ELECTRICAL CONDUCTION of $Bi_4Ti_3O_{12}$ CERAMICS SINTERED UNDER VARIOUS OXYGEN PARTIAL PRESSURES.

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Abstract

Influences of oxygen partial pressure (P_{O2}) during sintering at 1100°C of bismuth titanate (BIT) ceramics were investigated through the measurements of leakage current at 25°C and P_{O2} dependence of AC conductivity at 500 - 800°C. The P_{O2} dependence of conductivity of BIT ceramics sintered in air indicated the mixed conduction of oxide ion and electron hole (p-type). The samples sintered in nitrogen $(P_{O2}/atm = 5 \times 10^{-4})$ showed smaller leakage current than samples sintered in air and oxygen. The p-type electronic conduction due to electron holes would be generated by bismuth vaporization during sintering. In the BIT sintered at low P_{O2}, the formation of oxygen vacancies and electrons is enhanced and then the hole concentration is decreased. This charge compensation would lead to the smaller leakage current at 25°C observed in the samples sintered at low P_{O2}.

Key words: Bismuth layer-structured ferroelectrics, bismuth titanate, mixed conduction, leakage current, P_{O2} control

1. INTRODUCTION

Bismuth layer-structured ferroelectrics (BLSFs) have been intensively studied for various device applications to sensors, transducers, actuators and non-volatile memories, etc. due to their high Curie temperature (T_C), low dielectric dissipation, and anisotropic nature originating from their layered structure. The general formula of the composition for BLSF is expressed by $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$, where A represents Bi^{3+}, Pb^{2+}, Sr^{2+}, Ca^{2+}, etc. at the 12-coordinated site; B represents Fe^{3+}, Ti^{4+}, V^{5+}, Ta^{5+}, W^{6+} etc. at the 6-coodinated site; and m is an integer corresponding to the number of BO_6 octahedra in the pseudo-perovskite blocks. In the crystal, perovskite blocks, $(A_{m-1}B_mO_{3m+1})^{2-}$, are interleaved with $(Bi_2O_2)^{2+}$ layers along the c axis, and ferroelectricity arises mainly in the perovskite blocks. Bismuth titanate (BIT : $Bi_4Ti_3O_{12}$), a typical material of Bismuth layer-structured ferroelectrics ($m = 3$, A = Bi,

and B = Ti), is known to show a large spontaneous polarization [1] and large piezoelectric constants [2]. However, sintered specimens of BIT show relatively large leakage currents, resulting in unsaturated polarization properties. The crystal structure is shown in Fig. 1.
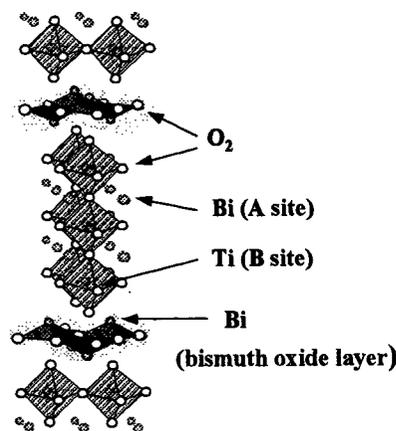

Fig. 1 The crystal structure of BIT

Up to now, the reason for such large leakage current is not revealed sufficiently. From measurements of the Seebeck coefficient above Tc, p-type electronic conduction in BIT single crystal was reported [3]. Shulman and co-workers suggested that p-type conduction in BIT is derived from hole compensation of cation vacancies or impurities in raw materials [4]. Recent years, several researchers have reported that doping of pentavalent (Nb^{5+}[5], V^{5+}[6]) or hexavalent (W^{6+}[6]) cation for B site in perovskite block improved the ferroelectric properties of BIT, probably due to a decrease in conduction carrier "hole". This fact indicates the control of the amount and species of defects are very essential for practical application. It is considered that large leakage current of BIT would be attributed to the vaporization of Bi during sintering at high temperature. In the present study, the mechanism of electrical conduction in BIT was investigated by measuring leakage current at room temperature and partial oxygen pressure (Po₂) dependence of electrical conductivity at 500-800°C.

2. EXPERIMENTS

Ceramic Samples of Bi₄Ti₃O₁₂ (BIT) were prepared by solid-state reaction. Powders of Bi₂O₃, TiO₂ of 99.99 % purity were mixed with the stoichiometric composition. Po₂ during sintering was controlled by flowing O₂, air, N₂ gasses. The powder calcined at 800°C for 7h was crushed, and then pressed into pellets. These pellets were sintered at 1100°C for 2h for electrical measurements. Here, the samples sintered in O₂ (Po₂ = 1 atm), air (Po₂ = 0.21 atm), and N₂ (Po₂ =

5x10⁻⁴ atm) atmosphere are referred to as BIT-O₂, BIT-air, and BIT-N₂ respectively. Dielectric properties were measured using HP4194A in a frequency range of 1KHz-1MHz at 25 - 800°C. Po₂ dependance of electrical conductivity were measured by two-probe alternating current (AC) method, using a HP4192A at 500-800°C in a frequency range of 5Hz-13MHz. During electrical measurements, Po₂ was controlled by mixing O₂ and N₂ gasses to desired ratio and monitored by zirconia oxygen sensor with platinum electrodes. Leakage current at 25°C was measured with an ultra high resistance meter (ADVANTEST R8340A) at room temperature in a electrical field range up to 100 kV/cm.

3. RESULTS AND DISCUSSION

Figure 2 (a) shows temperature dependence of dielectric loss measured in air at a heating rate of 3°C / min. Since measurement temperatures are much lower than sintering temperature, it can be assumed that lattice defects generated during sintering process were almost fixed and didn't change under the measurements. BIT-N₂ shows the lowest dielectric loss and BIT-O₂ shows the highest one. The results of dielectric loss are in agreement with that reported by Shulman et al [5]. At 600°C, as shown in Fig. 2 (b), the value of dielectric loss of BIT-N₂ is about 16% lower than that of BIT-O₂. This result can be attributed to a decrease in conduction carrier, hole. It is considered that the dominant carrier is hole generated from vaporization of bismuth during sintering in non-doped BIT, as expressed by the equation (1) using Kröger – Vink notation;
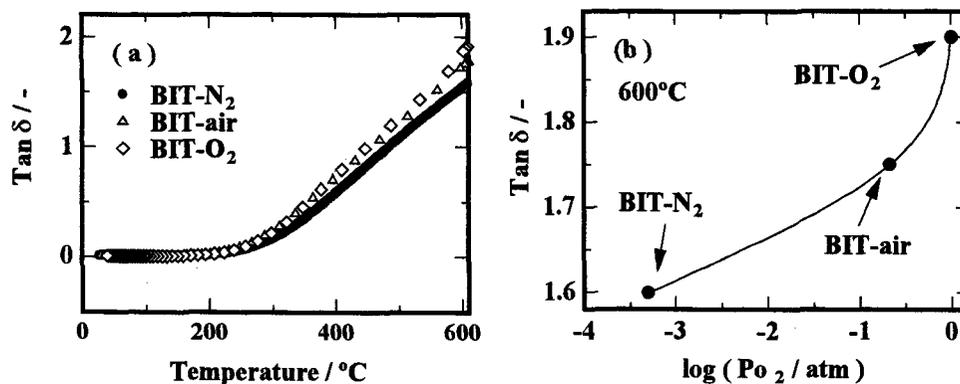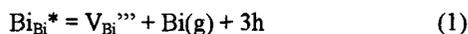
$$Bi_{Bi}^{\times} = V_{Bi}^{'''} + Bi(g) + 3h^{\cdot} \tag{1}$$

Fig. 2 Dielectric loss of BIT-N ₂, BIT-air and BIT-O ₂ in air
(a) at 25 to 600°C (b) at 600°C as a function of Po ₂ during sinterng

where $Bi_{Bi}*$ and V_{Bi}''' are bismuth at bismuth site and bismuth vacancy, respectively. Sintering BIT at lower Po_2 will enhance the formation of oxygen vacancies (Vo'') and resultant electrons (e^-), leading to a decrease in hole density, as expressed by the following equation;

$$Oo* = 1/2O_2 + Vo'' + 2e^- \qquad (2)$$
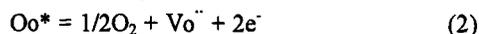
where $Oo*$ and Vo'' indicate lattice oxygen ion at oxygen site and oxygen vacancy, respectively. Lattice oxygen is reduced and diffuses into gas phase with formation of oxygen vacancy and electrons, resulting in a decrease of hole.

Figure 3 shows Po_2 and temperature dependences of AC electrical conductivity σ of BIT-air in a temperature range of 500-800°C and in a Po_2 range of 1 - 10^{-4} atm. The conductivity was measured after reaching an equilibrium state with Po_2. In the whole range of temperature, σ decreased with decreasing Po_2. At a low temperature, for example at 500°C, conductivity changed from 8.5×10^{-5} $S \cdot cm^{-1}$ ($Po_2 = 1$ atm) to 3.9×10^{-5} $S \cdot cm^{-1}$ (5×10^{-4} atm). If σ is derived only from hole (p-type) conduction expressed by the following equation;

$$1/2O_2 = Oo* + V_{Bi}'' + 2h^\cdot, \qquad (3)$$
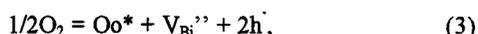
the slope in $\log\sigma$ - $\log Po_2$ plot would be 1/6. When there is a high concentration of oxygen vacancy, the following equation can be applicable;

$$Vo'' + 1/2O_2 = Oo* + 2h^\cdot \qquad (4)$$
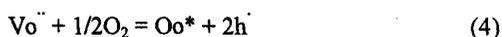
In this case, the slope would be 1/4.

As many researchers have reported [7][8], electrical conductivity shows no Po_2 dependence in the case that ionic conduction is dominant.
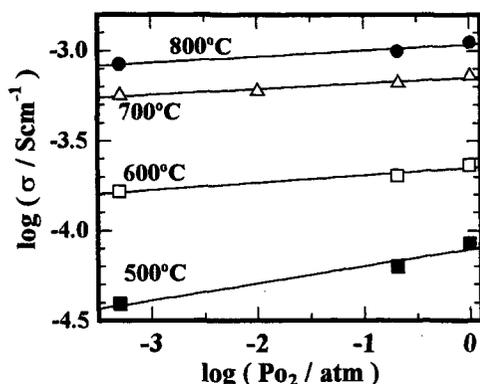
From Fig.3, the slope of the line at 500°C is about 0.1 and this value is much smaller than that of p-type conduction. This discrepancy indicates that the conduction carrier is the mixture of hole and oxide ion. At 800°C, σ showed very small Po_2 dependence, suggesting that dominant carrier is oxide ion. The relatively small concentration of hole compared with oxide ions is responsible for the slight Po_2 dependence of σ.

Fig. 4 shows the slope of the lines in Fig. 3 ($\Delta \log \sigma$ / $\Delta \log Po_2$) as a function of temperature. This slope indicates the contribution of p-type electronic conduction to total electrical conduction. At high temperatures above 650°C, the slope of the line is near to zero. This indicates that ionic conduction is dominant as described. At lower temperatures, the slope increased with decreasing temperature, indicating that the contribution of p-type conduction increases.

The shift in dominant carrier from hole to oxide ion with increasing temperature can be sometimes observed in ionic-p-type mixed conductors of such intermediate temperature region [9]. This will be due to a high activation energy for oxide ion conduction and to that an increase in hole concentration is inhibited by promotion of electron formation as eq. (2) with increasing temperatures. Same behaviors of electrical conductivity were also observed in $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ system, showing ionic - p-type mixed conduction. Y. Teraoka, et al. reported that the ionic conductivity increased with increasing temperature although the hole conductivity didn't increase [10]. In BIT ceramics, it
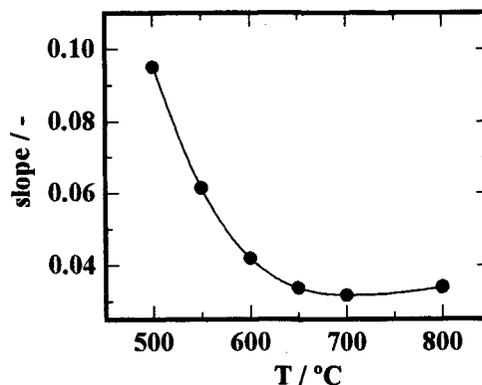

Fig. 3 Po_2 dependence of electrical conductivity of BIT.

Fig.4 Temperature dependence of the slope obtained from Fig. 3.

is considered that the shift of dominant carrier as mentioned above occurs in the ionic-p-type mixed conduction and therefore, electrical conductivity shows small dependence on Po_2 change at higher temperatures. Ionic conduction revealed in the present study is very important because the oxygen vacancy formation is closely related to the generation of electronic carriers but few reports described about ionic conduction in BIT [5][11].

The results of leakage current measurement at room temperature are shown in Fig. 5. Leakage current of BIT-N₂ was lower than that of BIT-O₂ at an electric field up to 100 kV/cm. This corresponds with the result of dielectric loss measurements. The leakage properties are assumed to be closely related to ionic and electronic defects generated during sintering process. Hole induced during sintering process was fixed in cooling step, resulting in the lower leakage current of BIT-N₂ than that of BIT-O₂. As described for Fig. 3 and Fig. 4, conduction mechanism shifted from ionic to p-type conduction with decreasing temperature (800°C to 500°C). In non-doped BIT system, the density of conductive carrier is determined during sintering process, mainly by Po_2 and temperature. Accordingly, Po_2 control at sintering process is important to conduction properties and to improve dielectric properties in BIT.

4. CONCLUSION

In non-doped BIT, samples sintered in nitrogen showed lower dielectric loss and leakage current than samples sintered in air and oxygen, indicating the decrease in hole concentration. It was revealed that BIT ceramics shows ionic − p-type electronic mixed conduction in a Po_2 range of 1 to 5×10^{-4} atm. The ionic conduction due to oxide ions was dominant at high temperature above 650°C, but the contribution of p-type conduction increased with decreasing temperature.
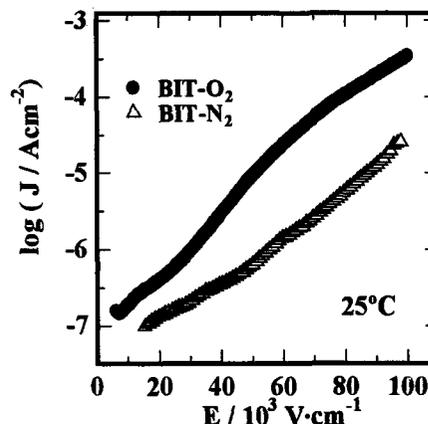

Fig. 5 Leakage current properties of BIT-N₂ and BIT-O₂.

5. REFERENCES

[1] S. E. Cummins, L. E. Cross, J. Appl. Phys., 39, 2268-2274.

[2] T. Takenaka, K. Sakata, Ferroelectrics, 38, 769 (1981).

[3] S. K. Kim, M. Miyayama, and H. Yanagida, Mat. Res. Bull., 31, 121-131 (1996).

[4] H. S. Shulman, M. Testorf, D. Damajanovic, and N. Setter, J. Am. Ceram. Soc., 79, 3124-3128 (1996).

[5] H. S. Shulman, M. Testorf, D. Damajanovic, and N. Setter, J. Am. Ceram. Soc., 83, 528-532 (2000).

[6] Y. Noguchi, I. Miwa, Y. Goshima, and M. Miyayama, Jpn. J. Appl. Phys., 39, L1259-L1262 (2000).

[7] W. D. Kingery, J. Pappis, M. E. Doty, and D. C. Hill, J. Am. Ceram. Soc., 42, 393-398 (1959).

[8] N. M. Sammes, Z. Cai, Solid State Ionics, 100, 39-44 (1997).

[9] M. Miyayama, S. Katsuta, H. Yanagida, Nihon-kagakukai-shi, 10, 1583-1588 (1981).

[10] Y. Teraoka, H. M. Zhang, K. Okamoto, and N. Yamazoe, Mat. Res. Bull., 23, 51-58 (1988).

[11] A. Huanosta, O. Alvarez-Fregoso, and E. Amano, J. Appl. Phys., 69, 404-408 (1994).