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Low-temperature sintering and microwave dielectric properties of $Mg_4Nb_2O_9$ ceramics

P. Liu · G. G. Yao · X. B. Bian · H. W. Zhang

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Abstract The effects of V_2O_5 and Li_2CO_3 on the sinterability and microwave dielectric properties of $Mg_4Nb_2O_9$ (MN) ceramics were investigated. With addition of 1.5wt% V_2O_5, the dielectric constant (ε) and $Q \cdot f$ value of MN ceramics sintered at 1,000 °C are comparable to those of pure MN sintered at 1,400 °C. The good results are because of the enhancement of the density by liquid sintering at the lower temperatures. With the mixtures of V_2O_5 and Li_2CO_3, the sintering temperature of MN was further reduced to 925 °C at the expense of the quality factor ($Q \cdot f$) value. Typically, ε of 13.7 and $Q \cdot f$ value of 78,000 GHz were obtained for the specimens with mixtures of 1.5wt% V_2O_5 and 1.5wt% Li_2CO_3 and sintered at 925 °C for 5 h.

Keywords Microwave dielectric ceramics · Low-temperature sintering · $Mg_4Nb_2O_9$ · V_2O_5 · Li_2CO_3

1 Introduction

Multilayer microwave devices have received much attention because of the rapid progress on the satellite and mobile communications such as cellar phone and GPS [1]. In such application dielectric materials with a low dielectric loss, an appropriate dielectric constant, and a near-zero temperature coefficient of resonant frequency have been explored for use as resonators and fillers. In the case of multilayer microwave devices, the low sintering temperatures, lower than the melting point of Ag (964 °C) or Cu (1,064 °C), are required to develop the low-temperature cofired ceramics (LTCC) [2]. Recently, a newly developed microwave dielectric material $Mg_4Nb_2O_9$ (MN) with a high quality factor [quality factor ($Q \cdot f$)=197,000 GHz, ε=12.6] was developed [3]. The microwave dielectric properties of MN ceramics are comparable to those of Al_2O_3 ceramics. Thus, MN is a suitable material for microwave applications, such as substrates and resonators at high frequency [4]. However, the sintering temperatures of MN ceramics (1,350–1,400 °C) are still too high for the practical applications for multilayer microwave integrated circuit [5]. Recently, Yokoi et al. [6] reported that with addition of 3.0wt% LiF, the MN ceramics could be well sintered at a temperature of as low as 850 °C. This work focused on the effects of V_2O_5 and Li_2CO_3 additions on the sintering behavior and microwave dielectric properties of MN ceramics.

2 Experimental procedure

High-purity MgO (99.9%) and Nb_2O_5 (99.5%) powders were weighted according to the stoichiometric composition of MN. They were mixed and ball-milled in a polyethylene bottle with agate balls using ethanol as medium, and then the mixtures were dried and calcined at 1,000 °C for 10 h, then remilled for 6 h with Li_2CO_3 and V_2O_5 additions. After drying, these powders were ground with an organic binder (polyvinyl alcohol) and pressed into pellets 15 mm in diameter and 7.5 mm in thickness under a pressure of 200 kg/cm^2. The samples were sintered at 850–1,050 °C

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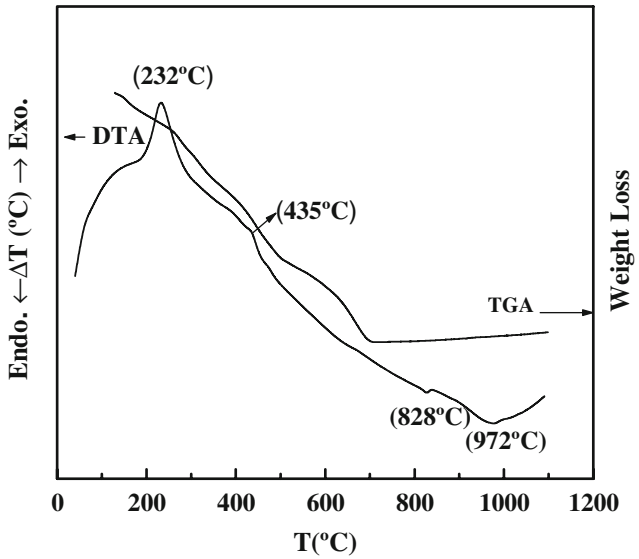

Fig. 1 TG-DTA curves of MN powders doped with 1.5wt% V_2O_5 and 3.0wt% Li_2CO_3

for 5 h with a heating rate of 5 °C/min and then cooled to room temperature.

The reactions of the calcined powders taking place during heat treatment were investigated by thermogravimetry and differential thermal analysis (TG-DTA) (SDTQ600, USA). The bulk densities of the sintered ceramics were measured by Archimedes method. The crystal structures of sintered samples were analyzed by X-ray diffraction (Rigaku D/MAX 2550, Japan). The microstructures of samples were observed by scanning electron microscopy (SEM) and energy-dispersive spectra (QUANTA200, Holand). The measurement of dielectric constant (ε) and unloaded Q of MN ceramics was performed in T_{011} mode at 8–11 GHz by the Hakki–Coleman dielectric resonator method [7] using a network analyzer (Agilent Tech., hp8720ES).

3 Results and discussion

The results of TGA-DTA measurements of the MN calcined powders mixed with 1.5% V_2O_5 and 3.0wt% Li_2CO_3 are shown in Fig. 1. In the TGA curve, a weight loss at the temperature around 600 °C is supposed to be related to the decomposing process of Li_2CO_3 compound. For the DTA results, the endothermic peak at 828 °C was because of the appearance of the liquid phase $LiVO_3$ [8, 9], which facilitates the sintering process of the MN ceramics as shown below.

The bulk density (ρ) and shrinkage of MN with 1.5wt% V_2O_5 and various Li_2CO_3 as a function of sintering temperatures are shown in Fig. 2. For the specimens with 1.5wt% V_2O_5, the maxim density of 4.137 g/cm^3 was obtained at 1,000 °C. The same ρ could be obtained for the pure MN specimens sintered at 1,400 °C [3]. As shown in Fig. 2(a), for the specimens with 1.5wt% V_2O_5 and designated weight percent of Li_2CO_3, ρ values changed with sintering temperature and Li_2CO_3 content. For MN with a mixture of 1.5wt% V_2O_5 and 3.0wt% Li_2CO_3, the maxim ρ value was obtained at 925–950 °C. As shown in Fig. 2(b), the shrinkage curve exhibited the same trend as bulk density as a function of sintering temperatures.

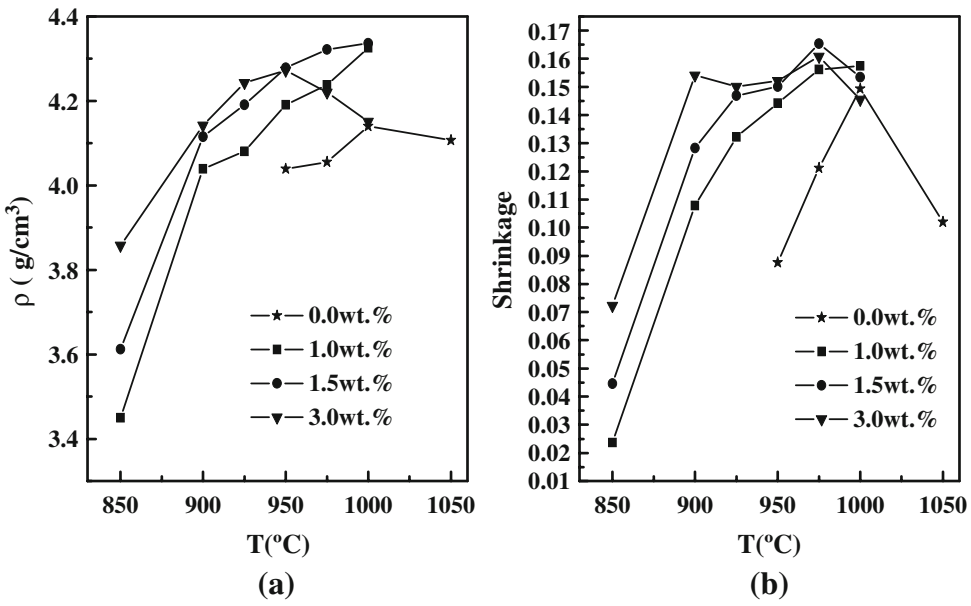

Fig. 2 The bulk density ρ (**a**) and shrinkage (**b**) of MN ceramics doped with 1.5wt% V_2O_5 and various Li_2CO_3 (0, 1.0, 1.5, and 3.0wt%) as a function of sintering temperatures

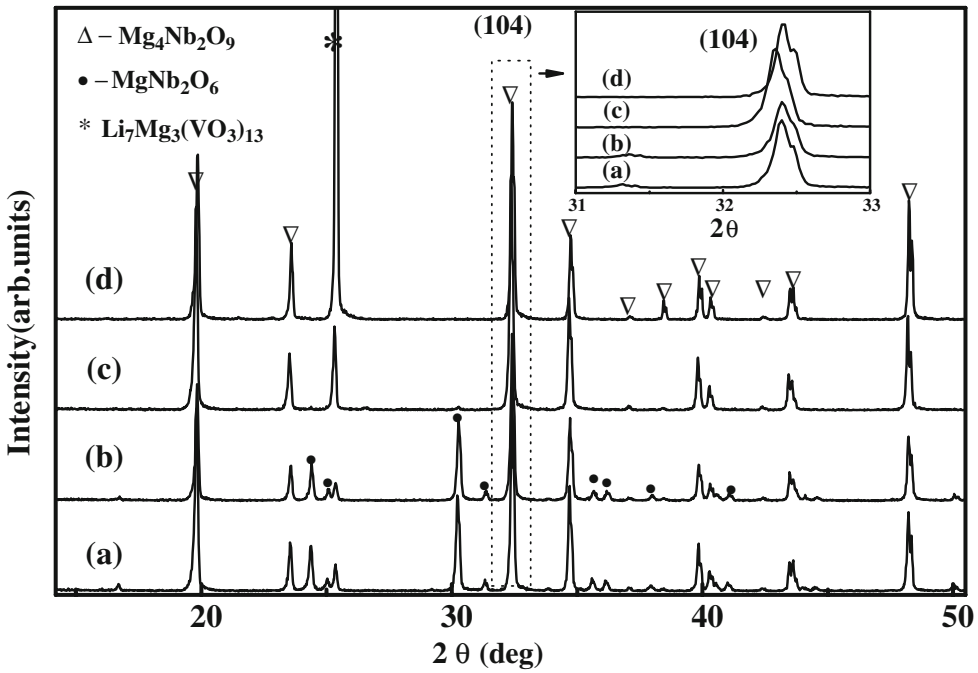

Fig. 3 XRPD patterns for MN ceramics doped with 1.5wt% V_2O_5 and various Li_2CO_3 sintered at 950 °C for 5 h. (**a**) 0.0wt%, (**b**) 1.0wt%, (**c**) 1.5wt%, and (**d**) 3.0wt%

X-ray powder diffraction (XRPD) patterns of the sintered MN specimens doped with 1.5wt% V_2O_5 and various Li_2CO_3 are shown in Fig. 3. For the specimens doped with 1.5wt% V_2O_5 alone, XRPD patterns could be indexed as the mixtures of MN associated with a minor of $MgNb_2O_6$ compound as a secondary phase (Fig. 3(a)). For the specimens doped with 1.5wt% and 3.0wt% Li_2CO_3, as shown in Fig. 3(c), (d), $MgNb_2O_6$ disappeared. In addition, as shown in the insert of Fig. 3, the main peak 104 shifts slightly toward lower angles (Fig. 3(b), (c)), indicating an increase of lattice parameters, but for the sample with 3.0wt % Li_2CO_3, 104 diffraction peak shifts toward higher angles (Fig. 3(d)) and the impurity phase of $Li_7Mg_3(VO_3)_{13}$ (JCPDS number of 33-0801) was detected (marked in a star symbol).

The effectiveness of sintering aids depends on several factors, such as sintering temperatures, viscosity, solubility, and wettability [10]. In the case of V_2O_5 additions, V_2O_5 as a sintering agent melted at 670 °C and wetted the MN powders. As a result, addition of 1.5wt% V_2O_5 is effective in reducing the sintering temperature of MN ceramics from 1,400 to 1,000 °C. With a combination of V_2O_5 and Li_2CO_3 the sintering temperature has been further lowered to 925 °C by the formation of $LiVO_3$ as a sintering agent [9]. On the other hand, some of Li^{1+} ions (coordination number, CN=6, 0.076 nm) substituted the smaller Mg^{2+} ions (CN=6, 0.072 nm) [11] with $(Mg_{1-x}Li_x)_4Nb_2O_{9-\delta}$ where oxygen vacancy was suggested to be produced. As a result, lattice parameters of MN phase increase with amount Li_2CO_3 contents (Fig. 3(a–c)). In addition, a chemical reaction of $MgNb_2O_6+2xLi_2O\rightarrow(Mg_{1-x}Li_x)_4Nb_2O_{9-\delta}$ leads to an elimination of $MgNb_2O_6$ phase in these Li-bearing ceramics. However, as Li_2CO_3 content increased up to 3.0wt%, the XRD peaks shift toward higher angles,

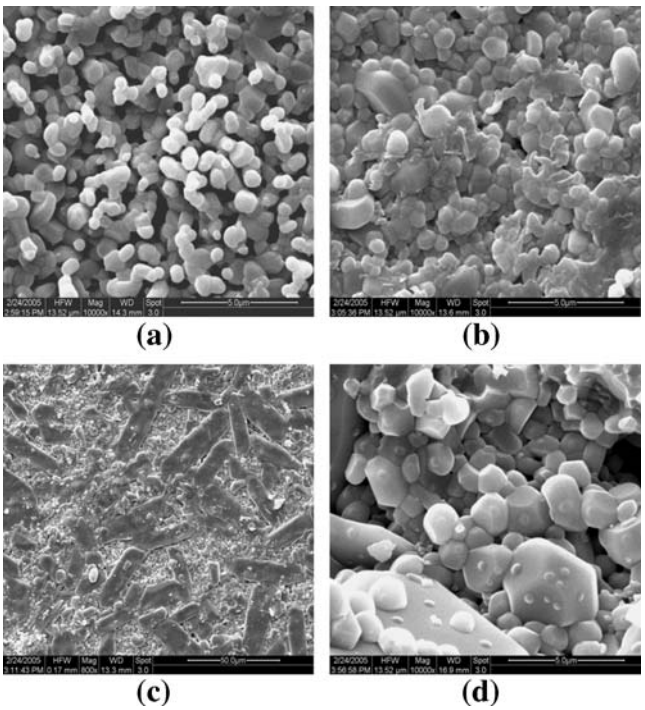

Fig. 4 SEM micrographs of MN ceramics doped with 1.5wt% V_2O_5 and 1.5wt% Li_2CO_3 sintered at various temperatures. (**a**) 850 °C, (**b**) 950 °C, (**c**) 1,000 °C, (**d**) 1,000 °C (fraction)

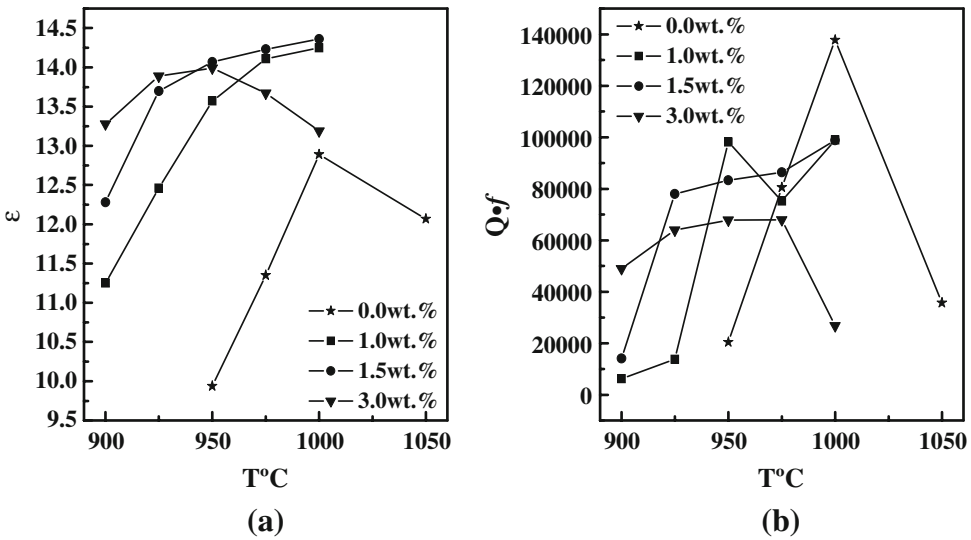

Fig. 5 The dielectric constant ε (**a**) and quality factor $Q \cdot f$ (**b**) of MN ceramics doped with 1.5wt% V_2O_5 and various Li_2CO_3 as a function of the sintering temperatures for 5 h

supposed to be related to the substitution of V^{5+} (CN=6, 0.054 nm) for Nb^{5+} (CN=6, 0.064 nm) [11] and the formation of the $Li_7Mg_3(VO_3)_{13}$ compound shown in (Fig. 3(d)).

Figure 4 shows the SEM micrographs of as sintered MN ceramics doped with 1.5wt% V_2O_5 and 1.5wt% Li_2CO_3. As shown in Fig. 4(a), the particles sintered at 850 °C have almost the same morphologies and the particles are highly agglomerated. As the sintering temperature increased up to 950 °C, the dense microstructures with grain size distributed from 0.2 to 1 μm were observed (Fig. 4(b)). When sintering temperature increased up to 1,000 °C, the grain size of the specimens increased (Fig. 4(d)), whereas the impurity phase with rectangle shape appeared at the surface of the as-sintered MN ceramics (Fig. 4(c)) was not detected in the body of the bulk (Fig. 4(d)).

The microwave dielectric properties of MN with V_2O_5 and Li_2CO_3 as a function of sintering temperature with ceramics are shown in Fig. 5. In Fig. 5(a), the relationship between dielectric constant (ε) and sintering temperature reveals the same trend as that for density and sintering temperature (Fig. 2(a)) because higher density represents lower porosity. The $Q \cdot f$ values of MN ceramics with V_2O_5 and Li_2CO_3 strongly depend on sintering temperatures and additives. The specimen doped with 1.5wt% V_2O_5 and sintered at 1,000 °C has the dielectric properties of ε= 12.9 and $Q \cdot f$=137,800 GHz, which is somewhat lower than the $Q \cdot f$ value of MN sintered at 1,400 °C [3, 12]. As shown in Fig. 5, the dielectric constant increased with sintering temperature, and then reached a saturated value. The mixtures of V_2O_5 and Li_2CO_3 have somewhat enhanced the saturated dielectric constant but suppressed $Q \cdot f$ values. The decrease of $Q \cdot f$ values may be related to the lattice defects in MN because of the substitution of Li^{1+} for Mg^{2+}, the small grain size, and formation of the secondary phase shown in Figs. 3 and 4. The ε of 13.7, $Q \cdot f$ value of 78,000 GHz were obtained for the specimens with 1.5wt% V_2O_5 and 1.5wt% Li_2CO_3 sintered at 925 °C. The excellent microwave dielectric properties and low-temperature sintering characteristics of V- and Li-bearing MN ceramics permit the potentional applications as a novel LTCC substrate, which is in agreement with the LiF-doped results [6, 13].

4 Summary

The MN ceramics doped with V_2O_5 and Li_2CO_3 were prepared by the conventional oxide mixture method to develop the new LTCC. With additions of 1.5wt% V_2O_5, sintering temperature of MN ceramics reduced from 1,400 to 1,000 °C without much degrading the microwave dielectric properties. With the mixtures of V_2O_5 and Li_2CO_3, the sintering temperature was lowed to 925 °C, but the $Q \cdot f$ values was suppressed because of the substitution of Li^{1+} for Mg^{2+} and the formation of secondary phase. The ε of 13.7 and $Q \cdot f$ value of 78,000 GHz were obtained for the specimens with 1.5wt% V_2O_5 and 1.5wt% Li_2CO_3 sintered at 925 °C, which permits a potentional application as a novel LTCC substrate.

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