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Preparation of $Bi_4Ti_3O_{12}$ particles by crystallization from glass

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Abstract

Glass from the Bi_2O_3–TiO_2–B_2O_3 system was formed by rapid quenching of the melt. After annealing at 500 °C, the glass crystallized in the form of plate-like particles. The particles thus formed were separated through an acid treatment. Field emission scanning electron microscopy showed a layered structure for the particles. XRD observations revealed that the crystalline form was $Bi_4Ti_3O_{12}$, a useful material in the electronics industry.

Keywords: Rapid quenching; Glass; Capacitors

1. Introduction

Bismuth titanate ($Bi_4Ti_3O_{12}$) is a typical bismuth-based ferroelectric compound with a stratified structure (bismuth layer-structured ferroelectrics, BLSF), and with a Curie temperature of 675 °C. $Bi_4Ti_3O_{12}$ is anticipated to be an excellent candidate material for next generation ferroelectric random-access memories.[1–4] Moreover, various reports indicate that ferroelectric materials could be the next generation capacitor material since they do not contain lead.[5,6]

Xu et al.[5] have reported hydrothermal synthesis of $Bi_4Ti_3O_{12}$ powders. Kimura et al.[6] have reported preparation of $Bi_4Ti_3O_{12}$ powders in the presence of molten salt, and they report that the morphology of the formed particles is plate-like. It is thought that plate-like particles could be useful as materials for making grain-oriented ferroelectric ceramics.[6] Although Gerth et al.[7] have reported the occurrence of crystallization of $Bi_4Ti_3O_{12}$ from glasses in the Bi_2O_3–TiO_2–B_2O_3 system, the material in their study was not obtained in the form of powders.

In this study, $Bi_4Ti_3O_{12}$ powder was fabricated from a glass of the Bi_2O_3–TiO_2–B_2O_3 system by rapid quenching of the melt.

2. Experimental details

TiO_2 (Kisida Chemical, 99.5%), Bi_2O_3 (Wako Pure Chemicals, 99.9%), and B_2O_3 (Merck, 99.99%) were mixed using a mortar and pestle for 20 min. The mixed powder was formed into a square rod shape (100 mm × 10 mm × 10 mm) using a mold. The specimens were sintered at 400 °C for 30 min in air. Rapidly quenched glass of the Bi_2O_3–TiO_2–B_2O_3 system was then formed by a plasma arc and twin rollers. The rapid quenching scheme is shown in Fig. 1.

The glass thus formed was annealed in a crucible at 500 °C for 24 h for the crystallization to occur. The glass was then ground and put into a 10% acetic acid solution which was then agitated for 8 h at 80 °C. $Bi_4Ti_3O_{12}$ powder was separated using a centrifugal separator for 15 min at 6000 rpm and dried at 75 °C.

X-ray diffraction analysis (XRD) of the powder was carried out in order to determine the glass formation region in the

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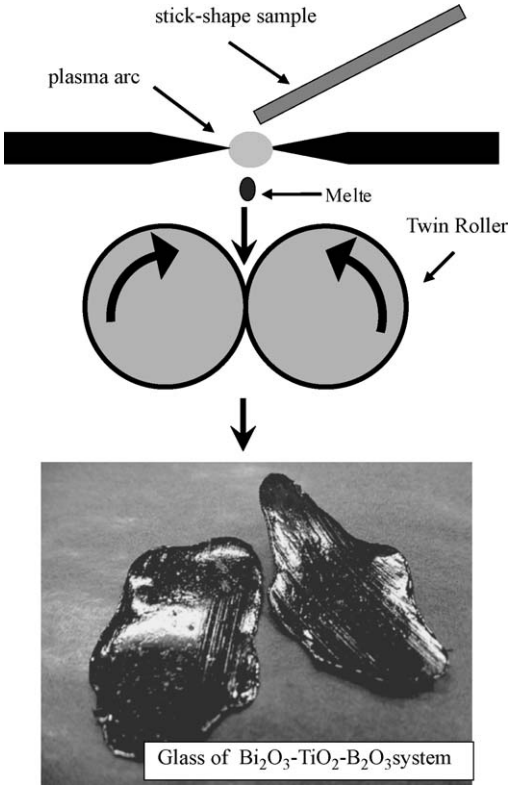

Fig. 1. The rapid quenching scheme used in the study.

Bi_2O_3–TiO_2–B_2O_3 system. Differential scanning calorimetry analysis (DSC) was carried out at a heating rate of 10 °C/min. The $Bi_4Ti_3O_{12}$ powder was examined using a field emission scanning electron microscope (FE-SEM) with an accelerating voltage of 30 kV.

3. Results and discussion

The rapidly-quenched products were thin films having a thickness of about 100 μm. They were crystalline or glassy depending on the composition. The dotted line in the phase diagram in Fig. 2 shows the compositions for which the ratio of Bi_2O_3/TiO_2 corresponds to $Bi_4Ti_3O_{12}$. XRD patterns for compositions along this line are shown in Fig. 3. When the content of B_2O_3 increased, a complete glass phase was obtained. Fig. 2 shows the phase relationship in the Bi_2O_3–TiO_2–B_2O_3 system resulting from the rapid quenching treatment. This phase diagram can be divided into three parts, glass, and glass + Bi_2O_3, and glass + $Bi_2Ti_2O_7$. A completely glassy state was observed for the material as long as the B_2O_3 was in amounts greater than 20 mol%. This value is lower than that obtained by Gerth et al. They reported that the minimum ratio of B_2O_3 ($B_2O_3 \times 100/(Bi_2O_3 + TiO_2 + B_2O_3)$) required for complete glass formation at a cooling rate of about 500 °C/min was 25 mol%. This difference was caused by the different quenching rates used (our cooling rate: <10,000 °C/s). In the lower

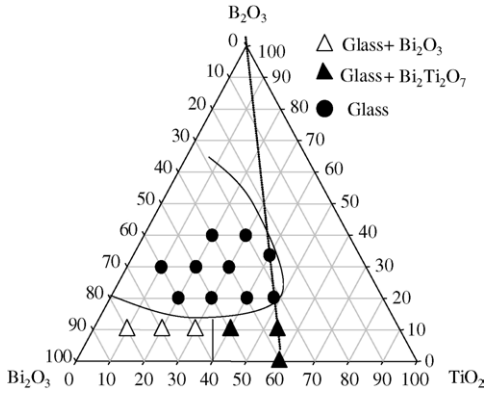

Fig. 2. Phase relationship in the Bi_2O_3–TiO_2–B_2O_3 system in terms of mol%.

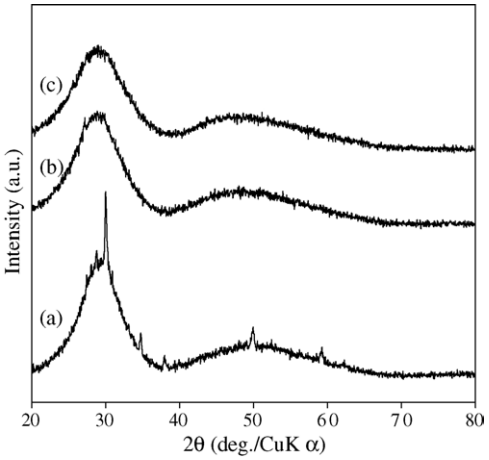

Fig. 3. XRD patterns for (a) Bi_2O_3:TiO_2:B_2O_3 = 36:54:10, (b) Bi_2O_3:TiO_2:B_2O_3 = 32:48:20 and (c) Bi_2O_3:TiO_2:B_2O_3 = 26.8:40.2:33.

B_2O_3 content region, the phases present are glass + $Bi_2Ti_2O_7$ or glass + Bi_2O_3.

Fig. 4 shows the DSC patterns for the glass whose composition is Bi_2O_3:TiO_2:B_2O_3 = 32:48:20. This sample

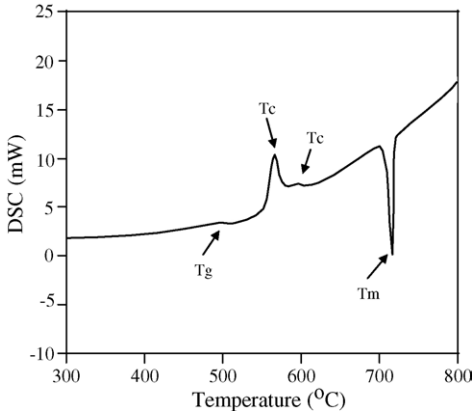

Fig. 4. DSC curve for a glass having a composition (Bi_2O_3:TiO_2:B_2O_3 = 32:48:20).

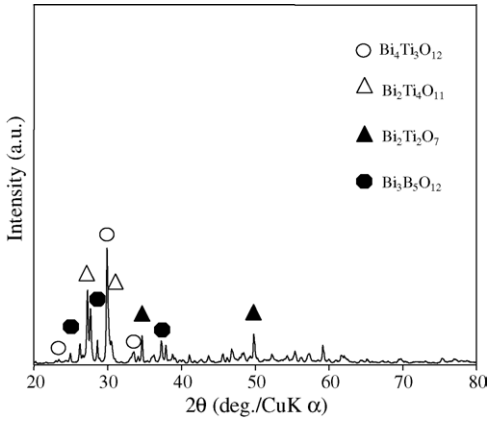

Fig. 5. XRD pattern for the glass after annealing at 500 °C for 24 h. Glass composition: Bi_2O_3:TiO_2:B_2O_3 = 32:48:20.

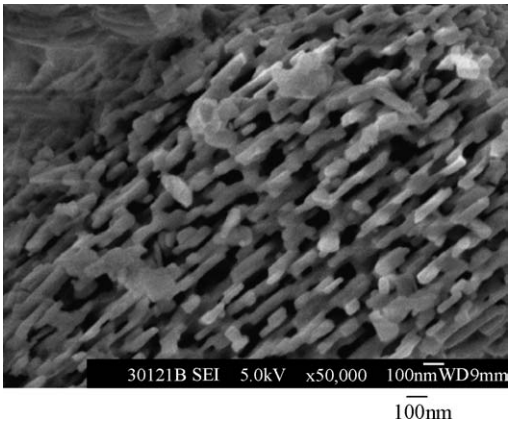

Fig. 7. FE-SEM image of the $Bi_4Ti_3O_{12}$ particles.

shows two exothermic peaks at 566 and 600 °C, representing crystallization of $Bi_3B_5O_{12}$ and $Bi_4Ti_3O_{12}$, respectively. Endothermic peaks were also observed at 499 and 716 °C. The peak at 499 °C corresponds to the glass transition temperature (T_g), and the peak at 716 °C is caused by melting of the glass. Although the crystallization temperature of the glass was around 580 °C according to the DSC result, crystallization occurred when the sample was heated to 500 °C. Fig. 5 shows the XRD pattern for the glass after annealing at 500 °C for 24 h. The composition of the glass is Bi_2O_3:TiO_2:B_2O_3 = 32:48:20. The XRD peaks in Fig. 5 are assigned to $Bi_4Ti_3O_{12}$, $Bi_2Ti_4O_{11}$, $Bi_2Ti_2O_7$ and $Bi_3B_5O_{12}$. As shown in Fig. 4, the crystallization of $Bi_3B_5O_{12}$ occurred prior to the crystallization of $Bi_4Ti_3O_{12}$. Bi in $Bi_3B_5O_{12}$ dose not contribute to the reaction with Ti. This causes decrease in Bi for reaction with Ti, resulting in the formation of compounds such as $Bi_2Ti_4O_{11}$ and $Bi_2Ti_2O_7$.

In order to compensate for the decrease of the amount of Bi, an excess amount of Bi_2O_3 was used. Glass having a composition (Bi_2O_3:TiO_2:B_2O_3 = 50:20:30) was prepared using rapid quenching and was crystallized at 500 °C for 24 h. The XRD pattern for this sample is shown in Fig. 6(a).

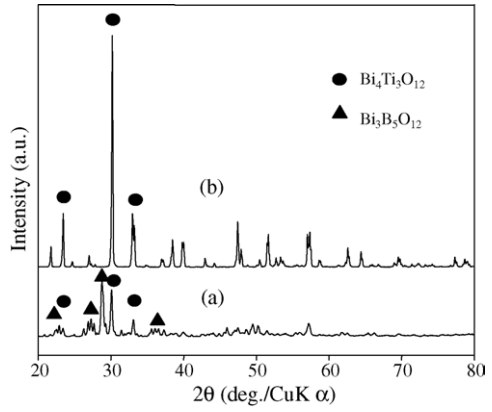

Fig. 6. XRD patterns of the glass. Before (a) and after (b) acid treatment.

The pattern shows that this sample consists of $Bi_3B_5O_{12}$ and $Bi_4Ti_3O_{12}$. $Bi_3B_5O_{12}$ can be removed by using an acid treatment with acetic acid. Then, a single phase of $Bi_4Ti_3O_{12}$ will be obtained. The XRD pattern of the sample after the acid treatment is shown in Fig. 6(b) indicating that a single phase of $Bi_4Ti_3O_{12}$ was obtained.

FE-SEM micrograph of the $Bi_4Ti_3O_{12}$ sample obtained as described above is shown in Fig. 7. The particles had a plate-like shape and were each about 10 nm thick and 100 nm wide. It is thought that the plate-like particles are useful as materials for making grain-oriented ferroelectric ceramics.

4. Conclusions

Glass made from the Bi_2O_3–TiO_2–B_2O_3 system was prepared using rapid quenching. Glass without crystallization was obtained for the composition having a lower content of B_2O_3 than previously reported. Part of the Bi reacted with B, causing the formation of compounds such as $Bi_2Ti_4O_{11}$ and $Bi_2Ti_2O_7$ after heat treatment. When an excess amount of Bi_2O_3 was used for the glass, crystalline phases of $Bi_3B_5O_{12}$ and $Bi_4Ti_3O_{12}$ were formed by the heat treatment at 500 °C. By removing $Bi_3B_5O_{12}$ using acid etching, particles of a single phase of $Bi_4Ti_3O_{12}$ were obtained. The particles had a plate-like shape, with a size of about 10 nm in thickness and 100 nm in width.

References

1. Du, X. and Chen, I., Ferroelectric thin films of bismuth-containing layered perovskites. *J. Am. Ceram. Soc.*, 1998, **81**(12), 3253–3259.
2. Nakanura, M., Higuchi, T., Hachisu, Y. and Tsukamoto, T., Preparation and characterization of *a*- and *b*-axes-oriented $Bi_4Ti_3O_{12}$ thin films using TiO_2 anataze buffer layer. *Jpn. J. Appl. Phys.*, 2004, **43**(4A), 1449–1453.
3. Toyoda, M., Hamuji, Y., Tomono, K. and Payne, D., Ferroelectric properties and fatigue characteristics of $Bi_4Ti_3O_{12}$ thin films by sol–gel processing. *Jpn. J. Appl. Phys.*, 1994, **33**, 5543–5548.

4. Chiu, T., Wakiya, N., Sinozuka, K. and Mizutani, N., Effect of substrate size on crystalline orientation and electrical properties of $(Bi,La)_4Ti_3O_{12}$ thin films. *J. Ceram. Soc. Jpn.*, 2004, **112**(5), 266–270.
5. Xu, H., Bowman, K. and Slamovich, E., Hydrothermal synthesis of bismuth titanate powders. *J. Am. Ceram. Soc.*, 2003, **86**(10), 1815–1817.
6. Kimura, T., Kanazawa, T. and Yamaguchi, T., Preparation of $Bi_4Ti_3O_{12}$ powders in the presence of molten salt containing LiCl. *J. Am. Ceram. Soc.*, 1983, **66**(8), 597–600.
7. Gerth, K. and Russel, C., Crystallization of $Bi_4Ti_3O_{12}$ from glasses in the system $Bi_2O_3/TiO_2/B_2O_3$. *J. Non-Cryst. Solids*, 1997, **221**, 10–17.