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Effects of type of additive and particle size of TiO_2 raw material powder on stabilization of $BaTi_2O_5$ phase during sintering

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 $BaTi_2O_5$ (BT2) calcined powder synthesized by a solid-phase reaction decomposed into $BaTiO_3$ (BT) and $Ba_6Ti_{17}O_{40}$ (B6T17) as the firing temperature was raised. This decomposition was suppressed by adding 1 wt % SiO_2 as an additive. SiO_2 did not dissolve in BT2 crystal grains and segregated as a secondary phase including Ba and Ti atoms. The incorporation of Ba and Ti into SiO_2 probably suppresses the decomposition of BT2. By using another TiO_2 powder with small particle sizes as one of the raw material powders, perfect BT2 single-phase calcined powder was obtained. The ceramic fired from this calcined BT2 powder maintained its BT2 single phase. This is probably attributed to the non-existence of any chemical compounds other than BT2 that can be the origin of BT2 decomposition during firing. On the one hand, in the case of using 1 wt % Fe_2O_3 as the additive, Fe_2O_3 dissolved in BT2 crystal grains, and the sintered samples exhibited relaxor behavior.

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1. Introduction

Lead zirconate titanate (PZT) based ceramics have been used in various fields since they have not only high piezoelectricity but also an excellent facility for designing materials for various applications. In recent years, from the concern of the Pb contamination of the global environment, many lead-free piezoelectric ceramics have been actively investigated. Bismuth layered structure ferroelectrics (BLSFs), (K,Na)-NbO₃ (KNN), and (Bi,Na)TiO₃ (BNT) are well-known representative lead-free piezoelectric ceramics.^{1–3)} Since the piezoelectricity of existing lead-free ceramics is low, grain orientation techniques have been studied to improve their piezoelectricity.^{4–9)} Furthermore, multilayer structures have been investigated for practical use.^{10–13)}

A new lead-free ferroelectric material, BaTi₂O₅ (BT2), was discovered under the above situation.^{14–16)} Having a Curie point (T_c) above 400 °C, BT2 is expected to be a high-temperature piezoelectric and dielectric material. After the discovery of the ferroelectricity of BT2, the crystal structure of BT2 was actively studied using single crystals,^{17,18} glass,¹⁹⁾ and powder^{20,21)} and analyzed by structural calculations.^{22,23)} From these studies, it was elucidated that the crystal structure at room temperature is monoclinic and belongs to the space group C2. The spontaneous polarization exists along only the *b*-axis direction and the relative permittivity in the *b*-axis direction comes up to about 30,000 at T_c .

BT2 is thermodynamically unstable and tends to decompose into BaTiO₃ (BT) and Ba₆Ti₁₇O₄₀ (B6T17) at temperatures higher than 1150 °C,^{24,25)} and it is also believed that BT2 powder with a single phase is not obtained in a conventional solid-phase reaction. Since calcined powders usually become mixed phases of mainly BT, BT2, and B6T17, BT2 powder was synthesized by the sol–gel method.^{26–29)} However, Zhu and West reported that BT2 powder with a trace amount of BT can be successfully obtained by calcining a mixture of BaCO₃ and TiO₂ (anatase) by a multistep method.³⁰⁾ Their results indicated that the synthesis is possible via a solid-phase reaction if the process is optimized. We improved the temperature profile of calcination for BT2 by introducing a slow-heating in the two temperature ranges, and obtained an almost single-phase BT2 calcined powder in a solid-phase reaction.³¹

During the sintering, the BT2 calcined powder obtained by the solid-phase reaction or sol–gel method gradually decomposed to BT and B6T17 with increasing firing temperature. Spark plasma sintering $(SPS)^{32}$ and hot pressing³³) were employed to fabricate dense BT2 ceramics at low temperatures. Furthermore, the effect of additives such as KF, B₂O₃, and MnO₂ was investigated to obtain BT2 ceramics by ordinary pressureless sintering.^{34–36} However, a perfect dense ceramic body with a BT2 single phase was not obtained.

Masuno et al. successfully synthesized $(Ba,Ca)Ti_2O_5$ ceramics by heating glass samples above the phase transition temperature to crystalline samples.³⁷⁾ (Ba,Ca)Ti₂O₅ showed relative permittivities from 2,000 to 3,000 near 300 °C. This indicates the potential of BT2 as a high-temperature dielectric material. They described that the BT2 phase is thermodynamically stable. This suggests that the decomposition of BT2 is caused by the local fluctuation in the composition of the ceramics.

In this paper, the effect of type of additive on BT2 phase stabilization during firing is discussed. We fabricated ceramics by adding additives to the calcined powder obtained by the method we have already reported.³¹⁾ On the basis of the results of experiments on these additive, the effect of TiO_2 raw material powder with small particle sizes on the stabilization of the BT2 phase was also investigated.

2. Experimental procedure

High-purity BaCO₃ powder (>99.5%, Sakai Chemical Industry) and two types of high-purity TiO₂ powders (rutile, >99.5%, Toho Titanium), which differ in specific surface area (SSA), were used as starting materials to prepare BT2 calcined powder. Table I shows the characteristics of these raw material powders. Various additives were added to the calcined powder obtained from the raw material powder of combination A, and the effect of type of additive on the stabilization of the BT2 phase was investigated. Another calcined powder obtained from combination B was fired without any additives in order to investigate the effect of the particle size of TiO₂ on the stabilization of the BT2 phase.

Table I. Two combinations of raw material powders used for the solid-phase reaction of $BaTi_2O_5$. Two TiO_2 powders of different particle sizes were used.

Combination	BaCO ₃ powder	TiO ₂ powder
А	Type: BW-K (SCI) SSA: 7.2 m ² /g	Type: HT0210 (TT) SSA: 2.3 m ² /g
В	Type: BW-K (SCI) SSA: 7.2 m ² /g	Type: HT1311 (TT) SSA: 9.0 m ² /g
SCI: Sal	ai Chemical Industry TT:	Toho Titanium



Fig. 1. Temperature profile of the calcination of BaTi₂O₅.

In both combinations mentioned above, $BaCO_3$ and TiO_2 were weighed at a molar ratio of 1 : 2 and ball-milled with zirconia balls in water for 12 h. After drying, poly(vinyl alcohol) (PVA) was added to the mixture as the binder, and the powders were pressed into disks of 60 mm diameter under a uniaxial pressure of 50 MPa. The resulting compacts were broken into pieces and calcined in an aluminum crucible at 1160 °C for 2 h according to the temperature profile shown in Fig. 1,³¹⁾ after removing the binder at 400 °C for 5 h. After the calcination, the compacts were pulverized using a mortar and a pestle and ball-milled with zirconia balls in water for 12 h.

The 22 additives listed in Table II were used. 0.05 g (1 wt%) of each additive was added to 5 g of the BT2 calcined powder obtained from combination A. Each powder was dry-mixed using a mortar and pestle. The PVA binder was added to these mixed powders, and the resulting mixture was pressed into disks of 15 mm diameter under a uniaxial pressure of 100 MPa. These disks were fired in an aluminum crucible at 1240 °C for 2 h in air. We estimated the production ratio of the BT2 phase using the index α .³⁰⁾ Since four of the 22 additives increased α value, their effects were again investigated in detail as follows: 0.5 g (1 wt%) of each additive was added to 50 g of BT2 calcined powder, and the mixture was mixed by ball milling with zirconia balls in water or ethanol for 12 h, instead of the previous dry mixing. After drying, each powder was pressed into disks of 15 mm diameter by the same method mentioned above. The resulting compacts were fired for 2 h in air, and their α and density ρ were estimated. Another BT2 calcined powder from combination B was pressed into disks and fired in air in the same manner.

The crystalline phases were analyzed by X-ray diffraction (XRD; Rigaku MiniFlex) analysis using Cu K α radiation. The morphologies of the powders and ceramics were observed with a scanning electron microscopy (SEM; JEOL

Table II.	BT2 production ratios and densities of samples fired at 1240 $^{\circ}\mathrm{C}$
without and	I with various additives of 1 wt% added to the calcined powder
fabricated f	rom combination A by dry-mixing.

Additive	α (%)	ρ (g/cm ³)
Without additives	80	4.94
Fe ₂ O ₃	100	4.84
K_2CO_3	100	4.49
SiO_2	88	
TiO ₂	87	4.78
BaCO ₃	70	5.04
CaCO ₃	68	4.75
NiO ₂	63	4.78
CoO	60	4.84
CuO	58	4.41
ZnO	49	4.91
Al ₂ O ₃	48	4.93
MgO	29	4.56
Na ₂ CO ₃	6	3.55
SrCO ₃	4	4.82
SnO_2	3	4.83
La_2O_3	0	4.46
Nd_2O_3	0	4.47
ZrO ₂	0	4.75
Bi ₂ O ₃	0	4.56
Sb_2O_3	0	4.64
Nb ₂ O ₅	0	4.69
Li ₂ O ₃	0	4.43

JCM-6000) system with an energy dispersion spectrometer (EDS; JEOL JED-2300). The so-called ZAF correction method was applied to the quantitative analysis of elements. The temperature dependence of permittivity was measured during the stage of cooling at a rate of about $200 \,^{\circ}\text{C/h}$ at $10 \,\text{kHz}$ or $1 \,\text{MHz}$, and the dielectric capacitance for calculating permittivity was measured with an LCR meter (NF ZM2410).

The BT2 production ratio index $\alpha = I_{BT2}/(I_{BT2} + I_{BT})$ was defined by Zhu and West,³⁰⁾ where I_{BT2} is the height of the diffraction peak due to (401) and (111) in BT2 at approximately $2\theta = 25.7^{\circ}$ and I_{BT} is that due to (110) in BT at approximately $2\theta = 31.6^{\circ}$. α is a useful semiquantitative index.

3. Results and discussion

3.1 Effects of additives

Figure 2 shows a SEM image of the BT2 calcined powder obtained from combination A. The particle sizes were about 2 µm or less. α was 93%. Table II shows the α and ρ values of the sintered samples with 1 wt% additives added by dry mixing that were fired at 1240 °C for 2 h in air. α and ρ were 80% and 4.94 g/cm³ in the sample without additives. The effects of type of additive on BT2 phase stabilization, i.e., on α , can be classified into three categories: (1) marked effect ($\alpha > 80$), (2) no effect (50 < $\alpha < 80$), and (3) decomposing effect (0 < $\alpha < 50$), as shown in Table II. The additives belonging to category (1) were Fe₂O₃, K₂CO₃, SiO₂, and TiO₂.

In order to improve the mixing state of the four additives mentioned above, they were mixed by wet ball milling



Fig. 2. SEM image of BT2 powder obtained by calcining the raw material powder mixture of combination A.



Fig. 3. Densities of samples with and without additives as functions of firing temperature.



Fig. 4. BT2 production ratios of samples with and without additives as functions of firing temperature.

instead of by dry mixing. Each disk compact was fired at various temperatures for 2 h in air. The densities of the samples with these additives are shown in Fig. 3. Since the samples with K₂CO₃ and SiO₂ partially melted at 1240 °C, their maximum temperature was 1220 °C. The maximum temperature of the other samples was 1240 °C since the partial melting occurred at 1260 °C. Figure 4 shows the change in α with the firing temperature. The α values of the samples with Fe₂O₃ and TiO₂ as well as that of the sample without additives gradually decreased with increasing firing



Fig. 5. XRD profile of the BT2 sample with 1 wt % SiO₂ fired at 1220 °C for 2 h and BaTi₂O₅ peak pattern.

temperature. Thus, no stabilization effect appeared for these two additives, in contrast to the result in the case of dry mixing. Although no further information is available, this difference in stabilization effect is probably attributed to the mixing state. The α values of samples with K₂CO₃ and SiO₂ are higher than those of the sample without additives. In particular, the sample with SiO₂ showed $\alpha = 100\%$, independent of the firing temperature. Thus, SiO₂ addition showed a marked effect in BT2 phase stabilization. Figure 5 shows the XRD profile of the sample with SiO₂ fired at 1220 °C for 2 h, together with the powder diffraction profile of BT2 (JCPDS 01-071-3822).³⁸) The BT2 single phase is successfully obtained, as shown in Fig. 5, although its XRD profile includes some unidentified small diffraction peaks.

Figures 6(a) and 6(b) respectively show SEM and EDS mapping images of Si of the sample with the SiO₂ additive fired at 1220 °C. The secondary phase, somewhat deeply colored, is shown in Fig. 6(a). Although the concentration distribution of Si is confirmed in Fig. 6(b), the deeply colored areas in Fig. 6(a) are not consistent with the Si distribution. Table III shows the elemental weight ratios estimated by EDS spot analysis of segregation areas with dense white spots showing the Si distribution in Fig. 6(b) (I) and of other areas without Si (II), as well as the whole surface estimated by the area analysis (III) of the image in Fig. 6(b). The results in Table III were converted to atomic ratio in terms of cations, as shown in Table IV. In area I, Ba and Ti atoms were detected at a ratio of about 8 : 5. The existence of these atoms probably produces some unidentified small diffraction peaks in the XRD profile in Fig. 5. On the whole surface (III), 0.5 wt % Si, corresponding to 1 wt % SiO₂, was detected, which was equal to the added amount. From these results, SiO₂ incorporated Ba and Ti atoms at a ratio of about 8:5, and this incorporation probably contributed to the stabilization of the BT2 phase. That is, SiO₂ incorporates unwanted compounds such as BT and B6T17 together with other substances rich in Ba in the calcined powder. The total Ba/Ti ratio of BT and B6T17 incorporated into the secondary phase should be equal to 1/2, which is the ratio of BT2. Since the Ba/Ti ratio 8/5 in the secondary phase is higher than 1/2, the deficiency in Ba should be supplied by BT2 grains. The Ba concentration of BT2 grains is therefore lower than the



Fig. 6. SEM image of the BT2 sample with $1 \text{ wt } \% \text{ SiO}_2$ added by wet ball milling and fired at 1220 °C for 2 h (a) and EDS mapping image of Si (b).

Table III. Elemental weight ratios estimated by EDS by point analysis of segregation areas of SiO_2 (I) and other areas without SiO_2 (II), and by area analysis of the whole surface in Fig. 6(b) (III).

Analyzed	Concentration in weight ratio (wt%)				– Domoulus
area	Ba	Ti	Si	0	Kemarks
Ι	55.5	11.5	9	24	Average of 3 points
II	45.5	29.5	0	25	Average of 3 points
III	45.6	28.8	0.5	25.1	

 $\label{eq:stable_stable} \begin{array}{ll} \textbf{Table IV.} & \mbox{Cation concentrations in atomic ratio calculated from the results} \\ \mbox{in Table III.} \end{array}$

A	Concentration in atomic ratio (at. %)			
Anaryzeu area	Ba	Ti	Si	
Ι	41.9	24.9	33.2	
II	35	65	0	
III	34.9	63.3	1.8	



Fig. 7. SEM image of the BT2 sample with 1 wt % $K_2\rm CO_3$ added by wet ball milling and fired at 1220 °C for 2 h (a) and EDS mapping image of K (b).

Table V. Elemental weight ratios estimated by EDS by point analysis of the segregation areas of K_2O (I) and other areas without K_2O (II), and by area analysis of the whole surface of Fig. 7(b) (III).

Analyzed	Concentration in weight ratio (wt%)				Dementer
area	Ba	Ti	К	0	Remarks
Ι	25.5	36.5	8.5	29.5	Average of 3 points
II	45	29	0.5	25.5	Average of 3 points
III	42.9	29.7	2.1	25.3	

 Table VI.
 Cation concentrations in atomic ratio calculated from the results in Table V.

A malagrad amon	Concentration in atomic ratio (at. %)		
Analyzed area	Ba	Ti	K
Ι	15.9	65.4	18.7
II	34.6	64	1.4
III	31.7	62.9	5.4

stoichiometric concentration of BT2. A similar absorption effect of SiO_2 is also confirmed in BT.³⁹⁾

A similar elemental analysis was performed in the sample with the K_2CO_3 additive fired at 1220 °C. SEM and EDS mapping images of K and the results of the elemental analysis of three areas are shown in Figs. 7(a) and 7(b) and Tables V and VI, respectively. As shown in Figs. 7(a) and 7(b), K also segregated in the same manner as Si. In area I, Ba and Ti atoms were incorporated into K_2O segregation

areas at a ratio of about 1 : 4. This Ba/Ti ratio indicates a Tirich composition, in contrast to that in the case of the SiO₂added sample. Thus, the stabilization of BT2 phase is independent of the Ba/Ti ratio in the secondary phase. This result shows that the stabilization of BT2 mainly depends on the disappearance of BT and B6T17. For the two samples with Fe₂O₃ and TiO₂, no segregation was observed when fired at 1240 °C for 2 h. It is thus considered that Fe₂O₃ uniformly dissolves in BT2 crystal grains.



Figure 8 shows SEM images of the fracture surfaces of the BT2 samples with SiO₂ and K₂CO₃ fired at 1220 °C, with Fe₂O₃ and TiO₂ fired at 1240 °C, and without additives fired at 1240 °C. All the samples showed intergranular fracture. The grains of the sample with K₂CO₃ are smaller than those of the other samples. Figures 9 and 10 respectively show the temperature dependences of the relative permittivity and dissipation factor of the five samples. Such dependences were measured at 1 MHz owing to their large dissipation factors, especially in the Fe₂O₃- and K₂CO₃-added samples. The sample with Fe₂O₃ showed a decreased Curie point *T*_c and relaxor behavior. This is probably caused by the substitution of Fe into Ti sites as well as of BT.^{40,41)} The depression of the relative permittivity curve for the K₂CO₃-added sample is probably affected by the sample's small grains.

Table VII shows the T_c values of all the samples shown in Fig. 9. The T_c values of the samples with TiO₂ and SiO₂ are higher than that of the sample without additives, whereas that of the sample with K₂CO₃ is lower than that of the sample without additives. It is estimated that the Ti concentration of BT2 crystal grains with TiO₂ additive is higher than the stoichiometric concentration obtained by dissolving excess TiO₂ in BT2 grains. Similar phenomena are confirmed in BT ceramics, i.e., excess TiO₂ dissolves in BT grains.⁴²⁾



Fig. 9. Temperature dependences of relative permittivities of samples with and without additives measured at 1 MHz.

Moreover, in the SiO₂-added sample, since Ba can be extracted from BT2 crystal grains into the secondary phase already mentioned above, the Ti concentration of BT2 crystal grains is probably higher. In the sample with K_2CO_3 , the Ti concentration is about 4 times higher than Ba in the K_2O segregation areas, as shown in Table VI. This result shows the extraction of Ti from BT2 grains to the secondary phase.



Fig. 10. Temperature dependences of dissipation factors $(\tan \delta)$ of samples with and without additives measured at 1 MHz.

 Table VII.
 Curie points derived from the temperature dependences in Fig. 9.

Additive	$T_{\rm c}$ (°C)
TiO ₂	436
SiO ₂	432
Without additives	426
K ₂ CO ₃	416
Fe ₂ O ₃	306



Fig. 11. SEM image of BT2 powder obtained by calcining raw material powder of combination B.

The Ti concentration of BT2 crystal grains is therefore lower than the stoichiometric concentration. Considering this estimation, we can see the correlation that T_c increases with decreasing Ba/Ti ratio of BT2 grains. This correlation accords with the results reported in BT.⁴³⁾

3.2 Effect of particle size of TiO₂ raw material powder

Figure 11 shows a SEM image of the calcined powder obtained using the raw material powder of combination B. The particles are larger than those of the calcined powder obtained using the raw material powder of combination A. This calcined powder showed $\alpha = 100\%$. Thus, the calcined powder of the BT2 single phase was obtained using small TiO₂ powder particles. As reported previously, it is necessary for BaO to be uniformly diffused on surfaces of TiO₂ particles in its initial reaction stage, in order to synthesize



Fig. 12. BT2 production ratios and densities of BT2 samples without additives obtained by firing the calcined powder compacts fabricated from combination B.



Fig. 13. SEM image of BT2 sample fired at 1220 °C for 2 h using raw material powder of combination B.

BT2 via a solid-phase reaction.³¹⁾ This initial stage reaction causes a subsequent homogeneous reaction. Since small TiO_2 powder particles promotes a homogeneous reaction, this result is consistent with previous our report.³¹⁾

Figure 12 shows the α and ρ values of the samples when the calcined powder was fired in air. The α value was 100% at temperatures below 1240 °C, and BT2 decomposition did not appear. However, the density fired at 1240 °C was $\rho = 4.69 \text{ g/cm}^3$ (91.6%). This is probably ascribed to big pores and microcracks produced by abnormal grain growth, as shown in Fig. 13. Figure 14 shows the temperature dependence of the permittivity of the sample measured at 10 kHz. T_c was 430 °C. This stability of the BT2 phase is probably due to the non-existence of any compounds other than BT2, which can be the origin of BT2 decomposition during sintering. This notion is consistent with the mechanism of stabilizing the BT2 phase by the absorption of unwanted compounds such as BT and B6T17 into SiO₂ or K₂O.

4. Conclusions

The effects of additives and the particle size of TiO_2 raw material powder on the stabilization of the BT2 phase during sintering were experimentally investigated. The additives SiO_2 and K_2CO_3 were effective for the stabilization of BT2.



Fig. 14. Temperature dependences of relative permittivity and dissipation factor (tan δ) of BT2 sample using the raw material powder of combination B sintered at 1240 °C for 2 h measured at 10 kHz.

In particular, the effect of SiO_2 was outstanding. Furthermore, the use of small TiO_2 raw material powder particles was effective. These results indicate that BT2 decomposition is attributed to the existence of unwanted compounds other than BT2, which can be the origins of BT2 decomposition. The additive Fe₂O₃ has no appreciable effect on BT2 phase stabilization. Fe₂O₃ uniformly dissolved in BT2 crystal grains and induced relaxor behavior.

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