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# Low temperature sintering and microwave dielectric properties of $Bi_4B_2O_9$-added $0.25CaTiO_3–0.75(Li_{1/2}Nd_{1/2})TiO_3$ ceramics

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ABSTRACT

The effects of $Bi_4B_2O_9$ addition on the sintering behaviour, microstructure and microwave dielectric properties of $0.25CaTiO_3–0.75(Li_{1/2}Nd_{1/2})TiO_3$ ceramics have been investigated. The addition of $Bi_4B_2O_9$ effectively reduced the sintering temperature to 1200 °C. The secondary phase was observed for the 7.5 wt% $Bi_4B_2O_9$-doped sample sintered at 1300 °C. The dense microstructure was developed and the grain size was increased with the creasing of $Bi_4B_2O_9$ content. $Bi_4B_2O_9$ addition significantly affected the microwave dielectric properties. The $Q \times f_0$ value was increased by the $Bi_4B_2O_9$ addition due to increased grain size and the temperature coefficient of resonant frequency ($\tau_f$) can be tailored by the $Bi_4B_2O_9$ addition as well. In particular, the excellent microwave dielectric properties of $\varepsilon_r = 114$, $Q \times f_0 = 2830$ GHz and $\tau_f = -7.8$ ppm/°C could be obtained for the 10 wt% $Bi_4B_2O_9$-doped sample sintered at 1200 °C.

## 1. Introduction

The growth of the wireless communications over the past three decades has resulted in an increasing demand for the dielectric loaded antennas materials with high permittivity ($\varepsilon_r$), low loss or high quality factor ($Q$; especially in the microwave frequency, $Q \times f_0$ is used instead of $Q$) and near-zero temperature coefficient of resonant frequency ($\tau_f$) [1–5]. The applications of such dielectric antennas materials ensure better performance along with reduction of weight and over all dimensions of the microwave devices. In general, as the permittivity increases, $Q$ decreases and $\tau_f$ increases [1]. The development of microwave ceramics with high permittivity and small dielectric loss together with near-zero $\tau_f$ is a big challenging problem in the area of dielectric antennas materials research.

Mirsaneh et al. [6] have introduced the existing ceramics suitable for dielectric loaded antennas applications. For the antenna community, there has been a significant effort in academia and industry to develop the high permittivity ceramics that are temperature stable and have high $Q \times f_0$ value, suitable for microstrip patch and quadrifilar helix designs. The application that drove this development was based on resonators and cavity filters for base stations and reached its peak in mid 1990s. The first generation of dielectric loaded antennas used materials based on $(Mg,Ca)TiO_3$, $ZrTiO_4$, and $BaTi_4O_9$, and then Ba-based complex perovskites, such as $BaZn_{1/3}Ta_{2/3}O_3$ and $BaMg_{1/3}Ta_{2/3}O_3$ based ceramics and $CaTiO_3$ and $SrTiO_3$ based solid solutions were developed for use of base station resonators [6].

Recent studies of $CaTiO_3–(Li_{1/2}RE_{1/2})TiO_3$ (RE = rare earth)-based solid solutions have shown that they could be a promising candidate material for dielectric loaded antennas applications, due to their high permittivity [7]. It is known that $CaTiO_3$ has a positive $\tau_f$ of +800 ppm/°C, an $\varepsilon_r$ of 170 and a $Q \times f_0$ value of 3600 GHz [8]. Therefore, this compound may be suitable for form a solid solution with $(Li_{1/2}RE_{1/2})TiO_3$ having a negative $\tau_f$ value in order to design a ceramic with a near-zero $\tau_f$ value. $CaTiO_3–(Li_{1/2}RE_{1/2})TiO_3$ based solid solutions were first reported by Ezaki et al. [9,10]. They proposed the non-stoichiometric composition of $CaO–Li_2O–RE_2O_3–TiO_2$ as a temperature stable dielectric material for the dielectric resonator use and the microwave dielectric properties of the ceramics with $\varepsilon_r = 110$, $Q \times f_0 = 4500$ GHz, and $\tau_f = 7.0$ ppm/°C with a composition of $CaO:SrO:Li_2O:Sm_2O_3:TiO_2 = 15:1:9:12:63$ (molar ratio), and $\varepsilon_r = 123$, $Q \times f_0 = 4150$ GHz, and $\tau_f = 10.8$ ppm/°C with $CaO:SrO:Li_2O:Sm_2O_3:Nd_2O_3:TiO_2 = 15:1:9:6:6:63$ (molar ratio) by SrO substitution for CaO. Huang et al. [11] reported that the BaO substitution for CaO partially could enhance the $Q \times f_0$ value and the dielectric properties of $\varepsilon_r = 103$, $Q \times f_0 = 7200$ GHz, and $\tau_f = 2$ ppm/°C were obtained with a composition of $CaO:BaO:Li_2O:Sm_2O_3:Nd_2O_3:TiO_2 = 14:4:8:10:2:63$ (molar ratio). Kim et al. [12] reported that $0.3CaTiO_3–0.7(Li_{1/2}Sm_{1/2})TiO_3$ sintered at 1300 °C exhibits $\varepsilon_r = 114$ $Q \times f_0 = 3700$ GHz, and = ″*si*34.*gif*″ > $\tau_f = 11.5$ ppm/°C. Aziz et al. [7] reported a high permittivity of 112, a $Q \times f_0$ of 2600 GHz and a positive $\tau_f$ of 65 ppm/°C for $0.2CaTiO_3–0.8(Li_{1/2}Nd_{1/2})TiO_3$ ceramic. Furthermore, the $0.4CaTiO_3–0.6(Li_{1/2}Nd_{1/2})TiO_3$ has a $\varepsilon_r$ of 126 and a $Q \times f_0$ value of 2600 GHz (measured at 2.1 GHz) and a $\tau_f$ of 127 ppm/°C [13].

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However, a wide range of microwave properties have been reported for this system which depends on RE ionic radius, so that the BaO substitution for CaO should yield a ceramic with a higher permittivity. Therefore, in this study, the $CaTiO_3$–$(Li_{1/2}Nd_{1/2})TiO_3$ has been investigated. The composition of $0.25CaTiO_3$–$0.75(Li_{1/2}Nd_{1/2})TiO_3$ (hereafter referred to as 0.25CT–0.75LNT) has been selected because of its high permittivity (∼126) and moderate positive $\tau_f$ (∼71.5 ppm/°C), which can be combined with the negative $\tau_f$ ceramic to produce the near-zero $\tau_f$ ceramics exhibiting high permittivity values. Due to its large negative $\tau_f$ (−203 ppm/°C) with $\varepsilon_r = 39$, $Q \times f_0 = 2600$ GHz and low melting temperature (675 °C), $Bi_4B_2O_9$ therefore is chosen to tune the $\tau_f$ and reduce the sintering temperature of $0.25CaTiO_3$–$0.75(Li_{1/2}Nd_{1/2})TiO_3$ ceramics without degrading their microwave dielectric properties. The effect of $Bi_4B_2O_9$ addition on sintering, structure and microwave dielectric properties of 0.25CT–0.75LNT has been examined.

## 2. Experimental

Specimens of the $Bi_4B_2O_9$ ceramics were prepared by a conventional mixed route from the dried, high-purity $Bi_2O_3$ (99.9%, Acros Organics) and $B_2O_3$ (99.9%, Sigma Aldrich). Stoichiometric proportions of the above raw materials were ball-milled for 8 h in iso-propanol medium, and then dried, and calcined at 580 °C for 2 h. Reagent-grade powders of $CaCO_3$ (99.9%, Sigma Aldrich), $Li_2CO_3$ (99.0%, Sigma Aldrich), $Nd_2O_3$ (99.90%, Sigma Aldrich) and $TiO_2$ (99.99%, Sigma Aldrich) were mixed according to the composition of $0.25CaTiO_3$–$0.75(Li_{1/2}Nd_{1/2})TiO_3$. The mixture was attrition milled in iso-propanol for 1 h with yttria stabilised zirconia media. The wet mixture was dried and calcined at 110 °C. The reacted powders were sieved through a 355 μm sieve and then attrition milled as above. After remilling with $Bi_4B_2O_9$ added, the powders were dried, pressed into pellets of 8 mm diameter and ∼3 mm thickness by uniaxial pressing at an applied load of ∼0.6 tonnes for 1 min. Pellets were then sintered 4 h in air at sintering temperatures ranging from 1200 to 1350 °C.

The bulk densities of the sintered samples were measured by the Archimedes method with distilled water. The phase composition of sintered samples were analysed by an X-ray diffractometer (D500, Siemens, Munich, Germany) with CuKα (λ = 1.5405 Å) radiation generated at 40 kV and 30 mA. The microstructures of well-polished and etched surfaces of the samples were observed under a scanning electron microscopy (SEM) (JSM-6400 JEOL Corporation, Tokyo, Japan). The JSM 6400 was equipped with a Link systems energy dispersive (EDS) X-ray detectors. The permittivity ($\varepsilon_r$) and quality $Q \times f_0$ at microwave frequency were measured by the transmission resonant cavity technique in an Au–coated brass cavity and fused silica support. A vector network analyser (R3767CH, Advantest Corporation, Tokyo, Japan) was used for the measurement. The temperature coefficient of resonant frequency ($\tau_f$) was measured in the temperature range from 25 to 80 °C. The $\tau_f$ value was defined as follows:

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

where $f_1$ and $f_2$ represent the resonant frequencies at $T_1$ and $T_2$, respectively.

## 3. Results and discussions

Fig. 1 represents bulk densities of $Bi_4B_2O_9$-doped 0.25CT–0.75LNT ceramics as a function of sintering temperature from 1100 to 1350 °C. The undoped 0.25CT–0.75LNT ceramic have an optimum sintering temperature of 1300 °C and the density is ∼4.96 g/cm$^3$. For the $Bi_4B_2O_9$-doped samples, the bulk densities increased with increasing $Bi_4B_2O_9$ content. As the melting temperature of the $Bi_4B_2O_9$ phase was about 680 °C, $Bi_4B_2O_9$ was considered to have been melted during the sintering and have assisted the densification of $Bi_4B_2O_9$-doped 0.25CT–0.75LNT ceramics. As shown in Fig. 1, the densities of the samples doped with 5 wt% $Bi_4B_2O_9$ were relatively high, which indicated that 5 wt% $Bi_4B_2O_9$ efficiently reduce the sintering temperature of 0.25CT–0.75LNT. When the $Bi_4B_2O_9$ content increased to 7.5–10 wt%, the samples could reach high densities (>95% theoretical density) at around 1200 °C. It could be also observed that the sintering curves of 5–10 wt% $Bi_4B_2O_9$-doped samples were similar, i.e., their densities slightly increased initially with increasing sintering temperature and then decreased slightly after reaching its maximum value. The highest densities could be obtained at about 1200 °C for the ceramics with 7.5–10 wt% $Bi_4B_2O_9$ and at about 1250 °C for the ceramics with 5 wt% $Bi_4B_2O_9$. All these results indicated that $Bi_4B_2O_9$ acted as effective sintering aid, appropriate $Bi_4B_2O_9$ addition could provide the liquid and enhanced the densification of 0.25CT–0.75LNT ceramics at lower sintering temperatures.

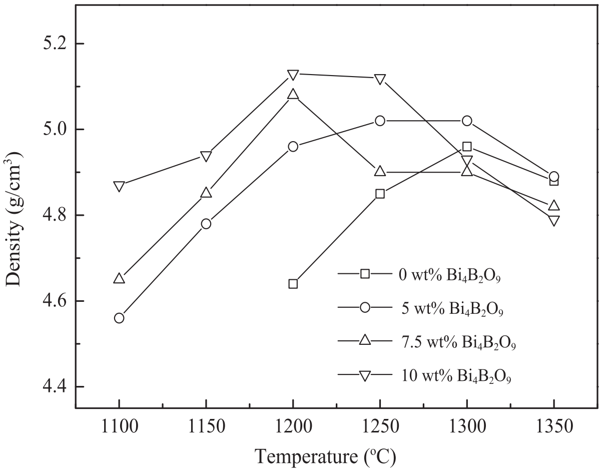

**Fig. 1.** Bulk densities of 0.25CT–0.75LNT ceramics with various $Bi_4B_2O_9$ additions as a function of sintering temperature.

Fig. 2a shows the X-ray diffraction (XRD) patterns of the 0.25CT–0.75LNT ceramics doped with 0–10 wt% $Bi_4B_2O_9$ sintered at 1200 °C for 4 h. The diffraction patterns were similar and matched with that for a perovskite phase with room temperature $CaTiO_3$ structure (JCPDS Card No. 42-0423). However, a secondary phase was detected for the ceramic with 7.5 wt% $Bi_4B_2O_9$. Moreover, for the samples with 7.5–10 wt% $Bi_4B_2O_9$ sintered at 1300 °C, as shown in Fig. 2b, several weak peaks of secondary phase could also be found in XRD patterns.

The SEM micrographs of the polished surface of 0.25CT–0.75LNT ceramics doped with 5 wt% $Bi_4B_2O_9$ addition sintered at different temperature are illustrated in Fig. 3. A porous microstructure was developed for the 0.25CT–0.75LNT ceramics with 5 wt% $Bi_4B_2O_9$ addition sintered at 1100 °C (see Fig. 3a). When the sintering temperature increased to 1200 °C, a dense microstructure with an average grain size ∼2 μm was formed, as shown in Fig. 3b. It could be observed that the grain size changed considerably with the sintering temperature. With the increase of sintering temperature, the grain size of specimen was significantly increased and the specimen sintered at 1350 °C exhibit a microstructure with an average grain size of 6 μm (see Fig. 3e). Table 1 lists the changes in grain size of 0.25CT–0.75LNT ceramics with $Bi_4B_2O_9$ addition sintered at different temperature. The grain size of the specimen was significantly increased with the $Bi_4B_2O_9$ content and the sample containing 7.5 wt% $Bi_4B_2O_9$ addition sintered at 1250 °C exhibited a microstructure with an average grain size of 4.1 μm (see Table 1), which is almost 2× of grain size for the undoped 0.25CT–0.75LNT ceramics (2.3 μm). However, the grain size decreased slightly when the $Bi_4B_2O_9$ content exceeded 7.5 wt%. The grain growth that occurred in the $Bi_4B_2O_9$-doped specimens could be explained by the liquid phase-assisted, abnormal grain growth [14]. Furthermore, the presence of a large amount of the $Bi_4B_2O_9$ addition increased the number of the nuclei for the abnormal grains during the sintering process, which eventually inhibited the grain growth and decreased the grain size, as shown in Table 2.

Fig. 3f shows the backscatter diffraction image of the 7.5 wt% $Bi_4B_2O_9$-doped 0.25CT–0.75LNT specimen sintered at 1350 °C. The dark grains were distributed in the matrix, indicating the