ELSEVIER

Journal of Alloys and Compounds 468 (2009) 338–342

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Influence of sintering temperature on microwave dielectric property and crystal structure of corundum-structured Mg_4NbSbO_9 ceramic

Akinori Kan*, Hirotaka Ogawa

Faculty of Science and Technology, Meijo University, 1-501 Shiogamaguchi, Tempaku-ku, Nagoya 468-8502, Japan

Received 2 May 2007; received in revised form 29 December 2007; accepted 2 January 2008
Available online 22 April 2008

Abstract

The relationships between the influence of the sintering temperature on the microwave dielectric properties and crystal structure of Mg_4NbSbO_9 (MNS) ceramics with corundum structure were investigated in this study. From the XRPD patterns, it was found that the MgO compound was identified as a secondary phase in the XRPD patterns of MNS ceramic when the samples were sintered at the sintering temperatures higher than 1500 °C because of the vaporization of Sb in MNS ceramic. The dielectric constants of MNS ceramic increased from 10 to 13 in the temperature range of 1375–1500 °C, whereas those of MNS ceramic decreased at the sintering temperatures above 1550 °C. The quality factors ($Q{\cdot}f$) of MNS ceramic also decreased from 275,000 to 5000 GHz at the sintering temperatures above 1550 °C. Such a decrease in $Q{\cdot}f$ values may be related to the vaporization of Sb and the formation of a secondary phase. The temperature coefficient of resonant frequency was ranged from −56 to −46 ppm/°C.

Keywords: X-ray diffraction; Dielectric response

1. Introduction

A variety of microwave dielectric ceramics are used for the dielectric applications including the filters and resonators in the wireless communication system. In the microwave dielectric applications, there are three main requirements. Firstly, in order to miniaturize the size of microwave dielectric resonator, a high dielectric constant (ε_r) is desirable because the size of resonator is known to be proportional to $1/\sqrt{\varepsilon_r}$, though a low dielectric constant is suitable for the application at high frequency. Secondary, the temperature coefficient of resonant frequency (τ_f) which ideally has near zero value is necessary because the resonant frequency must be stable at the various operating temperatures. Thirdly, the low dielectric loss ($\tan\delta = 1/Q$), i.e., high Q value, is required for the commercial applications; the $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) ceramic, which has a 1:2 ordering of B site cation in perovskite-type structure, is known to be one of the high-Q materials [1]. Therefore, most of recent works have been focused on the perovskite-structured microwave dielectric ceramics with the B site ordering such as BMT [2] and $Ba(Zn_{1/3}Ta_{2/3})O_3$ [3] ceramics.

Recently, in the corundum-structured ceramic, i.e., $Mg_4Nb_2O_9$ (MN) compound, it has been reported that the microwave dielectric properties of MN and their solid solutions are comparable to those of Al_2O_3. The $Q{\cdot}f$ values of $Mg_4(Nb_{2-x}Ta_x)O_9$ ($x = 0$–2) and $Mg_4(Nb_{2-x}Sb_x)O_9$ ($x = 0$–1) solid solutions are extremely improved depending on the composition x [4,5]. Although the effect of Sb substitution for Nb on microwave dielectric properties and crystal structure are investigated in the $Mg_4(Nb_{2-x}Sb_x)O_9$ ($x = 0$–1) solid solutions as described above, the relationships among the sintering time, the microwave dielectric properties and the crystal structure of MNS ceramic has not been clarified to date. Thus, the crystal structural refinement of MNS ceramic sintered at the various temperatures was performed by using the Rietveld method [6] and the stability of crystal structure and site occupancy of Sb site in MNS ceramic were determined to evaluate relationship between the possibility of Sb vaporization which depends on the sintering temperature and microwave dielectric properties.

* Corresponding author.
E-mail address: akan@ccmfs.meijo-u.ac.jp (A. Kan).

0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2008.01.002

2. Experimental method

The samples with nominal composition of Mg_4NbSbO_9 (MNS) were prepared via a conventional solid-state reaction method. The initial powder reactants, MgO (99.99%), Nb_2O_5 (99.9%) and Sb_2O_5 (99.9%), were weighed in stoichiometric proportions and mixed with acetone. These powders were calcined at a temperature of 1100 °C for 10 h in air. After calcining, the obtained powders were ground, mixed with polyvinyl alcohol and uniaxially pressed at 100 MPa into the pellets with 12 mm in diameter and 7 mm thickness. These pellets were sintered at the various temperatures ranging from 1375 to 1600 °C for 10 h in air in order to investigate the sintering dependence of microwave dielectric properties. Subsequently, the sintered pellets were polished, and then the dielectric constant (ε_r) and quality factor ($Q{\cdot}f$) were measured in the frequency range of 11–12 GHz by Hakki and Coleman method [7,8], using the vector network analyzer (Agilent 8720ES). The temperature coefficient of resonant frequency (τ_f) was determined from the resonant frequencies at 20 and 80 °C. The polycrystalline phase of the sintered samples was identified by using the X-ray powder diffraction (XRPD, Rigaku RINT-2200) with Cu Kα radiation at room temperature. In order to clarify the effect of sintering temperature on the possibility of Sb vaporization, the crystal structural refinements were performed in terms of the Rietveld analysis [6,9]; therefore, the site occupancy of Sb site of each sample sintered at the various temperature was determined in this study. The initial structural model for MNS ceramic was taken from the work obtained by Kumada et al. [10] who characterized the crystal structure of $Mg_4Nb_2O_9$ compound, using the neutron powder diffraction at the room temperature. The morphological changes in the sintered samples were also investigated by using field emission electron microscopy (FE-SEM, JEOL JFM-6330F).

3. Results and discussion

Fig. 1 shows the XRPD patterns of MNS ceramic sintered at the temperatures of 1375–1600 °C for 10 h in air. In the sintering temperature range of 1375–1500 °C, a single phase of MNS ceramic was obtained. When the samples were sintered at the temperatures above 1550 °C, the presence of secondary phase, i.e., MgO compound, was observed in the XRPD patterns of the ceramics; this result may be attributed to the Sb vaporization. As for the formation of the secondary phase which consists of the Nb_2O_5–MgO system, it is known that the Nb_2O_5–MgO system produces the liquid phase at the temperature above 1550 °C after formation of MN compound in the temperature range of 1200–1500 °C [11]. Moreover, the deviation of Nb_2O_5 and MgO concentrations from the stoichiometric composition of MN compound was also characterized by the evaluation of sintering temperature dependence of the MN compound [12], and such a deviation has an detrimental effect of the microwave dielectric properties of the MN compound. Based on these results, it is considered that the XRPD patterns of MNS ceramic did not show the presence of secondary phase which containing MgO and Nb_2O_5 in this study. The weight fraction of compounds, which are identified in XRPD patterns, is known to be estimated by using Rietveld analysis and the relationship between weight fraction and refined structural parameters is given by the following equation [13]:

$$W_p = \frac{S_p(ZMV)_p}{\sum_i S_i(ZMV)_i} \tag{1}$$

where S is refined scale factor of phase p and i is number of phase detected in XRPD patterns. Moreover, Z, M and V are formula number, mass of formula and unit cell volume, respectively. The variations in the weight fractions of MNS ceramic and MgO compounds are shown in Fig. 2. The significant variations in the weight fraction are observed at the temperatures above 1550 °C which correspond to the formation of secondary phase as mentioned above; therefore, such a variation in weight fraction may be related to the Sb vaporization of MNS ceramic. In order to confirm the possibility of Sb vaporization in MNS ceramic, the crystal structural parameters of MNS ceramic sintered at the various temperatures were refined by the Rietveld analysis [7] and the refined site occupancy of Sb site are shown in Fig. 3 as a function of sintering temperature. The site occupancy of Sb is refined to be 1.0 in the sintering temperatures of 1375–1500 °C; therefore, from these results, no Sb vocalization is observed in MNS ceramic sintered at such a sintering tempera-

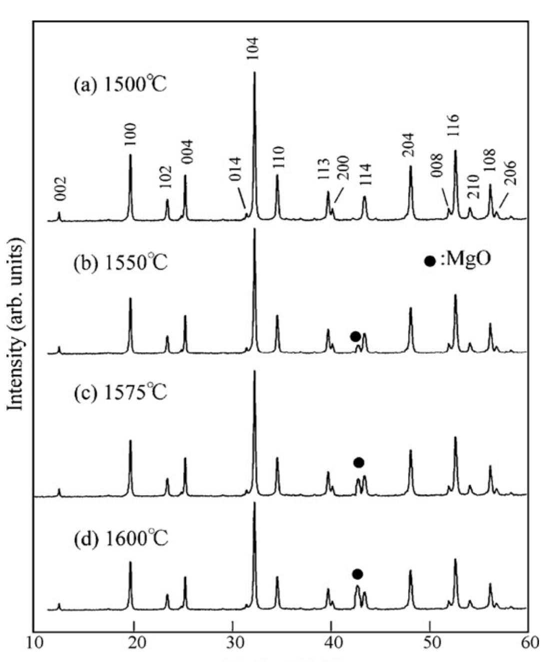

Fig. 1. XRPD patterns of MNS ceramic sintered at various temperatures for 10 h in air.

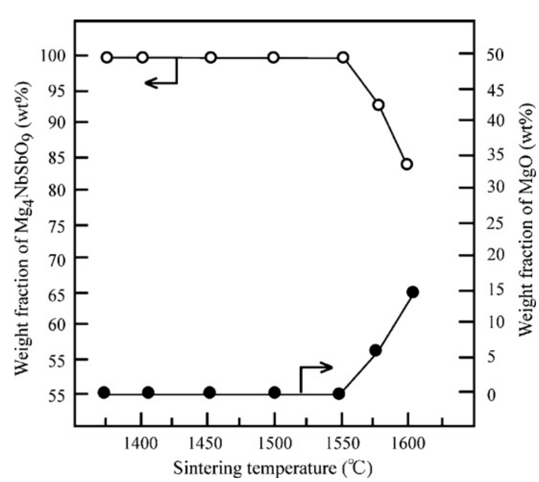

Fig. 2. Variations in weight fractions of MNS ceramic and MgO compounds as a function of sintering temperature.