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Dielectric properties of CuO-doped $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics at microwave frequency

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Abstract

The microwave dielectric properties of $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics prepared by the conventional solid-state method were investigated for application in mobile communication. A 100 °C reduction of the sintering temperature was obtained by using CuO as a sintering aid. A dielectric constant of 20.0, a quality factor ($Q \times f$) of 50,100 GHz and a temperature coefficient of resonant frequency τ_f of −78.3 ppm/°C were obtained when $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics with 0.25 wt.% CuO were sintered at 1500 °C for 4 h.

Keywords: A. Sintering; C. Dielectric properties; Ceramic; X-ray diffraction

1. Introduction

There are many commercial applications, such as mobile radio and wireless communications that use microwave devices. Three dielectric properties of materials must be considered for microwave devices: a high dielectric constant, a high quality factor and a near-zero temperature coefficient of resonant frequency. High dielectric constant, high quality factor and near-zero temperature coefficient of resonant frequency are required for small size, low loss and high temperature stability, respectively [1,2].

The advantages of using complex perovskite ceramics $A(B'_{0.5}B''_{0.5})O_3$ (A = Me^{2+}, Me^{3+}; B′ = Me^{2+}, Me^{3+}; B″ = Me^{4+}, Me^{5+}, Me^{6+}) are reportedly associated with their excellent dielectric properties at microwave frequencies [3–6]. $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics that were sintered at 1550 °C for 4 h had a dielectric constant of 15.6 and a $Q \times f$ of 30,600 GHz [7,8]. A liquid phase flux such as CuO and B_2O_3 was added to reduce the sintering temperature of $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics. A dielectric constant of 19.7 and a $Q \times f$ of 43,300 GHz were obtained for $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics with 0.5 wt.% CuO additive that were sintered at 1550 °C for 4 h [7]. Additionally, a dielectric constant of 19.7 and a $Q \times f$ of 45,000 GHz were obtained for $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics with 0.5 wt.% B_2O_3 additive that were sintered at 1500 °C for 4 h [8]. $BaLa_4Ti_4O_{15}$ compounds had good microwave dielectric properties compared to $CaLa_4Ti_4O_{15}$ compounds [9]. Since the ionic radius of Ba^{2+} ions (0.161 nm) is larger than that of La^{3+} ions (0.136 nm), they predominantly occupy A1-sites. This phenomenon motivated this study of the effect of the substitution of La^{3+} ions by Ba^{2+} ions to form $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics. $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics were synthesized herein by the conventional mixed-oxide method. The effects of the amounts of CuO addition and sintering temperature on the microwave dielectric properties of $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics were studied. For further understanding of these microwave dielectric properties, they were analyzed by densification and microstructure observations.

2. Experimental procedures

The starting raw chemicals were high-purity La_2O_3 (99.99%), $BaCO_3$ (99.9%), MgO (98.0%) and SnO_2 (99.0%) powders. The composition prepared was $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ doped with 0, 0.25 and 0.50 wt.% CuO. The raw material was weighed out in stoichiometric proportions, ball-milled in alcohol for 12 h, dried and then calcined at 1200 °C for 4 h. The calcined powder was then crushed into a finer powder through a sieve with a 200 mesh.

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The calcined powder with different amounts of CuO addition was re-milled for 12 h. PVA solution was used as a binder. The obtained fine powder was then axially pressed at 2000 kg/cm^2 into pellets with a diameter of 11 mm and a thickness of 6 mm. The specimens thus obtained were sintered at 1400–1600 °C for 4 h in air. Both the heating rate and the cooling rate were set to 10 °C/min.

After sintering, scanning electron microscopy (SEM; JEOL JSM-6500F) and energy-dispersive spectroscopy (EDS) were employed to examine the microstructures of the specimens. The apparent densities of the specimens were measured by the Archimede's method. The microwave dielectric properties of the specimens were measured with the postresonator method [10]. The method used a specimen in the form of a cylinder of diameter *D* and length *L*. The specimens used for microwave dielectric property measurements had an aspect ratio *D*/*L* of about 1.6 [11]. The TE_{011} resonant mode was optimal for measuring the dielectric constant and the loss factor of the specimen. An Agilent N5230A network analyzer was used to identify the TE_{011} resonant frequency of the dielectric resonator. The technique for measuring τ_f was the same as that for measuring the dielectric constant. The test cavity was placed in a chamber and the temperature was varied from 25 to 75 °C.

3. Results and discussion

Fig. 1 shows the microstructure of CuO-doped $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics obtained with different amounts of CuO additions and at different sintering temperatures for 4 h. The $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics with 0.25 wt.% CuO

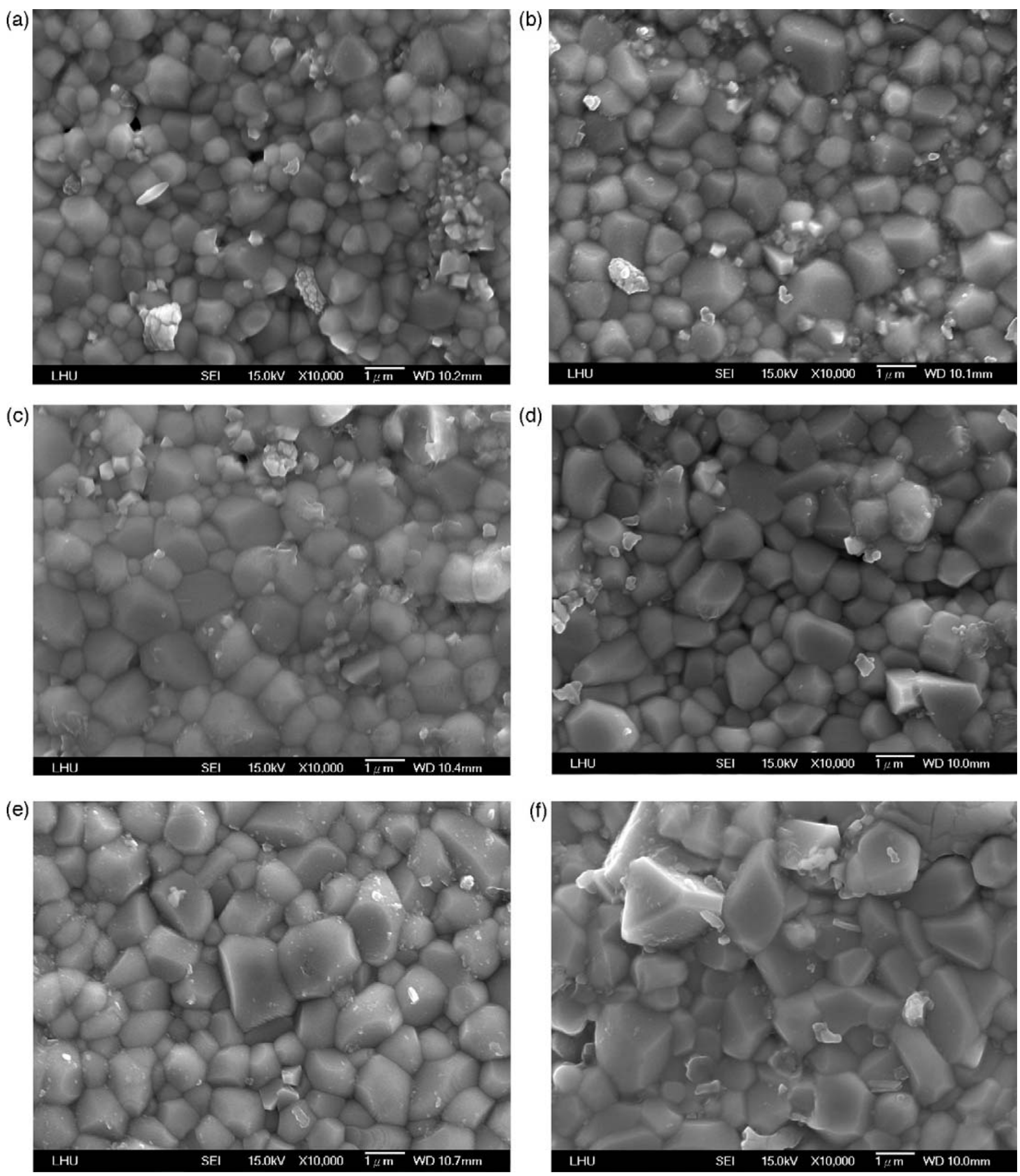

Fig. 1. The microstructures of the $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ (a) 0.25 wt.% CuO/1400 °C, (b) 0.25 wt.% CuO/1450 °C, (c) 0 wt.% CuO/1500 °C, (d) 0.25 wt.% CuO/1500 °C, (e) 0.50 wt.% CuO/1500 °C and (f) 0.25 wt.% CuO/1550 °C.

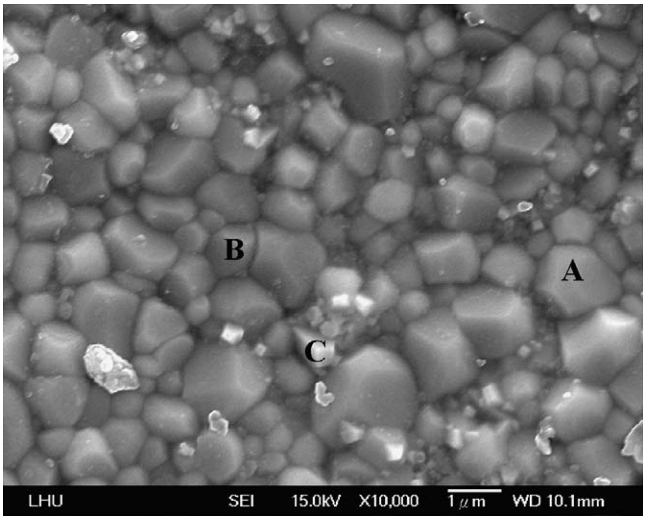

Fig. 2. Energy-disperse spectroscopy (EDS) analysis of grains of 0.25 wt.% CuO-doped $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics sintered at 1450 °C for 4 h.

addition were not dense, and grains did not grow after sintering at 1400 °C for 4 h. The pores of $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics almost disappeared upon sintering at 1500 °C for 4 h. The grain size did not increase significantly with the amounts of CuO addition, implying that the grain growth was not enhanced by increasing the amounts of CuO addition but mainly determined by the sintering temperature. An energy-dispersive spectroscopy was employed on the grains of 0.25 wt.% CuO-doped $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics sintered at 1450 °C for 4 h as shown in Fig. 2. As shown in Table 1, the grains of A and B were $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$, and the grain C was $La_2Sn_2O_7$.

Fig. 3 shows the apparent densities of $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics with different amounts of CuO addition that were sintered 1400–1600 °C for 4 h. Abnormal grain growth occurred at high sintering temperature, resulting in a decrease in apparent density. $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics with 0.25 wt.% CuO addition that were sintered at 1500 °C for 4 h had an apparent density of 6.61 g/cm^3. Fig. 4 shows the dielectric constant of $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics with different amounts of CuO addition that were sintered 1400–1600 °C for 4 h. The relationships between the dielectric constant and the sintering temperature were similar to that between the apparent density and the sintering temperature. The decrease in dielectric constant was associated with the low apparent densities of the ceramics. A higher apparent density is associated with lower porosity and, therefore, a higher dielectric constant. The dielectric constant of $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics with 0.25 wt.% CuO addition sintered at 1450 °C was almost the same as that of pure $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics sintered at 1550 °C. Adding CuO to the $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics enables a sintering temperature reduction of about 100 °C. Moreover, the dielectric constant of $La(Mg_{0.5}Sn_{0.5})O_3$ and $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics sintered at 1500 °C for 4 h were 15.6 and 19.5, respectively [8]. The dielectric constant of $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics can be improved by partially substituting La^{3+} ions by Ba^{2+} ions. This fact may be explained by the ionic polarization, as suggested by Tohdo et al. [9]. The dielectric constants depend on the ionic polarization. As the ionic polarization increases, the dielectric constant increases. The polarization of the Ba^{2+} ion and La^{3+} ion are 6.4 and 4.82 Å^3, respectively [12], so the dielectric constant of $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics is larger than that of $La(Mg_{0.5}Sn_{0.5})O_3$ ceramics.

Fig. 5 shows the $Q \times f$ of $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics with different amounts of CuO addition sintered at different temperatures for 4 h. The microwave dielectric loss is affected by many factors, and consists of intrinsic and extrinsic losses. Extrinsic loss is related to the density, porosity, second phases, impurities, oxygen vacancies, grain size and lattice

Table 1
EDS data of grains of 0.25 wt.% CuO-doped $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics sintered at 1450 °C for 4 h.

Atomic element	La (%)	Ba (%)	Mg (%)	Sn (%)	O (%)
A	18.46	0.79	9.19	8.76	62.80
B	16.41	0.63	8.61	8.26	66.09
C	11.49	0	0	9.70	78.81

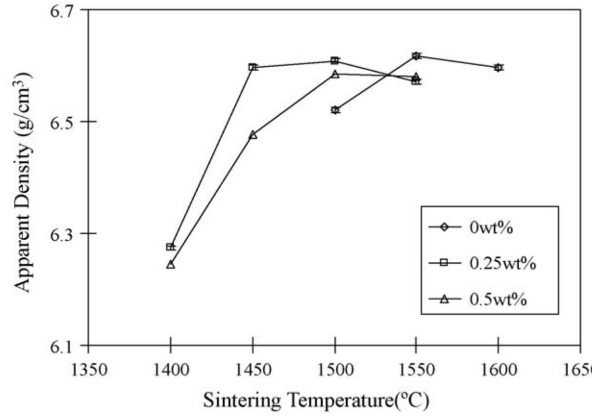

Fig. 3. The apparent densities of $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics with different amounts of CuO addition sintered in the range of 1400–1600 °C for 4 h.

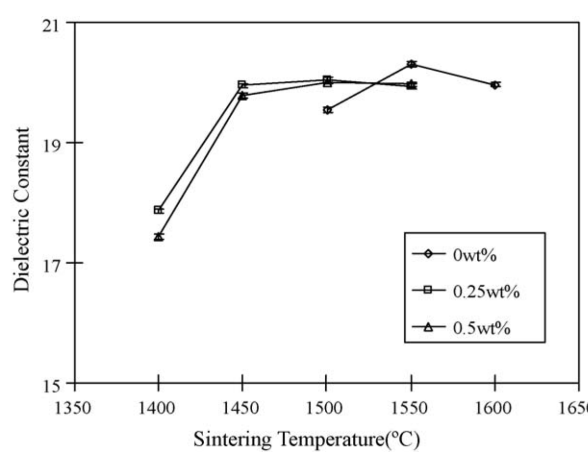

Fig. 4. The dielectric constant of $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics with different amounts of CuO addition sintered in the range of 1400–1600 °C for 4 h.

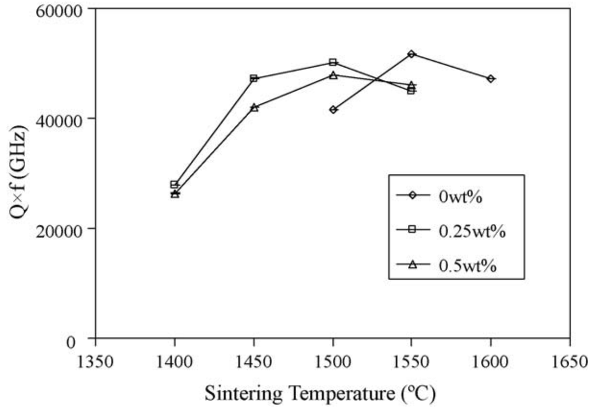

Fig. 5. The quality factor ($Q \times f$) of $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics with different amounts of CuO addition sintered in the range of 1400–1600 °C for 4 h.

defects [13,14]. The $Q \times f$ of $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics was consistent with the variation of the apparent density. The $Q \times f$ of $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics with 0.25 wt.% CuO additions sintered at 1450 °C was almost the same as that of pure $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics sintered at 1550 °C. Therefore CuO addition could reduce the sintering temperature of $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics. Furthermore, the $Q \times f$ of $La(Mg_{0.5}Sn_{0.5})O_3$ and $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics sintered at 1500 °C for 4 h were 30,600 and 41,500 GHz, respectively [7,8]. An increase in $Q \times f$ was successfully obtained by partially substituting La^{3+} ions by Ba^{2+} ions. Fig. 6 presents the τ_f of $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics with different amounts of CuO addition sintered at different temperatures for 4 h. Generally, τ_f is related to the composition, amount of additive and second phase [7,8]. Since the composition of $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics did not vary with sintering temperature with a fixed amount of CuO addition, no significant variation in τ_f with sintering temperature with a fixed amount of CuO addition was observed. A τ_f of −78.3 ppm/°C was measured for $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics with 0.25 wt.% CuO that were sintered at 1500 °C for 4 h.

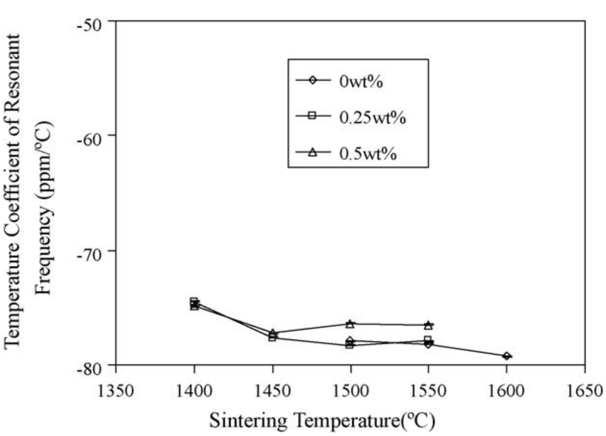

Fig. 6. The τ_f values of $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics with different amounts of CuO addition sintered in the range of 1400–1600 °C for 4 h.

4. Conclusions

The effects of CuO addition and sintering temperature on the microwave dielectric properties of $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics were investigated. Compared with earlier reports, improvement on the microwave dielectric properties was achieved by partially substituting La^{3+} ions by Ba^{2+} ions. An apparent density of 6.61 g/cm^3, a dielectric constant of 20.0, a $Q \times f$ of 50,100 GHz, and a temperature coefficient of resonant frequency (τ_f) of −78.3 ppm/°C were obtained for $La_{2.98/3}Ba_{0.01}(Mg_{0.5}Sn_{0.5})O_3$ ceramics with 0.25 wt.% CuO addition sintered at 1500 °C for 4 h. A sintering temperature reduction of about 100 °C was obtained by using CuO as a sintering aid.

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