New material properties and microstructure of $xLa(Mg_{1/2}Ti_{1/2})O_3-(1-x)Ca_{0.6}Sm_{0.8}/3TiO_3$ ceramics at microwave frequency

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The microstructure and microwave dielectric properties of $xLa(Mg_{1/2}Ti_{1/2})O_3-(1-x)Ca_{0.6}Sm_{0.8}/3TiO_3$ ceramics system with $B_2O_3$ additions (1 wt %) prepared by the conventional solid state route were investigated. Doping with $B_2O_3$ (1 wt %) can effectively promote the densification and the dielectric properties of $xLa(Mg_{1/2}Ti_{1/2})O_3-(1-x)Ca_{0.6}Sm_{0.8}/3TiO_3$ ceramics. $0.5La(Mg_{1/2}Ti_{1/2})O_3-0.5Ca_{0.6}Sm_{0.8}/3TiO_3$ ceramics with 1 wt % $B_2O_3$ addition possesses a dielectric constant ($\varepsilon_r$) of 48, a $Qxf$ value of 35.000 GHz (at 8 GHz) and a temperature coefficients of resonant frequency ($\tau_f$) of 9.1 ppm/°C sintering at 1450°C.

1. Introduction

The advances in microwave communication systems such as cellular radio and satellite communications demand new microwave dielectric ceramics. Using two or more compounds with negative and positive temperature coefficients to form a solid solution or mixed phases is the most promising method of obtaining a zero temperature coefficient of the resonant frequency, in our previous reports. Many kinds of dielectric ceramics have been developed for microwave applications. $La(Mg_{1/2}Ti_{1/2})O_3$ ($\varepsilon_r$ of 27, a Qxf value of 114,000 GHz, and a negative $\tau_f$ of −81 ppm/°C) is a promising microwave dielectric material with a dielectric constant of 27 and low dielectric loss, but its large negative $\tau_f$ requires modification for applications as a dielectric resonator. $Ca_{0.6}Sm_{0.8}/3TiO_3$ ($\varepsilon_r$ of around 101, a Qxf value higher than 14090 GHz and a $\tau_f$ value of +220 ppm/°C) have a positive $\tau_f$, so mixing $La(Mg_{1/2}Ti_{1/2})O_3$ with $Ca_{0.6}Sm_{0.8}/3TiO_3$ is expected to adjust the $\tau_f$ of $La(Mg_{1/2}Ti_{1/2})O_3$ near zero. To combine it with a compound having a positive $\tau_f$ should be the most convenient and promising way to achieve a zero $\tau_f$.

2. Experimental procedure

The $xLa(Mg_{8/3}Ti_{1/2})O_3-(1-x)Ca_{0.6}Sm_{0.8}/3TiO_3$ powders were prepared by the solid state reaction method by mixing individual high-purity oxide $La_2O_3$, $MgO$, $B_2O_3$, $Sm_2O_3$, $CaCO_3$ and $TiO_2$. The sample X-ray diffraction(XRD, Rigaku D/Max) spectra were collected using Cu Kα radiation (at 30 KV and 20 mA) and a graphite monochromator in the 2θ range. The microstructural observations and analysis of sintered surface were performed by a scanning electron microscopy (SEM, Philips XL-40FEG). Microwave dielectric properties such as dielectric constant and unloaded Q were measured by the post-resonant method as suggested by Hakki and Coleman. The temperature coefficient of resonant frequency was measured in the temperature range of 20–60°C. A system combined with a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement.

3. Results and discussion

In Fig. 1 shown the spectra for all the compositions were indexed according to an orthorhombic unit cell with space group Pbnm (No. 62, Pm nan standard setting for Pnma). Combinations of odd (O) and even (E) reflections indicate a distorted perovskite structure (individual peaks are identified by numbers in brackets). On the basis of Glazer’s notation, the (OEO, EEO, and EOE) reflections are assigned to an in-phase tilting of the oxygen (OOE, OEO, and EOO) reflections are assigned to an in-phase tilting of the oxygen.
octahedra surrounding the B-site cations. The (OOO) reflections are assigned to an antiphase tilting of the oxygen octahedra. The presence of reflections with (EOE, EOE, and OOE) combinations is associated with antiparallel displacement of A-site cations. The tilting mechanism defined by the present combination of distortions is consistent with an orthorhombic a–a–c+ tilt system. As a result the La(Mg1/2Ti1/2)O3 structure adopts a monoclinic P21/n space group which has similar systematic absences as in Pbnm except that the 0kl: k = 2n+1 condition is lifted. A disordered B-site sublattice structure is attained at x = 0.3. This is because the increase in the Ca0.6Sm0.8TiO3 content in the solid solution destroys the stoichiometric 1:1 ratio of Mg:Ti ions, manifested in (1-x)Ca0.6Sm0.8/3TiO3. The lattice parameters and unit-cell volumes of La(Mg1/2Ti1/2)O3–Ca0.6Sm0.8/3TiO3 ceramics are presented in Table 1 and Table 2.

Table 1. Lattice parameter, tolerance factor data for sintered xLa(Mg1/2Ti1/2)O3–(1-x)Ca0.6Sm0.8/3TiO3

| xLa(Mg1/2Ti1/2)O3–(1-x)Ca0.6Sm0.8/3TiO3 | a(Å) | b(Å) | c(Å) | Beta | Tolerance factor |
|----------------------------------------|------|------|------|------|-----------------|
| 0.9LaMg0.1CST–0.9CST                  | 5.523| 5.545| 7.8217| 89.96| 0.94113         |
| 0.8LaMg0.2CST–0.8CST                  | 5.517| 5.5286| 7.8009| 90| 0.935961        |
| 0.7LaMg0.3CST–0.7CST                  | 5.5035| 5.5121| 7.7800| 90| 0.930778        |
| 0.6LaMg0.4CST–0.6CST                  | 5.4891| 5.4956| 7.7592| 90| 0.925566        |
| 0.5LaMg0.5CST–0.5CST                  | 5.4747| 5.4791| 7.7383| 90| 0.920325        |
| 0.4LaMg0.6CST–0.4CST                  | 5.4603| 5.4626| 7.7175| 90| 0.915555        |

Table 2. Structural data for sintered xLa(Mg1/2Ti1/2)O3–(1-x)Ca0.6Sm0.8/3TiO3

| xLa(Mg1/2Ti1/2)O3–(1-x)Ca0.6Sm0.8/3TiO3 | Space group | Structure          |
|----------------------------------------|-------------|--------------------|
| x = 0.4                                 | Pbnm        | orthorhombic       |
| x = 0.5                                 | Pbnm        | orthorhombic       |
| x = 0.6                                 | Pbnm        | orthorhombic       |
| x = 0.7                                 | Pbnm        | orthorhombic       |
| x = 0.8                                 | Pbnm        | orthorhombic       |
| x = 0.9                                 | Pbnm        | orthorhombic       |
| x = 1                                   | P21/n       | monoclinic         |

Fig. 2. SEM photographs of 0.5La(Mg1/2Ti1/2)O3–0.5Ca0.6Sm0.8/3TiO3 ceramics (a) 1400, (b) 1425, (c) 1450 (d) 1475 and (e) 1500°C with 1 wt% B2O3 additions for 5 h.

The SEM photographs of 0.5La(Mg1/2Ti1/2)O3–0.5Ca0.6Sm0.8/3TiO3 ceramics at microwave frequency 1400 to 1500°C with 1 wt% B2O3 additive, which might degrade the microwave dielectric properties of the ceramics. The driving force in these systems is the surface tension which leads to a reduction of the total surface area of the grains.

The densities of 3.81–5.46 (g/cm³) were obtained for B2O3-doped xLa(Mg1/2Ti1/2)O3–(1-x)Ca0.6Sm0.8/3TiO3 ceramics at sintering temperatures from 1400 to 1500°C as shown in Fig. 3. The density increased with increasing sintering temperature due to enlarged grain size as observed as shown in Fig. 2, and was also affected by the composition and decreased with increasing x value. It suggested sintering at higher temperatures (above 1475°C owing to the over-sintering as shown in Fig. 2) would degrade the bulk density of the ceramics.
As the x value increased from 0.4 to 0.8, the dielectric constants decreased from 53 to 34.2 as could be seen in Fig. 4(a). The dielectric constants slightly decreased with increasing sintering temperature. The decrease of ¾ value with increasing sintering temperature could be explained owing to the over-sintering of xLa(Mg1/2Ti1/2)O3-(1-x)Ca0.6Sm0.8/3TiO3. With 1 wt % B2O3 addition, a ¾ value of 48 was obtained for 0.5La(Mg1/2Ti1/2)O3-0.5Ca0.6Sm0.8/3TiO3 ceramics sintered at 1450°C. The value increase with the increase of La(Mg1/2Ti1/2)O3 content and sintering temperature as shown in Fig. 4(b). It was expected since that the quality factor of La(Mg1/2Ti1/2)O3 is much higher than that of Ca0.6Sm0.8/3TiO3 and the bulk density increased with increasing sintering temperature due to the ceramics being denser. Many factors could affect the microwave dielectric loss of dielectric resonators such as the lattice vibration modes, the pores and the secondary phases. Generally, a larger grain size, i.e., a smaller grain boundary, indicates a reduction in lattice imperfection and the dielectric loss was thus reduced. It seems that the dielectric loss of xLa(Mg1/2Ti1/2)O3-(1-x)Ca0.6Sm0.8/3TiO3 ceramics system was dominated by the bulk density and the grain size. The highest Qxf value of 51,900 (GHz) for x = 0.8 is achieved at the sintering temperature 1475°C.

The temperature coefficients of the resonant frequency (f) of B2O3-doped xLa(Mg1/2Ti1/2)O3-(1-x)Ca0.6Sm0.8/3TiO3 ceramics sintered at various temperatures are shown in Fig. 5. The temperature coefficient of resonant frequency is well known to be related to the composition, additives, and secondary phases of a material. Higher Ca0.6Sm0.8/3TiO3 content made the f value more positive. The f value changed from ~61.1 to 41 ppm/°C when the amount of Ca0.6Sm0.8/3TiO3 addition was increased from 0.4 to 0.8 at a sintering temperature of 1450°C. In general, the temperature coefficient of the resonant frequency was found to be related to the composition and the phases in the ceramics.

4. Conclusions

xLa(Mg1/2Ti1/2)O3-(1-x)Ca0.6Sm0.8/3TiO3 ceramics exhibited perovskite structure. With 1 wt % B2O3 addition, a dielectric constant of 48, a Qxf value of 35000 (GHz) and a f value of 9 ppm/°C were obtained for 0.5La(Mg1/2Ti1/2)O3-0.5Ca0.6Sm0.8/3TiO3 ceramics at 1450°C for 4h. Therefore, the B2O3-doped 0.5La(Mg1/2Ti1/2)O3-0.5Ca0.6Sm0.8/3TiO3 ceramic is suitable for applications in microwave dielectric resonators and microwave device because of its excellent microwave dielectric properties.

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References

1) C.-L. Huang, Y.-B. Chen and C.-F. Tasi, J. Alloys Compd., 460, 675–679 (2008).
2) C.-L. Huang, Y.-B. Chen and C.-F. Tasi, J. Alloys Compd., 454, 454–459 (2008).
3) C.-L. Huang, C.-F. Tasi, Y.-B. Chen and Y.-C. Cheng, J. Alloys Compd., 453, 337–340 (2008).
4) N. Santha, I. N. Jawahar, P. Mohanan and M. T. Sebastian, Mater. Lett., 54, 318 (2002).
5) W. S. Kim, K. H. Yoon and E. S. Kim, J. Am. Ceram. Soc., 83, 2327 (2000).
6) V. M. Ferrei, F. Azough, R. Freer and L. Baptista, J. Mater. Res., 12, 3293 (1997).
7) W. S. Kim, K. H. Yoon and E. S. Kim, J. Am. Ceram. Soc., 83, 2327 (2000).
8) M. Avdeed, M. P. Seabra and V. M. Ferreira, Mater. Res. Bull., 37, 1459–1468 (2002).
9) W. S. Kim, E. S. Kim and K. H. Yoon, J. Am. Ceram. Soc., 82, 2111–2115 (1999).
10) K. H. Yoon, W. S. Kim and E. S. Kim, Mater. Sci. Eng., B, 99, 112–115 (2003).
11) K. H. Yoon, W. S. Kim and E. S. Kim, Mater. Sci. Eng., B, 99, 112–115 (2003).
12) M. A. Akbas and P. K. Davies, J. Am. Ceram. Soc., 81, 1061–1064 (1998).
13) S.-Y. Cho, H.-J. Youn, H.-J. Lee and K. S. Hong, J. Am. Ceram. Soc., 84, 753–758 (2001).
14) C.-L. Huang, Y.-B. Chen and C.W. Lo, Jpn. J. Appl. Phys., 44, 3147–3150 (2005).
15) B. W. Hakki and P. D. Coleman, IEEE Trans. Microw. Theory Tech., 8, 402–410 (1960).
16) R. D. Shannon, J. Appl. Phys., 73, 348–366 (1993).