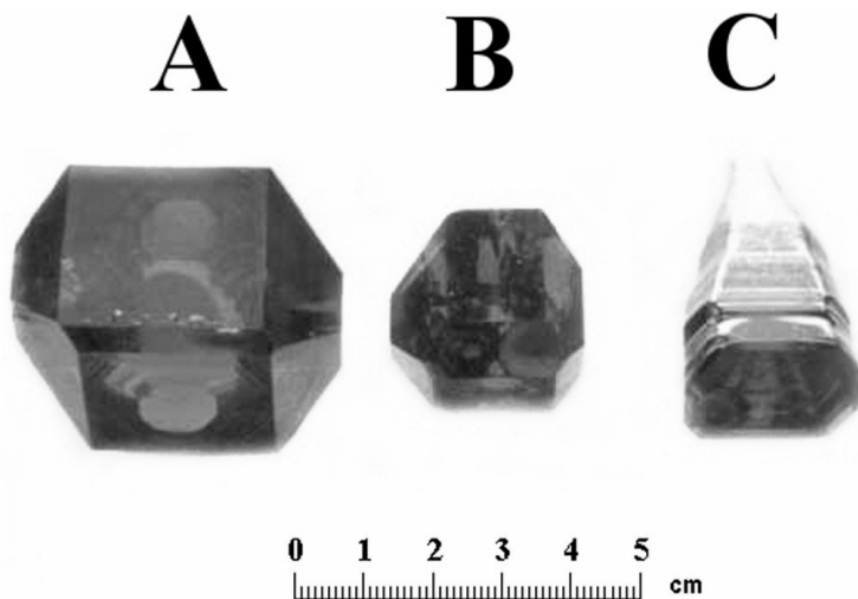


Fig. 1: Three BTO single crystals grown under different thermal conditions (see text).

In the initial stages of growth of mixed BTO crystals some defects were incorporated into crystals. Despite very small temperature gradients the natural convection existed in the melt when the crystal diameter was smaller than 5mm. After the diameter became bigger than approximately 5mm the rotations of the increasing crystal caused the inversion of flows, discussed earlier. Disturbances of melt flows influenced the thermal conditions in the vicinity of the interface, causing constitutional supercooling. As a result the crystal-melt interface

became unstable, although still flat, and some inclusions were incorporated. The distribution of the inclusions showed the shape of the interface in the initial stages of growth. After further increase of the crystal diameter the growth occurred under forced convection conditions and gave crystals free of such defects as inclusions, bubbles or cracks.

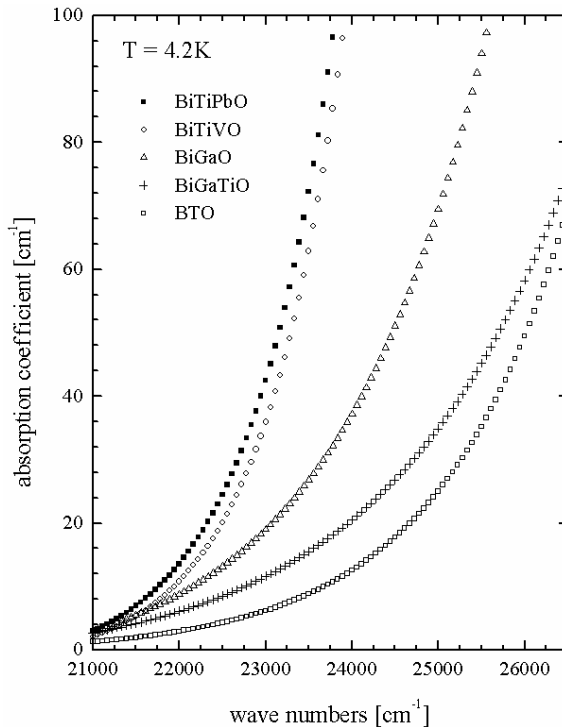


Fig. 2: Fundamental absorption edge for BTO, $\text{Bi}_{40}\text{Ga}_2\text{O}_{63}$ (BiGaO), $\text{Bi}_{12}\text{Ti}_{0.8}(\text{V},\text{Pb},\text{Ga})_{0.2}\text{O}_{20}$ (BiTiVO, BiTiPbO, and BiGaTiO) single crystals.

Spectral position of fundamental absorption edge is the main parameter characterising optical properties of single crystals. Its shape depends on the kind of transition between the valence and conductance bands. The dependence has power function character with power index depending on the kind of transition (direct, indirect; allowed, forbidden). In some cases it is connected with creation of excitons, while in others it may be influenced by strong defecting or doping of single crystals. In the last two cases, as a rule (KURIK), an exponential dependence of fundamental absorption edge is observed. For all described above sillenite single crystals (pure and mixed) coefficients of optical absorption in the region of fundamental absorption edge have been measured. The results are shown in Fig. 2. The shape of the absorption edges of all investigated sillenites is exponential. Sillenites, containing characteristic tetrahedral structures MO_4 (where $\text{M}=\text{Ge}, \text{Si}, \text{Ti}, \text{Pb}, \text{V}, \text{Ga}$ etc.), are cubic crystals in which metal ions stabilise $\gamma\text{-Bi}_2\text{O}_3$ phase (so called $\gamma^*\text{-Bi}_2\text{O}_3$ phase). Very profound influence of electronegativity of Ga^{3+} , V^{5+} and Pb^{2+} ions placed in tetrahedral positions can be seen. Decreasing electronegativity of the ions ($\text{Ti}^{4+} > \text{Ga}^{3+} > \text{V}^{5+} > \text{Pb}^{2+}$) leads to shift of fundamental edge towards lower energies (energy gap of a given material decreases).

This result clearly shows that electron states of tetrahedral ions define the energy gap (BOROWIEC 1990).

The photochromic effect was found in all pure (having no intentionally introduced dopants) investigated sillenites (BRIAT, OBERSCHMID, BOROWIEC 1997). In Fig. 3 the exemplary photochromic spectrum of a pure BTO crystal is presented. It consists of at least three bands and is very similar to photochromic spectra of pure BGO and BSO crystals. The main difference is a shift to lower energies (about 0.25 eV). The stability of the photochromic effect in pure BTO is shifted to lower temperatures - the characteristic temperature equals 165 K (see insert in Fig. 3) (NGUYEN).

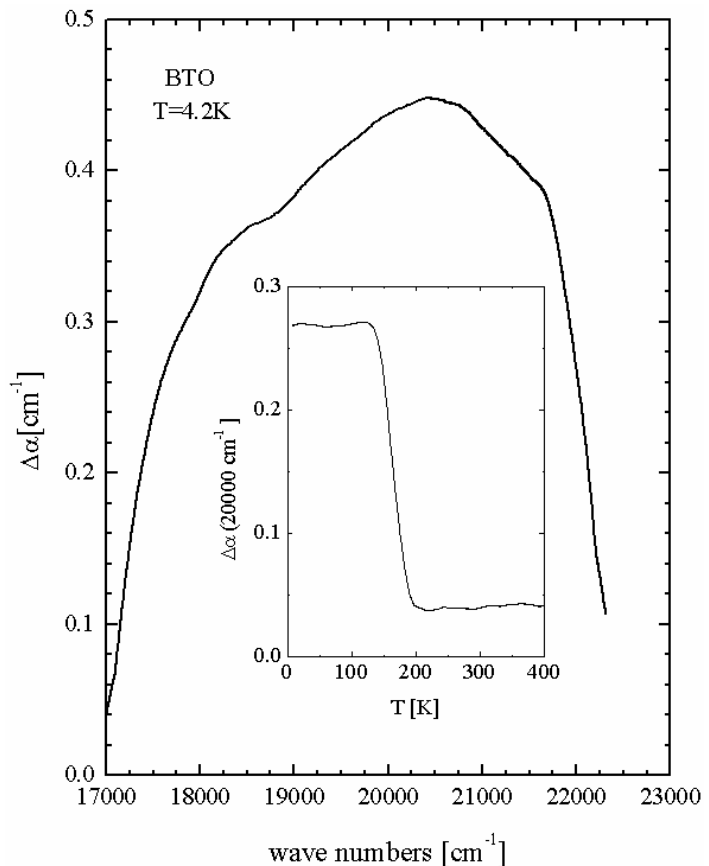


Fig. 3: Photochromic spectrum of BTO at 4.2 K after 1 min. Hg 436 nm illumination. Insert - dependence of photochromic absorption (at 20000 cm^{-1}) on temperature (photochromic stability curve).

4. Conclusions

Pure $\text{Bi}_{12}\text{TiO}_{20}$ and $\text{Bi}_{40}\text{Ga}_2\text{O}_{63}$, and mixed $\text{Bi}_{12}\text{Ti}_{0.8}(\text{V},\text{Pb or Ga})_{0.2}\text{O}_{20}$ single crystals have been grown with use of the TSSG technique. Good thermal stabilisation of growth parameters has been obtained due to two-zone resistance furnace. Growth under conditions of forced convection in the melt gave good quality mixed BTO crystals having flat (110) bottom. Some inclusions observed in the initial phase of growth were caused by the

constitutional supercooling occurring due to inversion of flows in the melt. Energy gap of investigated sillenites depends on electronegativity of ions placed in tetrahedral positions. Photochromic properties have been observed in all investigated samples.

Acknowledgments

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