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Molten salt synthesis of single-phase $BaNd_2Ti_4O_{12}$ powder

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The single-phase $BaNd_2Ti_4O_{12}$ powder was successfully prepared at 1000 to 1200 °C by the KCl molten salt method, and the sinterability of the powder was briefly studied. Longitudinal single-phase powders could be fully densified at 1450 °C. Measurements showed that the dielectric constant and Q-value of the densified ceramics were high, and the Q-value in particular was markedly affected by the preparatory conditions. These results indicate that single-phase $BaNd_2Ti_4O_{12}$ powder can easily be prepared by the KCl molten salt method and that the ceramics made from the powder show optimal properties for microwave dielectrics. © *1999 Kluwer Academic Publishers*

1. Introduction

The rapid growth of mobile telecommunication systems has hastened the need for a wide variety of new microwave dielectric materials [1]. Of these materials, the compounds in the BaO-Nd_2O_3-TiO_2 system have been found to demonstrate the desired properties such as high dielectric constant, high Q value, and a low temperature coefficient of resonant frequency at microwave frequencies [2–7]. The compounds such as $BaNd_2Ti_4O_{12}$ (designated BNT4 hereafter) and $BaNd_2Ti_5O_{14}$ (designated BNT5) were usually prepared via a solid-state reaction, and the properties of these ceramics have been evaluated. These studies have proven that the compounds are considered to be promising materials for microwave dielectrics [8, 9], but there are differing views concerning the correct compositions [10]. The actual properties of these compounds, however, have not been studied because single-phase ceramics of BNT4 and BNT5 have not been successfully prepared [11]. In this paper, the preparation of single-phase BNT4 powders by the molten salt method [12] is described, and a brief report is given of the sinterability of the powders and the dielectric properties of the resultant ceramics.

2. Experimental

The starting materials were commercially available, high-purity carbonate powder ($BaCO_3$), oxide powders (Nd_2O_3 and TiO_2), and analytical grade chlorides (LiCl, NaCl and KCl). Before the molten salt method, the mixed oxide method was carried out.

Stoichiometric amounts of $BaCO_3$, Nd_2O_3, and TiO_2 were weighed and mixed in ethanol in an agate mortar and pestle, and the stoichiometric mixture for BNT4 was prepared. After drying at 120 °C, the stoichiometric mixture was calcined at 1000 °C for 10 h. The calcined powder was mixed with 1 mass % stearic acid, pressed into pellets (10 mm diameter × 1 mm) in a stainless steel die at a pressure of 10 MPa. The pellets were fired in air at 900 to 1400 °C for 1 to 50 h. The phases present in the fired pellets were identified by X-ray diffraction (XRD).

In the molten salt method [13], the stoichiometric mixture of $BaCO_3$, Nd_2O_3, and TiO_2 was prepared in the same way as described above, and the alkaline chloride salts of LiCl, NaCl, or KCl were added and mixed in. The amount of each salt was varied from 0.1 to 20 moles in a 1 mole stoichiometric mixture of BNT4. The mixed powders were then heated to temperatures of 800 to 1200 °C in a covered alumina crucible for 0 to 10 h. The obtained products were washed in boiling water to remove alkaline salts and then filtered. The washing and filtering were repeated until no chloride ion was detected in the filtrate. The phases present in the powders were identified by XRD, and the morphology of the powders was observed using scanning electron microscopy (SEM). The amount of each phase present in the powders was quantified by determining the height of the highest peak for each compound. The particle size distribution was measured using a laser diffraction method with the dispersion of powders in ethanol by ultrasonic vibration. Single-phase powders prepared by the molten salt method were sintered in the same manner as that used in the mixed oxide method. The bulk density of the resultant ceramics was calculated from the weight and dimensions. The microstructure of the ceramics was observed by SEM. Dielectric properties were measured at a frequency of 10^6 Hz.

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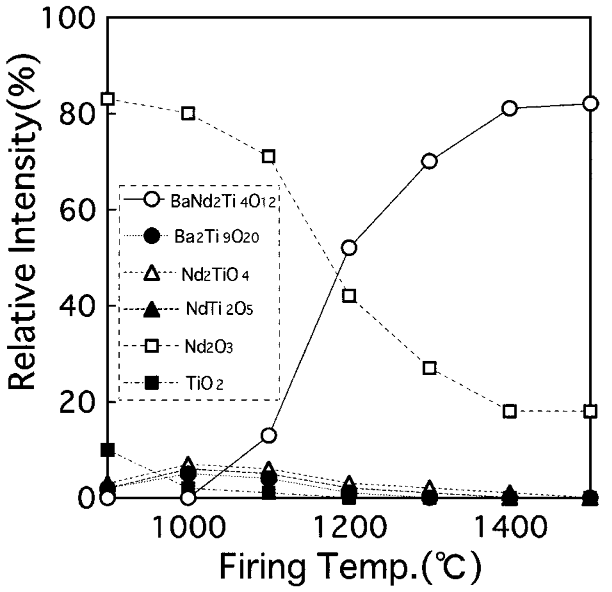

Figure 1 Relative intensity of specified XRD peaks for each phase as a function of heating temperature in the oxide mixing method. Duration of firing: 2 h.

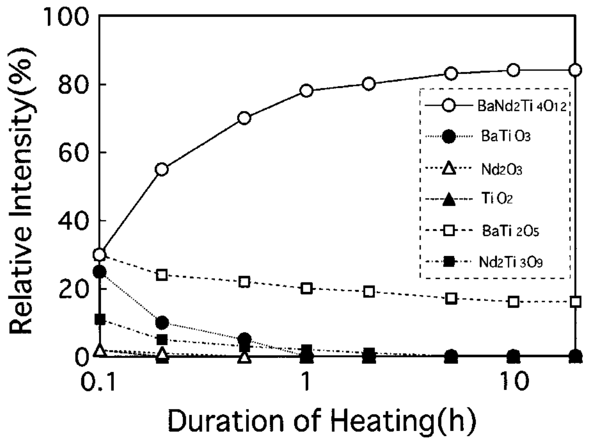

Figure 2 Relative intensity of specified XRD peaks for each phase as a function of heating duration in the NaCl molten salt method.

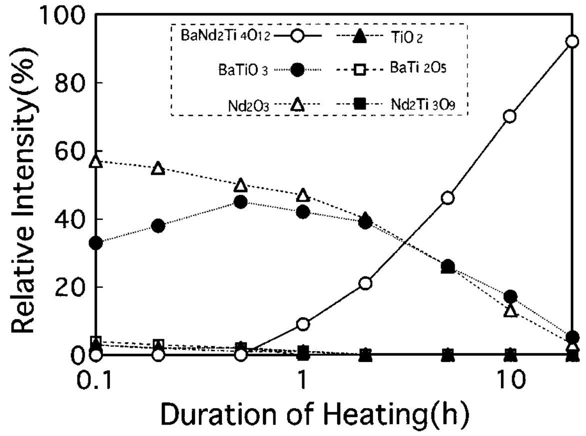

Figure 3 Relative intensities of specified XRD peaks for each phase as a function of heating duration in the KCl molten salt method at 900 °C.

3. Results and discussion

3.1. Mixed oxide method

Fig. 1 shows the relative intensity of specified XRD peaks for each detected phase in ceramics prepared by the oxide mixed method. The presence of several kinds of compound in addition to the objective compound (BNT4) was confirmed. BNT4 first appeared in the sample fired at 1100 °C, and the relative intensity of BNT4 increased continuously with increasing firing temperature, although it never reached 100%. In contrast, the intensity of unreacted Nd_2O_3 decreased with firing temperature but never disappeared entirely. Furthermore, the presence of other undesirable compounds such as $Ba_2Ti_9O_{12}$, Nd_2TiO_4, and $NdTi_2O_5$ was confirmed, but these compounds completely disappeared in the sample fired at 1500 °C. No single-phase BNT4 was obtained, although the firing temperature was increased up to 1600 °C. The change in the calcination temperature also did not improve the reactivity of Nd_2O_3 [14], which seemed to be the reason that single-phase BNT4 was not obtained [9].

3.2. Molten salt method

The molten salt method seems to be a promising preparation method for complex oxide compounds anisotropic in shape [12, 15]. The phases present in the powders prepared by the molten salt method varied according to the preparatory conditions. Fig. 2 shows the relative intensity of XRD peaks for each detected phase in the powders prepared at 1000 °C by the NaCl molten salt method. Compounds such as BNT4 and $BaTiO_3$ (designated BT), and starting materials Nd_2O_3 and TiO_2 were confirmed in the sample heated for 0.1 h. The relative intensity of BNT4 increased as the duration of heating increased, and those of BT and starting materials decreased. TiO_2 disappeared in the sample heated for 5 h, and the relative intensity of Nd_2O_3 also decreased but never disappeared, although the duration of heating exceeded 20 h. The change in the heating temperature did not affect the relative intensity of these phases. A similar preparation procedure was conducted with LiCl molten salt, but the objective phase of BNT4 could not be confirmed.

Fig. 3 shows the relative intensity for each detected phase in the powders prepared at 900 °C by the KCl molten salt method. Unlike the results shown in Fig. 2, TiO_2 disappeared in the sample heated for 20 h, while BT was confirmed even in the sample heated for 20 h. On the other hand, BNT4 was first confirmed in the sample heated for 0.5 h, and the intensity of BNT4 gradually increased with increasing duration. However, no single-phase BNT4 powder was obtained.

Fig. 4 shows the relative intensity of the phases in powders prepared at 1000 °C. Only three compounds, BNT4, BT, and Nd_2O_3, could be detected, and BT and Nd_2O_3 completely disappeared after 1 and 10 h duration, respectively. This result indicates that single-phase BNT4 powder can be prepared by the KCl molten salt method, and that ten hours is the minimum duration for obtaining single-phase BNT4 powder at 1000 °C. Similar experiments conducted at 1100 and 1200 °C revealed that the minimum duration for the preparation of single-phase BNT4 powder was 5 and 2 h, respectively. These experiments indicate that the differences in the melting temperatures of the salts and the reactivities

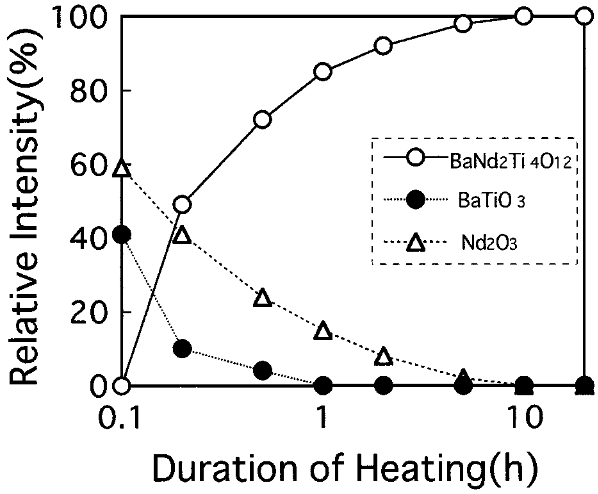

Figure 4 Relative intensities of specified XRD peaks for each phase as a function of heating duration in KCl molten salt method at 1000 °C.

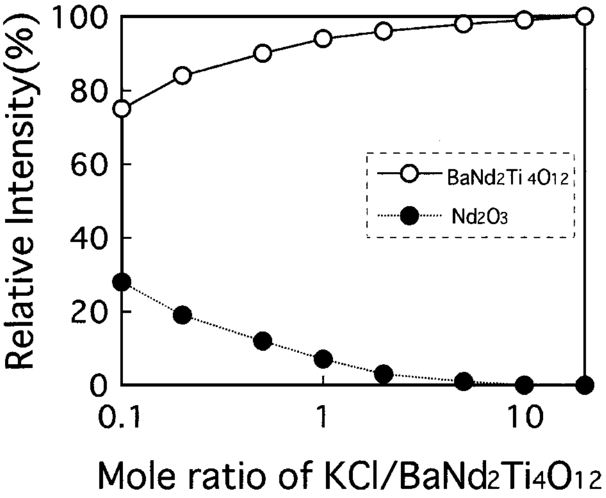

Figure 5 Effect of KCl amount on the preparation of single-phase powder heated at 1000 °C for 2 h.

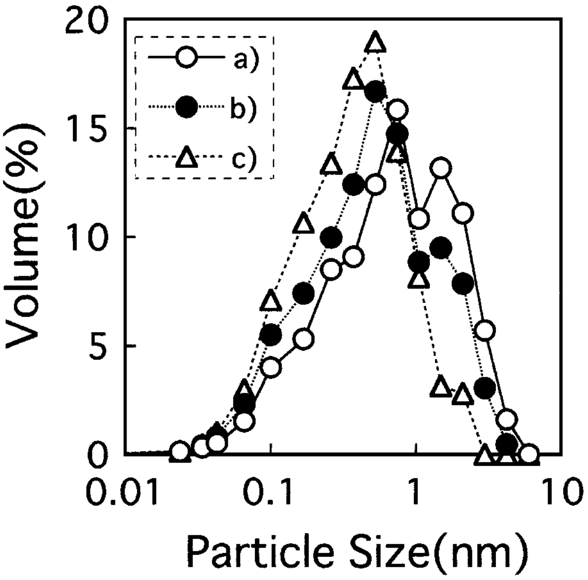

Figure 6 Particle size distribution of single-phase powders prepared at (a) 1000 °C (b) 1100 °C, and (c) 1200 °C.

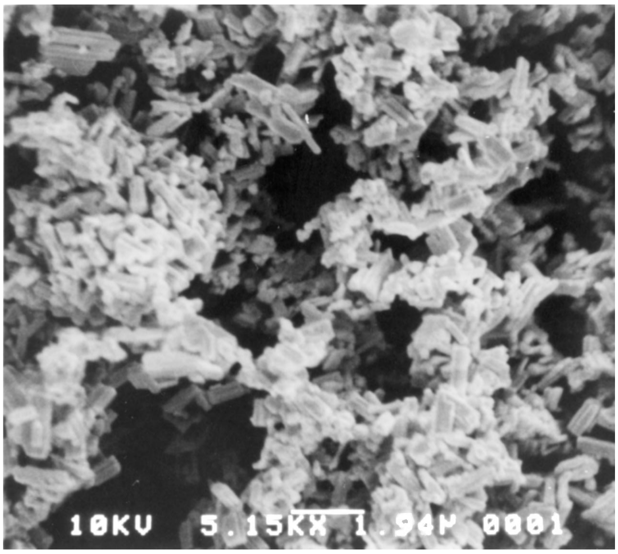

Figure 7 SEM micrograph of single-phase $BaNd_2Ti_4O_{12}$ powder prepared at 1100 °C for 5 h.

of the starting materials in these molten salts might be responsible for producing different phases [16].

The amount of KCl also affected the formation of BNT4 powder in the KCl molten salt method. Fig. 5 shows the relative intensity of BNT4 and Nd_2O_3 in powders prepared at 1000 °C with various amounts of KCl. The figure indicates that a ratio of ten moles of molten salts to one mole of stoichiometric mixture was necessary for the preparation of single-phase BNT4 powder. The minimum required amount of KCl did not vary, although the samples were heated to 1100 °C or more. Therefore, the experiment hereafter was conducted using a ratio of ten moles of KCl to one mole of molten salt.

The particle size distribution of single-phase BNT4 powders prepared at 1000 to 1200 °C is shown in Fig. 6, and the average diameter for each single-phase powder prepared at 1000, 1100, and 1200 °C was calculated to be 6.72, 4.44, and 2.52 μm, respectively. The single-phase BNT4 powder prepared at 1100 °C is shown in Fig. 7, which depicts the powder as having particles that are longitudinal in shape and that form aggregates. The single-phase BNT4 prepared at 1000 to 1200 °C had similar particle shape and size, although the degree of aggregation decreased with increasing preparing temperature. These results suggest that the molten salt method is useful not only for producing ultra-fine powders with anisotropy, but also for controlling the aggregation states of the powders [12].

3.3. Sintering single-phase BNT4 powder

The density of ceramics fired using three kinds of single-phase BNT4 powder are shown in Fig. 8. XRD confirmed that all the ceramics prepared here were single-phase BNT4. The density increased with increasing firing temperature, and the ceramics with higher density were obtained using BNT4 powder prepared at higher temperatures. Fully dense ceramics could be obtained by firing BNT4 powder prepared at 1450 or 1500 °C. A typical microstructure of the ceramics is shown in Fig. 9. The particles were also observed

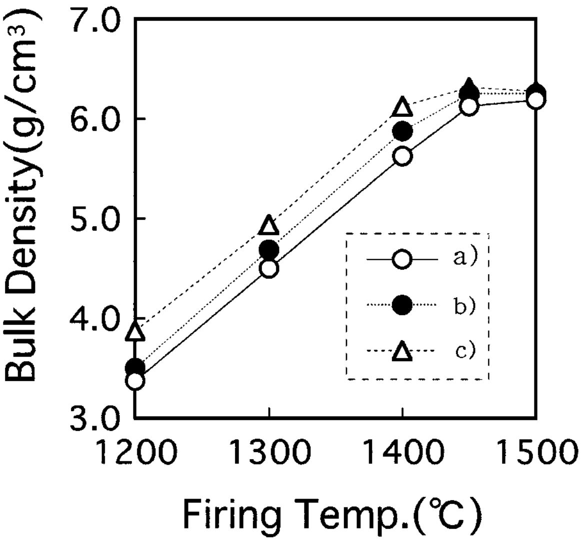

Figure 8 Bulk density of single-phase ceramics made from single-phase powder prepared at (a) 1000 °C, (b) 1100 °C, and (c) 1200 °C.

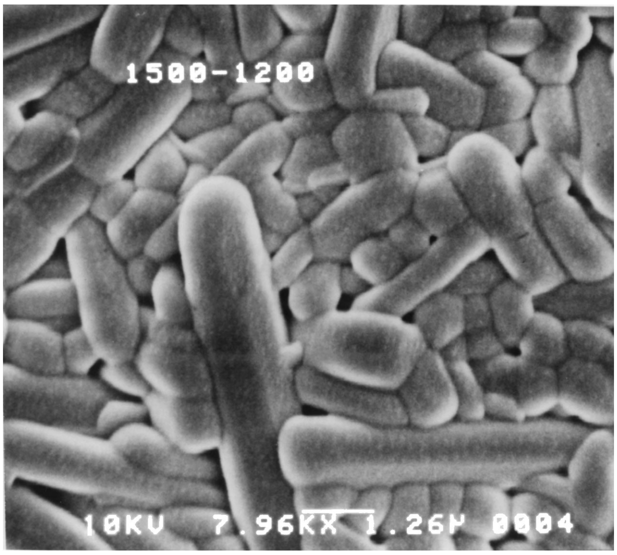

Figure 9 SEM micrograph of single-phase $BaNd_2Ti_4O_{12}$ ceramics sintered at 1450 °C for 2 h.

to be longitudinal in shape, and very few pores were observed. The required temperature for obtaining dense ceramics was higher than that reported in earlier papers [15]. The exact reason why higher densities were obtained is not known, but it is probably because the single-phase BNT4 powder with a precise stoichiometric composition can be prepared by this KCl molten salt method and because there is no liquid phase formed during sintering.

Figs 10 and 11 show the dielectric constants (σ) and Q-values of single-phase ceramics. The values in these dense ceramics were a little higher than those reported previously [17]. The σ increased with increasing firing temperature in the same manner as the variation in the density. On the other hand, the Q-value largely depended on the firing temperature. An exceptionally steep rise in the Q-value was observed at firing temperatures of 1400 to 1450 °C, and a precipitous fall was observed at 1450 to 1500 °C. SEM studies revealed that there is no liquid phase in single-phase ceramics, and that the grain size increases and the number of pores decreases with increasing firing temperature up to 1450 °C. However, exaggerated grain growth was observed in the ceramics fired at 1500 °C. These results indicate that the changes in σ and Q-values can be ascribed to variations in the microstructures of the ceramics [9, 18].

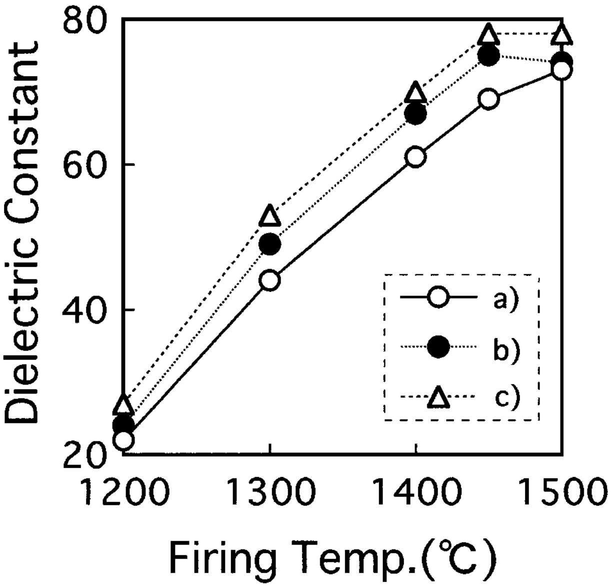

Figure 10 Dielectric constants at 1 MHz for single-phase ceramics sintered at 1200–1500 °C for 2 h using single-phase powder prepared at (a) 1000 °C, (b) 1100 °C, (c) 1200 °C.

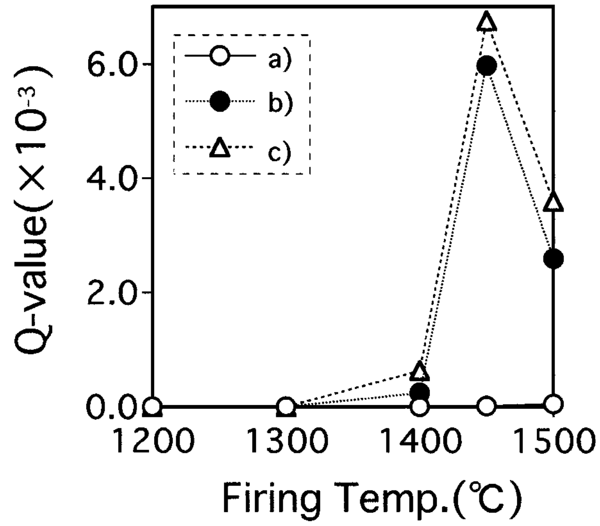

Figure 11 Q-values at 1 MHz for single-phase ceramics sintered at 1200–1500 °C for 2 h using single-phase powder prepared at (a) 1000 °C, (b) 1100 °C, and (c) 1200 °C.

4. Conclusion

BNT4 powder was prepared by the molten salt method, and single-phase BNT4 powder with a longitudinal shape could be prepared using KCl. The temperature and duration of heating, and the amount of KCl salt largely affected the formation of the single-phase powder. The single-phase BNT4 powder with a lesser degree of aggregation exhibited excellent sinterability, and the resulting dense ceramics exhibited favorable dielectric properties.

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