Ceramics International 27 (2001) 809–813

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Substitution of CaO by BaO to improve the microwave dielectric properties of CaO–Li_2O–Sm_2O_3–TiO_2 ceramics

Ying-Chung Chen[a], Ping-Shou Cheng[a], Cheng-Fu Yang[b,*], Wen-Cheng Tzou[a]

[a]Department of Electrical Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan, ROC
[b]Department of Electronic Engineering, Chinese Air Force Academy, PO Box 90277-4, Kangshan, Kaohsiung, Taiwan 82012, ROC

Received 19 October 2000; received in revised form 9 December 2000; accepted 3 January 2001

Abstract

Sintered CaO–Li_2O_3–Sm_2O_3–TiO_2(16:9:12:63) composition (CLST) at 1325°C shows microwave dielectric properties: $\varepsilon_r = 104.1$, $Q{*}f$ value = 4320 GHz, and $\tau_f = 13.2$ ppm/°C. When BaO is used to substitute CaO in the CLST composition to form CaO–BaO–Li_2O–Sm_2O_3–TiO_2 = 16−x:x:9:12:63 ($x = 2$ and 4 for CBLST2 and CBLST4), the sintered CBLST2 and CBLST4 ceramics show coexistence of two phases, the perovskite CaO–Li_2O_3–Sm_2O_3–TiO_2 (CLST) phase and $BaSm_2Ti_4O_{12}$ (BST). As the BaO content increases from 0 to 4 mol%, the dielectric constant of CBLST ceramics decreases from 104.1 to 94.5, the $Q{*}f$ value increases from 4320 to 6740, and the τ_f value changes from 13.2 to 3.24 ppm/°C. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Microwave properties; CaO–Li_2O–Sm_2O_3–TiO_2 ceramics; CaO, BaO additions

1. Introduction

The rapid growth of microwave frequencies in communications has created a need for the miniaturization of components of bandpass filters and microwave oscillators. To achieve this result, materials with a high dielectric constant (ε_r), a high quality value ($Q{*}f$), and a low temperature coefficient of resonant frequency (τ_f) are required [1–3]. In general, a dielectric material with a high dielectric constant has a large τ_f value [4,5]. To adjust τ_f value close to zero, two or more compounds having negative and positive τ_f values are employed to form a solid solution or mixed phases in order to obtain the desired τ_f values. Paladino reported that zero τ_f value was achieved at an intermediate composition of $CaTiO_3$–$Ca(Al_{1/2}Ta_{1/2})O_3$ system [4]. However, in general, it is not easy to realize a material with intermediate properties in a two components system because it is difficult for each component to retain its individual properties. Therefore, for the development of the properties of two compounds, it is necessary to investigate each system's microstructure and dielectric properties.

In the past, the CaO–Li_2O–Sm_2O_3–TiO_2 (CLST) system was investigated by Ezaki et al. [5]. The CLST system is made by combining the Li_2O–Sm_2O_3–TiO_2 system ($Li_{1/2}Sm_{1/2}TiO_3$, $\varepsilon_r = 52$, $Q{*}f = 2280$ GHz, and $\tau_f = -260$ ppm/°C, an orthorhombic structure) [5] and the CaO–TiO_2 system ($CaTiO_3$, $\varepsilon_r = 170$, $Q{*}f = 3600$ GHz, and $\tau_f = 800$ ppm/°C, an orthorhombic perovskite structure) [4]. The CLST system has a high dielectric constant ($\varepsilon_r = 104.1$), a lower temperature stability for the resonant frequency change ($\tau_f = 13.2$ ppm/°C), and a lower quality value ($Q{*}f = 4600$). In this study, the CaO–Li_2O_3–Sm_2O_3–TiO_2 system is used as the base material. BaO, which has similar chemical properties with CaO, is used to substitute for CaO in order to improve the microwave dielectric properties. The microwave dielectric properties of two different CaO–BaO–Li_2O–Sm_2O_3–TiO_2 compositions have been investigated. The microwave dielectric properties of the CaO–Li_2O_3–Sm_2O_3–TiO_2 composition and the $BaSm_2Ti_4O_{12}$ ceramics are also developed for comparison.

2. Experimental procedure

Reagent-grade raw materials of $BaCO_3$, $CaCO_3$, Li_2CO_3, Sm_2O_3, and TiO_2 with higher than 99.5% purity were used as starting materials. These powders were weighed first in accordance with the four different compositions: CaO–Li_2O–Sm_2O_3–TiO_2 = 16:9:12:63 (CLST),

---

* Corresponding author. Fax: +886-7-6114536.
E-mail address: cfyang@cc.cafa.edu.tw (C.-F. Yang).

PII: S0272-8842(01)00034-7

CaO–BaO–Li_2O:Sm_2O_3–TiO_2 = 16−x:x:9:12:63 for x = 2 (CBLST2) and x = 4 (CBLST4), and BaO:Sm_2O_3:TiO_2 = 1:1:4 (BST). The powders were mixed for 10 h in a milling pot containing agate balls and distilled water. The mixtures were then dried and calcined at 1100°C for 3 h. After grinding, organic binder was added to the powders. Cylindrical specimens for dielectric and sintering characteristics testing were pressed, then debinding was carried out. These shaped pellets were sintered at 1275–1350°C for 3 h. X-ray diffraction pattern (XRD) was used to determine the crystalline phases of the sintered ceramics. The surface observations of the BST, CLST, CBLST2, and CBLST4 ceramics were executed by scanning electron micrography (SEM). The electron microprobe analyses for Ca, Ba, Sm, and Ti were also executed by SEM. Dielectric characteristics at microwave frequency were measured by Hakki and Coleman's dielectric resonator method improved by Courtney [6] and Kobayashi et al. [7]. The dielectric constant of a cylindrical dielectric resonator can be accurately determined by measuring the resonant frequency of the TE_{011} mode and verified by $TE_{01\delta}$ resonant modes. The temperature coefficient of resonant frequency τ_f is defined as follows.

$$\tau_f = f_T - f_o/(f_t * \Delta T) \tag{1}$$

where f_T, f_t, and f_o are the resonant frequency at 85, 25, and 0°C, respectively.

3. Results and discussion

The XRD patterns of the 1325°C-sintered CLST, BST, CBLST2, and CBLST4 ceramics are recognized and the results are shown in Fig. 1. For CLST ceramic, the mainly crystalline structure in the system is the same as that of the $CaTiO_3$, which is an orthorhombic perovskite structure. This is not a typical simple cubic structure but an orthorhombic structure with slight distortion. The BaO–Sm_2O_3–TiO_2 = 1:1:4 composition reveals a single phase of $BaSm_2Ti_4O_{12}$. The XRD patterns of CBLST2 and CBLST4 ceramics reveal a large difference with that of the CLST ceramic. Many external lines are revealed in the CBLST2 and CBLST4 ceramics. As the external lines of the CBLST2 and CBLST4 ceramics are compared with the reflection lines of the BST ceramic, it is found that they are coincident. This result suggests that the BST phase may appear in the CBLST2 and CBLST4 ceramics.

Fig. 2 illustrates the optical micrograph of the 1325°C sintered CLST, CBLST2, and CBLST4 ceramics. The grain growth of the CBLST2 and CBLST4 ceramics can also be indicative of forming the $BaSm_2Ti_4O_{12}$ phase in the CBLST2 and CBLST4 ceramics. The CLST ceramic shows disk-type grains [Fig. 2(a)]. The BST ceramics show that the main crystals are bar-shaped grains with the occasional appearance of the block-shaped grains [8]. The CBLST2 and CBLST4 ceramics illustrate a texture of two-phase components, where bar-type and disk-type grains coexist [Fig. 2(b) and (c)]. As the micrographs of the CBLST2 and CBLST4 ceramics are compared, the size of the bar-type grains increases with the increase of the BaO content.

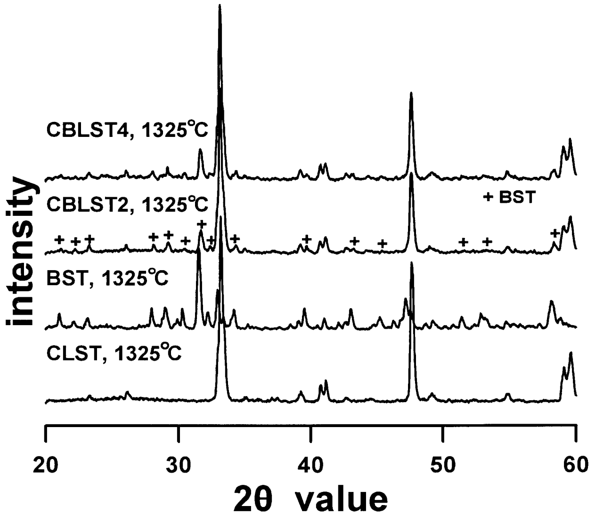

Fig. 1. The XRD patterns of CLST, BST, CBLST2, and CBLST4 ceramics. The sintering temperature is 1325°C.

To analyze the composition, X-ray diffraction pattern for Ca, Ba, Ti, and Sm on the bar-type and disk-type grains are carried out, and the results are shown in Fig. 3. However, Li could not be detected because of its small size and light atomic weight. As Fig. 3(a) shows, the Ca, Ba, Ti, and Sm elements can be detected in the disk-type grains. The Ba, Ti, and Sm elements can be detected but the Ca cannot be detected in the bar-type grains, as shown in Fig. 3(b). It is noted that the atomic ratio of the Ba–Sm–Ti in the bar-type grains is about 1:1:4, and this result suggests again that the bar-type grains may be the $BaSm_2Ti_4O_{12}$ phase and the disk-type grain is the CLST phase. The appearance of the extra peaks in Fig. 1 can be identified as the $BaSm_2Ti_4O_{12}$ phase.

The dielectric constants (ε_r) of the CLST, BST, CBLST2, and CBLST4 ceramics are tested as a function of sintering temperature, and the results are shown in Fig. 4. At first, independent of BaO content, the ε_r values of all compositions increase with the increasing of the sintering temperature and reach a saturation value at about 1325°C. The densities of all ceramics increase with the increase of the sintering temperature could account for this result. It is noted that the ε_r values of the CBLST-system (including CLST, CBLST2, and CBLST4) ceramics are strongly dependent on the BaO content. As 1325°C is used as the sintering temperature, the dielectric constants of the CBLST-system ceramics decrease from 104.1 for CLST ceramic to 98.7 and 94.5 for CBLST2 and CBLST4 ceramics.

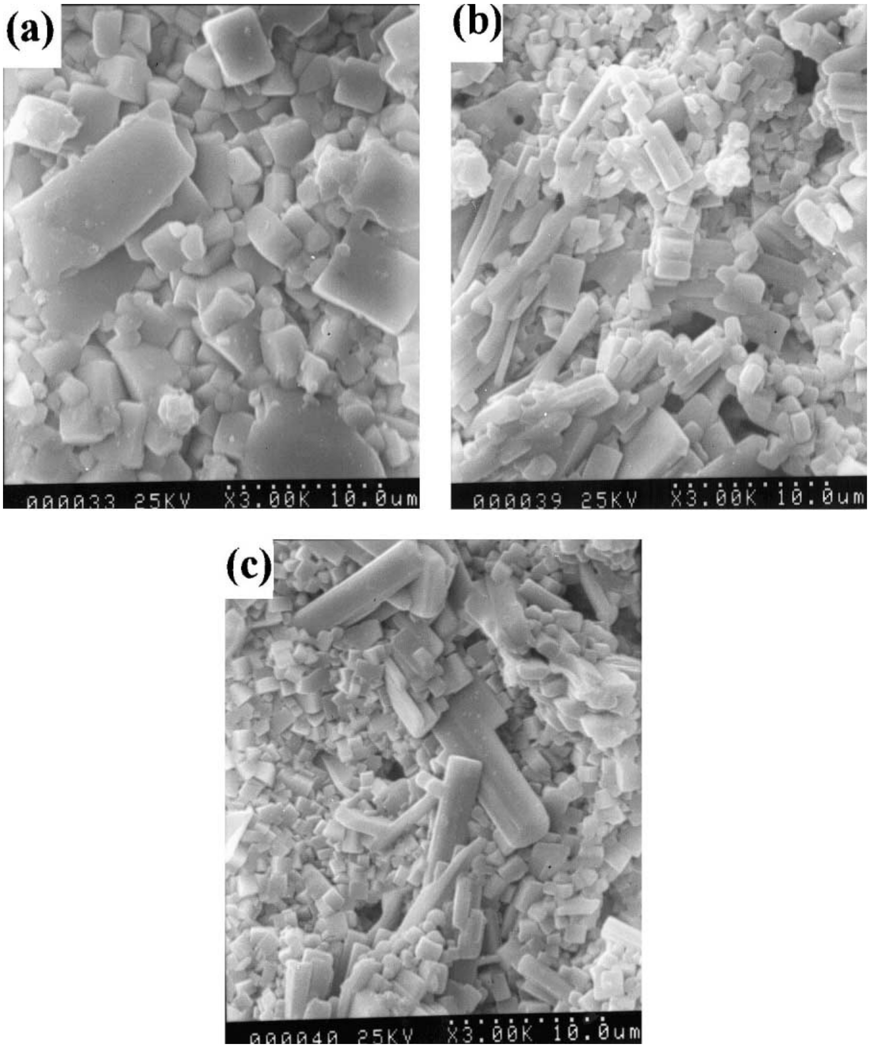

Fig. 2. The micrographs of (a) CLST, (b) CBLST2, and (c) CBLST4 ceramics. The sintering temperature is 1325°C.

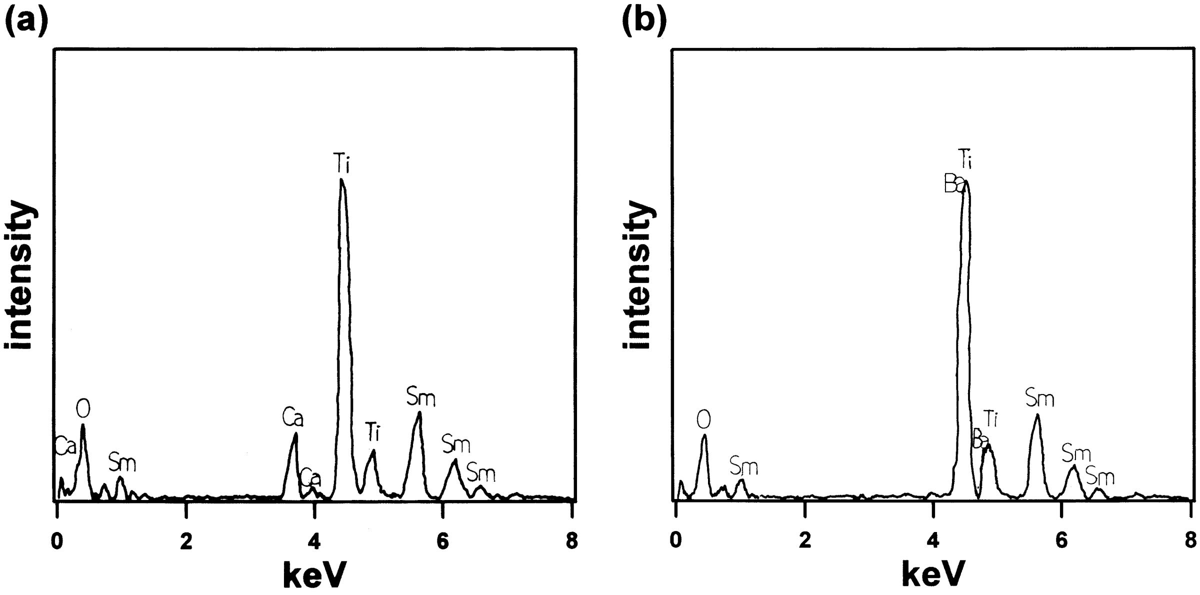

Fig. 3. The EPMA analyses of CBLST4 ceramics for (a) disk-type grains and (b) bar-type grain.

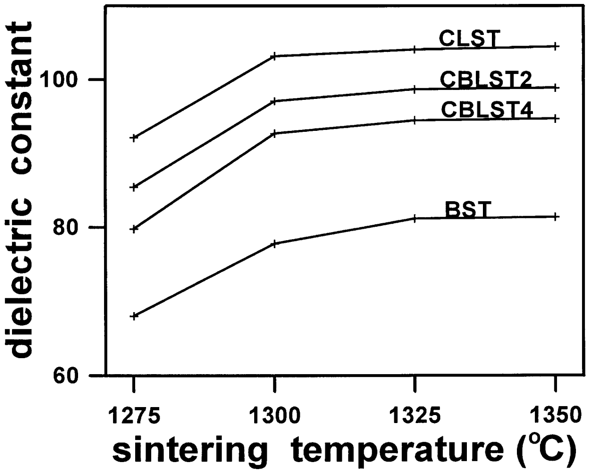

Fig. 4. The dielectric constants of CLST, BST, CBLST2, and CBLST4 ceramics as a function of sintering temperature.

Fig. 5 shows the microwave dielectric properties of the CBLST ceramics as a function of the BaO content, and the sintering temperature used is 1325°C. It is also noted that the Q^*f values of the CBLST-system ceramics are strongly dependent on the BaO content. The Q^*f values of the CBLST-system ceramics increase from 4320 for CLST ceramic to 6180 and 6740 for CBLST2 and CBLST4 ceramics. The τ_f values change from 13.4 ppm/°C for CLST ceramic to 7.85 ppm/°C and 3.24 ppm/°C for CBLST2 and CBLST4 ceramics. These results imply that the BaO content has a beneficial influence on the Q^*f and the τ_f values of the CBLST ceramics in which the CLST is a major component and the BST is a minor component. According to the XRD patterns, the crystalline phases of the CBLST-system ceramics are composed of the two phases of the $BaSm_2Ti_4O_{12}$ and the CLST. If that be so, the effect of the $BaSm_2Ti_4O_{12}$ phase on the ε_r values, the τ_f values, and the Q^*f values of the CBLST2 and CBLST4 ceramics is unavoidable. If the $BaSm_2Ti_4O_{12}$-CLST ceramics are thought of as heterogeneous phases in the CBLST2 and CBLST4 ceramics, the microwave dielectric properties of the CBLST2 and CBLST4 ceramics can be predicted by the empirical models [9]:

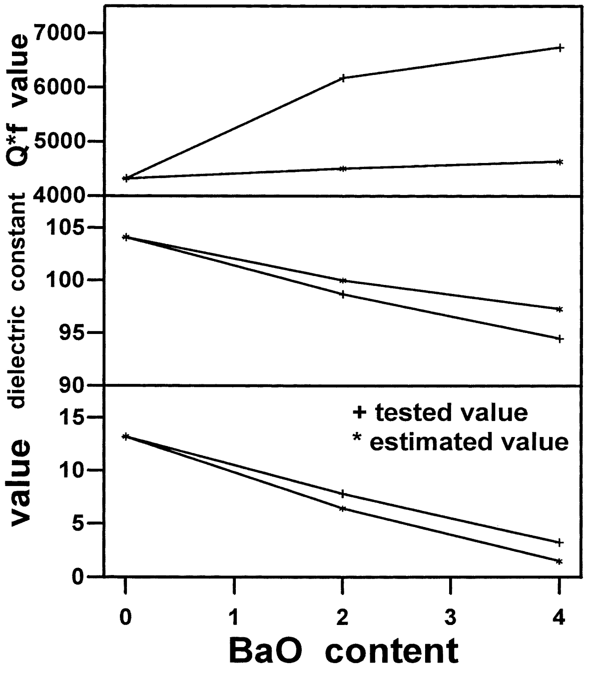

Fig. 5. The microwave dielectric properties of the CBLST ceramics as a function of BaO content. The sintering temperature is 1325°C.

$$V \ln(\varepsilon_r) = \Sigma\ V_i \ln(\varepsilon_{ri}) \tag{2}$$

$$1/Q = \Sigma V_i/Q_i \tag{3}$$

$$\tau_f = \Sigma\ V_i\ \tau_i \tag{4}$$

where V_i, ε_i, τ_i, and Q_i ($i=1$ and 2) are the volume fraction, the dielectric constant, the temperature coefficient of resonant frequency, and the quality value of each-phase dielectrics; while V, ε, τ, and Q are the volume fraction, the dielectric constant, the temperature coefficient of resonant frequency, and the quality value of the multi-phase components. In predicting the dielectric properties of the CBLST2 and CBLST4 ceramics, the dielectric constants are estimated from the CLST ceramic (sintered at 1325°C, $\tau_f = 13.2$ ppm/°C, $\varepsilon_r = 104.1$, and $Q^*f = 4320$) and the BST ceramic (sintered at 1325°C, $\tau_f = -19.2$ ppm/°C, $\varepsilon_r = 81.2$, and $Q^*f = 5280$).

According to the empirical modes, the τ_f values of the CBLST2 and CBLST4 ceramics have positive smaller τ_f values than does the CLST ceramic. Because the lower dielectric constants of the BST ceramics, the appearance of the $BaSm_2Ti_4O_{12}$ phase would decrease the dielectric constants of the CBLST2 and CBLST4 ceramics. As shown in Fig. 6, the dielectric constants decrease with the increase of the BaO content in the CBLST system. The experimentally tested results do not give a good agreement with the estimated values. It is believed that Ba has similar chemical properties to Ca and that some Ba will substitute in Ca site. The atomic ratios of the Ca, Sm, and Ti in CBLST2 and CBLST4 ceramics have some degree of distortion from the atomic ratios of Ca, Sm, and Ti in CLST ceramic.

4. Conclusions

In this study, using BaO to substitute the CaO site will improve the microwave dielectric properties of the CLST ceramics. However, it is believed that Ba will substitute the Ca site in the CLST composition because of their similar chemical properties. Even the CBLST2 and CBLST4 ceramics have lower dielectric constants than does the CLST ceramics, but the CBLST2 and CBLST4 ceramics show higher Q^*f values and better τ_f values than those of the CLST and the $BaSm_2Ti_4O_{12}$ ceramics. Although the CBLST2 and CBLST4 ceramics are composed of two phases, CLST and BST, the ε_r values, the Q^*f values, and the τ_f values of the CBLST2 and CBLST4 ceramics cannot be predicted from the CLST and the BST ceramics. From the EPMA analysis, the deviation of the CLST composition in the CBLST2 and CBLST4 ceramics may account for these results.

References

[1] T. Negas, G. Yeager, S. Bell, N. Coats, $BaTi_4O_9/Ba_2Ti_9O_{20}$-based ceramics resurrected for modern microwave applications, Am. Ceram. Soc. Bull. 72 (1993) 80–89.

[2] S.B. Desu, H.M. O'Bryan, Microwave loss quality of $Ba(Zn,Mg)_{1/3}Ta_{2/3}O_3$ ceramics, J. Am. Ceram. Soc. 68 (1985) 546–551.

[3] S. Nishigaki, H. Kato, S. Yano, R. Kamimura, Microwave dielectric properties of $(Ba,Sr)O–Sm_2O_3–TiO_2$ ceramics, Am. Ceram. Soc. Bull. 66 (1987) 1405–1410.

[4] S. Kucheiko, J.W. Choi, H.J. Kim, H.J. Jung, Microwave dielectric properties of $CaTiO_3–Ca(Al_{1/2}Ta_{1/2})O_3$ ceramics, J. Am. Ceram. Soc. 79 (1996) 2739–2743.

[5] K. Ezaki, Y. Baba, H. Takhashi, K. Shibata, S. Nakano, Microwave dielectric properties of $CaO–Li_2O–Ln_2O_3–TiO_2$ ceramics, Jpn J. Appl. Phys. 32 (1993) 4319–4322.

[6] W.E. Courtney, Analysis and evaluation of a method of measuring the complex permittivity and permeability of microwave insulators, IEEE Trans. MTT 18 (1985) 476–485.

[7] Y. Kobayashi, M. Katoh, Microwave measurement of dielectric properties of low-loss materials by the dielectric rod resonator method, IEEE Microwave Theory and Technol. 33 (1985) 586–592.

[8] P.-S. Cheng, C.-F. Yang, Y.-C. Chen, W.-C. Tzou, The reaction sequence and dielectric properties of $BaSm_2Ti_4O_{12}$ ceramics, Ceram. Int. 26 (2000) 877–881.

[9] W. Wersing: Electronic Ceramics, B.C.H. Steele (Ed.), Elsevier, London, 1991, p. 67.