Phase Relationship in a BaO–Bi$_2$O$_3$–TiO$_2$ System and Electrical Properties of BaTiO$_3$ with Addition of Bi$_4$Ti$_3$O$_{12}$

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A phase relationship of the BaO–Bi$_2$O$_3$–TiO$_2$ system at 1273 K was studied using a solid state reaction. A new compound of BaBi$_6$Ti$_{20}$O$_{50}$ was found in this ternary system. In the BaTiO$_3$–Bi$_4$Ti$_3$O$_{12}$ pseudo-binary system, the solid solution of Bi$_4$Ti$_3$O$_{12}$ into BaTiO$_3$ was observed up to 4 mol% Bi$_4$Ti$_3$O$_{12}$. The lattice parameters of tetragonal BaTiO$_3$ varied depending on Bi$_4$Ti$_3$O$_{12}$ content in the solid solution range. The structure of BaTiO$_3$ became cubic with the addition of more than 4 mol% Bi$_4$Ti$_3$O$_{12}$. The temperature dependence of permittivity obeyed the Curie-Weiss-like behavior in the solid solution range. The highest permittivity of BaTiO$_3$ decreased and the peak of permittivity became broader with increasing Bi$_4$Ti$_3$O$_{12}$ content.

1. Introduction

BaTiO$_3$ is a well-known ferroelectric material,[1-3] which is widely applied in various devices in the electroceramic industry. However, the sharp increase in its permittivity at the Curie temperature is a serious obstacle to its application in capacitors. To solve this problem, the doping of BaTiO$_3$ with several elements has been conducted to modify the temperature dependence of permittivity. For example, the Curie temperature shifted to lower temperatures with SrTiO$_3$ doping.[4] On the other hand, the Curie temperature shifted to higher temperatures with PbTiO$_3$ doping.[4,5] With ZrO$_2$ doping, the Curie temperature shifted to lower temperatures and a broad temperature dependence around the Curie temperature was attained.[6]

There have been a few reports on the doping of BaTiO$_3$ with Bi$_4$Ti$_3$O$_{12}$.[7,8] However, the solubility range of BaTiO$_3$ with Bi$_4$Ti$_3$O$_{12}$ and the effect of the addition of Bi$_4$Ti$_3$O$_{12}$ to BaTiO$_3$ on the dielectric properties of BaTiO$_3$ are not understood. In this study, we constructed a phase diagram of the BaO–Bi$_2$O$_3$–TiO$_2$ ternary system at 1273 K and investigated the effect of the addition of Bi$_4$Ti$_3$O$_{12}$ on the electrical properties of BaTiO$_3$.

2. Experimental Procedures

BaCO$_3$, Bi$_2$O$_3$ and TiO$_2$ (purity: 99.9%) were mixed with a small amount of ethanol in an agate mortar. The mixed powder was calcined at 973 K for 12 h. The calcined powders were pressed into disk-shaped pellets and sintered at 1273 K for 12 h. The crystal structure was examined by powder X-ray diffraction (XRD) and a precession camera. The compositions of the specimens were determined by induction plasma spectroscopy (ICP).

To obtain dense specimens for dielectric measurements, disk-shaped pellets were sintered at 1373 to 1623 K for 24 h. The permittivity and the electrical conductivity were measured by an a.c. impedance analyzer (Solartron 1260, 1296) at temperatures from 293 to 1133 K in air in the frequency range between 0.1 Hz and 10 MHz.

3. Results and Discussions

Figure 1 shows the phase relationship of the BaO–Bi$_2$O$_3$–TiO$_2$ systems at 1273 K obtained in the present study. We examined the phases of about 80 compositions as indicated in Fig. 1. Ba$_2$TiO$_4$, BaTiO$_3$, Ba$_4$Ti$_{13}$O$_{30}$ and BaTi$_4$O$_9$ in the BaO–TiO$_2$ pseudo-binary system have already been reported. In the Bi$_2$O$_3$–TiO$_2$ pseudo-binary system, Bi$_4$Ti$_3$O$_{12}$ and Bi$_2$Ti$_4$O$_{11}$ have been identified. In the BaO–Bi$_2$O$_3$–TiO$_2$ pseudo-ternary system, BaBi$_4$Ti$_4$O$_{15}$ has been confirmed. Aurivillius et al.[9] synthesized Ba$_2$Bi$_4$Ti$_5$O$_{18}$ by cooling the melt at 1427 K. Subbanna et al.[10] prepared BaBi$_8$Ti$_7$O$_{27}$ by heating a mixture of BaCO$_3$, Bi$_2$O$_3$ and Cr$_2$O$_3$ between 1200 and 1300 K. In the present study, the phases of Ba$_2$Bi$_4$Ti$_5$O$_{18}$ and BaBi$_8$Ti$_7$O$_{27}$ were not observed at 1273 K.
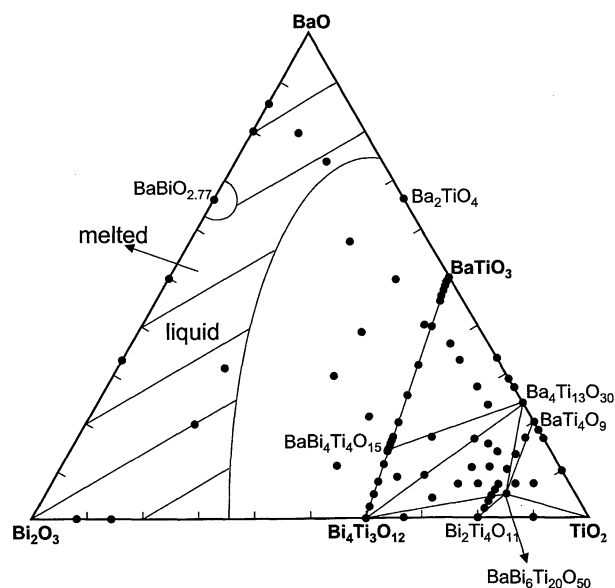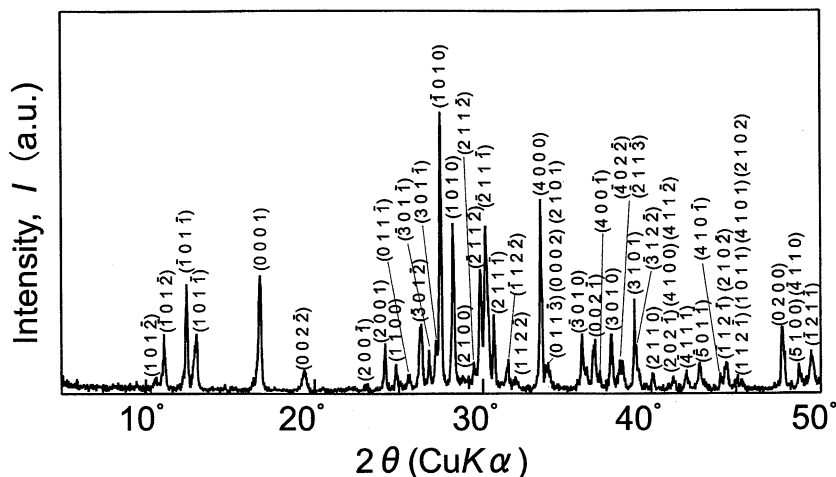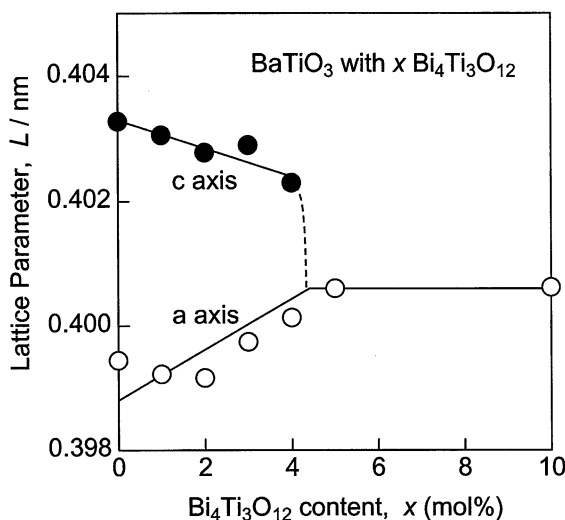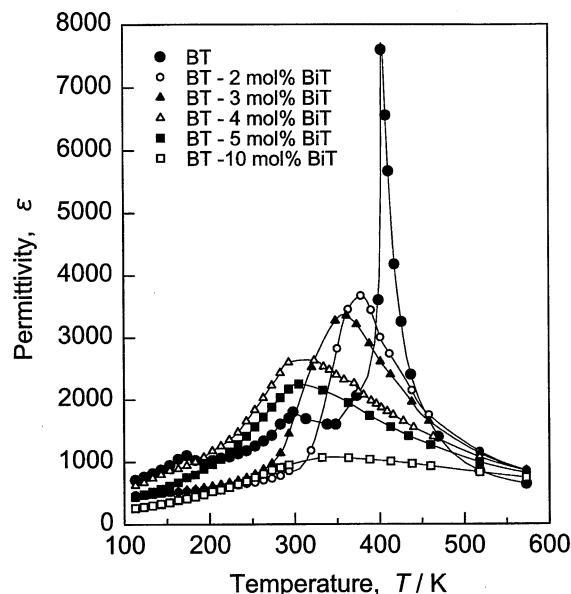

Fig. 1 Phase relationship in the BaO–Bi$_2$O$_3$–TiO$_2$ system at 1273 K.

Fig. 2　X-ray diffraction pattern of $BaBi_6Ti_{20}O_{50}$.

Fig. 3　Variation of lattice parameters of $BaTiO_3$ with the addition of $Bi_4Ti_3O_{12}$.

Fig. 4　Temperature dependence of permittivity of $BaTiO_3$ with the addition of $Bi_4Ti_3O_{12}$ at 10^4 to 10^6 Hz. BT: $BaTiO_3$, BiT: $Bi_4Ti_3O_{12}$.

A new compound of $BaBi_6Ti_{20}O_{50}$ was found in the $BaO–Bi_2O_3–TiO_2$ ternary system. The single crystal of the new compound was synthesized by cooling the melted $BaBi_6Ti_{20}O_{50}$. The new compound had a modulated structure[11] having a main lattice structure and a sublattice structure. The space group of the main lattice structure was not precisely determined (either I2, Im or I2/m), but the lattice parameters were determined to be $a = 1.073$ nm, $b = 0.381$ nm, $c_1 = 0.336$ nm and $\beta = 92.5°$. The space group of the sublattice structure was $P2_1/a$, and the lattice parameters of a, b and β were the same as those of main lattice, but the lattice parameter $c_2 = 0.529$ nm. Figure 2 shows the XRD pattern of the new compound. Each XRD peak in Fig. 2 was completely indexed by calculation ($hklm$) using those lattice parameters. A detailed structural analysis of this new compound will be reported elsewhere.[12]

Figure 3 shows the variation of lattice parameters of $BaTiO_3$ with the addition of $Bi_4Ti_3O_{12}$. In the $BaTiO_3–Bi_4Ti_3O_{12}$ pseudo-binary system, $BaTiO_3$ had a tetragonal structure having lattice parameters a and c in the range of $Bi_4Ti_3O_{12}$ content between 0 and 4 mol%. The tetragonality of $BaTiO_3$ decreased with increasing $Ba_4Ti_3O_{12}$

content. The structure of $BaTiO_3$ became cubic at more than 4 mol% $Bi_4Ti_3O_{12}$. Therefore, the solubility of $Bi_4Ti_3O_{12}$ in $BaTiO_3$ was estimated to be 4 mol%.

Figure 4 shows the temperature dependence of the permittivity of $BaTiO_3$ with the addition of $Bi_4Ti_3O_{12}$ at 10^4 to 10^6 Hz. The value of permittivity and the Curie temperature of undoped $BaTiO_3$ were in agreement with the reported values.[1–3] As shown in Fig. 4, the temperature at the highest permittivity (T_{max}) shifted to lower temperatures with increasing $Bi_4Ti_3O_{12}$ content. Three peaks of the temperature dependence of permittivity were observed for $BaTiO_3$ corresponding to the three phase transition of $BaTiO_3$.[1] (i.e., cubic to tetragonal to orthorhombic with decreasing temperature). In $BaTiO_3$ with $Bi_4Ti_3O_{12}$, on the other hand, one broad peak was observed to become broader and lower with increasing $Bi_4Ti_3O_{12}$ content. M'Peko et al.[7] have reported the temperature dependence of permittivity of $BaTiO_3$ with $Bi_4Ti_3O_{12}$ in the range between 1 and 4 mol% $Bi_4Ti_3O_{12}$. They reported that the Curie temperature of $BaTiO_3$ was unchanged by the

addition of Bi$_4$Ti$_3$O$_{12}$. The different results between the study by M'Peko *et al.* and the present study may be due to the sintering times of M'Peko *et al.* being too short (1.9 ks) to obtain stable and homogeneous specimens. Figure 5 shows the relation between the reciprocal permittivity and temperature for BaTiO$_3$ with the addition of Bi$_4$Ti$_3$O$_{12}$ at temperatures above T_{max}. The experimental data for BaTiO$_3$ obeyed the Curie-Weiss law. For BaTiO$_3$ with less than 4 mol% Bi$_4$Ti$_3$O$_{12}$, the relationship between reciprocal permittivity and temperature was almost linear, exhibiting Curie-Weiss-like behavior. For BaTiO$_3$ with more than 4 mol% Bi$_4$Ti$_3$O$_{12}$, the behavior deviated from the Curie-Weiss law significantly.

Figure 6 depicts the effect of the addition of Bi$_4$Ti$_3$O$_{12}$ to BaTiO$_3$ on T_{max} and ε_{max}, where T_{max} is the temperature at the peak permittivity shown in Fig. 4 and ε_{max} is the highest permittivity at T_{max}. The ε_{max} decreased with increasing Bi$_4$Ti$_3$O$_{12}$ content. The T_{max} showed the minimum at around 4 to 5 mol% addition of Bi$_4$Ti$_3$O$_{12}$. The second phase which appeared in the samples with more than 4 mol% Bi$_4$Ti$_3$O$_{12}$

was BaBi$_4$Ti$_4$O$_{15}$, whose Curie temperature and highest permittivity were 700 K and 3000, respectively. The reason for the slight increase of T_{max} for the sample with more than 5 mol% Bi$_4$Ti$_3$O$_{12}$ may be the high Curie temperature of BaBi$_4$Ti$_4$O$_{15}$ phase.

Figure 7 shows the temperature dependence of permittivity for the samples with 4 mol% Bi$_4$Ti$_3$O$_{12}$ at frequencies from 100 Hz to 100 kHz. The ε_{max} increased and T_{max} decreased with increasing frequency. This relaxor-type behavior was observed for the sample with 4 to 5 mol% Bi$_4$Ti$_3$O$_{12}$. Several researchers reported that BaTiO$_3$ could be changed to relaxor-type materials by substitution of aliovalent elements.[6,13] However, the present study first showed that BaTiO$_3$ could be changed to relaxor-type material by the addition of Bi$_4$Ti$_3$O$_{12}$. It is still not well-understood why relaxor-type behavior appears in some materials, but this phenomenon is probably closely associated with the so-called diffuse phase transition. The solid solution of Bi$_4$Ti$_3$O$_{12}$ into BaTiO$_3$ may cause the substitution of Ba^{2+} by Bi^{3+} associated with the formation of oxygen vacancies. This may introduce significant disordering in BaTiO$_3$ resulting in diffuse phase transition. Further study is needed to understand the mechanism of relaxor-type behavior. Such relaxor-type behavior has also been obtained for other non-stoichiometric perovskites derived from BaTiO$_3$.[14,15]

Figure 8 shows the temperature dependence of the electrical conductivity (σ) for BaTiO$_3$ with the addition of Bi$_4$Ti$_3$O$_{12}$. The activation energy (93 kJmol^{-1}) and σ values for undoped BaTiO$_3$ shown in Fig. 8 are almost in agreement with values reported in the literature.[3] The effect of the addition of Bi$_4$Ti$_3$O$_{12}$ to BaTiO$_3$ on the electrical conductivity has not been reported in the past. In the present study, the σ values decreased with increasing Bi$_4$Ti$_3$O$_{12}$ content. The activation energy slightly increased from 93 to 134 kJmol^{-1} with increasing Bi$_4$Ti$_3$O$_{12}$ content from 0 to 10 mol%. It is known that BaTiO$_3$ is usually a p-type semiconductor. The trivalent substitution of Ba^{2+} by Bi^{3+} may have caused the electron
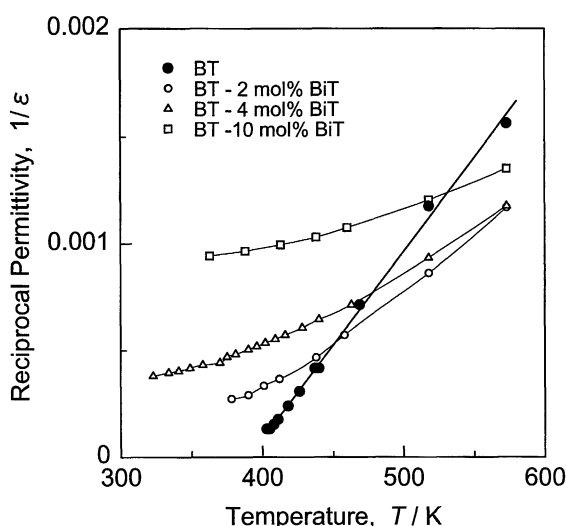

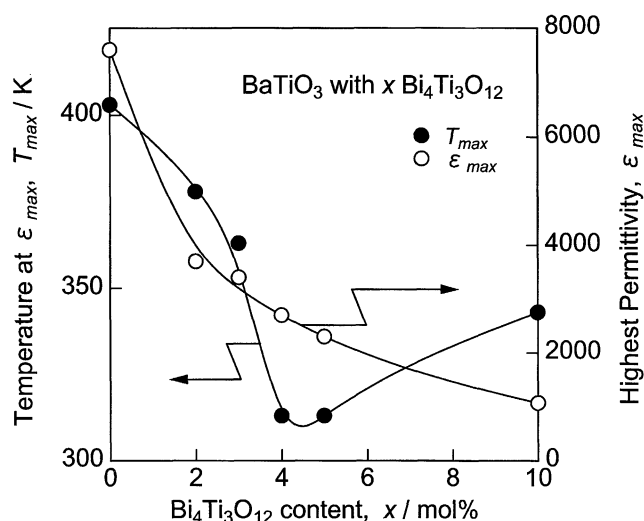Fig. 5   Temperature dependence of the reciprocal permittivity of BaTiO$_3$ with the addition of Bi$_4$Ti$_3$O$_{12}$. BT: BaTiO$_3$, BiT: Bi$_4$Ti$_3$O$_{12}$.

Fig. 6   Effect of the addition of Bi$_4$Ti$_3$O$_{12}$ to BaTiO$_3$ on T_{max} and ε_{max}. T_{max}: the temperature at the peak permittivity shown in Fig. 4. ε_{max}: the highest permittivity at T_{max}.
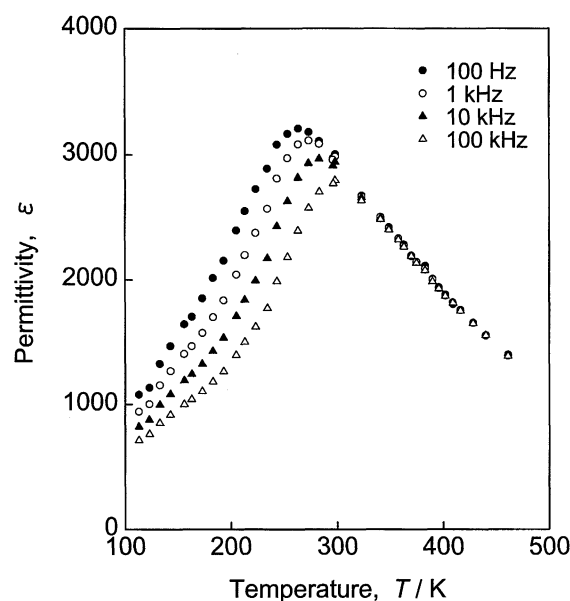

Fig. 7   Temperature dependence of permittivity of BaTiO$_3$ with 4 mol% Bi$_4$Ti$_3$O$_{12}$ at 100 Hz to 100 kHz.
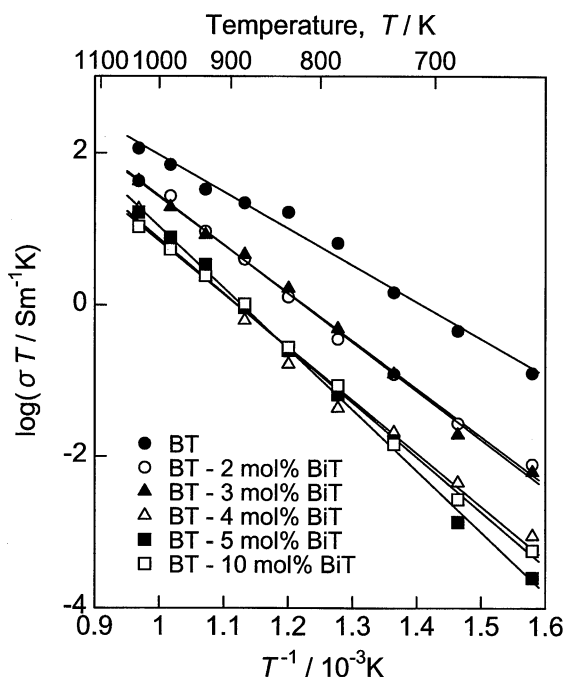
Fig. 8 Temperature dependence of electrical conductivity of $BaTiO_3$ with the addition of $Bi_4Ti_3O_{12}$. BT: $BaTiO_3$, BiT: $Bi_4Ti_3O_{12}$.

formation. This may compensate the intrinsic p-type carrier in $BaTiO_3$, resulting in a decrease in electrical conductivity.

4. Conclusions

A phase relationship of the $BaO–Bi_2O_3–TiO_2$ ternary system at 1273 K was proposed, and the electrical properties of $BaTiO_3$ with the addition of $Bi_4Ti_3O_{12}$ were measured.

(1)   A new compound of $BaBi_6Ti_{20}O_{50}$ was found. The lattice parameters were $a = 1.073$ nm, $b = 0.381$ nm,

$c_1 = 0.336$ nm, $c_2 = 0.529$ nm and $\beta = 92.5°$.

(2)   The solid solution of $Bi_4Ti_3O_{12}$ into $BaTiO_3$ was observed in the range up to 4 mol% of $Bi_4Ti_3O_{12}$. The structure of $BaTiO_3$ was tetragonal at less than 4 mol% $Bi_4Ti_3O_{12}$, and was cubic at more than 4 mol%$Bi_4Ti_3O_{12}$.

(3)   With increasing $Bi_4Ti_3O_{12}$ content, the temperature dependence of permittivity became broader and the highest permittivity values decreased. The temperature at the highest permittivity was also lowered with increasing $Bi_4Ti_3O_{12}$ content.

(4)   A relaxor-like frequency dependence of permittivity was observed for the $BaTiO_3$ with 4 to 5 mol% $Bi_4Ti_3O_{12}$.

(5)   The electrical conductivity of $BaTiO_3$ was decreased with increasing $Bi_4Ti_3O_{12}$ content.

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