Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 39 (2013) 9763–9766
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Short communication

Low-firing high permittivity $Ca_{0.6}Sm_{0.8/3}TiO_3$–$(Li_{0.5}Nd_{0.5})TiO_3$ ceramics with $BaCu(B_2O_5)$ addition

Guo-hua Chen*, Chang-lai Yuan, Chang-rong Zhou, Yun Yang

Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, Guilin, Guangxi 541004, PR China

Received 22 March 2013; received in revised form 8 May 2013; accepted 8 May 2013
Available online 16 May 2013

Abstract

High permittivity $0.4Ca_{0.6}Sm_{0.8/3}TiO_3$–0.6 $(Li_{0.5}Nd_{0.5})$ TiO_3 ceramics with low firing temperature by $BaCu(B_2O_5)$ addition were prepared and the ceramic sintering behavior, phase purity, microstructure and microwave dielectric properties were investigated. Addition of $BaCu(B_2O_5)$ can effectively lower the firing temperature by about 200 °C. The $0.4Ca_{0.6}Sm_{0.8/3}TiO_3$–0.6 $(Li_{0.5}Nd_{0.5})$ TiO_3 ceramics with 3 wt% $BaCu(B_2O_5)$ sintered at 1100 °C exhibit good microwave dielectric properties with a permittivity of 96.3, a *Qf* value of 3133.3 GHz, and a temperature coefficient of resonant frequency of −19.5 ppm/°C, which is suitable for dielectric loaded antenna applications.
© 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: C. Dielectrics properties; Ceramics; Low firing

1. Introduction

New applications have emerged for microwave ceramics with the development of hand satellite navigation devices and phones, which require antennas with higher gain to deal with the low power signals from satellites in geostationary orbit. Improved efficiency can be achieved in antennas loaded with a high permittivity medium, the so called dielectric loaded antenna (DLA) [1,2]. Most of the current generations of DLAs, however, still use the microwave dielectric materials originally fabricated for cavity filters and resonators in cellular base stations. The latter applications have stringent material property requirements: quality factor $Qf_0 > 30000$ GHz, τ_f ± 5 ppm/°C and relative permittivity of $20 < \varepsilon_r < 50$. The materials suitable for such applications typically require a high sintering temperature (> 1400 °C), which adds greatly to production costs. For DLAs, property requirements of dielectric loss and τ_f can be relaxed as compared to those of cavity filters, and materials with larger values of τ_f and lower Q may be utilized in such devices [3].

Barium neodymium titanate ($\varepsilon_r > 80$) [4] and $Ca_{2/5}Sm_{2/5}TiO_3$–$Li_{1/2}Nd_{1/2}TiO_3$ ($\varepsilon_r > 100$) [5] ceramics are two of the most common ceramics currently used in DLAs. These materials possess high Qf_0 value and close to zero τ_f but a high sintering temperature of > 1400 °C. These ceramics are therefore ideal candidates for the incorporation of sintering aids to lower sintering temperature, thereby significantly decreasing production costs and carbon emission. $BaCu(B_2O_5)$ (BCB) addition is commonly used to decrease the sintering temperature of many ceramic materials [6,7]. For example, with 1.5 wt% BCB addition, the $Ba_5Nb_4O_{15}$ ceramic can be sintered at 875 °C and good microwave dielectric properties of ε_r=40.2, Qf_0=28,655 GHz, τ_f=60 ppm/°C are obtained [6]. In our recent work, we find that the $0.4Ca_{0.6}Sm_{0.8/3}TiO_3$–$0.6(Li_{0.5}Nd_{0.5})TiO_3$ (CSLNT) ceramics sintered at 1300 °C exhibit good microwave dielectric properties of $\varepsilon_r = 123.2$, $Qf_0 = 3546$ GHz, $\tau_f = 8.9$ ppm/°C. In this work, the effects of BCB addition on the CSLNT ceramics are studied with the aim of fabricating a low sintering temperature and high permittivity dielectric material suitable for DLA applications.

2. Experimental procedure

High-purity $CaCO_3$, TiO_2, Li_2CO_3, $BaCO_3$, CuO, and H_3BO_3, Sm_2O_3, Nd_2O_3 (> 99.5%), (Guo-Yao Co. Ltd., Shanghai, China) powders were used as the starting materials. The ceramics were prepared by the conventional solid state reaction method. Stoichiometric quantities of starting materials according to the general formula of $0.4Ca_{0.6}Sm_{0.8/3}TiO_3$–0.6 $(Li_{0.5}Nd_{0.5})$ TiO_3 (CSLNT)

*Corresponding author. Tel.: +867732291434; fax: +867732191903.
E-mail addresses: cgh1682002@163.com, chengh@guet.edu.cn (G.-h. Chen).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.05.028

was ball-milled in a polyethylene jar for 6 h using ZrO_2 balls with ethanol. The mixtures were heated at 1100 °C in air for 3 h after drying and sieving. The BCB powder was synthesized according to Zhou's report [6]. The CSLNT powders were ball-milled together with the 1–7 wt% BCB in alcohol medium for 12 h and then dried and sieved. The granulated powders were pressed into disks of 12 mm in diameter and 6 mm in thickness and then sintered at 1100 °C in air for 3 h.

The bulk densities of the sintered ceramics were measured by the Archimedes method. The crystal phases were identified by the X-ray diffractometry (XRD: D8-ADVANCE, Bruker, Germany). The microstructures were examined using a scanning electron microscope (SEM: JEOL JSM-5610LV, Tokyo, Japan) coupled with energy-dispersive X-Ray spectroscopy (EDS).The microwave dielectric properties were measured by a Vector Network Analyzer (N5230C, Agilent Technologies).

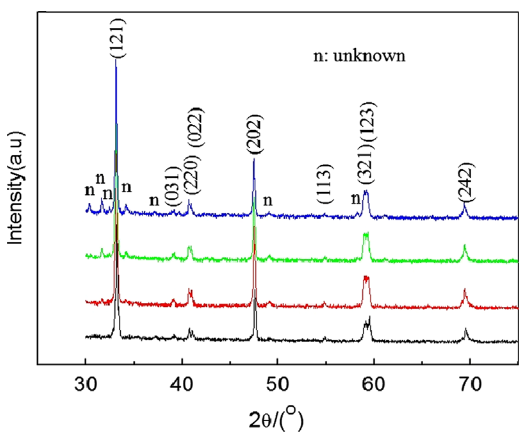

Fig. 1. XRD patterns of the CSLNT ceramics with different BCB contents sintered at 1100 °C for 3 h (a) 1 wt%, (b) 3 wt%, (c) 5 wt%, and (d) 7 wt%.

The temperature coefficient of resonant requency (τ_f) was measured in the temperature range of 25–75 °C using the equation [8]: $\tau_f=((f_{75}-f_{25})\ \times 10^6/(50\times f_{25}))$, where f_{75} and f_{25} are the resonant frequencies at 75 °C and 25 °C, respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns of the CSLNT ceramics with different BCB contents, sintered at 1100 °C for 3 h. All the peaks for 1 wt% BCB added samples are indexed based on the JCPDS file number 42-0423 for $CaTiO_3$ with an orthorhombic perovskite structure and no additional peaks are observed (Fig. 1a), which suggests that a single solid-solution between $Ca_{0.6}Sm_{0.8/3}TiO_3$ and $(Li_{0.5}Nd_{0.5})$ TiO_3 is obtained. However, some peaks associated with unknown secondary phases are observed when BCB is ≥3 wt%, and the intensity of peaks associated with unknown secondary phases increases with further increase of BCB contents.

Fig. 2 shows the SEM images of BCB added CSLNT ceramics sintered at 1100 °C for 3 h. The dense microstructures are obtained in the sintered ceramics as BCB is ≥3wt% (Fig. 2b–d). The melting temperature of the BCB is approximately 850 °C [6,7], the addition of BCB effectively lowers the sintering temperature from 1300 °C to 1100 °C due to the liquid-phase effect. The morphology of the CSLNT ceramics varies with BCB contents. Only one type of grains with an average size of 2–3 μm is observed in the 1 wt% BCB added CSLNT sample (Fig. 2a). Obviously, in Fig. 2b–d, at least two kinds of grains are observed, the square platelike and long straplike grains are present in the specimens of the CSLNT ceramics added with 3–7 wt% of BCB. It is noted that the size of long straplike grains increases with increase of BCB

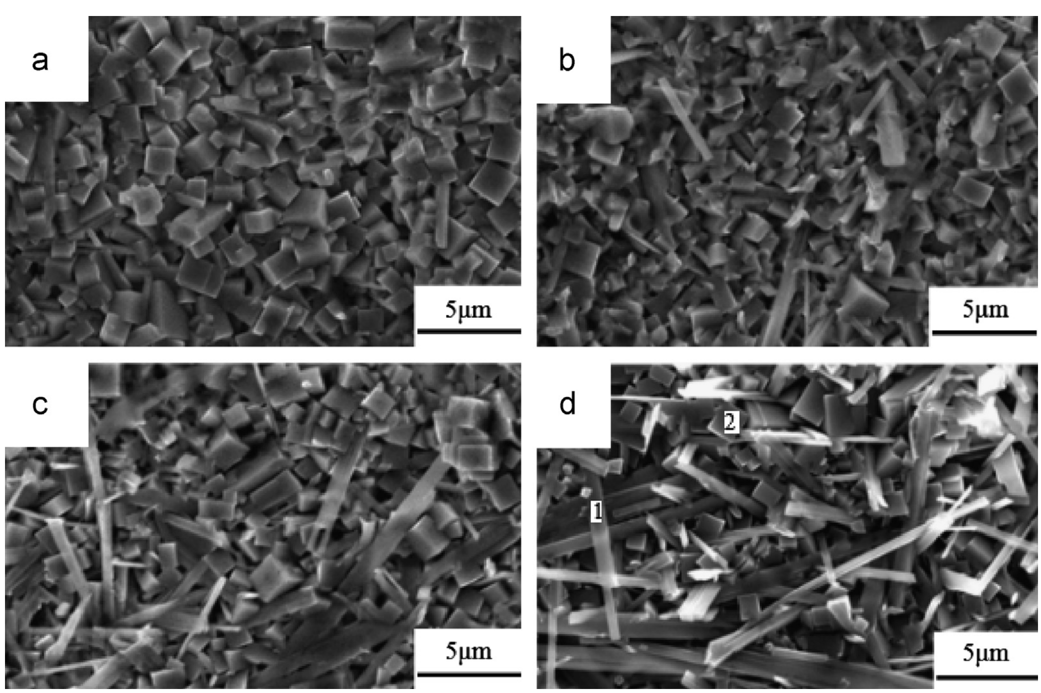

Fig. 2. SEM images of the CSLNT ceramics doped with various BCB contents sintered at 1100 °C for 3 h (a) 1 wt%, (b) 3 wt%, (c) 5 wt%, and (d) 7 wt%.

Table 1
EDS analysis results for long straplike grains (spot 1) and square platelike grains (spot 2) as seen in Fig. 2d.

Element	Spot 1(at%)	Spot 2 (at%)
O–K	69.59	69.33
Ca–K	3.24	3.25
Ti–K	16.90	17.15
Nd–L	4.29	4.43
Sm–L	1.96	2.11
Ba–L	2.00	1.83
Cu–K	2.02	1.91
Totals	100.00	100.0

contents. Typically, the average grain size of straplike grains is about 8–12 μm for the sample with 7 wt% of BCB. As mentioned earlier the presence of small amount of liquid phase while sintering which facilitates the grain growth and improves the sinterability. Similar behavior has been reported in case of SBN ceramics in which the addition of CASP glass gives rise to an increased grain size [9]. However, the presence of excessive liquid phase will facilitate the grain egregious growth, or abnormal grain growth in one direction, which restrains the elimination of inner pores in the ceramic bodies and leads to the decrease in the density [10].

The EDS analysis results for long straplike grains (spot 1) and square platelike grains (spot 2) as seen in Fig. 2d are shown in Table 1. It is observed that two kinds of grains (long strap and plate grains) have the same elemental composition of Ca, Nd, Sm, Ti, Ba, Cu and O, and almost same concentration for every element. It is impossible to detect boron and lithium ions using an EDS detector. The BCB may incorporate into matrix CSLNT or exist in amorphous state. In a word, the addition of BCB indeed influences the microstructure of the samples.

Fig. 3a shows the dependence of BCB content on the permittivity (ε_r) and the relative density of the CSLNT ceramics sintered at 1100 °C for 3 h. With increase of BCB contents, the relative densities and the permittivity first increase, and then decrease. When BCB = 3 wt%, a maximum value of the relative density and permittivity is obtained. The variation of the relative densities corresponds to that of the microstructure of the samples as seen in Fig. 2. For the CSLNT ceramics with 5–7 wt% BCB, the decrease of the permittivity may be attributed to the low densification degree and secondary phases. The Qf and τ_f values of the CSLNT ceramics as a function of BCB content are shown in Fig. 3b. The Qf value first has a tendency to increase due to the increasing relative density of the ceramics. When BCB = 3wt%, the Qf value reaches its maximum value of 3111 GHz, and then the Qf value decreases with further increase in BCB content because the unknown secondary phase may has a low Qf value itself. Hence, it is concluded that the variation of the Qf value with BCB can be attributed to the dual effect of the densification degree (or porosity) and unknown secondary phase content. It is found that the τ_f value exhibits monotone decrease with the increase of BCB content. The optimized CSLNT ceramics with 3 wt% BCB sintered at 1100 °C exhibit good microwave dielectric properties of $\varepsilon_r = 98.5$, $Qf_0 = 3111.0$ GHz (at $f_0 = 3.1$ GHz), $\tau_f = -19.5$ ppm/°C.

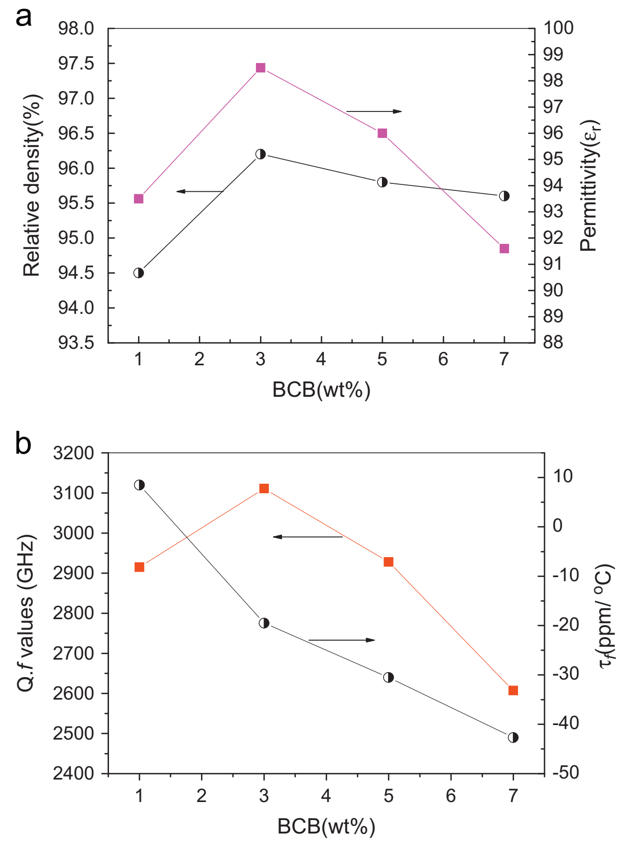

Fig. 3. The dependence of BCB content on the permittivity and the relative density (a), and the Qf and τ_f values (b) of the CSLNT ceramics.

4. Conclusion

Addition of BCB can effectively lower the sintering temperature of the CSLNT ceramics to 1100 °C and degrades the microwave dielectric properties to a certain degree. The CSLNT ceramics added with 3 wt% BCB sintered at 1100 °C have reasonable microwave dielectric properties, which may be suitable for DLA applications.

Acknowledgments

This work was supported by the Research funds of The Guangxi Key Laboratory of Information Materials (No.1210908-05-Z) and Natural Science Foundation of Guangxi (No. 2010GXNSFA013029). This work was also supported by the Research funds of Guangxi Experiment Center of Information Science, Guilin University of Electronic Technology.

References

[1] M. Mirsaneh, O.P. Leisten, B. Zalinska, I.M. Reaney, Circularly polarized dielectric-loaded antennas: current technology and future challenges, Advanced Functional Materials 18 (16) (2008) 2293–2300.

[2] I.M. Reaney, D. Iddles, Microwave dielectric ceramics for resonators and filters in mobile phone networks, Journal of American Ceramic Society 89 (7) (2006) 2063–2072.

[3] M. Mirsaneh, I.M. Reaney, Y. Han, I. Sterianou, O.P. Leisten, Low sintering temperature high permittivity glass ceramic composites for dielectric loaded microwave antennas, Advances in Applied Ceramics 110 (7) (2011) 387–393.

[4] L. Zhang, X.M. Chen, N. Qin, X.Q. Liu, Upper limit of x in $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ new tungsten bronze solid solution, Journal of European Ceramic Society 27 (8-9) (2007) 3011–3016.

[5] W.S. Kim, K.H. Yoon, E.S. Kim, Microwave dielectric characteristics of the $Ca_{2/5}Sm_{2/5}TiO_3$–$Li_{1/2}Nd_{1/2}TiO_3$ ceramics, Japanese Journal of Applied Physics 39 (9B) (2000) 5650–5653.

[6] H.F. Zhou, H. Wang, M.H. Zhang, H.B. Yang, Microwave dielectric properties and compatibility with silver of low-fired $Ba_5Nb_4O_{15}$ ceramics by $BaCu(B_2O_5)$ addition, Journal of Materials Research 25 (9) (2010) 1793–1798.

[7] J.B. Lim, K.H. Cho, S. Nahm, J.H. Paik, J.H. Kim, Effect of $BaCu(B_2O_5)$ on the sintering temperature and microwave dielectric properties of BaO–Ln_2O_3–TiO_2 (Ln, Sm, Nd) ceramics, Materials Research Bulletin 41 (2006) 1868–1873.

[8] Jun Liang, Wen-Zhong Lu, Microwave dielectric properties of Li_2TiO_3 ceramics doped with ZnO–B_2O_3 frit, Journal of American Ceramic Society 92 (4) (2006) 952–954.

[9] G.H. Chen, B. Qi, Effect of CASP glass doping on sintering and dielectric properties of SBN ceramics, Journal of Alloys and Compounds 473 (2009) 414–417.

[10] P.K. Patro, A.R. Kulkarni, C.S. Harendranath, Combustion synthesis of $Sr_{0.5}Ba_{0.5}Nb_2O_6$ and effect of fuel on its microstructure and dielectric properties, Materials Research Bulletin 38 (2003) 249–259.