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Effect of grain size and secondary phase on microwave dielectric properties of $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Ba([Mg,Zn]_{1/3}Ta_{2/3})O_3$ systems

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Abstract

Here we report the influence of the grain size of the $Ba(Mg_{1/3},Ta_{2/3})O_3$ (BMT) and secondary phase formed in $Ba([Mg_{0.8}Zn_{0.2}]_{1/3},Ta_{2/3})O_3$ (BMZT) ceramics on the microwave dielectric properties. BMT and BMZT ceramics were prepared by conventional mixed-oxide reaction method using high purity reagents. Samples with different grain size and secondary phase content were obtained by controlling the sintering time of the BMT and BMZT. The secondary phase comprised of $BaTa_2O_6$, which includes small amount of Zn, was formed due to the vaporization of ZnO from BMZT by the high temperature sintering. The Qf value of BMT increased up to 400 THz with increasing the grain size of ceramics, whereas the Qf value of BMZT decreased with increase of the $BaTa_2O_6$ content. This second phase also caused an increase in the temperature coefficient of the resonant frequency of BMZT.

Keywords: Dielectric properties; Perovskites; Grain size; Grain growth; Secondary phase

1. Introduction

Development of advanced dielectric materials in Japan plays an important role in the rapid spread of the wireless communication systems worldwide. Japan has pioneered commercial production of many types of new communication systems, the latest example being the third generation (3G) of the mobile phones. The major research and development efforts are now focused on utilization of the multiple high-frequency bands for the future multipurpose communication systems. Essentially every high frequency communication system employs low-loss dielectric ceramics as passive components of the RF devices. Improvement of the overall performance of the microwave devise is achieved by meticulous investigation and perfection of the dielectric resonators (DR) and other components. Over the last 30 years, significant improvement of the Q-factor and temperature coefficient of the resonant frequency, τ_f, of the dielectric resonators made a great impact on the development of higher frequency devices. $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) and $Ba([Mg,Zn]_{1/3}Ta_{2/3})O_3$ (BMZT) dielectric resonators are widely used in the microwave devices, such as base station filters and output power multiplexers of communication satellites. While BMT and BMZT have superior dielectric properties, it is often necessary to tune their permittivity and τ_f to meet the requirements of the microwave devices. The research on the ion substitution of the BMT ceramics has been carried out by many workers.[1–5] Fang et al. investigated the formation process of several secondary phases during the calcination of the BMT system.[6] However, the relation between the microwave dielectric properties and the secondary phase in the sintered BMT or BMZT and also effect of the grain size on the microwave dielectric properties have been poorly understood.

In the present paper, we report the effect of the grain size on the dielectric properties of the BMT and also the role of the secondary phase on the microwave dielectric properties of BMZT.

2. Experimental procedure

BMT and BMZT were prepared by a conventional mixed-oxide reaction method. High purity reagents of magnesium, zinc and tantalum oxides and barium carbonate were used. The raw materials were weighed according to the stoichiometric compositions of the BMT and BMZT, mixed by ball-milling using zirconia balls in deionized water and then dried. Both BMT and BMZT powders were calcined for 4 h at 1573 K in air. The cal-

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cined powders were subjected to ball-milling again until the D_{50} of the particle size distribution reached about 1 μm. The powders were pressed to form pellets of 12 mm in diameter and 20 mm in height. The BMT pellets were sintered at 1873 K using an electric furnace. The sintering time was programmed in the range of 4–300 h to obtain BMT with various grain sizes. The sintering of the BMZT was carried out in the time range of 50–400 h. As a result, eight types of the BMZT were obtained with various amount of the secondary phase. The secondary phase is formed by Zn vaporization from the BMZT, but its detail will be described in Section 3. The shrinkage of the BMT and BMZT ceramics was within 18–20%. The sintered pellets were sliced to evaluate their dielectric properties. The samples were shaped into the disc resonators having 9.0 mm diameter and 4.5 and 9.0 mm height. After the measurement of the microwave properties, the samples were thermally etched at 1673 K for 30 min.

X-ray diffraction analysis was performed to determine the crystal parameters of the constituents. Also it was confirmed that there were no secondary phase which affects IR measurements in the BMT. The thermally etched surface of BMT was examined by the SEM to determine the grain size of the samples prepared at various sintering time. The composition of the secondary phase of the BMZT was determined by the Electron Probe Microanalyzer (EPMA). The dielectric properties of the samples were measured by Hakki & Coleman's open resonator method in the microwave range, using a network analyzer (HP8720D).

3. Results and discussion

3.1. Grain size and dielectric properties of BMT

Fig. 1 shows the SEM micrographs of the BMT sintered for 4 and 50 h at 1873 K. The significant difference in grain size was observed between two samples. The Qf values of the former and latter were 100 and 300 THz, respectively. The grain size was found to depend linearly on the sintering time. The average grain sizes were about 5, 8 and 14 μm for 100, 150 and 300 h sintering, respectively. Fig. 2 shows the variation of the Qf value as a function of the grain size of the BMT. The Qf gradually increased with the grain size and reached its maximum value of 400 THz for the mean grain size over 9 μm. The grain size dependence of the permittivity and temperature coefficient of the resonant frequency was not observed in the present study. Regarding the Qf value of BMT, Shimada reported that the BMT sintered at 1873K for 4 h or shorter possessed an extremely low Qf value.[1] He concluded that the small Qf value was due to damped vibration of the oxygen layer. Fig. 3 shows the part of the far infrared spectrum attributed to the vibrations of the oxygen layers in the BMT sintered for 30 h. The grain size of the BMT ceramics has reached 2 μm during this sintering time. From this spectrum, the damping constant of the 4th oxygen layer mode is about 39 cm^{-1} and its value is smaller than that of the BMT sintered for 4 h. Hence, we could confirm that the damping of the 4th oxygen layer sufficiently weakened after sintering for 30 h because of the improvement of the degree of ion ordering. Therefore, we consider that the grain size has influenced the Qf value as appeared in the BMT having the grain size between 2 and 9 μm. In this grain size range, as shown in Fig. 2, the most pronounced increase in the Qf value with the grain size is observed.

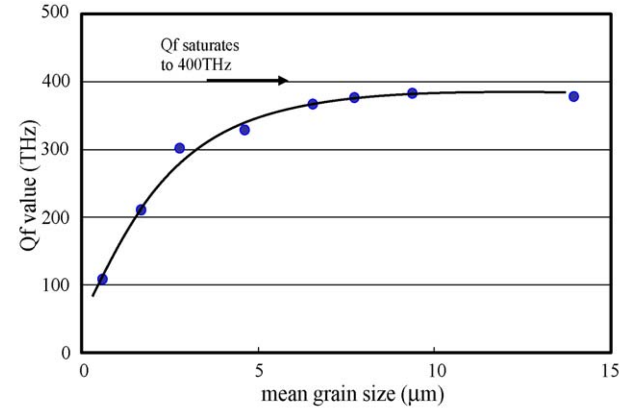
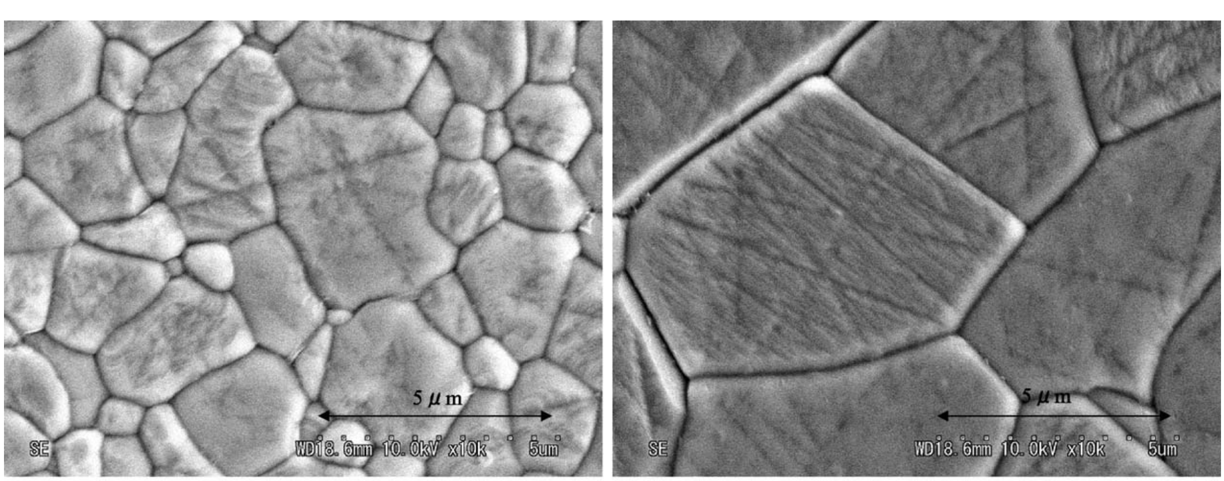


Fig. 2. Grain size dependence of Qf value in BMT.



(a) BMT sintered for 4h at 1873 K (b) BMT sintered for 50h at 1873 K

Fig. 1. Dependence of the grain size on the sintering time of BMT.