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Low-temperature fabrication of $BaBi_2Nb_2O_9$ ceramics by reaction controlled sintering

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Abstract

Reaction controlled sintering was applied to the fabrication of $BaBi_2Nb_2O_9$ (BBN) ceramics at lower temperature. A powder mixture of $BaCO_3$ and Nb_2O_5 was heated at 600°C in a 1st step calcination to produce a binary precursor of $BaNb_2O_6$. The pre-heated powder was then mixed with a fixed amount of Bi_2O_3, which was subsequently pressed into a disk pellet. After a powder compact of the mixture was subjected to heating at 950°C for 4 h, a BBN bulk sample with a relative density of 92% was successfully obtained. The low-temperature fabrication of dense BBN ceramics could be attributed to the inhibited formation of an intermediate phase of $Ba_5Nb_4O_{15}$ and the production of submicron powder with an appropriate reactivity during a 1st step calcination.

Keywords

$BaBi_2Nb_2O_9$, reaction controlled sintering, low-temperature sintering, phase formation, densification

1. Introduction

BaBi$_2$Nb$_2$O$_9$ (BBN) is a ferroelectric compound belonging to the well known Aurivillius family of layer-structured oxides [1]. BBN shows a broadened ferroelectric - paraelectric transition at 100-150°C with a relaxor characteristic, and the origin of the behavior has been intensively discussed [1-7]. In addition, the doping effects on the modification of the dielectric properties are also extensively studied [8-11]. Recently, Ando et al. reported that solid solution of Ba$_{1-x}$Sr$_x$Bi$_2$Nb$_2$O$_9$ were quite adequate for the fine tolerance resonator applications because they have the thermally stable characteristics and small electromechanical coupling coefficients [12]. In most of the studies, BBN powders were prepared by the conventional solid state reaction of BaCO$_3$, Bi$_2$O$_3$, and Nb$_2$O$_5$ [6-9, 11-12]. This method requires calcination at high temperature to synthesize a powder consisting of the BBN single phase, usually resulting in grain coarsening. Thus, densification of the powder compact prepared by this method requires sintering at a considerably high temperature. For example, Miranda et al. obtained a BBN powder at 950°C, which was followed by sintering at 1100°C [6]. Some authors have proposed different methods to prepare an ultrafine precursor powder to BBN: (i) citrate gel method [13], (ii) co-precipitation method [14], and (iii) chemical precursor decomposition method [15]. Nevertheless, high temperatures were still required to obtain dense BBN ceramics, e.g., 1050°C for the citrate gel method and 1000°C for the co-precipitation method. Sintering at high temperature involves a risk of an undesirable compositional change and resulting material degradation due to the volatilization of Bi species [16-17]. Therefore, it is preferable to employ an alternative synthesis and sintering procedure by which functional BBN ceramics can be fabricated at lower temperatures.

Lu et al. fabricated $BaBi_2Ta_2O_9$ (BBT) ceramics at lower sintering temperature by about 50°C than that of the conventional solid state reaction method, using a BBT powder obtained by a novel process [18]. In this process, referred to as a reaction controlled process, pre-reacting Bi_2O_3 and Ta_2O_5 to form $BiTaO_4$ prior to the reaction with $BaCO_3$ led to the production of a BBT powder with a reduced particle size. The present authors applied this process using $BiNbO_4$ as a precursor to the fabrication of BBN ceramics and obtained the bulk sample with the relative density of 90% by sintering at 950°C for 4 h [10]. This result indicates that modified processes based on the reaction controlled process are a promising approach to further lowering of the sintering temperature of BBN ceramics. Therefore, several modified processes were employed in this study in order to fabricate BBN ceramics by sintering at lower temperatures below 1000°C. At first, the phase formation behavior of BBN by the conventional solid state reaction was studied. Then, the reaction controlled process using different precursors of $BaBi_2O_4$, $BaNb_2O_6$, or $Ba_5Nb_4O_{15}$ was examined for the synthesis and sintering of powders consisting of the BBN single phase. Finally, the reaction controlled sintering (RCS) was applied to achieve the low-temperature fabrication, in which oxide mixtures of pre-reacted $BaNb_2O_6$ and Bi_2O_3 were directly sintered.

2. Experimental Procedure

2.1 Powder preparation for the conventional solid state reaction

BBN powders were prepared using $BaCO_3$, Bi_2O_3, and Nb_2O_5 as starting materials (All from Kojundo Chemical Lab.). Stoichiometric amounts of the starting materials were simultaneously ball-milled with distilled water for 24 h.

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The mixed slurry was dried and heated at 600-1000°C for 4 h under an oxygen flow.

2.2 Powder preparation for the reaction controlled process

Three different binary precursors of $BaBi_2O_4$, $BaNb_2O_6$, and $Ba_5Nb_4O_{15}$ were prepared by mechanical mixing of the corresponding oxide powders and heating at 750-800°C for 4 h under an oxygen flow (1st calcination). Each precursor powder was subsequently mixed with Bi_2O_3 or Nb_2O_5 to give the final composition of BBN. The mixtures were calcined again at 700-1000°C for 4 h in air (2nd calcination) in order to complete the reaction to BBN.

2.3 Powder preparation for the reaction controlled sintering (RCS)

In the case of the RCS, oxide mixtures were prepared by the procedure based on the $BaNb_2O_6$-route mentioned above. The equi-molar mixture of $BaCO_3$ and Nb_2O_5 was pre-heated at 600°C or 800°C for 4 h under an oxygen flow (The precursor powder is referred to as RCS-600 or RCS-800), and then the precursor powder was subsequently mixed with Bi_2O_3 required to the BBN stoichiometry. The obtained mixtures are referred to as RCS-600/Bi or RCS-800/Bi hereafter. A further calcination was not carried out prior to sintering.

2.4 Characterization and sintering of the heat-treated powders

The heat-treated powders were characterized by phase identification with X-ray diffraction (XRD; Mac Science, M03XHF), microstructure observation with scanning electron microscope (SEM; JEOL, JSM-5800LV), particle size

distribution measurement (Microtrac, HRA 9320-X100), and surface area measurement (three-point BET method; Quanta Chrome, Auto sorb-1). These powders were pressed into pellets and sintered at 800-1000°C (heating rate of 5°C min^{-1}) for 0-4 h in air. The sintered samples were characterized by density measurement (for the samples sintered at 950°C for 4 h), phase identification with XRD, microstructure observation with SEM. To examine the densification behavior under a constant heating rate (5°C min^{-1}), linear shrinkage was measured with thermo-mechanical analysis (TMA; Seiko Instruments Inc, EXSTAR-6000) using rod-shaped compacts. For dielectric measurement, both sides of the sintered sample were painted with silver paste and fired at 600°C for 10 min to form electrodes. The dielectric properties were measured at temperatures ranging from 50-300°C with a LCR meter (HP, 4274A) at 1-100 kHz.
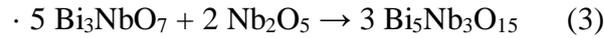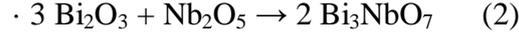
3. Results and Discussion

3.1 The phase formation behavior of BBN by the conventional solid state reaction

In order to draw out a reaction scheme for fabricating BBN ceramics by sintering at lower temperature, the phase formation behavior of BBN was examined.
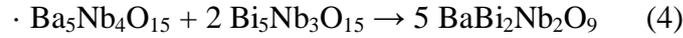
Figure 1 shows the XRD patterns of the conventionally prepared powders heated at 600-1000°C for 4 h. In the 600°C-heated powder, a five-phase mixture consisting of $BaCO_3$, Nb_2O_5, $Ba_5Nb_4O_{15}$, Bi_3NbO_7, and $Bi_5Nb_3O_{15}$ was obtained. BBN phase did not form at this temperature. After heating at 800°C, the intended BBN phase (•) began to form distinctly with the presence of $Ba_5Nb_4O_{15}$ and $Bi_5Nb_3O_{15}$ phases. Heating at 1000°C could cause the production of the BBN

single phase. From the phases identified and their intensity ratio changes of the X-ray peaks with heating temperature, the reactions occurring in the conventional solid state reaction are described as follows:

[<800°C]

$\cdot$ 5 $BaCO_3$ + 2 Nb_2O_5 → $Ba_5Nb_4O_{15}$ + 5 CO_2 (1)

$\cdot$ 3 Bi_2O_3 + Nb_2O_5 → 2 Bi_3NbO_7 (2)

$\cdot$ 5 Bi_3NbO_7 + 2 Nb_2O_5 → 3 $Bi_5Nb_3O_{15}$ (3)

[800-1000°C]

$\cdot$ $Ba_5Nb_4O_{15}$ + 2 $Bi_5Nb_3O_{15}$ → 5 $BaBi_2Nb_2O_9$ (4)

Lu et al. proposed a similar reaction sequence for BBT, in which BBT was formed by the reaction between two intermediates, cubic Bi_2O_3 and $Ba_5Ta_4O_{15}$ [18]. Compared with the present XRD result, $Ba_5M_4O_{15}$ (M = Ta or Nb) phase was produced in both systems, while there was a difference between cubic Bi_2O_3 phase and Bi_3NbO_7 and $Bi_5Nb_3O_{15}$ phases. For the present solid state reaction, the $Ba_5Nb_4O_{15}$ phase was produced at 600°C and still existed up to a higher temperature of 900°C. Thus, the heating at 1000°C was required to obtain the BBN single phase in this method. The presence of the intermediate $Ba_5Nb_4O_{15}$ phase might inhibit the further phase formation of BBN.

3.2 Synthesis of the BBN powders by the reaction controlled process and their sinterability

The formation process of the intermediate $Ba_5Nb_4O_{15}$ phase should be bypassed for the synthesis and sintering of the BBN powders at lower temperatures. Then, the reaction controlled process was applied.
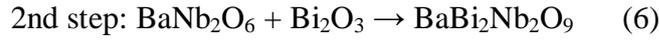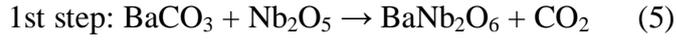
Table 1 summarizes the preparation conditions and obtained phases in this process, in which the BBN powders were synthesized from the binary precursors

of $BaBi_2O_4$, $BaNb_2O_6$, $Ba_5Nb_4O_{15}$, or $BiNbO_4$ (BaB-, BaN-, B5N-, or BiN-route, respectively). The BiN-route was previously reported [10]. The synthesizing temperature of the BBN single phase was different depending on the route. In the case of BaB-route, it reached 1000°C, being as high as that of the conventional solid state reaction method [6-12]. Both B5N- and BiN-routes required heating at 800°C to prepare the BBN powders. For the BaN-route, however, the BBN single phase could be synthesized at 700°C, which was the lowest of all synthesizing temperature required. Thus, since the BaN-route was found to substantially lower the synthesizing temperature, low temperature fabrication of the BBN ceramics would be expected by this BaN-route.

Sintering characteristics at 950°C were examined for the synthesized BBN powders in order to achieve the low-temperature fabrication of BBN ceramics by sintering below 1000°C. The relative densities of the samples sintered at 950°C for 4 h were 60%, 51%, and 54% for the BaB-, BaN-, and B5N-route, respectively. No densification occurred at the sintering temperature in these samples, even for the BaN-route powder. Probably, the densification of these BBN powders at 950°C would be promoted by some powder treatment such as mechanical grinding. However, the achievement of low-temperature fabrication of BBN ceramics by such a physical process is not the aim of this study. So no further examination based on the mechanical grinding was conducted for the powders prepared by the reaction controlled process.

3.3 Phase formation and densification behaviors by the reaction controlled sintering (RCS)

In the previous section, the BaN-route in which following stepwise reactions could take place during heating

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1st step: $BaCO_3 + Nb_2O_5 \rightarrow BaNb_2O_6 + CO_2$ (5)

2nd step: $BaNb_2O_6 + Bi_2O_3 \rightarrow BaBi_2Nb_2O_9$ (6)

was found to be the optimum method to obtain the single phase BBN powder at temperature as low as possible. Therefore, as a modified approach to produce densified BBN ceramics by low-temperature sintering, the RCS method was applied in this study, in which powder compacts consisting of a mixture of $BaNb_2O_6$ (prepared by 1st step calcination in eq. (5)) and Bi_2O_3 were heated at 950°C for 4 h. Especially, the effect of the 1st step calcination temperature on the sintering behavior was examined in this RCS method.

Figures 2(a) and 2(b) show the XRD patterns of the RCS-600 and RCS-800 powders, respectively. At 600°C, $BaCO_3$, Nb_2O_5, and $Ba_5Nb_4O_{15}$ coexisted. After heating at 800°C, the $BaNb_2O_6$ single phase could be obtained via the reaction between them. The RCS-600 or RCS-800 powder was then mixed with Bi_2O_3 for subsequent reaction and sintering. Figures 2(c)-(e) show the XRD patterns of the sintered samples using RCS-600/Bi and RCS-800/Bi powders. The BBN single phase could be obtained for the RCS-800/Bi sample by sintering at 800°C for 0 h (Fig. 2(e)). For the RCS-600/Bi sample, although three phases including $Ba_5Nb_4O_{15}$ coexisted in the calcined powder (Fig. 2(a)), almost single phase was observed by sintering at 900°C for 0 h (Fig. 2(d)). Therefore, RCS-600/Bi or RCS-800/Bi sample suppressed partially or completely the formation of the intermediate $Ba_5Nb_4O_{15}$ phase, respectively, and the BBN single phase could be obtained at the relatively low temperature of 800-900°C as expected.

Figure 3 indicates the TMA results of the powder compacts for RCS, which was heated at 5°C min^{-1} from room temperature to 1000°C. Both samples showed an expansion from about 700°C. This expansion probably corresponded to the BBN phase formation because BBN has a larger molar volume than the sum of

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the individual reactants. As can be seen in Fig. 3, the RCS-600/Bi sample started shrinking at 850°C and a shrinkage of 17% was achieved at 1000°C, whereas RCS-800/Bi sample showed no shrinkage in this heating schedule. Furthermore, the total linear shrinkage of the powder compact after sintering at 1000°C for 4 h was only 5%. Thus, the significant difference in the densification behavior was observed depending on the pre-heating temperature.

In order to clarify the factors causing the different densification behavior between RCS-600/Bi and RCS-800/Bi, microstructural analysis was conducted. Figure 4 shows the SEM micrographs of the RCS-600 and RCS-800 powders. For the RCS-600 powder (Fig. 4(a)), fine particles were observed and they seemed to be softly agglomerated. In the case of the RCS-800 powder (Fig. 4(b)), on the other hand, the primary particles whose size could be estimated to be about 0.5 μm were slightly larger than that of the RCS-600, and they tightly bound with each other to form large agglomerates of more than 1 μm. Figure 5 illustrates the particle size distributions of the RCS-600 and RCS-800 powders. Both powders have a peak located at 0.3 μm, and the RCS-800 powders have an additional clear peak located at 1.0 μm, having a bimodal distribution. The latter peak for the RCS-800 powder corresponds to the large agglomerated particles shown in Fig. 4(b). The specific surface areas of the RCS-600 and RCS-800 powders were estimated to be 4.4 and 3.0 m^2g^{-1}, respectively. These results indicated that heating at 800°C enhanced the agglomeration of the calcined powder in addition to the phase formation of $BaNb_2O_6$.

Figure 6 shows the micrographs of the fractured surfaces of the RCS-samples obtained by sintering at 900°C for 0 h, which was just after the onset of the shrinking of the RCS-600/Bi powder compact as shown in Fig. 3(a). The RCS-600/Bi sample exhibited the microstructure containing no distinct agglomeration

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and fine particles with a broad size distribution (Fig 6(a)). On the other hand, the RCS-800/Bi sample sintered at 900°C, which showed no densification, exhibited the microstructure consisting of a network of partially sintered and coarsened grains through the solid materials (Fig. 6(b)). The formation of this aggregated grain network could be attributed to the fact that the BBN single phase particles have already formed at lower temperature of 800°C (Fig. 2(e)). For very porous materials, a grain coarsening process would be generally favored more than a densification process [19]. Thus, once such a porous network microstructure observed in the RCS-800/Bi sample has been built up, no further densification occurs. In order to densify such porous materials, prolonged heating at a high temperature or an applied pressure is required [20]. In this way, each sample having different sinterability showed different microstructure depending on the pre-heating temperature and resulting reaction route and powder properties.

When the RCS-600/Bi mixture with appropriate reactivity and sinterability was used, low-temperature sintering could be successfully achieved. The densified BBN ceramics sintered at 950°C for 4 h showed its relative density of 92%.

3.4 Dielectric properties of the RCS-sample

Figure 7 illustrates the temperature dependence of the dielectric constant (εr) for the RCS-600/Bi sample sintered at 950°C for 4 h with a tan δ change at different frequencies (1- 100 kHz). A general relaxor behavior was observed in the ε-T curves, where the temperatures of the maximum dielectric constant shifted to higher temperatures and the maximum values of the dielectric constant decreased with increasing frequency. This sample showed a well-known diffuse phase transition character with a dielectric constant peak at 130-180°C (1 kHz).

From the intense discussion on the cause of the broadened phase transition in BBN, Blake et al. concluded that it could be attributed to the Ba and Bi atoms disordering [3]. At high temperatures, both εr and tan δ started to increase most probably due to an electrical conduction. Therefore, the dielectric properties obtained from the BBN ceramics fabricated by RCS at lower temperature were comparable to those previously reported [8-9, 11-12].

4. Conclusions

Densified BBN ceramics were fabricated by sintering at below 1000°C. Examination of the phase formation behavior of BBN by the conventional solid state reaction revealed that the inevitable intermediate $Ba_5Nb_4O_{15}$ phase was present up to the high temperature of 900°C. This phase might inhibit the further phase formation of BBN. In order to bypass the formation of the $Ba_5Nb_4O_{15}$ phase, the reaction controlled process was applied, in which the BBN powders were synthesized from three different binary precursors of $BaBi_2O_4$, $BaNb_2O_6$, and $Ba_5Nb_4O_{15}$. However, the sintering of the BBN powders indicated that the single phase powder obtained by repeated heating showed the limited densification. For the reaction controlled sintering, the $BaNb_2O_6$ powders obtained by pre-heating at 600°C and 800°C were mixed with Bi_2O_3 to give the final BBN composition (RCS-600/Bi and RCS-800/Bi). If the RCS-800/Bi powder compacts were used, enhanced reaction with the Bi_2O_3 powder caused the network formation between coarsened grains, therefore no densification occurred. On the contrary, when the RCS-600/Bi powder compacts were used, its appropriate reactivity could lead to the formation of BBN submicron powder during early stage of the sintering, followed by densification at later stage. Thus,

densified BBN ceramics (the relative density of 92%) were obtained by RCS at

950°C for 4 h.

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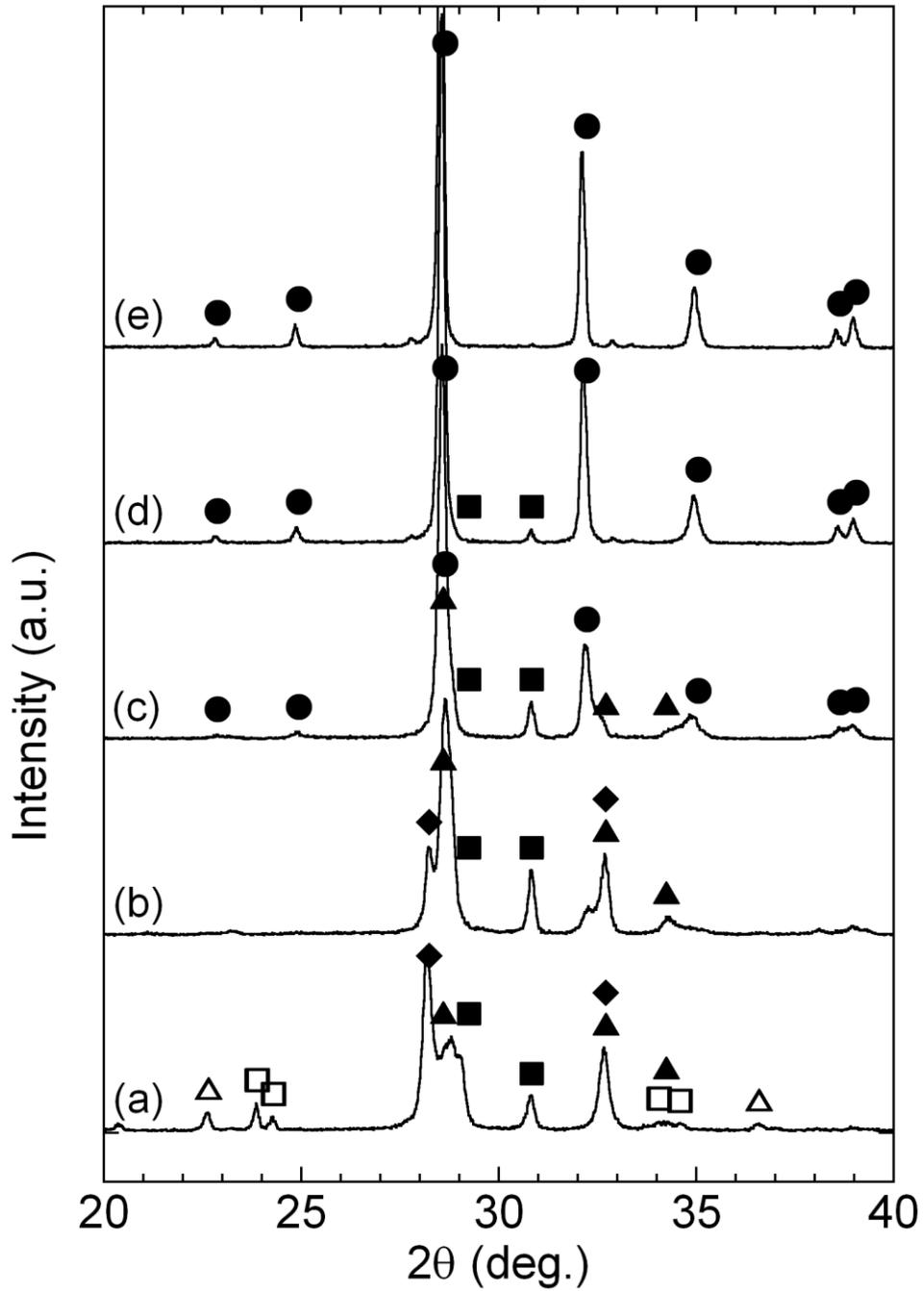20. M. Adamczyk, L. Kozielski, M. Pawełczyk, Ceram. Inter. 34, 1617 (2008)

Figure Legends

Fig. 1 XRD patterns of the conventionally prepared powders heated at (a) 600°C, (b) 700°C, (c) 800°C, (d) 900°C, and (e) 1000°C for 4 h; (●) $BaBi_2Nb_2O_9$, (■) $Ba_5Nb_4O_{15}$, (▲) $Bi_5Nb_3O_{15}$, (♦) Bi_3NbO_7, (□) $BaCO_3$, (Δ) Nb_2O_5
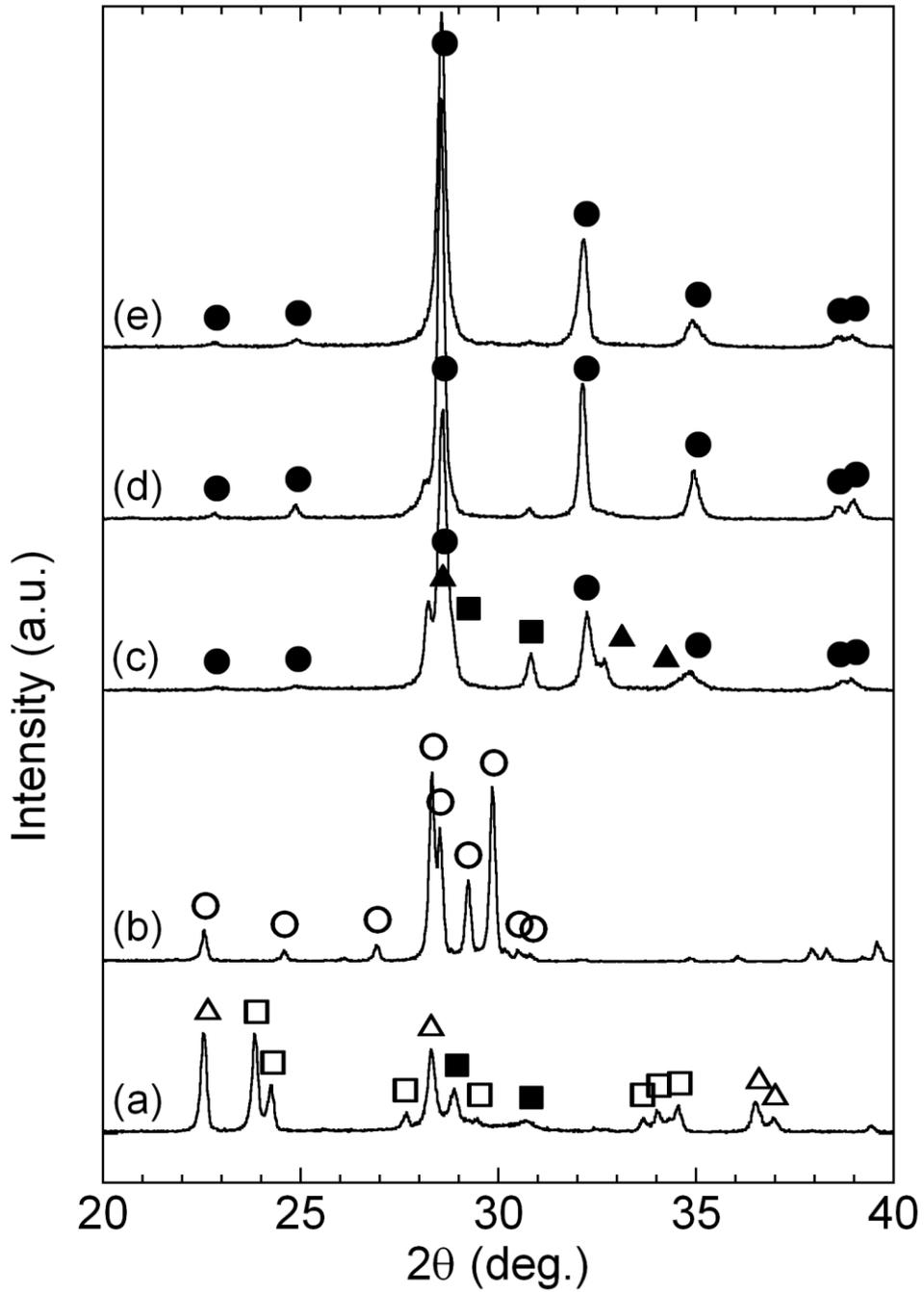
Fig. 2 XRD patterns of the RSC-samples: (a) RCS-600 and (b) RCS-800 powders and the bulk samples using RCS-600/Bi sintered at (c) 800°C and (d) 900°C for 0 h, and (e) using RCS-800/Bi sintered at 800°C for 0 h; (●) $BaBi_2Nb_2O_9$, (■) $Ba_5Nb_4O_{15}$, (▲) $Bi_5Nb_3O_{15}$, (○) $BaNb_2O_6$, (□) $BaCO_3$, (Δ) Nb_2O_5
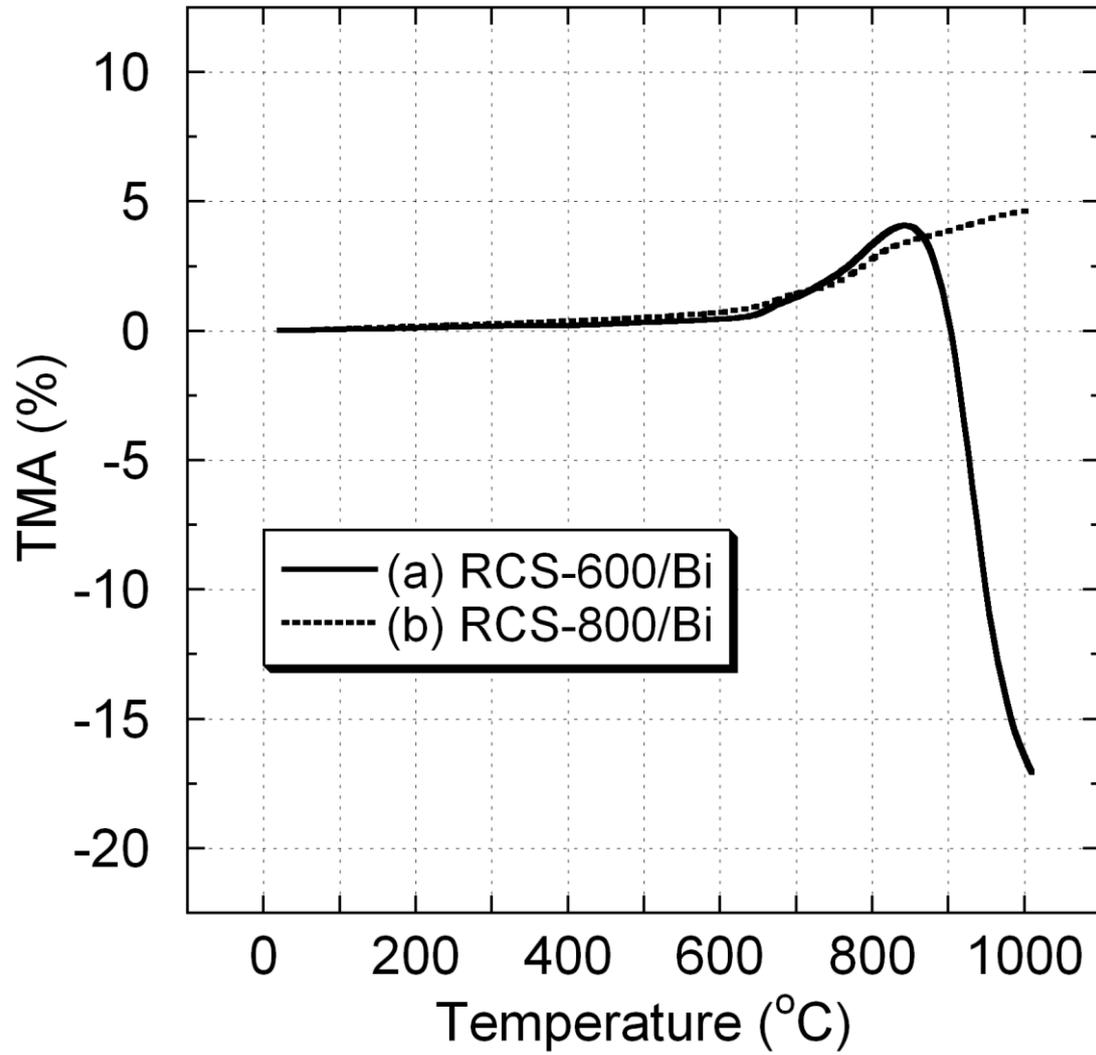
Fig. 3 TMA results of the powder compacts prepared for RCS: (a) RCS-600/Bi and (b) RCS-800/Bi
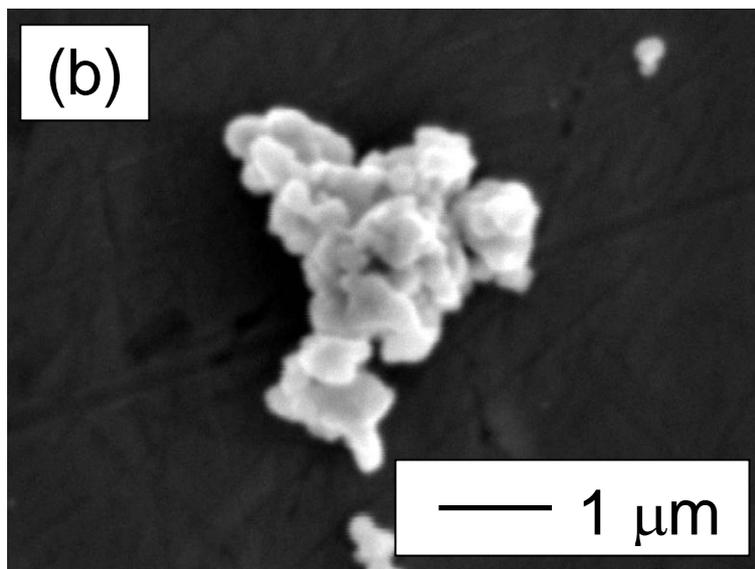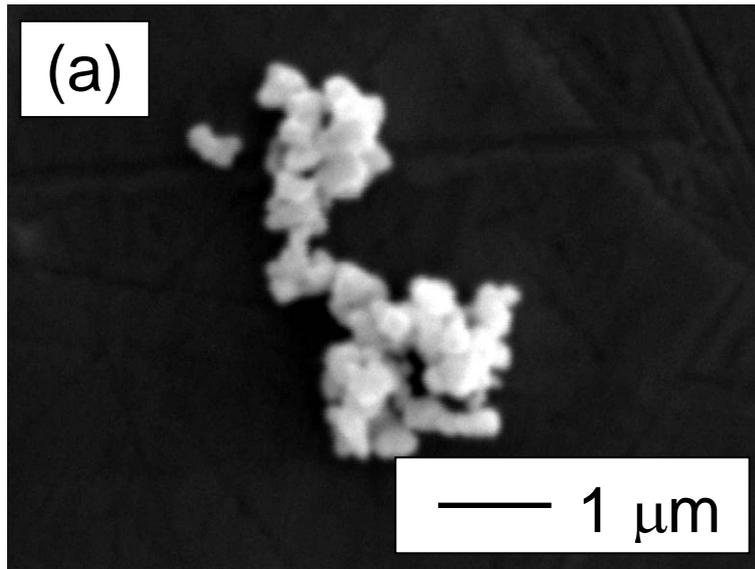
Fig. 4 SEM micrographs of the (a) RCS-600 and (b) RCS-800 powders

Fig. 5 Particle size distributions of the (a) RCS-600 and (b) RCS-800 powders

Fig. 6 SEM micrographs of the fractured surfaces of the RCS-samples obtained by sintering at 900°C for 0 h: (a) RCS-600/Bi and (b) RCS-800/Bi powders

Fig. 7 Temperature dependence of the dielectric constant and dielectric loss for the RCS-600/Bi sample sintered at 950°C for 4 h

Table 1 Preparation conditions and obtained phases for synthesizing the BBN powders using different binary precursors

Fig. 1 XRD patterns of the conventionally prepared powders heated at (a) 600°C, (b) 700°C, (c) 800°C, (d) 900°C, and (e) 1000°C for 4 h; (●) $BaBi_2Nb_2O_9$, (■) $Ba_5Nb_4O_{15}$, (▲) $Bi_5Nb_3O_{15}$, (♦) Bi_3NbO_7, (□) $BaCO_3$, (△) Nb_2O_5

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Fig. 2 XRD patterns of the RSC-samples: (a) RCS-600 and (b) RCS-800 powders and the bulk samples using RCS-600/Bi sintered at (c) 800°C and (d) 900°C for 0 h, and (e) using RCS-800/Bi sintered at 800°C for 0 h; (●) $BaBi_2Nb_2O_9$, (■) $Ba_5Nb_4O_{15}$, (▲) $Bi_5Nb_3O_{15}$, (○) $BaNb_2O_6$, (□) $BaCO_3$, (△) Nb_2O_5

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Fig. 3 TMA results of the powder compacts prepared for RCS: (a) RCS-600/Bi and (b) RCS-800/Bi

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Fig. 4 SEM micrographs of the (a) RCS-600 and (b) RCS-800 powders
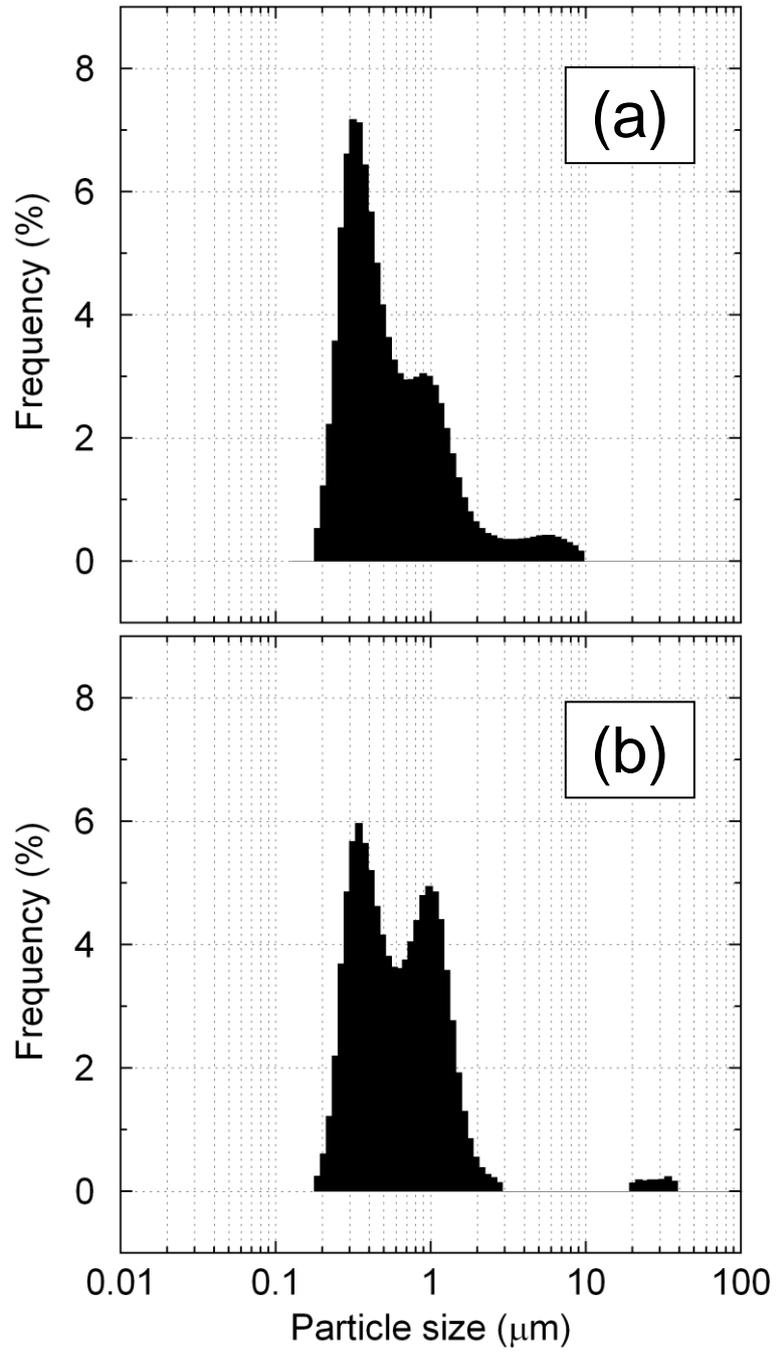
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Fig. 5 Particle size distributions of the (a) RCS-600 and (b) RCS-800 powders
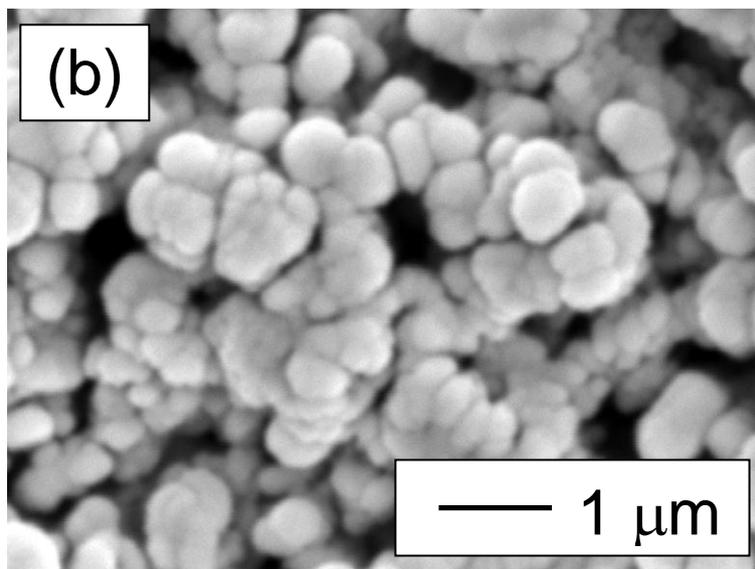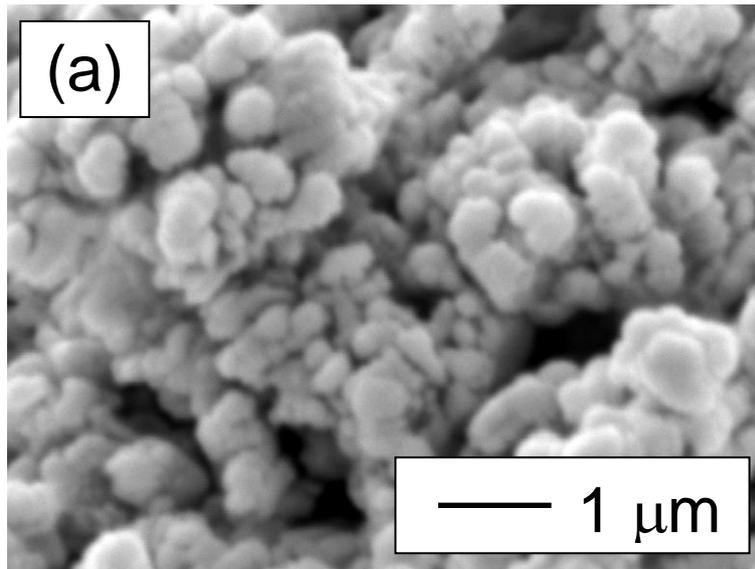
Fig. 6 SEM micrographs of the fractured surfaces of the RCS-samples obtained by sintering at 900°C for 0 h: (a) RCS-600/Bi and (b) RCS-800/Bi powders
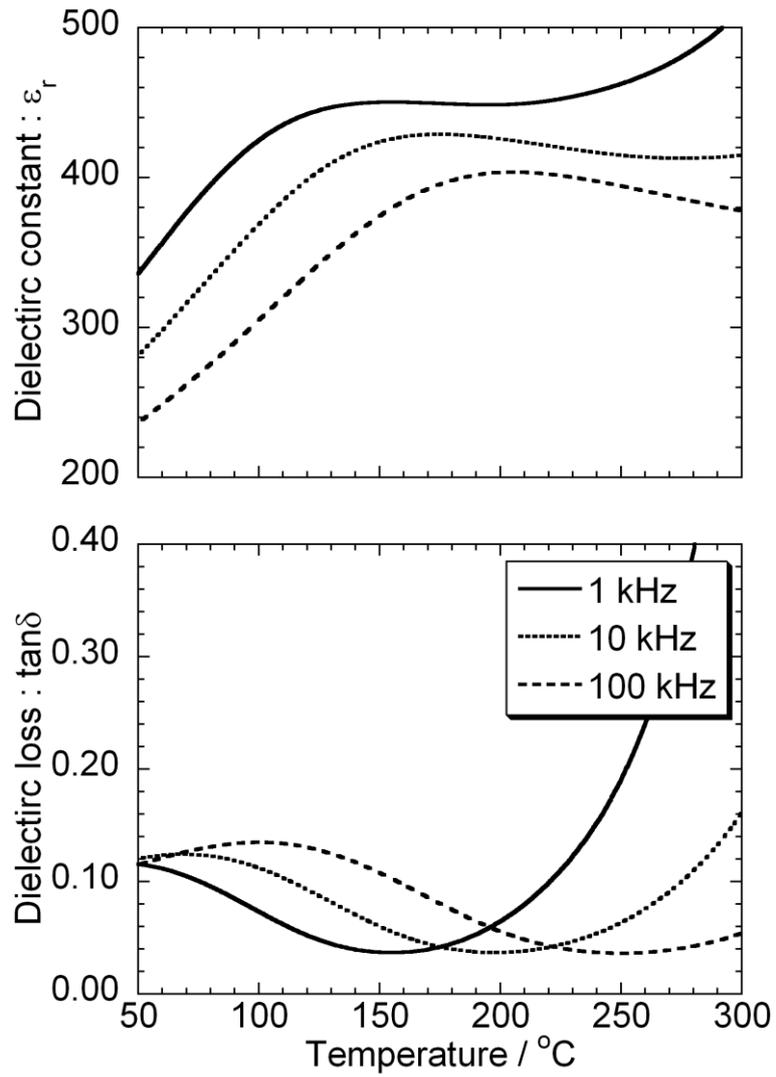
Fig. 7 Temperature dependence of the dielectric constant and dielectric loss for the RCS-600/Bi sample sintered at 950°C for 4 h

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Table 1 Preparation conditions and obtained phases for synthesizing the BBN powders using different binary precursors

Route	Materials and mixing ratio (molar ratio)	1st calcination temperature	obtained precursor	Materials and mixing ratio (molar ratio)	2nd calcination temperature	obtained phase
BaB	$BaCO_3 : Bi_2O_3 = 1 : 1$	750°C [a)]	$BaBi_2O_4$	$BaBi_2O_4 : Nb_2O_5 = 1 : 1$	1000°C	BBN
BaN	$BaCO_3 : Nb_2O_5 = 1 : 1$	800°C	$BaNb_2O_6$	$BaNb_2O_6 : Bi_2O_3 = 1 : 1$	700°C	BBN
B5N	$BaCO_3 : Nb_2O_5 = 5 : 2$	800°C	$Ba_5Nb_4O_{15}$	$Ba_5Nb_4O_{15} : Bi_2O_3 : Nb_2O_5 = 1 : 5 : 3$	800°C	BBN
BiN	$Bi_2O_3 : Nb_2O_5 = 1 : 1$ [b)]	800°C	$BiNbO_4$	$BiNbO_4 : BaCO_3 = 2 : 1$	800°C	BBN

a) The powder was heated twice at 750°C with intermediate grinding.
b) The preparation conditions and obtained phases are from reference [10].

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