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Synthesis, Crystal Growth and Characterization of γ-Phase Bismuth Titanium Oxide with Gallium

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Gallium solubility in the $Bi_{12}TiO_{20}$ (BTO) matrix was investigated by solid state reaction synthesis and $Bi_{12}Ti_{(1-x)}Ga_xO_{20}$ (BTGaO) single crystals were grown by Top Seeded Solution Growth (TSSG). We determined that it is possible to obtain a continuous solid solution from $(x)Bi_{12}TiO_{20}$: $(1-x)Bi_{12}[Ga_{0.7}Bi_{0.3}]O_{20}$ and that Ga replaces Ti in the BTO matrix giving $Bi_{12}Ti_{(1-x)}Ga_{(x)}O_{20}$ up to $x < 0.2$. BTGaO single crystals grown with an excess of Bi_2O_3 were transparent, a bleaching effect was observed due to the presence of gallium in the crystalline sillenite structure and their lattice parameter was higher than for pure BTO. The results for BTGaO single crystals showed an increase in the optical activity from $\rho_0 = 6.4° \pm 0.3°/mm$, for BTO, to $\rho_0 = 9.7° \pm 0.3°/mm$, for BTGaO grown with $x = 0.30$ in the melt. The BTGaO crystal presented an activation energy value of 0.48 ± 0.02 eV for $100\ °C \le T \le 300\ °C$.

Keywords: *crystal growth, bismuth titanium oxide, optical material*

1. Introduction

Bismuth oxide (Bi_2O_3) is an interesting dielectric material with potential applications such as optical coatings, in metal/insulator/semiconductor (MIS) capacitors and integrated microwave circuits[1]. The Bi-O system is rather complicated and can have four different main crystalline phases, usually indicated by the letters α, β, γ and δ. Recently, a new polymorphic form of Bi_2O_3 with the A-type rare-earth sesquioxide structure was synthesized by a high-pressure technique[2]. Each of these phases has different electrical and optical properties[3]. The γ-phase bismuth oxide is a very important material for optical applications when stabilized at room temperature. The γ-phase can be stabilized by adding some ions to its crystalline structure. When this is done, the resulting compounds are known as sillenite, named after Sillen, who discovered this special class of materials[4,5].

Sillenite crystals are of the $Bi_{12}MO_{20}$ type, where M = Si, Ge, Ti and others, and crystallize in the I23 space group. They have a number of interesting properties, including piezoelectric, electro-optical, elasto-optical, optical activity and photoconductivity. Of particular interest is the combination of electro-optical and photoconductivity properties, which results in the so-called photorefractive effect, consisting of a reversible light-induced change in the refractive index[6]. Because of these properties, sillenite crystals are useful for many advanced and potentially promising applications, such as a reversible recording medium for real-time holography or for image processing applications[7,8]. Bismuth titanium oxide, $Bi_{12}TiO_{20}$ (BTO), has some practical advantages in terms of its isomorphous $Bi_{12}SiO_{20}$ (BSO) and $Bi_{12}GeO_{20}$ (BGO), including lower optical activity, higher electro-optic coefficient and increased sensitivity to red light[8].

In recent years, many articles have been published about the influence of impurities added to these crystals in the attempts that have been made to improve their optical properties[9]. Gallium doped BTO crystals (BTO:Ga) and pure $Bi_{12}Ga_xBi_{1-x}O_{19.5}$ (BGaO), in particular, have lately been prepared but few reports discuss the synthesis, growth process and properties of these crystals[10-11]. This paper discusses our investigation of the solubility of gallium in the BTO matrix using solid state reaction synthesis, the growth of $Bi_{12}Ti_{(1-x)}Ga_xO_{20}$ (BTGaO) single crystals by the Top Seeded Solution Growth (TSSG) method and struc-

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tural (X-ray powder diffraction technique, differential thermal analysis (DTA), electron probe microanalysis, optical microscopy), optical (optical absorption, optical activity, electro-optic coefficient, photocurrent response) and electrical (impedance spectroscopy) characterization.

2. Experimental

Bismuth oxide (Johnson Matthey, 99.9995%), titanium oxide (Johnson Matthey, 99.995%) and gallium oxide (Trikol/Ventron Division, 99.99%) were employed as starting materials in the solid state reaction used as synthesis process. After being weighed in suitable molar proportions, the compounds were mechanically mixed to obtain a homogeneous product, which was put into a pure platinum crucible, placed in a resistive furnace and heated to 800 °C. After one hour at this temperature, the material was removed and finely ground with a mortar, after which it was returned to the furnace. This procedure was repeated eleven times over a 96-hour period. In the first grinding procedure, isopropyl alcohol was used as a liquid medium to improve the mixing. In this case, the material was air dried before being returned to the furnace.

The crystals were made through the Top Seeded Solution Growth method using a resistive heating furnace equipped with an 808 Eurotherm microprocessor-based digital temperature controller unit attached to a Pt-Pt10%Rh thermocouple. The temperature fluctuations were typically lower than 0.3 °C, as measured near the crucible. An axial temperature gradient above the melt of about 10 °C/cm was measured with a platinum thermocouple attached to the seed holder. High purity cylindrical platinum crucibles, with approximate dimensions of 35 x 35 mm, were used. The starting batch melt was prepared by thoroughly mixing appropriate amounts of bismuth oxide (Johnson Matthey, 99.9995%), titanium oxide (Johnson Matthey, 99.995%) and gallium oxide (Trikol/Ventron Division- 99.99%), followed by melting. All runs were carried out in an open-air environment. BGO seeds oriented along the [001] direction, contained in a pure platinum seed holder, were used to initiate crystal growth. Pulling rates ranging from 0.25 to 0.30 mm/h and 25 to 30 rpm rotation rates were used. After their growth was completed, the crystals were annealed at 700 °C in an appropriate furnace to reduce thermal stresses.

X-ray powder diffraction spectra were collected using CuKα radiation from an automatic diffractometer RIGAKU-ROTAFLEX RU-200B equipped with a rotatory anode. Data collection was made in the step scan mode in the 2θ range from 5 to 120° with 0.02° step interval and a step time of 3 s. The samples were very fine powder. Lattice parameters were calculated by the least square method using a computational program. Differential Thermal Analysis (DTA) measurements were carried out in a TA Instrument DSC 2090 at 10 °C/min. The samples (~35 mg) used were very fine powder obtained from single crystals. Pure platinum crucibles were used in all the trials.

Single crystal optical quality was evaluated using an optical microscope with and without polarized light. The presence of gallium in the crystals was verified with a ZEISS Digital Scanning Electron Microscope (DSM960) equipped with a QX 2000 Link Energy Dispersive Spectrometer (EDS).

All optical measurements were performed at room temperature using carefully polished BTGaO samples. Optical absorption in the visible region was measured with a Cary 17 spectrophotometer. The photocurrent response was measured in a transverse geometry with silver electrodes arranged as two strips separated by 1 mm. The applied d.c. voltage was of 100 V. A Keythley 602 electrometer was used for current detection. The spectral range of excitation light used was from 700 to 400 nm. For optical activity measurements the crystal was placed between a polarizer and an analyzer and was illuminated by a 633 nm line of a He-Ne laser. The angle of rotation of the polarization plane was measured by rotating the analyzer until extinction. The rotatory power (ρ_0) was obtained by the ratio of the rotation's angle and the crystal's thickness. The effective electro-optic coefficient (r_{41}) was measured for $\lambda = 633$ nm, by using the method described in the literature[12, 13].

The electrical characterization was performed by impedance spectroscopy on 8 x 8 x 2 mm samples oriented along [100] direction. The samples were cleaned with acetone in an ultrasonic cleaner for 3 min and dried at 100 °C. The electrodes required for the eletrical measurements were deposited on both faces of the sample by applying silver paste, which was dried at 400 °C for 15 min.

The electrical measurements were made from 5 Hz to 13 MHz, with an applied potential of 500 mV, using a Solartron 1260 Impedance Analyzer controlled by a personal computer. The samples were placed in an appropriate sample holder with a two-electrode configuration. The ac measurements were made from 100 °C to 300 °C with a 20 °C temperature step. A 30-minute interval was adopted prior to thermal stabilization after each measurement. All the measurements were carried out in atmospheric air.

The data were analyzed using the "Equivalent Circuit" (Equivcrt) software, a package for the analysis of complex immittance spectra.

3. Results and Discussion

3.1. Solid state reaction synthesis

An initial series of solid state reaction experiments was made using the molar proportion $6Bi_2O_3$: $(1-x)TiO_2$: $x/2Ga_2O_3$ for x = 0.10, 0.20, 0.45 and 0.50. We verified that gallium can replace titanium in the BTO matrix giving the chemical formula $Bi_{12}Ti_{(1-x)}Ga_xO_{20}$ for x = 0.10 and 0.20.

Under these conditions, a homogeneous phase with sillenite structure is obtained, as verified by X-ray powder diffraction. For higher values of x (x = 0.5) another phase appears in addition to the sillenite. Some X-ray reflections resulting from this new phase, not identified, are shown in the insert in Fig. 1. This suggests that, for lower concentrations of gallium, the BTO structure can easily accommodate the gallium ions in the tetrahedral position, partially replacing the titanium ions. However, higher concentrations of gallium in the solid solution require an excess of bismuth oxide in comparison with the stoichiometric composition to obtain a single sillenite structure. This is due to the non-stoichiometric character of BGaO, whose chemical formula should be written $Bi_{12}[Ga_xBi_{(1-x)}]O_{19.5}$, where x can range from 0.5 to 0.7[10].

Considering the non-stoichiometric character of BGaO it was possible to obtain a homogeneous solid sillenite structure solution with the $Bi_{12}Ti_{0.5}[Ga_{0.35}Bi_{0.15}]O_{19.75}$ and $Bi_{12}Ti_{0.05}[Ga_{0.665}Bi_{0.285}]O_{19.525}$ compositions. The X-ray powder patterns of the materials thus obtained are shown in Fig. 1. Table 1 shows the lattice parameters values for differents gallium concentrations. The diffraction lines due to $K\alpha_2$ radiation were extracted by software to calculate ones. The lattice parameters of BTO and BGaO are also given for comparison. Our results show that it is possible to obtain a continuous solid solution of the $(x)Bi_{12}TiO_{20}$:$(1-x)Bi_{12}[Ga_{0.70}Bi_{0.30}]O_{19.5}$ type with x ranging from 0 to 1. However, there is a solubility limit if one attempts to directly substitute Ti with Ga in the $Bi_{12}Ti_{(1x)}Ga_xO_{20}$ chemical formula.

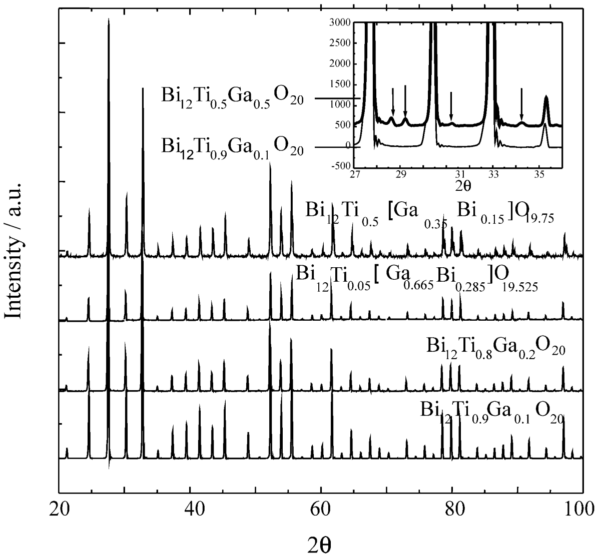

Figure 1. X-ray powder diffraction of $Bi_{12}Ti_{0.90}Ga_{0.10}O_{20}$; $Bi_{12}Ti_{0.80}Ga_{0.20}O_{20}$; $Bi_{12}Ti_{0.05}[Ga_{0.665}Bi_{0.285}]O_{19.525}$; $Bi_{12}Ti_{0.5}[Ga_{0.35}Bi_{0.15}]O_{19.75}$. Insert see details in text. In $Bi_{12}Ti_{0.5}[Ga_{0.35}Bi_{0.15}]O_{19.75}$ the $K\alpha_2$ diffraction lines are present.

Table 1. Lattice parameter for materials with different gallium concentrations obtained by solid state reaction synthesis.

Samples	Lattice parameter (Å)
$Bi_{12}TiO_{20}$ (BTO)	10.173(5)
$Bi_{12}Ti_{0.9}Ga_{0.1}O_{20}$	10.177(6)
$Bi_{12}Ti_{0.8}Ga_{0.2}O_{20}$	10.182(3)
$Bi_{12}Ti_{0.05}$ $[Ga_{0.665}$ $Bi_{0.285}]$ $O_{19.525}$	10.182(6)
$Bi_{12}Ti_{0.5}$ $[Ga_{0.35}$ $Bi_{0.15}]$ $O_{19.75}$	10.183(4)
$Bi_{12}GaO_{20}$ (BGaO)	10.182(3)

3.2. Crystal growth

BTGaO single crystals were grown from a liquid phase with the $10Bi_2O_3$: $(1x)TiO_2$: $x/2Ga_2O_3$ composition, where x = 0, 0.10 and 0.30. The melting point of the crystals decreases from 875 °C for nominally pure BTO to 822 °C for BGaO, as determined by DTA. Figure 2 shows a BTGaO crystal as grown. An evident characteristic of BTGaO crystals was the bleaching effect associated to the presence of gallium.

Only around one third of the starting charges in all growth experiments were crystallized. Figure 3 shows the X-ray emission spectrum of a BTGaO sample, obtained by EDS, where $K\alpha$ gallium line is noticed. An accurate quantitative gallium concentration measurement using EDS was not possible because of the superimposition of the gallium $K\alpha$ and bismuth $L\iota$ lines. Despite the difficulties involved in the growth of these crystals, good optical quality samples were obtained from the principal crystal body parts.

Growth defects such as striations, core and inclusions are frequent in sillenite family crystals. Optical microscopy was used to analyze these defects in our crystals. We found that the greater the gallium content, the more difficult the growth process and that there was a drastic increase in the occurrence of such defects. Growth striations are frequent in doped-crystals or in crystals that show some degree of non-stoichiometry. They correspond to compositional variations associated to the growth rate fluctuations that derive from changes in the solid-liquid interface temperature due to the convective process in the liquid phase[14]. The striations in our crystals are more evident owing to the higher gallium content in the liquid phase. The inclusions and voids that appear are associated mainly to the highly convex

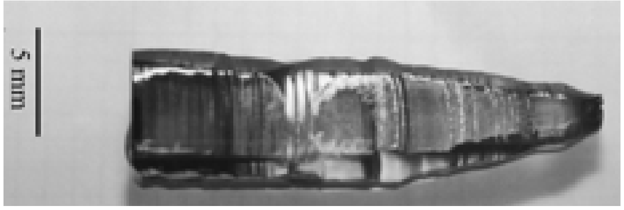

Figure 2. BTGaO single crystal grown by top seeded solution growth.

growth interface, which is characteristic of the crystal shoulder region. They can also appear during the interface shape transition from convex to planar owing to growth interface instabilities produced by changes in the liquid convective fluxes that occur during this process. The core, a darker central column, is a characteristic defect in sillenite family crystals when the solid/liquid interface is convex. A core with a markedly darker coloration in comparison with nominally pure BTO appears in crystals with a high concentration of gallium. The core is absent in regions of crystals with a planar or slightly concave solid/liquid interface.

3.3. Optical properties

The optical activity grows linearly with the increase of the gallium content in the crystals from $\rho_0 = 6.4 \pm 0.3$ °/mm, for nominally pure BTO, to $\rho_0 = 9.7 \pm 0.3$ °/mm, for BTGaO grown with x = 0.30 in the melt. The gallium doping decreases the optical absorption coefficient by about 80% in the wavelength range of 700 to 550 nm and it causes the displacement of the absorption edge to smaller wavelengths. The dark current is increased approximatelly by four orders of magnitude in gallium-doped crystals, and no photocurrent response was detected in the range of 700 to 400 nm. The gallium presence doesn't cause significant change in the electro-optic coefficient value of BTO crystals ($r_{41} = 5.6$ pm/V).

3.4. Electrical properties

The electrical characterization of BTGaO, grown with x = 0.30 in the melt, was carried out by impedance spectroscopy. Figure 4 shows the impedance spectra present in the Z'' *vs.* Z' plots of the BTGaO obtained at different temperatures. The diagrams show only the contribution in the high frequency region assigned to bulk response. No electrode effect was seen in the analyzed frequency range. The fitting curve showed good agreement with experimental data. The electric response was further fitted by a parallel RC equivalent circuit in the frequency range analyzed, where R represents the bulk resistance and C the bulk or geometric capacitance of the samples.

The electric conductivity of the bulk was plotted as a function of the temperature in an Arrhenius plot (Fig. 5). The activation energy for conduction was derived from slope plot was equal to 0.48 ± 0.02 eV. Only one slope is apparent over an entire set of the measurements. By extrapolation of the curve log σ x 1/T (Fig. 5) the resistivity value of 2.9×10^9 Ω cm at room temperature was obtained.

The $Bi_{12}TiO_{20}$ phase presents an activation energy value of 0.99 eV for 400 °C ≤ T ≤ 700 °C with a resistivity of 8.5×10^{14} Ω cm at room temperature[16,17]. Thus, the gallium doped BTO exhibit a significant change in the activation energy and resistivity values (four orders of magnitude for 100 °C ≤ T ≤ 300 °C). By comparison with the $Bi_{12}TiO_{20}$

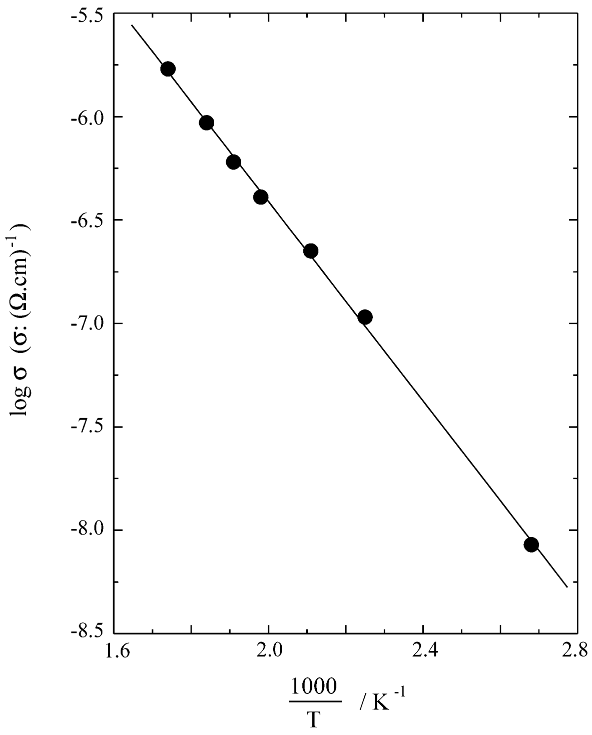

Figure 5. Arrhenius plot of electrical conductivity of BTGaO single crystal.

According to literature[8], the $(Bi_{Si}^{3+} + h_o^{+})$ defect is observed in $Bi_{12}SiO_{20}$ in view of the ultrasonic attenuation center with tetrahedral symmetry, which has been associated with an absorption shoulder. In gallium doped $Bi_{12}SiO_{20}$ this absorption shoulder is absent. This bleaching effect have been explained by assuming the transformation of the intrinsic defect $(Bi_{Si}^{3+} + h_o^{+})$ to Bi_{Si}^{5+}. Considering the $Bi_{12}TiO_{20}$ structure similar to the $Bi_{12}SiO_{20}$ one, the addition of the gallium can result in the Bi_{Ti}^{5+} defect in $Bi_{12}TiO_{20}$, as suggested by Oberschmid[19]. Substitution of Ga on Ti sites, however, result in acceptors levels responsible for the p type conduction. Thus, the activation energy value of 0.48 ± 0.02 eV can be associated to the sub-level in band gap edge below the conduction band.

4. Conclusions

In solid state reaction synthesis process gallium can replace titanium in the BTO matrix giving $Bi_{12}Ti_{(1x)}Ga_xO_{20}$ chemical formula for x up to 0.20. A continuous solid solution was possible when considered the non-stoichiometric character of BGaO. BTGaO single crystals of optical quality were grown from a liquid phase with up to 30% of gallium ions in the nominal liquid composition. Growth defects as striations were more evident in crystals with higher gallium content in the liquid phase. A bleaching effect was observed due to the presence of gallium in the crystalline sillenite structure. Its optical absorption was decreased for holographic applications. The electrical properties of BTGaO single crystal can be described as parallel RC circuits. The electrical conductivity follows an Arrhenius law with an activation energy of 0.48 ± 0.02 eV, which can be associated to the sub-level in band gap edge below the conduction band.

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