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Letter

Improvements in the sintering behavior and microwave dielectric properties of $Mg_4Nb_2O_9$ by adding Fe_2O_3

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ABSTRACT

The influences of Fe_2O_3 additives on the sintering behavior and microwave dielectric properties of $Mg_4Nb_2O_9$ ceramics were investigated. The prepared ceramics exhibits a mixture of phases $Mg_4Nb_2O_9$ and $Mg_5Nb_4O_{15}$. Lowering the sintering temperature (as low as 1240 °C) and promoting the $Q \times f$ value of $Mg_4Nb_2O_9$ ceramics could be effectively achieved by adding Fe_2O_3 (up to 1 wt%). At 1270 °C, 0.75 wt% Fe_2O_3-doped $Mg_4Nb_2O_9$ ceramics possess a dielectric constant (ε_r) of 13.46, a $Q \times f$ value of 280,000 GHz, and a temperature coefficient of resonant frequency (τ_f) of −62 ppm/°C. In contrast to that of pure $Mg_4Nb_2O_9$ ceramics, incorporating additional Fe_2O_3 helps to render a dielectric material with a >40% dielectric loss reduction, a higher dielectric constant and retains a comparable τ_f, which makes it a very promising candidate for applications requiring an extremely low microwave dielectric loss.

1. Introduction

As the carrier frequency of interest in communication systems is being extended to a higher frequency regime, it has been driving the need for new materials with an extremely low dielectric loss (high quality factor, Q) in the last few years [1,2]. Although materials having extremely low dielectric loss have been reported for high frequency applications, research on new microwave dielectrics is still ongoing and has become a primary issue recently [3–8].

Several corundum-structured $A_4B_2O_9$ (A = Co and Mg, B = Nb and Ta) had been reported due to their excellent microwave dielectric properties [1,9–13]. Among these materials, $Mg_4Nb_2O_9$ was investigated to possess a dielectric constant ε_r of ∼12.4, a temperature coefficient of resonant frequency τ_f of ∼−70 ppm/°C and in particular, a high $Q \times f$ of ∼194,000 GHz [13]. However, it also required a sintering temperature of as high as 1350–1400 °C/10 h. Obviously, the high sintering temperature of the ceramics will limit its applications for practical cases. In addition, the $Q \times f$ also required an effective promotion to adapt high frequency applications.

In this paper, Fe_2O_3-doped $Mg_4Nb_2O_9$ ceramics were synthesized by solid-state method and its microwave dielectric properties and microstructures were also investigated. Consequently, the compound under study not only showed a tremendous lowering in the dielectric loss but also achieved a substantial sintering temperature reduction and retained comparably decent values of ε_r and τ_f.

2. Experimental

Samples of $Mg_4Nb_2O_9$ were synthesized by conventional solid-state methods from individual high-purity oxide powders (>99:9%): MgO and Nb_2O_5. The starting materials were mixed according to a stoichiometric ratio to synthesize $Mg_4Nb_2O_9$ ceramics. The powders were ground in distilled water for 12 h in a ball mill with agate balls. All mixtures were dried at 100 °C and calcined at 1200 °C for 4 h. The calcined powders were then doped with 0.5–1 wt% Fe_2O_3 ceramics and remilled for 12 h. The fine powder with 3 wt% of a 10% solution of PVA as a binder (Polyvinyl alcohol 500, Showa, made in Japan) was pressed into pellets 11 mm in diameter and 5 mm thick under a pressure of 2000 kg/cm^2. These pellets were sintered at temperatures of 1210–1360 °C for 4 h in air. The heating rate and the cooling rate were both controlled at 10 °C/min.

The X-ray diffraction (XRD, Rigaku D/Max III.V) data of powder and bulk samples were collected using Cu Ka radiation (at 30 kV and 20 mA) and a graphite monochromator in the 2θ range of 10–60°. The microstructural observations and analysis of sintered surface were performed using a scanning electron microscopy (SEM, Philips XL-40FEG) and an energy dispersive X-ray spectrometer (EDS). The density of the sintered specimens was measured by the Archimedes method using distilled water as the liquid.

The dielectric constant (ε_r) and the quality factor values (Q) at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method [14,15]. The dielectric resonator was positioned between two parallel conductor plates. A system combining a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement. For the temperature coefficient of resonant frequency (τ_f), the technique is the same as that for quality factor measurement. The test cavity is placed over a thermostat and the temperature range used is 25–80 °C [12]. The τ_f (ppm/°C) is calculated by noting the change in resonant frequency (Δf):

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

where f_1 is resonant frequency at T_1 and f_2 is the resonant frequency at T_2.

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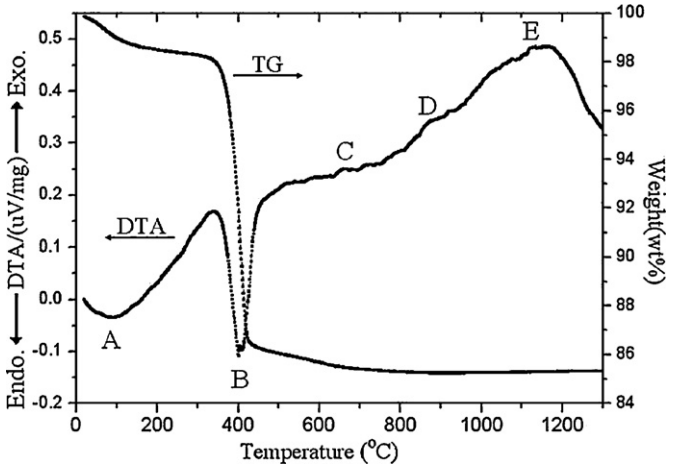

Fig. 1. TG–DTA curves for the mixture of MgO–Nb_2O_5 powder.

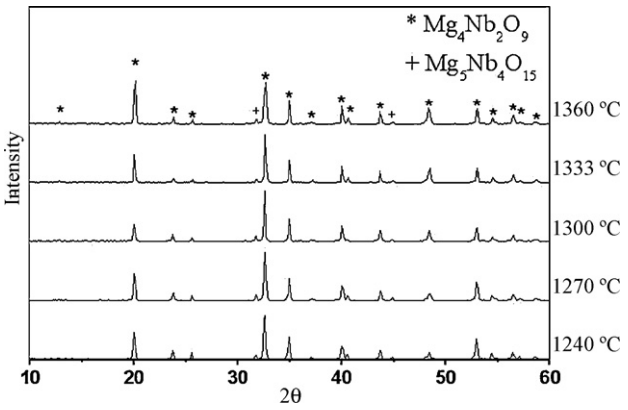

Fig. 2. XRD patterns of 0.75 wt% Fe_2O_3-doped $Mg_4Nb_2O_9$ ceramics at different sintering temperatures.

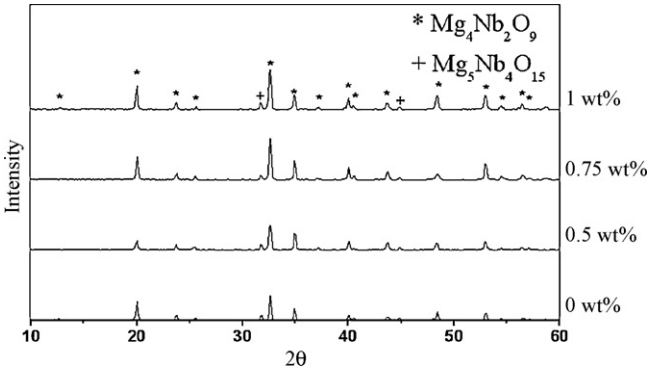

Fig. 3. XRD patterns of $Mg_4Nb_2O_9$ ceramics with different amounts of Fe_2O_3 addition sintered at 1270 °C.

3. Results and discussion

It is well known that several phases, $Mg_4Nb_2O_9$, $Mg_5Nb_4O_{15}$, and $MgNb_2O_6$, co-exist in the MgO–Nb_2O_5 system. The TG–DTA result for a powder, mixed in the stoichiometric proportions of $Mg_4Nb_2O_9$, is shown in Fig. 1. The DTA curve shows the broad endothermic peak at the temperature ~90 °C (point A), which are related to the first weight loss. This peak is considered to be caused by the loss of water. Moreover, the sharp endothermic peak and a rapid weight loss is observed at ~400 °C (point B), this endothermic peak is attributed to the decomposition of $MgO{\bullet}H_2O$. No further significant weight loss was observed for the temperatures above 650 °C in the TG curve. With the increasing temperature, the DTA curve shows that there are small exothermic peaks observed at ~660 °C (point C), ~875 °C (point D) and ~1120 °C (point E). These small peaks are likely to correspond to crystallization of $MgNb_2O_6$, $Mg_4Nb_2O_9$ and $Mg_5Nb_4O_{15}$.

Fig. 2 illustrates the X-ray diffraction (XRD) patterns recorded from the 0.75 wt% Fe_2O_3-doped $Mg_4Nb_2O_9$ ceramics sintered at different temperatures for 4 h. According to the XRD results, the corundum-type hexagonal structured $Mg_4Nb_2O_9$ was identified as the main phase. In addition to the main phase, crystalline phase of $Mg_5Nb_4O_{15}$ was spotted as a second phase. There is no significant variation in the weak second phase $Mg_5Nb_4O_{15}$ for Fe_2O_3-doped $Mg_4Nb_2O_9$ and identical XRD patterns (Fig. 3) were also recorded for specimens using different amount of Fe_2O_3 additions.

To investigate the morphologies of the samples, the surfaces of the sintered specimens were examined. The SEM micrographs of specimens using 0.75 wt% Fe_2O_3-doped $Mg_4Nb_2O_9$ ceramics sintered at different temperatures for 4 h are illustrated in Fig. 4. Grain growth was promoted by increasing the sintering temperature of the specimen. The result also indicated that fine microstructures and nearly full densification of specimen can be achieved at suitable sintering temperatures. Further increase in the sintering temper-

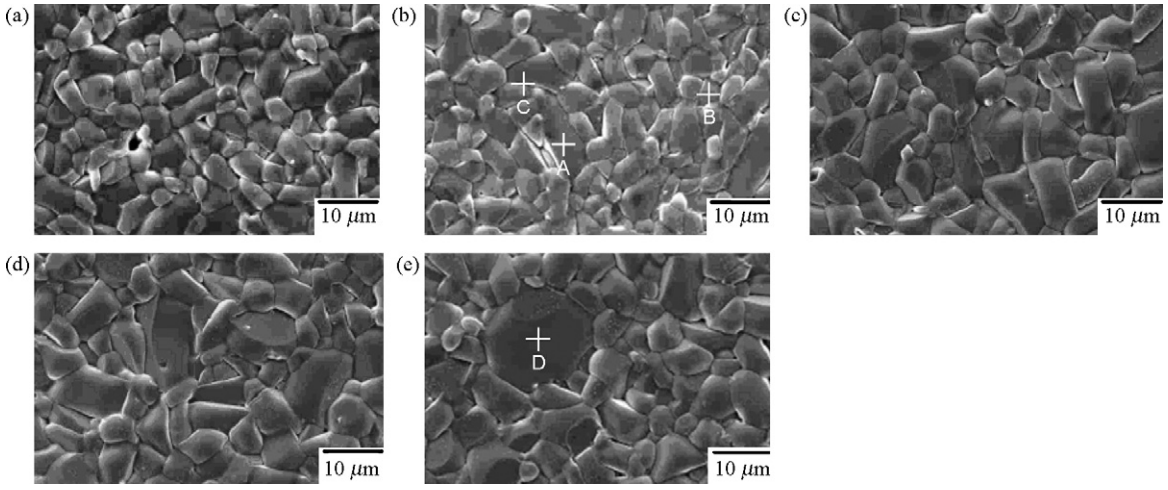

Fig. 4. The SEM micrographs of the specimens using 0.75 wt% Fe_2O_3-doped $Mg_4Nb_2O_9$ ceramics sintered at (a) 1240 °C, (b) 1270 °C, (c) 1300 °C, (d) 1330 °C and (e) 1360 °C for 4 h.

Table 1
The EDX data of the spots A–D shown in Fig. 4.

Spots	Atom (%)			
	Mg	Nb	Fe	O
A	25.69	13.91	0.06	60.34
B	25.54	14.23	0.12	60.11
C	23.23	12.95	1.25	62.57
D	25.65	13.79	0.10	60.46

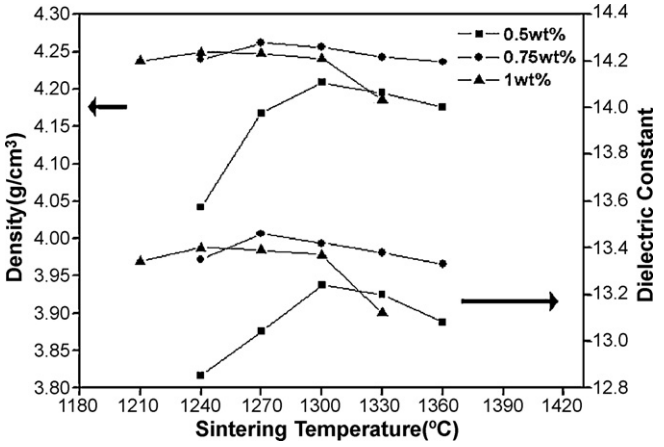

Fig. 5. The density and dielectric constant of Fe_2O_3-doped $Mg_4Nb_2O_9$ ceramics as functions of sintering temperature.

ature would lead to an abnormal grain growth as observed in Fig. 4(e). In addition, all the grains under test showed a small content of Fe (Table 1) suggesting the liquid phase was residual in the grains at the final stage.

Fig. 5 shows the apparent densities and dielectric constant of Fe_2O_3-doped $Mg_4Nb_2O_9$ ceramics at different sintering temperatures for 4 h. With increasing sintering temperature, the apparent density of specimen increased to a maximum and thereafter it slightly decreased. Notice that the breaking point temperature decreases with increasing Fe content indicating the forming of liquid phase does contribute to the densification of ceramics. The maximum density 4.26 g/cm^3 is obtained for $Mg_4Nb_2O_9$ with 0.75 wt% Fe_2O_3 addition sintered at 1270 °C. The results suggest that a higher amount of Fe_2O_3 is not required for producing dense ceramics. The variation of ε_r was consistent with that of density and a maximum ε_r of 13.46 was obtained for specimen using 0.75 wt% Fe_2O_3-doped $Mg_4Nb_2O_9$ ceramics sintered at 1270 °C for 4 h. It is higher than that of the pure $Mg_4Nb_2O_9$ (ε_r ~12.4).

The $Q \times f$ and τ_f values of Fe_2O_3-doped $Mg_4Nb_2O_9$ ceramics at different sintering temperatures for 4 h are shown in Fig. 6. The variation of $Q \times f$ was also consistent with that of density suggesting it was mainly dominated by the density of the specimens. A maximum of 280,000 GHz can be achieved for $Mg_4Nb_2O_9$ with 0.75 wt% Fe_2O_3 addition sintered at 1270 °C for 4 h. Further increase in the Fe_2O_3 content would lower the $Q \times f$ and similar phenomenon was also reported previously due to an over-added sintering aid [16,17]. In comparison with that of the pure $Mg_4Nb_2O_9$ ($Q \times f$ ~194,000 GHz), it shows a >40% increase in $Q \times f$ suggesting the $Q \times f$ of $Mg_4Nb_2O_9$ can be effectively promoted by adding Fe. The temperature coefficient of resonant frequency is well known, related to the composition, the additives and the second phase of the material.

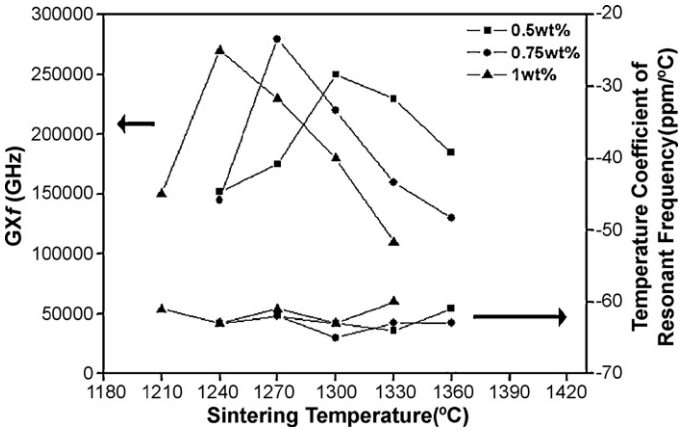

Fig. 6. The $Q \times f$ and τ_f values of Fe_2O_3-doped $Mg_4Nb_2O_9$ ceramics as functions of sintering temperature.

It was almost independent of sintering temperature and Fe_2O_3 content since there was no significant compositional change observed and all τ_f values were in the range of −60 to −65 ppm/°C, which is also comparable with that of the pure $Mg_4Nb_2O_9$ (−70 ppm/°C).

4. Conclusion

The influences of Fe_2O_3 additives on the sintering behavior and microwave dielectric properties of $Mg_4Nb_2O_9$ ceramics were investigated. Densification of the specimens can be improved by the forming of liquid phase resulted from the addition of Fe_2O_3. The $Mg_4Nb_2O_9$ compound with Fe_2O_3 addition not only showed a substantial lowering in the sintering temperature (~130 °C), it also indicated a tremendous dielectric loss reduction (>40%), which makes it a very promising dielectric for ultra high frequency applications.

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