Preparation and photoconduction of rapidly quenched films in the Bi_2O_3-TiO_2 system

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The rapidly quenched films in the Bi_2O_3-TiO_2 system (0 to 60% TiO_2) were prepared using a twin-roller type apparatus. The films precipitated Bi_2O_3 solid solutions of different types in the composition ranges, with TiO_2 contents of 0 to 5, 7.5 to 10 and 12.5 to 40%, respectively. The first solid solution had a tetragonal structure of β-form. The second, though also crystallized in the tetragonal structure, adopted a disordered modification of the β-form. The third solid solution was δ-form (defect fluorite structure). The formation of amorphous phase commenced in the composition with 30% TiO_2, and the films became completely amorphous beyond 50% TiO_2. The quenched films showed a certain instability to decompose or transform into the different phase assemblage by annealing at higher temperatures (about 400 to 500° C, except 260° C for the pure Bi_2O_3 film). The quenched films were also characterized by a high photoconductivity. The photoconduction mechanism was suggested to be associated with a structural imperfection of Bi_2O_3 accompanied by a certain amount of pentavalent bismuth ion.

1. Introduction

Crystals of the γ-family (b c c structure), such as $Bi_{12}SiO_{20}$, $Bi_{12}GeO_{20}$ and $Bi_{12}TiO_{20}$, are of interest because of their photo-effects [1–4]. Photoconductors based on Bi_2O_3, other than these γ-type crystals, were little known, until the present authors prepared a new type of photoconductive film by rapidly quenching the Bi_2O_3 melts containing a small amount of a second oxide of M_2O_5 and MO_3 types using a twin-roller type apparatus [5, 6]. The crystal phases formed in the photoconductive films were related to δ-Bi_2O_3 in structure, which adopts a defect fluorite structure (f c c); that is, the films precipitated the crystal phase with a tetragonally distorted δ-structure when the amount of second oxide was relatively poor, while the crystal phase with δ-structure was precipitated by a further increase in the amount of additive. The addition of a second oxide was essential to produce photoconductive films. As a result of examining the effect of addition of other oxides, it was confirmed that a number of oxides have this effect. Amongst these, titanium dioxide (TiO_2) proved to be one of the important additives.

In this report, the preparation of rapidly quenched films in the Bi_2O_3-TiO_2 system using a twin-roller type apparatus, and their characterization, are described. In particular, the phase relation in the quenched films is discussed together with the grain-orientation, thermal stability and photoconductivity.

2. Experimental techniques

Reagent grade Bi_2O_3 and TiO_2 were used for preparing the samples. Oxide mixtures with different TiO_2 content (0 to 60 mol % TiO_2) were heated in air at 750° C for 5 h. After being finely ground, they were pressed into rods (5 × 5 × 30 mm^3) and sintered under the same heating conditions. The sintered samples were melted and quenched to produce films by using a twin-roller type apparatus attached to an infrared image furnace [7].

Phase analysis was carried out by X-ray diffractometry. The lattice parameters of the crystal phases formed in the samples were measured where possible. The thermal stability of the quenched films was examined by differential thermal analysis (DTA). Electrical contacts to the film surface were made by commercial conductive silver paste. Photoconductivity was then measured at room temperature using an electrometer (Advantest, TR8652) while scanning the wavelength of the incident light from a spectroirradiator (Jasco, CRM-FA) in the range 300 to 700 nm. The intensity of the light was high enough to saturate the photoconductivity, although it was distributed in the range 8×10^4 to $2 \times 10^5 \, erg \, cm^{-2} \, sec^{-1}$ in compliance with the wavelength.

3. Results and discussion
3.1. Solid phase reaction
In Table I, the results of phase analysis in the samples

x in $(Bi_2O_3)_{1-x}(TiO_2)_x$	Solid phase reaction $(750°C, 5h, \times 2)$	Rapid quenching (twin-roller method)
0	α	$\alpha + \beta$
0.025	$\alpha + \gamma$	$\alpha + \beta$
0.05	$\alpha + \gamma$	β
0.075	$\alpha + \gamma$	β'
0.1	$\alpha + \gamma$	β'
0.125	$\alpha + \gamma$	δ
0.143	γ	δ
0.2	$\gamma + BT$	δ
0.3	$\gamma + BT$	$\delta + AM$
0.4	$\gamma + BT$	$\delta + AM$
0.5	$\gamma + BT$	AM
0.6	BT	AM

α, α-Bi_2O_3; β, β-Bi_2O_3 solid solution (ss); β', β'-Bi_2O_3 ss; γ, γ-$Bi_{12}TiO_{20}$; δ, δ-Bi_2O_3 ss; BT, $Bi_4Ti_3O_{12}$; AM, amorphous.

prepared by two heat treatments at $750°C$ for $5h$ with a grinding process in between, is shown together with the data observed in the quenched films. From the phase diagrams in the Bi_2O_3–TiO_2 system reported by Levin and Roth [8] and Bruton [9], it can be seen that two stable compounds γ-$Bi_{12}TiO_{20}$ and $Bi_4Ti_3O_{12}$ exist in the composition range containing up to 60 mol % TiO_2. The phase relation observed through the solid phase reaction in the present work also supported the existence of these two compounds.

3.2. Rapid quenching

As a result of rapid quenching treatment of the Bi_2O_3–TiO_2 melts, thin films (about $20\,\mu m$ thick) were obtained in fragments (less than 10 mm long) because of the fragility. The colour of the quenched films changed from an orange–red to a pale yellow as the TiO_2 content increased. Blackening was assumed on the films above 30% TiO_2. The crystalline films were translucent while the amorphous state was transparent.

Compared to the samples prepared by the solid phase reaction, the quenched samples showed a quite different feature in the phase relation. In the compositions examined, tetragonal solid solution, cubic solid solution and amorphous phase are formed, in that order, with increasing TiO_2 content. The tetragonal phase existed in two types. The first is formed in the pure Bi_2O_3 and in the composition containing up to 5% TiO_2 and has β-structure which is a two-dimensional superstructure of δ-structure [10]. The second was obtained when the TiO_2 content was 7.5 to 10%, and the structure looked like a disordered modification of β-structure because of the absence of superstructure reflection in the X-ray diagram. This phase is termed the "β'-phase". The cubic phase formed in the composition range with 12.5 to 40% TiO_2 is of δ-form. The formation of amorphous phase commenced in films containing 30% TiO_2, and a completely amorphous state was realized when the TiO_2 content was 50% or above. This may be due to the action of TiO_2 as glass former.

In Fig. 1, lattice parameters, a_0, c_0 and $V_0^{1/3}$ for the β-and β'-phases and a_0 for the δ-phase are plotted together as a function of the TiO_2 content. In this figure, however, the lattice parameter of the β-phase is
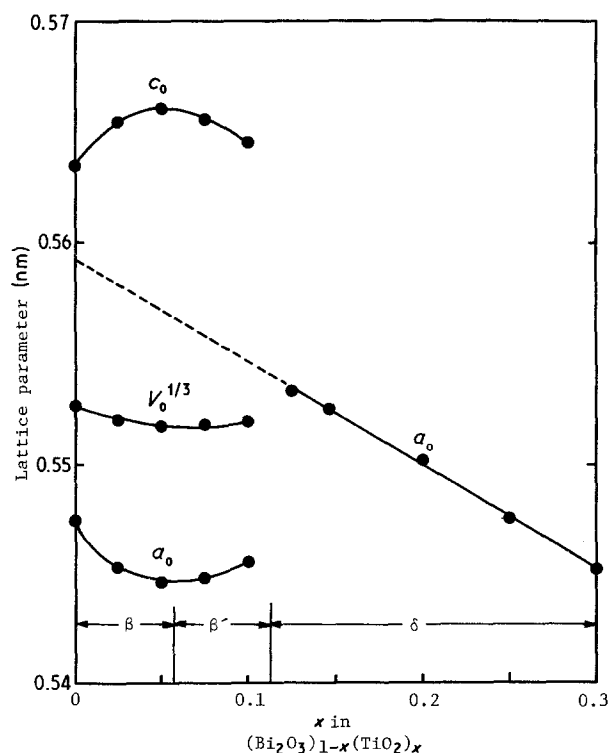

Figure 1 Lattice parameters, a_0, c_0 and $V_0^{1/3}$, of Bi_2O_3 solid solutions formed in the quenched films as a function of TiO_2 content.

represented in the same manner as in the δ-phase in order to make the structural interrelation between these phases easier. Because the a-axis of β-structure is parallel to the $\langle 1\,1\,0 \rangle$ of the δ-structure [11], $2^{1/2}a_0$ is the true parameter for the β-structure. A deflection is seen on the curves of a_0 and c_0 at 5% TiO_2. This is considered to be due to a change in the nature of the cation distribution coincident with the change from β-structure to its disordered form. As previously reported [5], the lattice parameters were measured for the tetragonal phases obtained by rapidly quenching the Bi_2O_3–M_2O_5 melts, and a deflection was also observed at 2.5% M_2O_5 on the curves of lattice parameter against M_2O_5 content. Although no attention was particularly paid to whether the β-phase existed or not in the quenched phase in that study, the quenched phase containing 2.5% M_2O_5 may be β-form from the analogy of the deflection. In practice, it is difficult to judge if the crystal is β-form or not, because the intensity of the superstructure reflection is very weak. In the present work, judgment was made easier by passing a high intensity X-ray beam through a monochromator.

The curve of $V_0^{1/3}$ against TiO_2 content deviates sharply downwards from the dotted line drawn by extrapolation of linear a_0 against TiO_2 content for the δ-phase. The deviation means that the β- and β'-structures are more contracted than the δ-structure. When a melt is cooled at a sufficiently high speed, it is usually crystallized in a more open and symmetrical form, even though an amorphous state is not realized. From this viewpoint, the formation of the tetragonal phase through rapid quenching is conflicting, because it is neither open nor symmetric compared to the δ-phase. Considering that the β- and β'-structures are not widely different from the δ-structure, the occurrence of the denser structure is inexplicable so far as

they consist only of the ions Bi^{3+}, Ti^{2+} and O^{2-}, and oxygen vacancy. As β-Bi_2O_3 is said to maintain its structure over a wide nonstoichiometric composition range ($BiO_{1.5}$ to $BiO_{1.75}$), suggesting the existence of pentavalent bismuth (Bi^{5+}) [10], it is probable that the quenched phases prepared in this work also dissolve an excess amount of oxygen. If the β- and β'-phases contain a certain amount of Bi^{5+}, the reason for the formation of denser structure is rationalized, because Bi^{5+} is smaller than Bi^{3+}. The reason for the preference of tetragonal structure in the Bi_2O_3-rich side is also believed to be associated with the existence of Bi^{5+}. In addition, it is seen that $V_0^{1/3}$ changes little despite the increase of TiO_2 content. This is considered to be because the Bi^{5+} turns into Bi^{3+} with increasing TiO_2 content.

From the linear relation of a_0 with TiO_2 content for the δ-phase, it can be seen that the δ-phase has a wide solid solution range. The δ-form, though stable at higher temperatures in pure Bi_2O_3, can be stabilized by the addition of a certain amount of second oxide [12–16]. As can be seen from the phase diagram of the Bi_2O_3–TiO_2 system [8] and from our results on the solid phase reaction, TiO_2 cannot play the role of stabilizer for the δ-form. Therefore, it is likely that the δ-phase is formed as a metastable phase when TiO_2 is present. The crystallization in the δ-structure in preference to the γ-structure is thought to occur in connection with a structural closeness between the δ-phase and the mother melt. In general, the metastable phase is formed when the energy barrier for its formation is much lower than that for the formation of the stable phase. The energy barrier is low when the crystal is like the mother melt in structure. A crystal with a more open, defective and symmetrical structure, therefore, would be formed from the melt much easier than a crystal with a compact, complete and asymmetrical structure. In this regard, the δ-phase would be closer to the mother melt in structure than the γ-phase, and accordingly the energy barrier for the formation of the δ-phase is much lower than that in the case of γ-phase. This is why the metastable δ-phase is formed in preference to the γ-phase through the quenching treatment of Bi_2O_3–TiO_2 melts.

3.3. Grain-orientation

As previously reported [5, 6, 17, 18], the crystallization of the Bi_2O_3-based melts in the rapid quenching results in a high crystallographic orientation. The same phenomenon was observed in this system. Although the films consisted of either tetragonal phase or cubic phase, the grains were oriented as (1 1 1) is parallel to the film plane; (2 0 1) corresponds to that plane for the β-structure.

The degree of grain-orientation, f, was estimated by adopting Lotgering's method [19]: a comparison of the X-ray diffraction intensities between the as-quenched films and the corresponding powders. The value was 0.9 to 0.95 for the films containing up to 20% TiO_2 and 0.75 to 0.80 for the specimens with 30 to 40% TiO_2, respectively. From the difference in these values, it is considered that one of the important factors for driving grain-orientation is the viscosity of
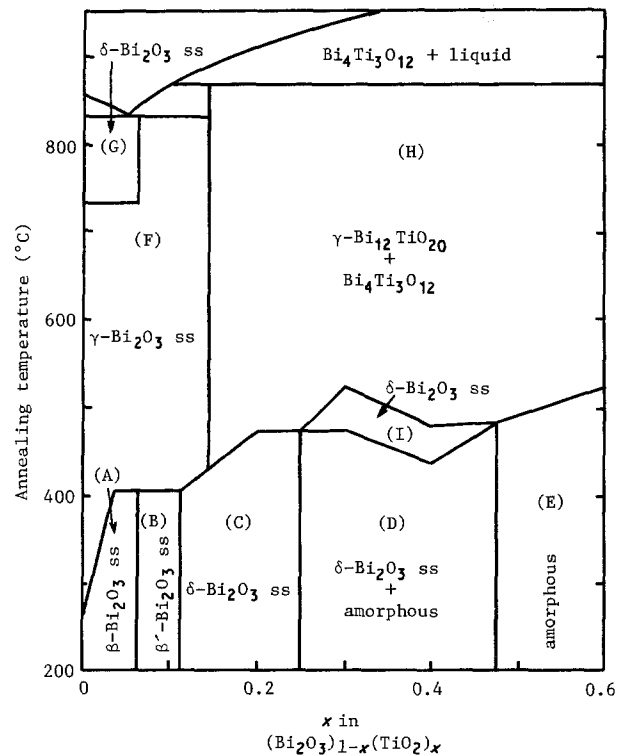

Figure 2 Diagram representing the phase change occurring on annealing the quenched films: relation between TiO_2 content and annealing temperature.

the melt, i.e. the lower the viscosity, the higher the grain-orientation. As TiO_2 has a higher melting point than Bi_2O_3, the addition results in an increase in viscosity of the Bi_2O_3 melt and accordingly in a decrease of the degree of grain orientation.

3.4. Thermal stability of films

The quenched films showed a certain instability on annealing at higher temperatures. Fig. 2 is the diagram representing the phase relation after annealing, investigated by DTA and X-ray diffractometry. As can be seen from this diagram, a wide variety of phase changes occur depending on the difference in the film compositions and annealing temperatures. The main reactions which occurred on annealing are summarized as follows:

1. The quenched phases containing up to 14.4% TiO_2 (A, B, C), although consisting either of β-, β'- or δ-Bi_2O_3 ss, transform into γ-Bi_2O_3 ss (F). The transition temperature is about $400°$C, but $260°$C for the pure Bi_2O_3.

2. The γ-Bi_2O_3 ss thus obtained and containing a small amount of TiO_2 transforms into the δ-form at about $730°$C (G); however, this cannot be brought to room temperature.

3. The single phase of δ-Bi_2O_3 ss containing more than 14.3% TiO_2 (C) decomposes to the mixed phase of γ-$Bi_{12}TiO_{20}$ and $Bi_4Ti_3O_{12}$ crystals at about 430 to $470°$C (H).

4. The phase assemblage of δ-Bi_2O_3 coexisting with amorphous phase (D) first changes to the single phase of δ-Bi_2O_3 ss(I), because of the crystallization of the amorphous phase into the δ-Bi_2O_3 ss, and then it decomposes to the same phases as above at 480 to $520°$C (H).
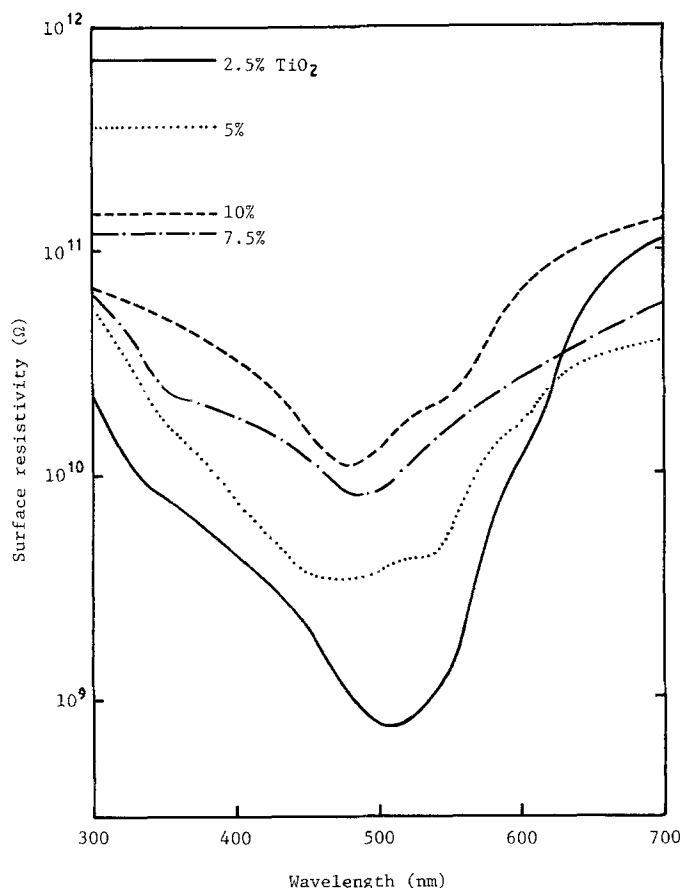
5. The amorphous phase containing 50% or more

10^{12}

2.5% TiO_2

5%

10%
7.5%

10^{11}

10^{10}

10^{9}

Surface resistivity (Ω)

300   400   500   600   700

Wavelength (nm)

Figure 3 Spectral response curves of the photoconductivities of the quenched films in the Bi_2O_3–TiO_2 system. The horizontal lines represent the resistivities in the dark state.

$TiO_2(E)$, however, directly precipitates the crystals γ-$Bi_{12}TiO_{20}$ and $Bi_4Ti_3O_{12}$ at temperatures from 480 to 520° C (H).

3.5. Photoconduction

The most striking character of the quenched films in the Bi_2O_3–TiO_2 system is to exhibit a high photoconductivity, in the same manner as observed in the Bi_2O_3–M_2O_5 [5] and Bi_2O_3–MO_3 [6] systems. Photoconductivity was detected only in films containing up to 10% TiO_2. In Fig. 3, the photoconductivity curves are shown as the relation between the surface resistivity of the film and the wavelength of irradiated light. The spectral response curves indicate a peak around 500 nm, suggesting that the photoconducting carrier is excited by absorbing a blue–greenish light. This photoconduction mode is also the same as in films of the Bi_2O_3–M_2O_5 and Bi_2O_3–MO_3 systems. Among these photoconductive films, that containing 2.5% TiO_2 and consisting of β-phase shows the highest photoconductivity: the resistivity difference between the dark state and photoexcited state is of three orders of magnitude. In order to make a comparison, photoconductivity was also measured on the sintered samples. As a result, it was found that they showed a weak photoconductivity in the range 350 to 600 nm, based on α-Bi_2O_3 and/or γ-$Bi_{12}TiO_{20}$ crystals: the difference in resistivity between the dark state and the photoexcited state was less than one order of magnitude. From this fact, it is obvious that the rapid quenching treatment causes the materials to have a higher photoconductivity. The greatest drawback of the quenched films is that they show a very high resistivity. However, they can find application in photodetectors or photoswitching elements, because the photosensitivity is relatively high.

In this system, the appearance of photoconductivity is limited in the films consisting of tetragonal phase. This agrees with the case in the Bi_2O_3–M_2O_5 films [5]. In the Bi_2O_3–MO_3 system [6], however, a high photoconductivity was observed in the films including not only tetragonal phase but also cubic phase. In general, materials form a structural imperfection by thermal excitation, a deviation from the stoichiometric composition etc., and consequently, electron or positive holes are trapped on a level in the forbidden band. When the carrier moves from such a position to the conduction band by light-excitation, this phenomenon is called photoconduction. In the case of quenched films based on Bi_2O_3, it is considered that a situation where the structural imperfection equilibrated at higher temperatures is brought to room temperature, results in the formation of a band structure favourable to photoconduction. Accordingly, the importance of this for photoconductivity lies in what is the situation of imperfection rather than what is the crystal structure. The aspect of imperfection in the quenched phase is not clear at present. However, it is likely that the existence of Bi^{5+} is of importance for the formation of imperfections and the appearance of photoconductivity.

4. Conclusion

As a result of the rapid quenching treatment of the BiO_2O_3–TiO_2 melts (0 to 60% TiO_2), the films precipitated Bi_2O_3 solid solutions of three types and amorphous phase according to the TiO_2 content. The solid solutions were β-phase (tetragonal structure;

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O to 5% TiO_2), β'-phase (disordered modification of β-form; 7.5 to 10% TiO_2) and δ-phase (cubic structure; 12.5 to 40% TiO_2), respectively. The formation of amorphous phase began at 30% TiO_2, and the films became completely amorphous at 50% TiO_2 or more. The crystalline films were characterized by a high crystallographic orientation; (1 1 1) of the grains were parallel to the film plane. The quenched phases decomposed or transformed into other assemblages on annealing at about 400 to 500° C. The quenched films showed a high photoconductivity. The photoconduction mechanism was suggested to be related to a structural imperfection in which a certain amount of Bi^{5+} was contained.

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