Journal of Alloys and Compounds 509 (2011) L150–L152

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Letter

High-Q microwave dielectrics in the $(Mg_{1-x}Zn_x)Al_2O_4$ ($x = 0$–0.1) system

Cheng-Liang Huang[a,*], Yu-Hua Chien[a], Chen-Yi Tai[a], Chi-Yuen Huang[b]

[a] Department of Electrical Engineering, National Cheng Kung University, Tainan 70101, Taiwan
[b] Department of Resource Engineering, National Cheng Kung University, Tainan, Taiwan

ARTICLE INFO

Article history:
Received 8 December 2010
Received in revised form
28 December 2010
Accepted 29 December 2010
Available online 4 January 2011

Keywords:
Crystal growth
Dielectric response

ABSTRACT

The microwave dielectric properties and the microstructures of $(Mg_{1-x}Zn_x)Al_2O_4$ ($x = 0$–0.1) ceramic system prepared by the conventional solid-state route were investigated. The forming of spinel-structured $(Mg_{1-x}Zn_x)Al_2O_4$ ($x = 0$–0.1) solid solutions was confirmed by the XRD patterns and the measured lattice parameters, which linearly varied from $a = b = c = 8.0815$ Å for $MgAl_2O_4$ to $a = b = c = 8.0828$ Å for $(Mg_{0.9}Zn_{0.1})Al_2O_4$. By increasing x, the $Q \times f$ of $(Mg_{1-x}Zn_x)Al_2O_4$ can be tremendously boosted from 82,000 GHz at $x = 0$ to a maximum of 156,000 GHz at $x = 0.05$. The Zn substitution was effective in reducing the dielectric loss without detrimental effects on the ε_r and τ_f values of the ceramics.

1. Introduction

Ceramic materials utilized for microwave components such as dielectric resonators and filters must satisfy three main criteria; a high dielectric constant for miniaturization, a low dielectric loss ($Q > 5000$, where $Q = 1/\tan\delta$) for better selectivity and a near-zero temperature coefficient of resonant frequency (τ_f) for stable frequency stability [1]. However, as the carrier frequency of communication system is being extended to ISM (industrial, scientific and medical) bands or even to millimeter wave range, materials with high dielectric constant tend to become a less of interest [2]. High quality factor instead, would play a more prominent role and the search for low-loss dielectric ceramics has become a primary issue in the last few years [3–12].

Being one of the spinel-type ceramics with general formula of AB_2O_4, $MgAl_2O_4$ ($\varepsilon_r = 8.8$, $Q \times f \sim 68{,}900$ GHz, $\tau_f = -75$ ppm/°C) was first proposed for microwave applications by Surendran et al. [9]. A significant improvement in the $Q \times f$ could be achieved by combining it with $MgZn_2O_4$ or $MgNi_2O_4$ to form a $(Mg_{1-x}Zn_x)Al_2O_4$ or $(Mg_{1-x}Ni_x)Al_2O_4$ solid solution (with an increment of 0.2–0.25 in x) and still retained a similar ε_r and τ_f [10–12]. The $Q \times f$ value was a function of x and could be promoted up to 106,000 and 130,000 GHz for $ZnAl_2O_4$ and $(Mg_{0.75}Ni_{0.25})Al_2O_4$, respectively [5,6]. Several reports pointed out that small amount substitution could effectively promote the $Q \times f$ value of specimen and the obtained $Q \times f$ is usually higher than that of both end members [13–15]. For instance, microwave dielectrics $MgTiO_3$ and Mg_2TiO_4 showed a great promotion in the $Q \times f$ by replacing 0.05 mol% Mg^{2+} with other ions [13–15]. Therefore, it should be of interest to characterize the dielectric response of the $(Mg_{1-x}Zn_x)Al_2O_4$ ($x = 0$–0.1) solid-solution system at microwave frequency.

In this paper, $(Mg_{1-x}Zn_x)Al_2O_4$ ($x = 0$–0.1) solid solutions with a smaller increment in x were synthesized by solid-state method and its microwave dielectric properties and microstructures were also investigated. Consequently, the compound under study not only showed a tremendous lowering in the dielectric loss but also retained comparably decent values of ε_r and τ_f.

2. Experimental procedure

$(Mg_{1-x}Zn_x)Al_2O_4$ ceramics where $x = 0$–0.1 were synthesized by conventional solid-state methods from high purity grade MgO, Al_2O_3 and ZnO powders (>99.9%). Because MgO is hygroscopic, it was initially fired at 650 °C for 5 h to avoid moisture contain. The weighed raw materials were ball-milled with alumina balls in ethanol for 12 h at a speed of 200 rpm. After milling, the slurry was dried in microwave oven, and then calcined at 1200 °C for 2 h. Prepared powders were dried, ball-milled for 24 h with 5 wt% of a 10% solution of PVA solution as a binder. The fine powders were forced through a 200 mesh sieve, and pressed into pellets with 11 mm in diameter and 5 mm in thickness under a pressure of 300 MPa. The pellets were sintered at 1480–1600 °C in air for 3 h at a heating rate of 10 °C/min.

The crystalline phases of the sintered ceramics were identified by XRD using Cu Kα ($\lambda = 0.15406$ nm) radiation with a Siemens D5000 diffractometer operated at 40 kV and 40 mA. The microstructural observations and analysis of the sintered surface were performed by scanning electron microscopy and an energy-dispersive X-ray spectrometer. The apparent densities of the sintered pellets were measured by microwave the Archimedes method. The dielectric constant (ε_r) and the quality factor values (Q) at frequencies were measured using the Hakki–Coleman dielectric resonator method [16,17]. A system combining a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement. For temperature coefficient of resonant frequency (τ_f), the technique implemented is identical to that of quality factor measurement. The τ_f at microwave frequencies was measured in the temperature range from 25 to 80 °C.

* Corresponding author. Tel.: +886 6 2757575x62390; fax: +886 6 2345482.
E-mail address: huangcl@mail.ncku.edu.tw (C.-L. Huang).

0925-8388/$ – see front matter © 2011 Published by Elsevier B.V.
doi:10.1016/j.jallcom.2010.12.202

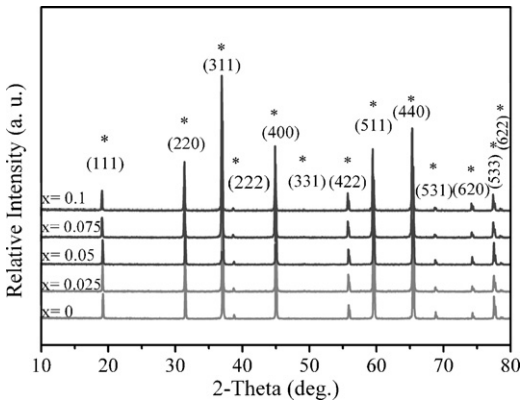

Fig. 1. The X-ray diffraction (XRD) patterns of the $(Mg_{1-x}Zn_x)Al_2O_4$ (x = 0–0.1) ceramics sintered at 1570 °C for 3 h.

3. Results and discussion

Fig. 1 illustrates the room temperature X-ray diffraction (XRD) patterns recorded from the $(Mg_{1-x}Zn_x)Al_2O_4$ (x = 0–0.1) ceramics sintered at 1570 °C for 3 h. All compositions show a single spinel phase without the evidence of any additional second phase over the entire compositional range indicating the forming of solid solutions. The diffraction peak slightly shifts to a lower angle as x increases due to the incorporation of larger Zn^{2+} (0.6 Å, CN = 4) in place of Mg^{2+} (0.57 Å, CN = 4) [18]. The theoretical density of the $(Mg_{1-x}Zn_x)Al_2O_4$ (x = 0–0.1) ceramics calculated from XRD patterns increases from 3.58 g/cm^3 at x = 0 to 3.68 g/cm^3 at x = 0.1 corresponding to a lattice parameter of 8.0815(5) Å and 8.0828(4) Å (Table 1), respectively. It is also found that the strength of (1 1 1) reflections decreases from 43.1% to 13.8% (compared to that of (3 1 1) reflections) as x value increases from 0 to 0.1 because of the partial replacement of Mg^{2+} by Zn^{2+}.

Fig. 2 shows the fracture section scanning electron microscopy (SEM) micrographs of specimens using $(Mg_{0.95}Zn_{0.05})Al_2O_4$ ceram-

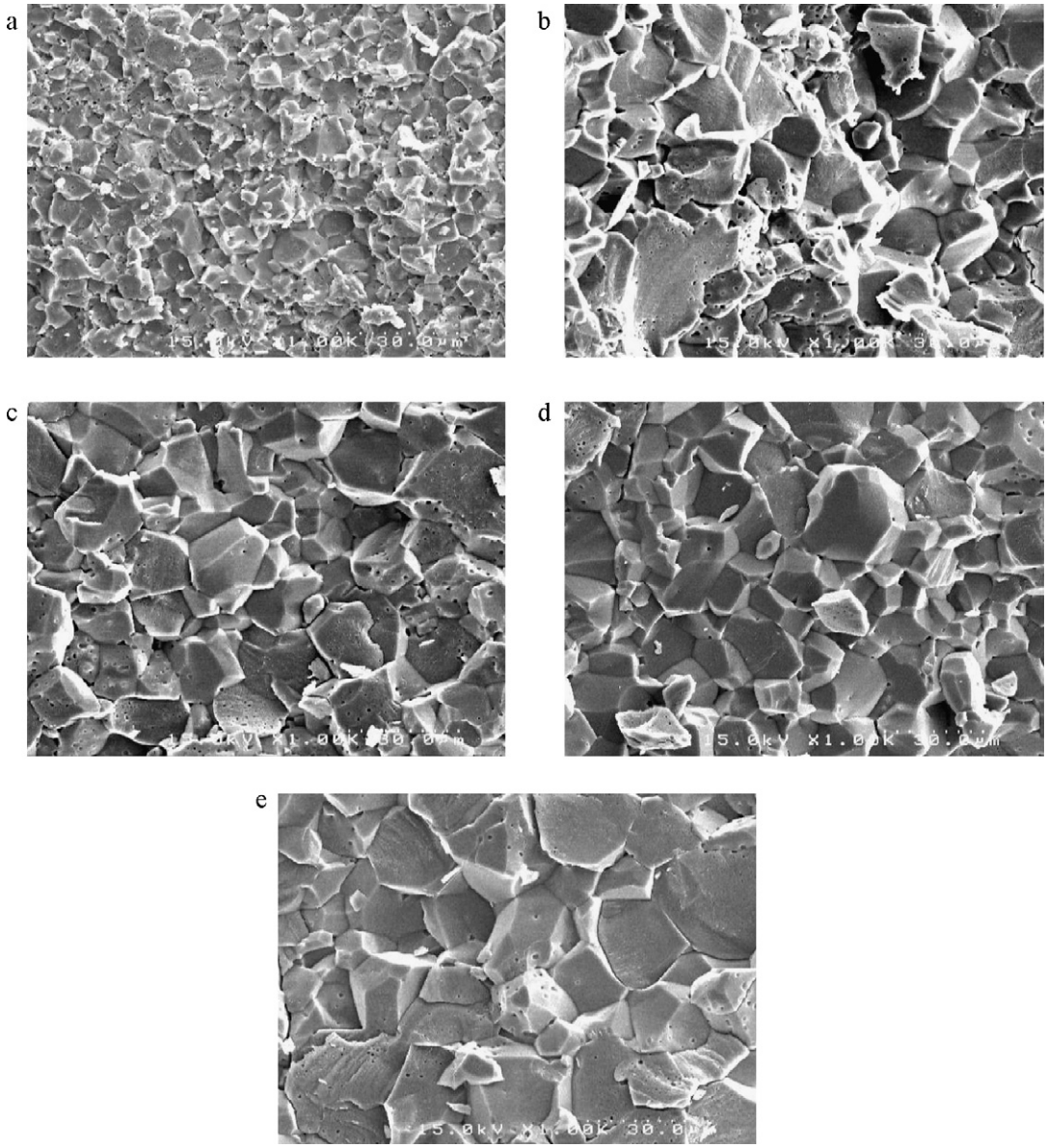

Fig. 2. The scanning electron microscopy (SEM) micrographs of $(Mg_{1-x}Zn_x)Al_2O_4$ (x = 0.05) cross section sintered at (a) 1480, (b) 1510, (c) 1540, (d) 1570, and (e) 1600 °C for 3 h.

Table 1
Lattice parameter, cell volume and theoretical density of $(Mg_{1-x}Zn_x)Al_2O_4$ (x = 0–0.1) ceramic system.

x value	Lattice parameter (Å)	Cell volume (Å^3)	Theory density (g/cm^3)
0	8.0815(5)	527.71	3.58
0.025	8.0792(3)	527.36	3.61
0.05	8.0819(4)	527.89	3.63
0.075	8.0811(3)	527.93	3.66
0.1	8.0828(4)	528.06	3.68

ics sintered at different temperatures for 3 h. The result indicated that the grain size of the specimen was small, approximately 3–6 μm, for specimen sintered at 1480 °C. The increase of sintering temperature helped to promote the grain growth and a relative increase in the grain size was achieved for specimen sintered at 1540 °C and the grains are of relatively large size up to 30 μm at 1600 °C. In addition, the EDS chemical analysis results indicated the Zn content decreased from 3.8 at% at 1480 °C to 2.14 at% at 1600 °C due to the volatilization of Zn at high temperatures [4,19].

The relative density and ε_r values of $(Mg_{1-x}Zn_x)Al_2O_4$ (x = 0–0.1) solid solutions sintered at different temperatures for 3 h are demonstrated in Fig. 3. The relative density of $(Mg_{1-x}Zn_x)Al_2O_4$ ceramics is already higher than 93% at 1480 °C. The relative density increases with increasing sintering temperature to a maximum at 1570 °C and 1540 °C for specimens with x = 0.05 and 0.1, respectively, and thereafter it decreases. It indicates the Zn substitution would lower the sintering temperature of the specimen. The increase of density was a result from grain growth; whereas oversintering or Zn volatilization would lead to a decrease of density of the specimen. Moreover, the variation of dielectric constant was consistent with that of relative density. For specimen using $(Mg_{0.95}Zn_{0.05})Al_2O_4$ sintered at 1570 °C, a maximum ε_r value of 8.11 can be obtained. In comparison with that of pure $MgAl_2O_4$, the effect of Zn substitution for Mg on the ε_r value of specimen is insignificant.

Fig. 4 shows the $Q \times f$ values and the temperature coefficient of resonant frequency (τ_f) of the $(Mg_{1-x}Zn_x)Al_2O_4$ (x = 0–0.1) solid solutions sintered at different temperatures for 3 h. The variation of $Q \times f$ follows the same trend with that of relative density suggesting the $Q \times f$ of the specimen was mainly related to its corresponding relative density. The $(Mg_{0.95}Zn_{0.05})Al_2O_4$ possesses a $Q \times f$ value of 156,000 GHz, which is not only much higher than that of pure $MgAl_2O_4$ ($Q \times f \sim$ 68,900 GHz) or $ZnAl_2O_4$ ($Q \times f \sim$ 106,000 GHz), it

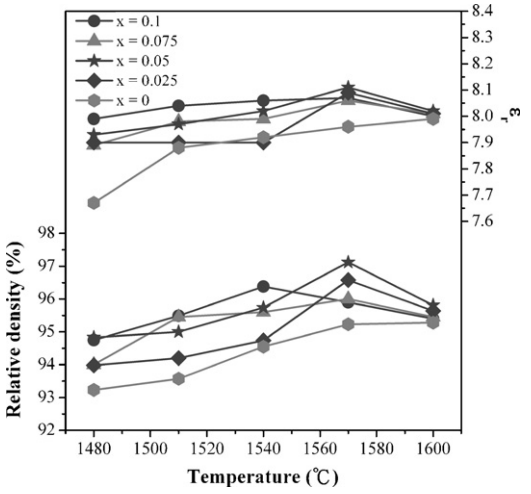

Fig. 3. The relative density and ε_r values of $(Mg_{1-x}Zn_x)Al_2O_4$ (x = 0–0.1) solid solutions sintered at different temperatures for 3 h.

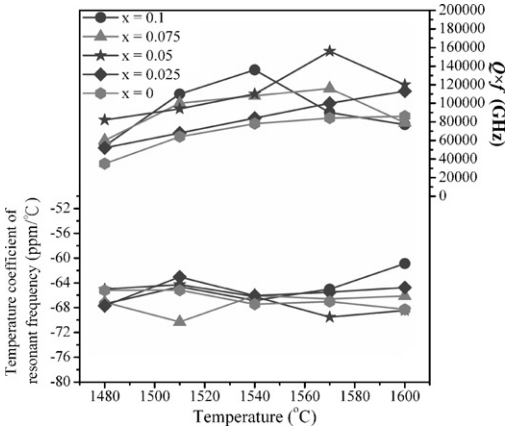

Fig. 4. The $Q \times f$ values and the temperature coefficient of resonant frequency (τ_f) of the $(Mg_{1-x}Zn_x)Al_2O_4$ (x = 0–0.1) solid solutions sintered at different temperatures for 3 h.

is also higher than those reported for $(Mg_{1-x}Zn_x)Al_2O_4$ solid solutions such as $(Mg_{0.5}Zn_{0.5})Al_2O_4$ ($Q \times f \sim$ 95,000 GHz) [3] implying the small amount of Zn substitution for Mg has significant effects on the $Q \times f$ value. Moreover, it indicates the maximum $Q \times f$ can be obtained from entire $(Mg_{1-x}Zn_x)Al_2O_4$ solid solutions appears at x = 0.05. The τ_f value is well-known to be related by the composition and the second phase of the material. Since the XRD shows there is no second phase, no significant different was noted in the τ_f value and it varied between −64 and −70 ppm/°C.

4. Conclusions

The microstructure, densification and microwave dielectric properties of $(Mg_{1-x}Zn_x)Al_2O_4$ (x = 0–0.1) ceramics were investigated. The $Q \times f$ can be tremendously boosted to a value of 165,000 GHz corresponding to the highest relative density for specimen using $(Mg_{0.95}Zn_{0.05})Al_2O_4$ and retains a comparably decent value of ε_r and τ_f compared to that of pure $MgAl_2O_4$ or $ZnAl_2O_4$.

Acknowledgement

This work was financially supported by the National Science Council in Taiwan under grant NSC 97-2221-E-006-013-MY3.

References

[1] C.L. Huang, J.J. Wang, Y.P. Chang, J. Am. Ceram. Soc. 90 (2007) 858–862.
[2] C.L. Huang, J.Y. Chen, J. Am. Ceram. Soc. 93 (2010) 1248–1251.
[3] C.F. Tseng, H.H. Tung, C.K. Hsu, C.C. Yu, C.H. Hsu, J. Alloys Compd. 502 (2010) 136–138.
[4] C.F. Tseng, C.L. Huang, W.R. Yang, C.H. Hsu, J. Am. Ceram. Soc. 89 (2006) 1465–1470.
[5] W. Lei, W.Z. Lu, D. Liu, J.H. Zhu, J. Am. Ceram. Soc. 92 (2009) 105–109.
[6] M.E. Song, J.S. Kim, M.R. Joung, S. Nahm, J. Am. Ceram. Soc. 91 (2008) 2747–2750.
[7] Y.C. Chen, Y.H. Chang, J. Alloys Compd. 477 (2009) 450–453.
[8] C.L. Huang, J.J. Wang, C.Y. Huang, J. Am. Ceram. Soc. 90 (2007) 1487–1493.
[9] K.P. Surendran, P.V. Bijumon, P. Mohanan, M.T. Sebastian, Appl. Phys. A 81 (2005) 823–826.
[10] K.P. Surendran, N. Santha, P. Mohanan, M.T. Sebastian, Eur. Phys. J. B 41 (2004) 301–306.
[11] C.W. Zheng, S.Y. Wu, X.M. Chen, K.X. Song, J. Am. Ceram. Soc. 90 (2007) 86–1483.
[12] C.L. Huang, C.Y. Tai, C.Y. Huang, Y.H. Chien, J. Am. Ceram. Soc. 93 (2010) 1999–2003.
[13] H.J. Lee, I.T. Kim, K.S. Hong, Jpn. J. Appl. Phys. 36 Part 2 (1997) L1318–L1320.
[14] C.L. Huang, J.Y. Chen, J. Am. Ceram. Soc. 92 (2009) 379–383.
[15] C.L. Huang, S.S. Liu, J. Am. Ceram. Soc. 91 (2008) 3428–3430.
[16] B.W. Hakki, P.D. Coleman, IEEE Trans. Microwave Theory Tech. 8 (1960) 402–410.
[17] W.E. Courtney, IEEE Trans. Microwave Theory Tech. 18 (1970) 476–485.
[18] R.D. Shannon, Acta Crystallogr. Sect. A: Found. Crystallogr. 32 (1976) 751.
[19] S. Solomon, J.T. Joseph, H.P. Kumar, J.K. Thomas, Mater. Lett. 60 (2006) 2814–2818.