Article ID: 1000-324X(2011)06-0664-05 **DOI:** 10.3724/SP.J.1077.2011.11060

Microwave Dielectric Properties of the (1–*x*)($Mg_{0.9}Co_{0.1}$)TiO_3-*x*($Ca_{0.61}La_{0.26}$)TiO_3 Ceramics

LIU Hao, SHEN Chun-Ying, LU Zheng-Dong, QIU Tai

(College of Materials Science and Engineering, Nanjing University of Technology, Nanjing 210009, China)

Abstract: The microwave dielectric properties of the (1–*x*)($Mg_{0.9}Co_{0.1}$)TiO_3-*x*($Ca_{0.61}La_{0.26}$)TiO_3(MCT-CLT) ceramics were investigated. The system was prepared using a conventional solid-state ceramic route. The objective of the present work is to compensate for the negative temperature coefficient of resonant frequency (τ_f) of ($Mg_{0.9}Co_{0.1}$)TiO_3 (MCT) by the addition of ($Ca_{0.61}La_{0.26}$)TiO_3 (CLT). The microwave dielectric properties are strongly correlated with the sintering temperature and the composition. Very dense MCT-CLT ceramics were prepared by sintering at 1300℃. When the ceramics were sintered at temperatures above 1300℃, the bulk density decreased and the dielectric properties deteriorated. With the increasing of *x*, the relative dielectric constant (ε_r) of the ceramics increases and the product of quality factor and resonant frequency ($Q\times f$) decreases. For practical application, 0.87($Mg_{0.9}Co_{0.1}$)TiO_3-0.13($Ca_{0.61}La_{0.26}$)TiO_3 (87MCT-13CLT) ceramics sintered at 1300℃ with a dielectric constant ε_r=22.4, a $Q\times f$ value of 35000 GHz and a temperature coefficient of resonance frequency (τ_f) of -8.7×10^{-6}/℃ was proposed in this paper.

Key words: (1–*x*)($Mg_{0.9}Co_{0.1}$)TiO_3-*x*($Ca_{0.61}La_{0.26}$)TiO_3 ceramics; microwave dielectric ceramics; dielectric constant; quality factor; temperature stable resonant frequency

Microwave dielectric ceramics are important materials used in microwave devices such as resonators, filters and oscillators in microwave communication systems[1]. For a good microwave dielectric ceramics, three dielectric characteristics should be satisfied, which are high dielectric constant (ε_r) to reduce the size of devices, high quality factor ($Q\times f$) for achieving prominent frequency selectivity and stability, and a near zero temperature coefficient of resonance frequency (τ_f)[2] for temperature stability respectively.

$MgTiO_3$-based ceramics is one of the leading dielectric materials for microwave frequency applications. In the past, $CaTiO_3$ or $SrTiO_3$ were incorporated to adjust temperature coefficient of resonance frequency of $MgTiO_3$-based ceramics[3-4]. Recently, Lu *et al* reported that through partial replacement of Mg by Co, the ($Mg_{0.9}Co_{0.1}$)TiO_3 (MCT) ceramics with ilmenite-type structure possesses good dielectric characteristics (ε_r = 18.99, $Q\times f$ =154000 GHz and τ_f = -45.6×10^{-6}/℃)[5]. Moreover, ($Ca_{0.61}La_{0.26}$)TiO_3 (CLT) was another important microwave dielectric ceramic, which shows a positive τ_f value of 213×10^{-6}/℃ associated with a high ε_r of 109 and a $Q\times f$ value of 17600 GHz[6]. This work intends to further improve the dielectric properties of MCT, particularly in terms of the $Q\times f$ and τ_f values, by modifying it sequentially with certain contents of CLT. The correlation between the microstructure and the $Q\times f$ value was also investigated.

1 Experimental

High-purity oxide powders (>99.9%) MgO, TiO_2, Co_2O_3, La_2O_3 and $CaCO_3$ were used as raw materials. MgO and La_2O_3 was separately heated at 700℃ and 900℃ for 2h before weighing to remove any hydroxides. The powders were weighed according to the desired stoichiometry of CLT and MCT respectively, and mixed for 6 h with distilled water. Then the two mixed powders were calcined at 1100℃ for 3h to produce CLT and MCT respectively, and mixed according to the compositon of MCT-CLT and re-milled for 6h. After being dried, the resultant mixed powder were pressed into pellets of ϕ11mm×5mm in thickness under a pressure of 300MPa, which was followed by sintering at 1250–1400℃ for 2h.

The microstructures of the sintered samples were observed by scanning electron microscope (SEM) and energy dispersive spectroscope (EDS). X-ray power diffrac-

Received date: 2010-01-18; **Modified date:** 2011-03-02; **Published online:** 2011-03-30
Biography: LIU Hao(1987–), male, candidate of master. E-mail: kyleliu@sohu.com
Corresponding author: SHEN Chun-Ying, professor. E-mail: shency@njut.edu.cn

tion (XRD) data were collected for phase identification using CuKα radiation. The densities of the samples were measured by the Archimedes method. The dielectric properties of the samples at microwave frequency were measured by the modified Hakki and Coleman's method in the TE011 mode using a network analyzer[7-8]. τ_f was evaluated in the temperature range from 25℃ to 80℃.

2 Results and discussion

2.1 Sintering properties

Figure 1 shows the bulk density of MCT-CLT ceramics sintered at different temperatures. With the increase of sintering temperature, the porosity decreased to a minimal at 1300℃ and thereafter slightly increased. Dense ceramics can be obtained when sintered at 1300℃. The decrease of density at 1400℃ as compared with 1300℃ was owing to the increase of pore size[9]. The increase of pore size at 1400℃ is well visible from the Fig. 3(d). Bulk density was also influenced by the composition and increased with the increase of CLT content, which possesses a higher density than MCT[10].

2.2 Phase composition

The XRD patterns of MCT-CLT ceramics system did not significantly change with x value ranging from 0.11 to 0.19 sintered at 1300℃ for 2 h, as shown in Fig. 2. CLT has perovskite structure. CLT also has a high ε_r of around 109, a $Q\times f$ value higher than 17600 GHz and a large τ_f value of 212×10^{-6}/℃. According to the well-known mixing rules, the addition of CLT to the MCT system can enhance the dielectric constant and adjust the temperature coefficient of dielectric constant to near zero. When CLT was added to MCT to form a ceramic system of MCT-CLT, the lattice parameters of MCT did not change with CLT content. Furthermore, the formation of mixed phases in the MCT-CLT ceramics system was due to structural differences and because the average ionic radii of Ca^{2+} (0.099 nm) and La^{3+} (0.115 nm) were larger than those of Mg^{2+} (0.066 nm) and Co^{2+} (0.0745 nm).

2.3 Microstructure

The SEM micrographs of 0.87MCT-0.13CLT ceramics sintered at different temperatures are illustrated in Fig. 3. The grain size of the materials slightly increased with increasing sintering temperature and very dense materials with uniform grain size and morphology was obtained. However, inhomogeneous grain growth was observed at the sintering temperatures higher than 1350℃, indicating 1300℃ should be an appropriate sintering temperature for the ceramics. The EDS patterns of 0.87MCT-0.13CLT ceramics sintered at 1300 ℃ are shown in Fig.4. EDS analysis of Fig. 3(b) indicated that the grain A and B were MCT and CLT respectively, which further verified the MCT-CLT system.

2.4 Microwave dielectric properties

Figure 5 demonstrates the dielectric constant of the MCT-CLT ceramics sintered at different temperatures. Variation of the ε_r value was consistent with that of density and the maximum dielectric constant was obtained for each composition when sintered at 1300℃. As can be expected from mixing rule, the dielectric constant increased from 21.86 to 26.65 as the content of CLT increased from 0.11 to 0.19, owing to a much higher ε_r value of CLT than MCT. It also suggests an ε_r-tunable system through the control of the x value. The quality factor value ($Q\times f$) of

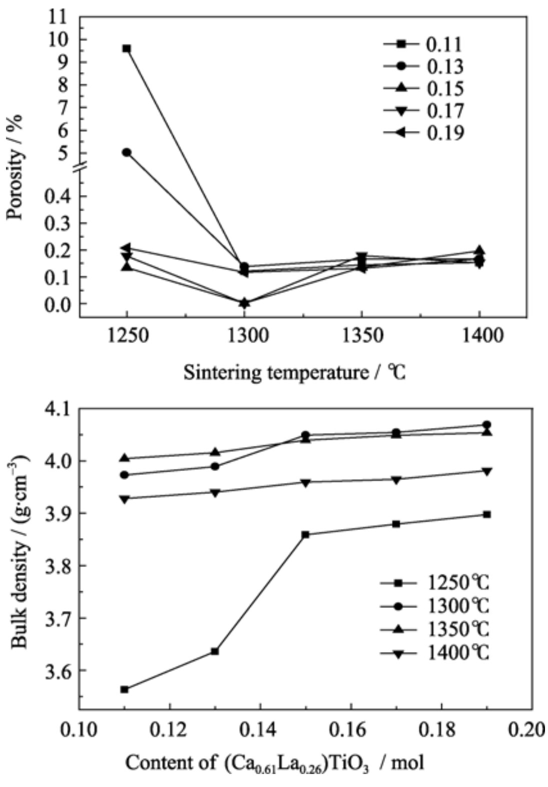

Fig. 1 Bulk density and Porosity of MCT-CLT ceramics system sintered at different temperatures

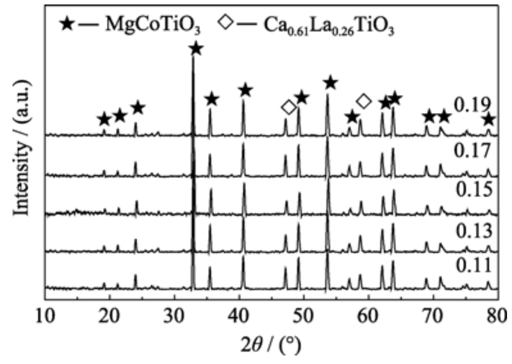

Fig. 2 XRD patterns of MCT-CLT ceramics sintered at 1300℃ for 2 h

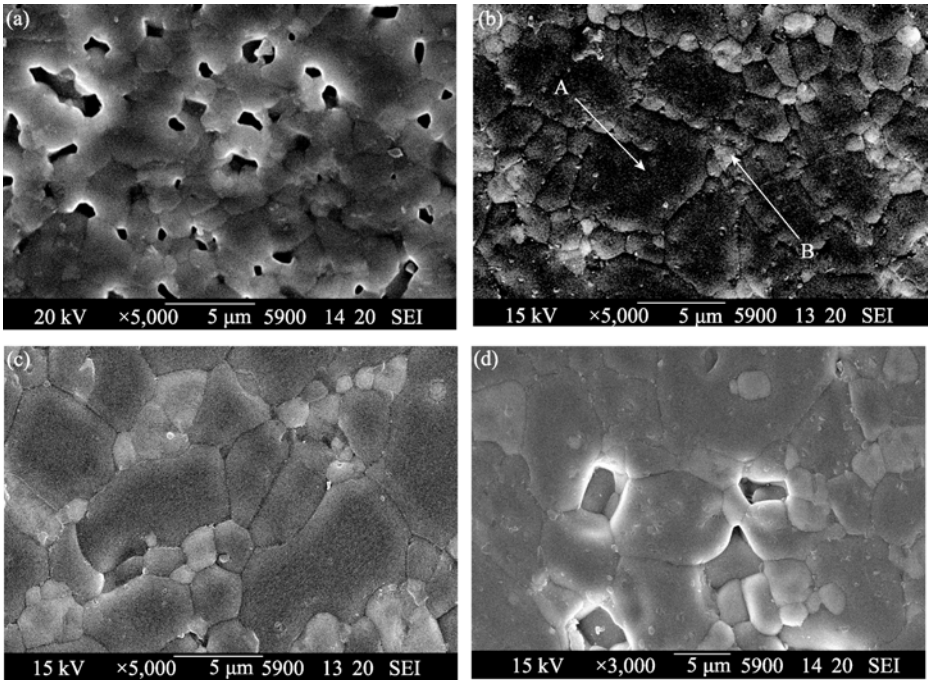

Fig. 3 SEM images of 0.87MCT-0.13CLT ceramics sintered at different temperatures
(a) 1250 ℃; (b) 1300 ℃; (c) 1350 ℃; (d) 1400 ℃

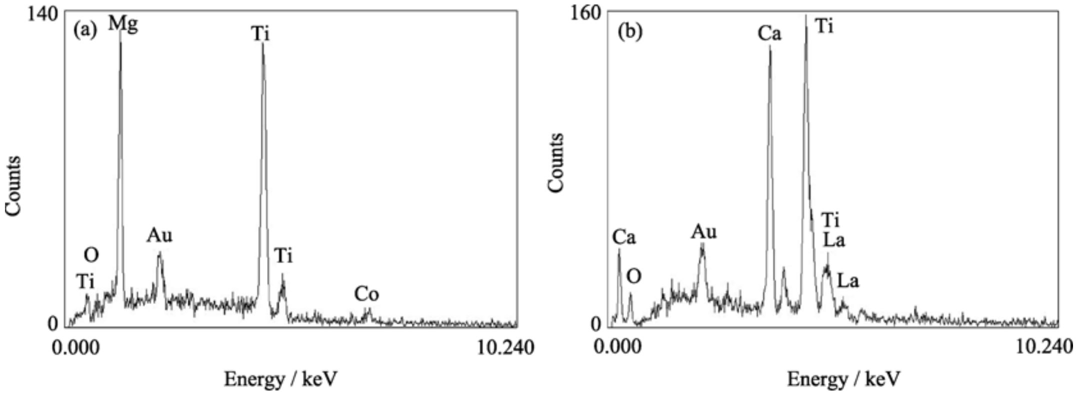

Fig. 4 EDS patterns of 0.87MCT-0.13CLT ceramics in Fig.3 (b)
(a) A spot; (b) B spot

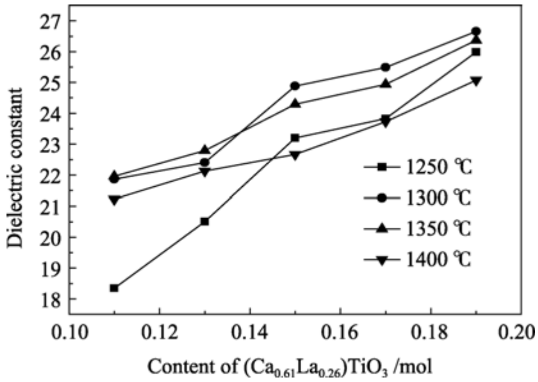

Fig. 5 ε_r value of MCT-CLT ceramics system sintered at different temperatures

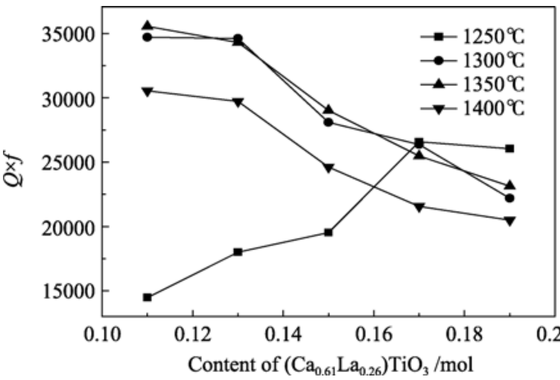

Fig. 6 $Q\times f$ value of MCT-CLT ceramics system sintered at different temperatures

MCT-CLT ceramics sintered at different temperatures are shown in Fig. 6. Many factors are believed to affect the microwave dielectric loss which consists of intrinsic loss and extrinsic loss. Intrinsic losses are mainly caused by lattice vibration modes while extrinsic losses are dominated by the second phases, oxygen vacancies, grain size. Meanwhile, relative density also plays an important role in controlling the dielectric loss, and has been shown for other microwave dielectric materials[11-12].

Since the quality factor of MCT ($Q\times f$ =154000GHz) is much higher than that of CLT ($Q\times f$ =17600GHz), a decrease in the $Q\times f$ value is expected as the amount of CLT increased. The $Q\times f$ value of MCT-CLT ceramics decreased with increasing x value in all cases. The 0.87MCT-0.13CLT ceramics possessed an excellent $Q\times f$ value of 35000 GHz at 1300℃ for 2h.

Figure 7 illustrates the temperature coefficient of the resonant frequency (τ_f) of MCT–CLT ceramics sintered at 1300℃. In general, τ_f is related to the phase composition of the ceramics and insensitive to the sintering temperature. A higher CLT (τ_f=213×10^{-6}/℃) content leads to a variation of τ_f toward positive value, which increases from −19.4×10^{-6}/℃ to 27.8×10^{-6}/℃ as the addition of CLT increases from 0.11 to 0.19. It gives a cross-zero line which implies that zero τ_f can be achieved through appropriate adjustment of the x value in the system.

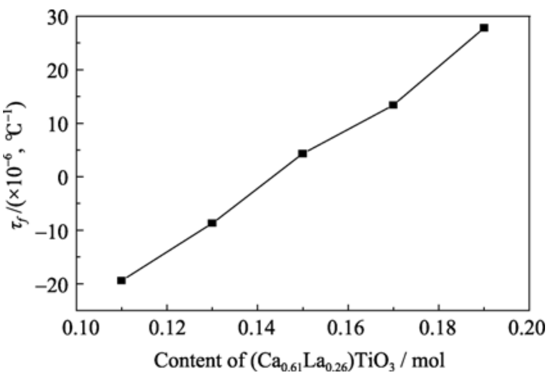

Fig.7 The τ_f value of MCT-CLT ceramics system sintered at different temperatures

3 Conclusions

Very dense MCT-CLT ceramics were prepared by sintering at 1300℃, which exhibited optimum dielectric properties. When the ceramics were sintered at temperatures above 1300℃, the increase of pore size resulted in the decrease in density and degradation in dielectric properties.

With the molar fraction of CLT in MCT-CLT ceramics increasing from 0.11 to 0.19, both ε_r and τ_f value increased, whereas $Q\times f$ value decreased gradually. The ε_r, $Q\times f$ and temperature coefficient of resonant frequency (τ_f) of 0.87MCT-0.13CLT ceramic sintered at 1300℃ are 22.4, 35000GHz and −8.7×10^{-6}/℃, respectively.

References:

[1] Long S A, Mcallister M W, Shen L C. The resonant cylindrical dielectric cavity antenna. *IEEE Trans.*, 1983, **31(3):** 406−412.

[2] Wersing W. Microwave ceramics for resonators and filters. *Curr.Opin. Solid State. Mater. Sci.*, 1996, **1(5):** 715−731.

[3] Huang C L, Weng M H. Improved high *q* value of $MgTiO_3$-$CaTiO_3$ microwave dielectric ceramics at low sintering temperature. *Mater. Res. Bull.*, 2001, **36(15):** 2741−2750.

[4] Cho W W, Kakimoto K, Ohsato H. High-Q microwave dielectric $SrTiO_3$-doped $MgTiO_3$ materials with near-zero temperature coefficient of resonant frequency. *Jpn. J. Appl. Phys.*, 2004, **43(9A):** 6221−6224.

[5] Lu Z D, Shen C Y, Qiu T. Studies on microwave dielectric properties of $(Mg_{1-x}Co_x)TiO_3$ system ceramics. *Bulletin of the Chinese Ceramics Society*, 2010, **29(2):** 284−287.

[6] Zhao L, Shen C Y, Qiu T. Studies on the $(1-x)Mg_{0.7}Zn_{0.3}TiO_3$-$xCa_{0.61}La_{0.26}TiO_3$ microwave dielectric ceramics system. *Journal of Inorganic Materials*, 2011, **26(2):** 219−224.

[7] Hakki B W, Coleman P D. A dielectric resonator method of measuring inductive capacities in the millimeter range. *Microwave Theory Technol*. 1960, **8(4):** 402−410.

[8] Kobayshi Y, Katoh M. Microwave measurement of dielectric properties of low-loss materials by the dielectric rod resonator method. *IEEE Trans. Microwave Theory Technol.*, 1985, **33(7):** 586−592.

[9] German R M. Liquid Phase Sintering. Plenum: New York, 1987: 127−151.

[10] Huang C L, Chung L P, Jui F H, *et al*. Microwave dielectric properties and mixture behavior of $(Mg_{0.95}Co_{0.05})TiO_3$-$Ca_{0.6}La_{0.8/3}TiO_3$ ceramic system. *J. Alloys Compd.*, 2008, **461(1):** 521−526.

[11] Huang C L, Pan C L, Hsu J F. Dielectric properties of $(1-x)(Mg_{0.95}Co_{0.05})TiO_3$-$xCaTiO_3$ ceramic system at microwave frequency. *Mater. Res. Bull.*, 2002, **37(15):** 2483−2490.

[12] Huang C L, Chen Y B, Lo C W. New dielectric material system of $La(Mg_{1/2}Ti_{1/2})O_3$-$CaTiO_3$ at microwave frequencies. *Jpn. J. Appl. Phys.*, 2005, **44:** 3147−3150.

$(1-x)(Mg_{0.9}Co_{0.1})TiO_3$-$x(Ca_{0.61}La_{0.26})TiO_3$ 陶瓷的微波介电性能

刘 昊, 沈春英, 卢正东, 丘 泰

(南京工业大学 材料科学与工程学院, 南京 210009)

摘 要: 研究了 $(1-x)(Mg_{0.9}Co_{0.1})TiO_3$-$x(Ca_{0.61}La_{0.26})TiO_3$(MCT-CLT) 体系陶瓷的微波介电性能. 目的是通过 $(Ca_{0.61}La_{0.26})TiO_3$ (CLT)协调$(Mg_{0.9}Co_{0.1})TiO_3$(MCT)陶瓷的谐振频率温度系数. 实验发现, 烧结温度和陶瓷组成对微波介电性能影响显著, 当烧结温度为 1300℃时, 可以获得良好的致密度, 当烧结温度超过 1300℃时, 陶瓷致密度和介电性能下降. 此外, 随着 CLT 含量的增加, 材料的介电常数增大, 品质因数减小. 当 CLT 含量为 13%, 烧结温度为 1300℃, 保温 2h, (MCCLT)陶瓷具有优良微波介电性能, ε_r =22.4, $Q\times f$ =35000 GHz, $\tau_f = -8.7\times10^{-6}$/℃, 从而达到实用要求.

关 键 词: $(1-x)(Mg_{0.9}Co_{0.1})TiO_3$-$x(Ca_{0.61}La_{0.26})TiO_3$ 陶瓷; 微波介质陶瓷; 介电常数; 品质因数; 谐振频率温度系数

中图分类号: TQ174 **文献标识码:** A