J Mater Sci: Mater Electron (2013) 24:3546–3550
DOI 10.1007/s10854-013-1283-2

Improved microwave dielectric properties of $Mg_4Nb_2O_9$ ceramics with $CaO–B_2O_3–SiO_2$ glass additions

Haikui Zhu · Wei Shen · Yu Jin · Hongqing Zhou · Xiaodong Shen · Weijuan quan

Received: 17 March 2013 / Accepted: 3 May 2013 / Published online: 23 May 2013

Abstract The effects of $CaO–B_2O_3–SiO_2$ (CBS) glass addition on the sintering temperature and dielectric properties of $Mg_4Nb_2O_9$ ceramics have been investigated using X-ray diffraction, Scanning electron microscopy and Differential thermal analysis. The CBS glass can change to liquid phase at about 750 °C and a small amount of CBS glass addition to $Mg_4Nb_2O_9$ ceramics can greatly decrease the sintering temperature to about 1,125 °C. It is revealed that the reduced sintering temperature is attributed to the formation of liquid phase. The major phases of the sample are $Mg_4Nb_2O_9$ and $MgNb_2O_6$. The relationship between τ_f values and the content of glass additions have the reverse change trends. The $Mg_4Nb_2O_9$ ceramics with 2wt% glass addition sintered 1,125 °C exhibit good microwave dielectric properties: dielectric constant (ε_r) of 13 and $Q{\cdot}f$ value of 69,000 GHz.

1 Introduction

Several types of dielectric materials have been developed and investigated to suit the requirements of various applications in recent years [1, 2]. The unique electrical properties of ceramic dielectric resonators have revolutionized the microwave-based wireless communications industry by reducing the size and cost of filter and oscillator components in circuit systems [3]. Several corundum-structured $A_4B_2O_9$ ceramics have been found due to their excellent microwave dielectric properties. Among these materials, the magnesium niobate ($Mg_4Nb_2O_9$) is a suitable material for microwave applications such as substrates and resonators at high frequency, because its dielectric constant and high $Q{\cdot}f$ are comparable to those of sintered Al_2O_3 [4]. Many experiments have also been conducted to study the preparation and properties of $Mg_4Nb_2O_9$-based ceramics [5–10]. According to previous report, $Mg_4Nb_2O_9$ possesses dielectric constant about 11 and low dielectric loss [3, 11]. However, the $Mg_4Nb_2O_9$ ceramics usually need to be sintered at higher temperature to achieve high enough density. Recently, there are several ways to reduce the sintering temperature of dielectric ceramics, such as low melting glass additions, chemical processing, using smaller size materials and liquid phase sintering aids [12, 13]. Among these methods, low melting glass addition for liquid-phase sintering is lower in cost and easier to process than the others [14, 15]. Recently, $CaO–B_2O_3–SiO_2$ (CBS) system glass used as low melting glass additions has also attracted much attention [16]. A small amount of CBS glass addition to $Ba_xSm_yTi_7O_{20}$ ceramics can greatly decrease the sintering temperature from 1,350 to 1,260 °C, which is attributed to the formation of liquid phase [17].

In this paper, the effects of CBS glass addition on the sintering properties and dielectric properties are studied. The relationships among sintering temperatures, microstructures and the dielectric properties are also discussed.

2 Experimental procedure

The compositions of the glass in this paper contained 30wt% CaO + 35wt% B_2O_3 + 35wt% SiO_2 were determined according to the phase diagram of the $CaO–B_2O_3–SiO_2$ system. Reagent-grade raw materials of $CaCO_3$, H_3BO_3 and SiO_2 with purities higher than 99wt% were

H. Zhu (✉) · W. Shen · Y. Jin · H. Zhou · X. Shen · W. quan
College of Materials Science and Engineering, Nanjing University of Technology, Nanjing 210009, People's Republic of China
e-mail: Zhuhaikui@eyou.com

chosen as the starting materials. After mixed uniformly, the raw materials were put into a platinum crucible and melted by an electric furnace at 1,200 °C for 1 h. The molten glass was quenched into distilled water to form cullet. The cullet was dried and milled with a mixture of agate balls in different diameters of 5–30 mm to an average particle size of less than 5 μm.

$Mg_4Nb_2O_9$ ceramics were prepared using MgO and Nb_2O_5 powders with purities higher than 99wt%. The powders were ball-milled in a polyethylene bottle and agate media for 12 h using ethanol, and then rapidly dried and calcined at 1,000 °C for 10 h. The crystalline phases of the calcined powders were identified by X-ray diffraction. The calcined powders were re-milled with different content of CBS glass for 12 h, mixed with 5wt% polyvinyl alcohol (PVA), uniaxially pressed under a pressure 100 MPa to obtain green compacts with diameter of 13 mm and thickness of 6 mm, and then sintered in air at different temperatures for 5 h.

The physical properties of those sintered bodies were measured, such as dielectric constant, dielectric loss and microstructure. The properties of the CBS glass were measured by Differential thermal analysis (DTA STA 449C/6/F). The compositions of these samples were determined by X-ray diffraction with CuKα radiation (XRD ARL X′TRA). Polished and thermally etched surfaces of sintered samples were examined by Scanning electron microscopy (SEM JSM-5900). The dielectric properties were measured by Agilent 8722ET network analyzer.

3 Results and discussion

3.1 DTA analysis of CBS glass

Figure 1 shows the result of DTA measurement of the CBS glass and the DTA curve is obtained in air up to 900 °C by a heating rate of 10 °C min^{-1}. An endothermic peak appears at about 750 °C, so that the soften point of the CBS glass can be identified to be about 750 °C. Thus, the CBS glass can change to liquid phase at about 750 °C.

3.2 Sintering and characterization of $Mg_4Nb_2O_9$ ceramics

The bulk densities of $Mg_4Nb_2O_9$ specimens with 0, 2, 4, 6 and 8wt% CBS glass additions are shown in Fig. 2. The densities of the samples increase dramatically when the sintering temperatures rise from 1,075 to 1,125 °C. But the samples show slightly worse sinterabilities with the higher sintering temperatures than 1,125 °C, especially for 6 and 8wt% glass doped samples. The densities of $Mg_4Nb_2O_9$ without glass addition increase only from 2.71 to 3.32 g

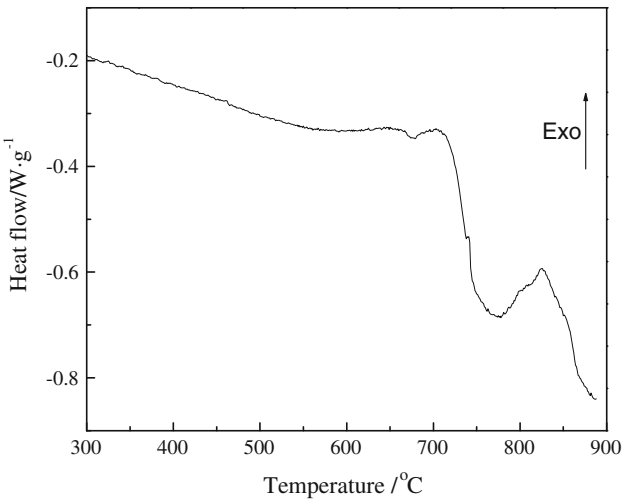

Fig. 1 DTA curve of CBS glass at a heating rate of 10 °C min^{-1}

cm^{-3} as the sintering temperatures increase from 1,100 to 1,175 °C, while the densities of samples with 2wt% glass addition increase from 3.71 to 4.05 g cm^{-3}. Since the low melting temperature of CBS addition, the liquid phase sintering occurs during sintering, which will reduce the activation energy and promote the rapid grain growth, leading to the densification of $Mg_4Nb_2O_9$ ceramics. However, the densities decrease with the enhancing glass addition from 2 to 8wt% in the temperature range of 1,075 to 1,175 °C, which is mainly due to the small density of the CBS glass addition (only about 2.5 g cm^{-3}).

3.3 XRD analysis results and SEM observations

XRD patterns of $Mg_4Nb_2O_9$ ceramics with different glass additions sintered at 1,125 °C are displayed in Fig. 3. The pure and CBS doped ceramics are all composed of

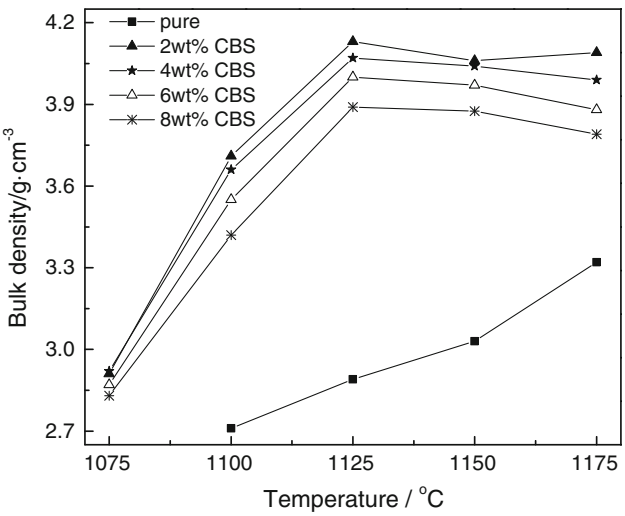

Fig. 2 Relationship between the bulk densities of $Mg_4Nb_2O_9$ ceramics and sintering temperatures

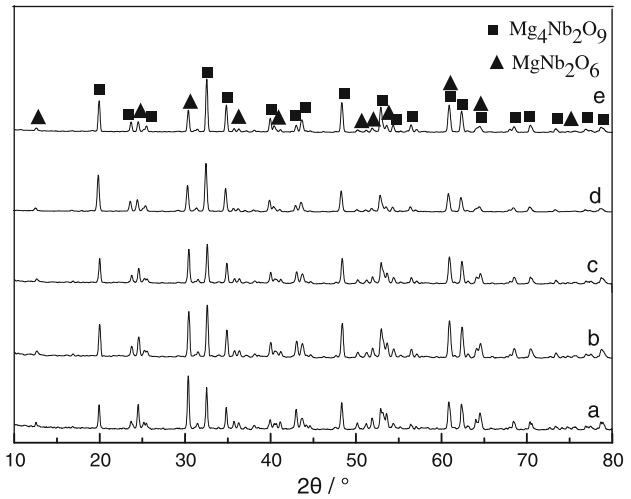

Fig. 3 XRD patterns of $Mg_4Nb_2O_9$ ceramics with different glass additions sintered at 1,125 °C: **a** pure; **b** 2wt%; **c** 4wt%; **d** 6wt%; **e** 8wt%

$Mg_4Nb_2O_9$ and $MgNb_2O_6$. The single $Mg_4Nb_2O_9$ phase is difficult to obtain via the conventional solid state reaction method and the residual $MgNb_2O_6$ phase is detected in the samples. In addition, the glass additions also affect the phase compositions and reaction between glass and $MgNb_2O_6$ may also occur during the sintering process. It causes the peak intensity at about $2\theta = 19.9°$ decreases obviously with the CBS glass addition rising from 2 to 8wt%. However, the exact reactions are not well understood and still need more study in future.

The SEM images of $Mg_4Nb_2O_9$ ceramics sintered at 1,125 °C are illustrated in Fig. 4. The $Mg_4Nb_2O_9$ sample without CBS glass is more porous and crystalline grains are very small (Fig. 4a), which is caused by low sintering temperature. As shown in Fig. 4b–e, viscous flow of the flux coalesce the $Mg_4Nb_2O_9$ particles and densification become more complete as the amount of CBS glass rises. The effects of CBS additions on samples are exerted not

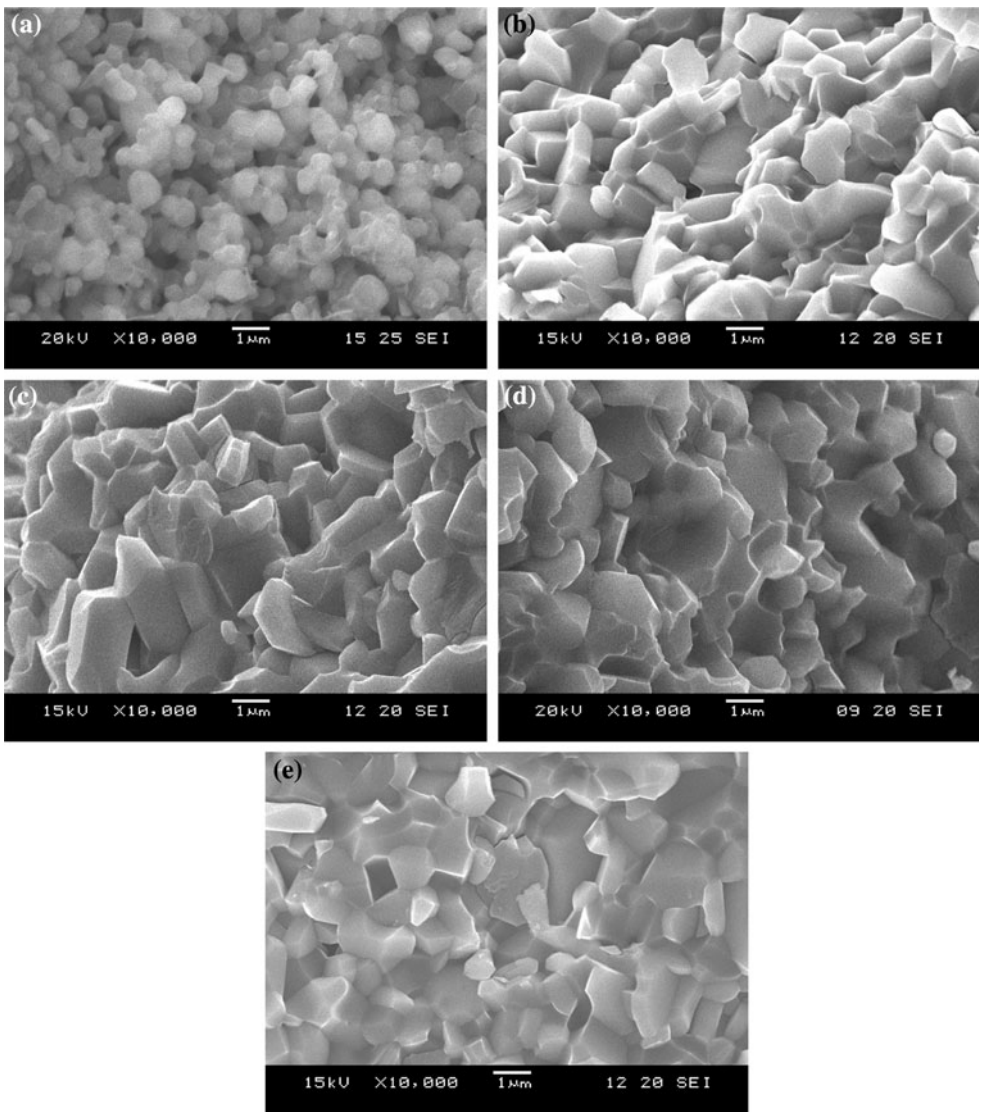

Fig. 4 SEM images of $Mg_4Nb_2O_9$ ceramic surfaces with different glass additions sintered at 1,125 °C: **a** pure; **b** 2wt%; **c** 4wt%; **d** 6wt%; **e** 8wt%

only by the decrement of the sintering temperatures, but also by the reduction of porosity. The 2wt% CBS addtion promotes the grain growth efficiently and the sample has a much uniform grain size about 2 μm. However, the higher CBS contents (>2wt%) leads to inhomogeneous grains and intragranular pores, which is caused by liquid phase during sintering processes.

3.4 Dielectric properties of $Mg_4Nb_2O_9$ ceramics

Figure 5 displays the dielectric properties of $Mg_4Nb_2O_9$ ceramics with different glass additions as a function of sintering temperatures. The dielectric constant ε_r and $Q{\cdot}f$ values increase rapidly and then keep slight decrement, that reveals the same trend as that between the densities and sintering temperatures. As Fig. 5 shows, the ε_r values of $Mg_4Nb_2O_9$ ceramics with different CBS glass additions sintered from 1,125 to 1,175 °C are all about 12.9. The $Q{\cdot}f$ values decrease with the increasing CBS glass additions, as the sintering temperatures rise from 1,075 to 1,175 °C. It is clear that the amount of CBS glass addition is much important to the $Mg_4Nb_2O_9$ ceramics. The effect of glass addition on dielectric loss is dependent on the chemistry of the glass, the chemical reactions, the phase changes during the sintering and the final density. There are three main types of dielectric loss for ceramics: resonance-type vibration loss, migration loss and deformation loss [14, 17]. Just as shown in Fig. 4, in the microstructures of these samples, the 2wt% CBS addition promotes the grain growth efficiently and the sample has a much uniform grain size about 2 μm. The dielectric properties not only have related to the density, but also depend strongly on the grain size and porosity. The homogeneous microstructure is to the benefit of dielectric loss decrement. However, the higher CBS contents (>2wt%) cause inhomogeneous larger grains separated by poorly conducting glass phase, leading to less grain boundaries per unit volume and lower resistivity. Therefore, the increment of the dielectric loss may be caused by the glass deformation loss and abnormal grain growth when the amount of CBS glass increasing from 4 to 8wt%. The $Mg_4Nb_2O_9$ ceramics with 2wt% CBS glass addition sintered 1,125 °C exhibit good microwave dielectric properties, i.e. dielectric constant (ε_r) of 13 and $Q{\cdot}f$ value of about 69,000 GHz.

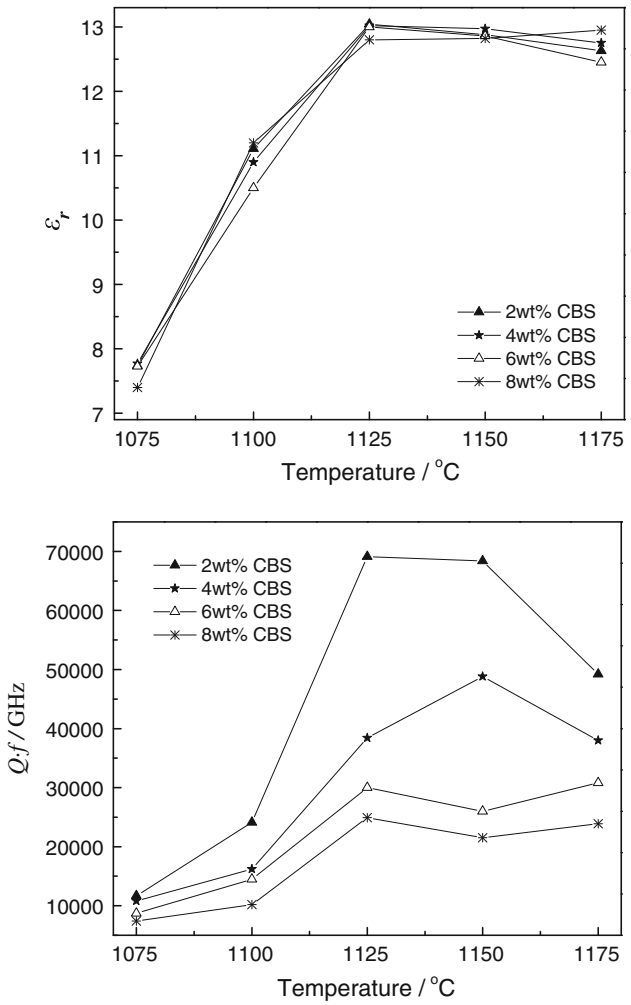

Fig. 5 Dielectric properties of $Mg_4Nb_2O_9$ ceramics as a function of sintering temperatures

Figure 6 displays the frequency temperature coefficients (τ_f) of $Mg_4Nb_2O_9$ ceramics as a function of the content of glass additions. The τ_f value is determined by the following formula:

$$\tau_f = \frac{f_{T_2} - f_{T_1}}{(T_2 - T_1) f_{T_1}}$$

Where f_{T1} and f_{T2} are resonant frequencies at temperatures T_1 and T_2 respectively. The temperature range used is

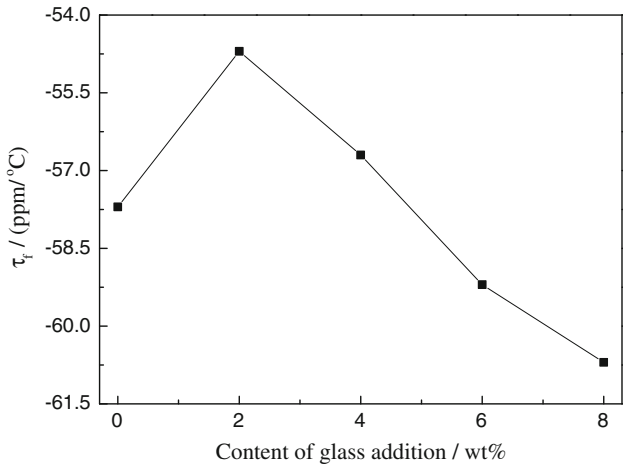

Fig. 6 Frequency temperature coefficients of $Mg_4Nb_2O_9$ ceramics as a function of the content of glass additions

from 20 to 80 °C. The τ_f value of pure $Mg_4Nb_2O_9$ ceramic is about −57.7 ppm/°C. The relationship between τ_f values and the content of glass additions have the reverse change trends. Just as shown in Figs. 2 and 3, it may be attributed to the density, formation of liquid phase and phase compositions. It implies that the τ_f value of $Mg_4Nb_2O_9$ ceramics can be adjusted by controlling the amount of CBS additions.

4 Conclusions

A small amount of CBS glass addition to $Mg_4Nb_2O_9$ ceramics can greatly decrease the sintering temperature to about 1,125 °C. It is revealed that the reduced sintering temperature is attributed to the formation of liquid phase. The major phases of the sample are $Mg_4Nb_2O_9$ and $MgNb_2O_6$. The relationship between τ_f values and the content of glass additions have the reverse change trends. The $Mg_4Nb_2O_9$ ceramics with 2wt% glass addition sintered 1,125 °C exhibit good microwave dielectric properties: dielectric constant (ε_r) of 13 and $Q{\cdot}f$ value of 69,000 GHz.

Acknowledgments This work is partly supported by Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT) under Grant no. IRT1146

References

1. J.Y. Chen, C.L. Huang, Mater. Lett. **64**, 2585–2588 (2010)
2. H. Su, S.H. Wu, Mater. Lett. **59**, 2337–2341 (2005)
3. C.L. Huang, J.Y. Chen, C.C. Liang, Mater. Res. Bull. **44**, 1111–1115 (2009)
4. H.T. Wu, L.X. Li, J. Sol-Gel. Sci. Technol. **58**, 48–55 (2011)
5. V.V. Deshpande, M.M. Patil, V. Ravi, Ceram. Int. **32**, 353–355 (2006)
6. H. Ogawa, A. Kan, S. Ishihara, Y. Higashida, J. Eur. Ceram. Soc. **23**, 2485–2488 (2003)
7. D.C. Sun, S. Senz, D. Hesse, J. Eur. Ceram. Soc. **26**, 3181–3190 (2006)
8. R. Wongmaneerung, T. Sarakonsri, R. Yimnirun, S. Ananta, Mater. Sci. Eng. B **130**, 246–253 (2006)
9. R. Wongmaneerung, R. Yimnirun, S. Ananta, Mater. Chem. Phys. **114**, 569–575 (2009)
10. C.L. Huang, J.Y. Chen, C.C. Lian, J. Alloys. Compd. **478**, 554–558 (2009)
11. C.L. Huang, W.R. Yang, J. Alloys. Compd. **509**, 2269–2272 (2011)
12. P. Liu, E.S. Kim, S. Gu Kang, H.S. Jang, Mater. Chem. Phys. **79**, 270–272 (2003)
13. D.W. Kim, D.G. Lee, K.S. Hong, Mater. Res. Bull. **36**, 585–595 (2001)
14. C.L. Huang, M.H. Weng, C.T. Lion, C.C. Wu, Mater. Res. Bull. **35**, 2445–2456 (2000)
15. N. Santha, M.T. Sebastian, V. George, J. Philip, Mater. Chem. Phys. **100**, 423–429 (2006)
16. H.K. Zhu, W. Shen, Y. Jin, H.Q. Zhou, J. Mater. Sci.: Mater. Electron. **24**, 1090–1094 (2012)
17. H.K. Zhu, H.Q. Zhou, M. Liu, Mater. Res. Bull. **44**, 674–677 (2009)