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Sintering behavior and microwave dielectric properties of $(Mg_{0.95}Zn_{0.05})_2(Ti_{0.8}Sn_{0.2})O_4$ ceramics

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The sinterability and microwave dielectric properties of pure and LiF-added $(Mg_{0.95}Zn_{0.05})_2(Ti_{0.8}Sn_{0.2})O_4$ (MZTS) ceramics were investigated. X-ray diffraction analysis indicated that all specimens show a cubic spinel structure with lattice parameters ($a = b = c = 8.48794$ Å). In the case of the pure MZTS ceramic, the optimum calcination and sintering temperatures were 1150 °C for 3 h and 1325 °C for 5 h, respectively, for the best density and dielectric properties. The MZTS ceramic sintered at 1325 °C for 5 h had $\varepsilon_r = 13.1$, $Q{\cdot}f = 131\ 170$ GHz (10 GHz), $\tau_f = -55.6$ ppm/K. A small addition (3.0 wt%) of LiF into the MZTS ceramic allowed a noticeable reduction in its sintering temperature by 200 °C without a significant detrimental effect on the dielectric properties. The MZTS-3.0 wt% LiF ceramic sintered at 1150 °C for 5 h showed $\varepsilon_r = 13.05$, $Q{\cdot}f = 119\ 316$ GHz (10.1 GHz), $\tau_f = -59.2$ ppm/K.

Key words: $(Mg_{0.95}Zn_{0.05})_2(Ti_{0.8}Sn_{0.2})O_4$, Dielectric properties, Sintering aids, LiF.

Introduction

With the current tendency of increasing operating frequencies of microwave wireless communications, new low-cost dielectric ceramics with an extremely high quality factor in the microwave frequency are urgently required [1]. In the case of advanced substrate materials for microwave integrated circuits they should have a low dielectric constant ($\varepsilon_r \leq 15$), in order to minimize the cross-coupling effect with the conductor and increase the signal propagation velocity, a high quality factor ($Q{\cdot}f > 50\ 000$ GHz) for selectivity, and a near-zero temperature coefficient of resonant frequency (τ_f) for temperature stability [2, 3]. Besides, the basic physical property requirements, the cost, and the toxicity should also be considered in these applications [4].

Recently, the spinel structure material Mg_2TiO_4 has attracted attention in the field of materials science [5-7]. Mg_2TiO_4-based ceramics are good candidates for microwave dielectrics [8]. Mg_2TiO_4 can also be used as a novel substrate for epitaxial growth of high temperature superconducting thin films [9]. Belous *et al.* first reported its microwave dielectric properties ($\varepsilon_r = 14$, $Q{\cdot}f = 150\ 000$ GHz, and $\tau_f = -50$ ppm/K) [10]. Presently active investigations are being done to improve its microwave dielectric properties by suitable substitution with ions, preparing various composites [11-15]. Among these, Huang *et al.* reported an improvement in $Q{\cdot}f$ of the Mg_2TiO_4 series by partial substitution for Mg or Ti-site ions [11-15]. To the best of our knowledge, no research has been performed to modify the microwave dielectric properties of Mg_2TiO_4 by both Mg- and Ti-site ions co-substitution. The present study was first undertaken to understand the effects of partial Zn substitution for Mg and Sn substitution for Ti on the microwave dielectric properties of MZTS ceramics. In addition, in order to lower its sintering temperature, a small amount of LiF was added to the ceramic, and the sintering behavior, microstructure and microwave dielectric properties of the MZTS-3.0 wt% LiF ceramic were also studied.

Experimental

The starting materials were high-purity oxide powders (> 99.9%) : TiO_2, MgO, ZnO and SnO_2. Predried raw materials were weighed in stoichiometric amount $(Mg_{0.95}Zn_{0.05})_2(Ti_{0.8}Sn_{0.2})O_4$ (MZTS) and ball milled for 6 h in a nylon jar with agate balls and ethanol as media. The milled powders were dried and then initially calcined at 1150 °C for 3 h. Then some powder was re-milled to obtain homogeneous pure MZTS powder. The other powder was re-milled with a 3.0 wt%LiF addition for 6 h. After drying, the powders with 5 wt% PVA as a binder were pressed into pellets 10 mm in diameter and 5 mm in thickness under a pressure of 200 MPa. Samples were sintered in the temperature range of 1250-1350 °C and 1100 to 1175 °C for 5 h, respectively, for pure and MZTS-3.0 wt% LiF specimens.

The apparent densities of the sintered ceramics were measured by the Archimedes' method. The crystal structures

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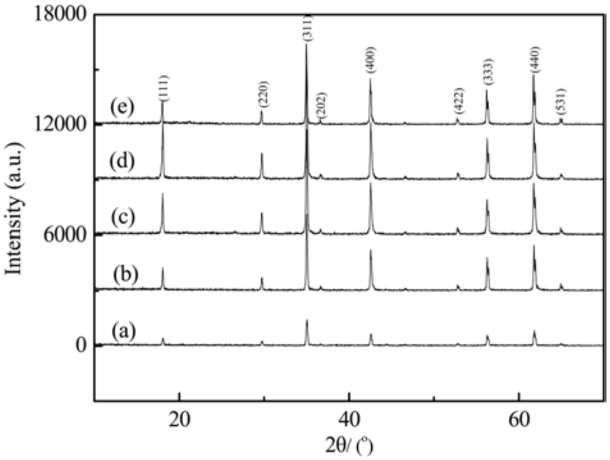

Fig. 1. XRD patterns of the MZTS-$x$wt% LiF ceramics sintered at various temperatures : (a) $x = 0$, 1325 °C, (b) $x = 3.0$, 1100 °C, (c) $x = 3.0$, 1125 °C, (d) $x = 3.0$, 1150 °C, (e) $x = 3.0$, 1175 °C.

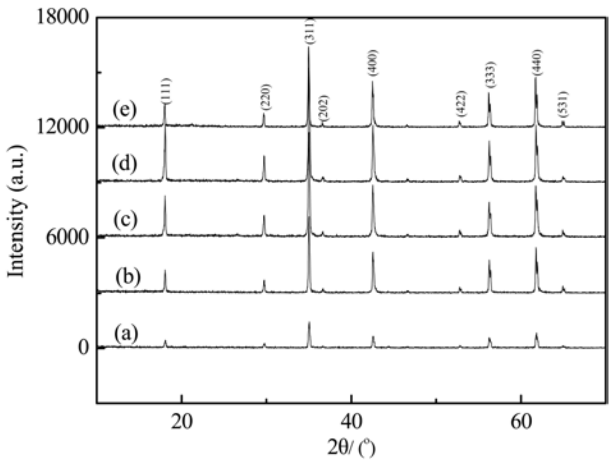

Fig. 2. Typical SEM images of the surfaces of the MZTS-$x$wt% LiF ceramics sintered at different temperatures : (a) $x = 0$, 1300 °C, (b) $x = 0$, 1325 °C, (c) $x = 0$, 1350 °C, (d) $x = 3.0$, 1125 °C, (e) $x = 3.0$, 1150 °C, (f) $x = 3.0$, 1175 °C.

were analyzed using X-ray diffraction (XRD) with CuKα radiation (Rigaku D/MAX2550, Japan). The microstructure of the pellets was investigated using a scanning electron microscope (SEM, Fei Quanta 200, Holland). The microwave dielectric properties of sintered samples at the microwave frequency were measured using a network analyses (HP8720ES, Agilent, Palo Alto, CA) with the $TE_{01\delta}$ shielded cavity method. The temperature coefficient of the resonant frequency (τ_f) was calculated with the following equation:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times (85 - 25)} \tag{1}$$

Results and Discussion

Fig. 1 shows the XRD patterns of the pure $(Mg_{0.95}Zn_{0.05})_2(Ti_{0.8}Sn_{0.2})O_4$ (MZTS) ceramic sintered at 1325 °C for 5 h and the MZTS-3.0 wt% LiF ceramic sintered at various temperatures. As can be seen, for all samples, a single phase was detected within the detectable level of XRD. Moreover, the XRD patterns of the MZTS-3.0 wt% LiF ceramic showed no significant change with sintering temperatures in the range from 1100 to 1175 °C. All of the diffraction peaks are consistent with a cubic spinel structure with space group $Fd\bar{3}m$. The lattice parameters were calculated to be $a = b = c = 8.48794$ Å, which are a littler larger than that reported earlier [16].

Typical SEM images of the pure and the MZTS-3.0 wt% LiF ceramic sintered at different temperatures are presented in Fig. 2. The pure MZTS ceramic sintered at 1300 °C had a porous microstructure with a grain size in the range of 1-3 μm as shown in Fig. 2(a). The pores were almost eliminated for the sample sintered at 1325 °C and a melted nature was observed for the MZTS ceramic sintered at 1350 °C as shown in Figs 2(b) and (c). However, for the MZTS-3.0 wt% LiF sintered ceramic [Figs 2(d)-(f)] a large amount of what had been a liquid phase covering small grains was observed, which showed the typical characteristics of liquid-phase sintering. The formation of a liquid phase arose from the addition of LiF.

The apparent densities of the sintered bodies, with respect to the sintering temperature, are demonstrated in Fig. 3. As the sintering temperature increased to 1325 °C, the density of the pure MZTS ceramic increased to a maximum value and a further increase in the sintering temperature decreased its density. The improvement in densification is due to the elimination of pores in the ceramic, as mentioned above. On the other hand, densification of the MZTS-3.0 wt% LiF is completed at a temperature that is much lower than 1325 °C. It seems to be around 1125 °C, 200 °C lower than that of the un-doped one. This indicates that LiF is an effective sintering aid for MZTS ceramics. The decrease of sintering temperature could be attributed to the liquid-phase effect, which comes from the melting of LiF as the sintering temperature exceeded 845 °C [17].

The variation of ε_r and $Q{\cdot}f$ values of the pure MZTS and the MZTS-3.0 wt% LiF ceramics with sintering tem- perature are illustrated in Figs. 4(a) and (b), respectively. It appears that the variation of ε_r and $Q{\cdot}f$ values for all samples with the sintering temperature is similar to that of the density. Both ε_r and $Q{\cdot}f$ values increased to a maximum value and then declined thereafter as the sintering temperature increased, a result closely correlated with the porosity, grain size and the residual liquid phase in the ceramics. The maximum $Q{\cdot}f$ values of the pure MZTS ceramic sintered at 1325 °C and the MZTS-3.0 wt% LiF specimens sintered at 1150 °C were 131, 170 and 119, 316 GHz, respectively. This indicated that the addition of LiF can lower the sintering temperature by around 200 °C without much deterioration in the $Q{\cdot}f$ value of the MZTS ceramics, and the slight decrease in $Q{\cdot}f$ could mainly be attributed to

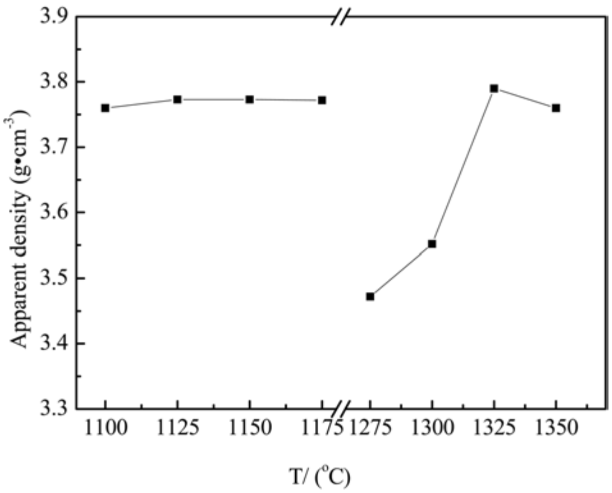

Fig. 3. Apparent densities of pure MZTS and MZTS-3.0 wt% LiF ceramics as a function of the sintering temperature.

the presence of what had been residual liquid phases. In addition, the $Q{\cdot}f$ values of MZTS and MZTS-3.0 wt% LiF specimens in our research were much lower that that of the $Mg_2(Ti_{0.95}Sn_{0.05})O_4$ and $(Mg_{0.95}Zn_{0.05})_2TiO_4$ ceramics reported by Huang *et al*. [12, 15]. It is generally accepted that ceramics having larger grains show a relatively better microwave dielectric properties in addition to their inherent properties [18]. Hence, the difference in $Q{\cdot}f$ value between our results and Huang's is due to the small grain size combined with the different chemical composition. The τ_f of all specimens was constant at values around −58 ppm/K. The variation of τ_f with sintering temperature is not shown here. Further research is in process to reduce the τ_f values for practical applications. The overall microwave dielectric properties of pure MZTS sintered at 1325 °C can be summarized as $\varepsilon_r = 13.1$, $Q{\cdot}f = 131, 170$ GHz (10 GHz) and $\tau_f = -55.6$ ppm/K, while MZTS-3.0 wt%LiF samples at 1150 °C had $\varepsilon_r = 13.05$, $Q{\cdot}f = 119, 316$ GHz (10.1 GHz), and $\tau_f = -59.2$ ppm/K.

Conclusions

MZTS and MZTS-3 wt%LiF ceramics were prepared by a solid-state reaction method. MZTS sintered at 1325 °C for 5 h had $\varepsilon_r = 13.1$, $Q{\cdot}f = 131\ 170$ GHz (10 GHz), $\tau_f = -55.6$ ppm/K. A small addition of LiF can effectively lower its sintering temperature to 1150 °C due to a liquid phase effect. The MZTS-3.0 wt% LiF sintered at 1150 °C for 5 h showed good microwave dielectric properties of $\varepsilon_r = 13.05$, $Q{\cdot}f = 119\ 316$ GHz (10.1 GHz), and $\tau_f = -59.2$ ppm/K. Further research is in process to reduce the τ_f values.

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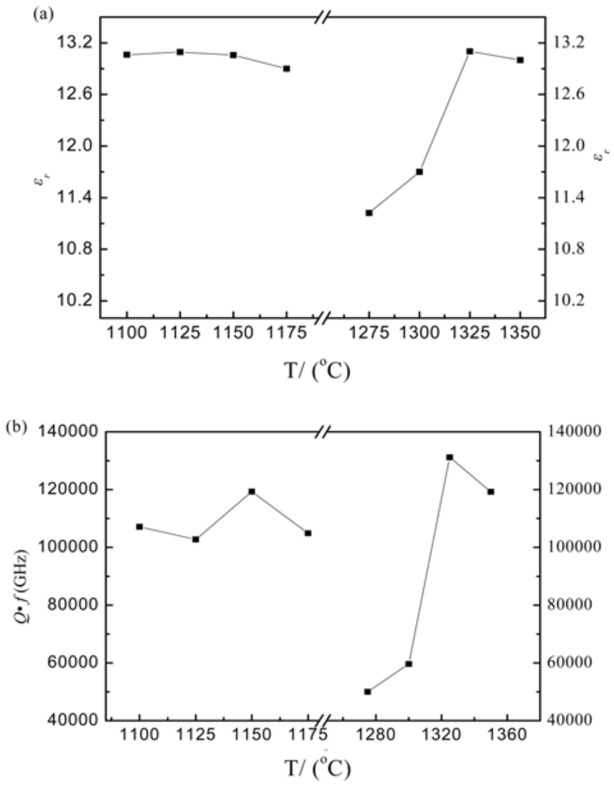

Fig. 4. Variation of (a) ε_r and (b) $Q{\cdot}f$ values of pure MZTS and MZTS-3.0 wt% LiF ceramics with sintering temperature.

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References

1. A. Belous, O. Ovchar, D. Durylin and M. Valant, J. Eur. Ceram. Soc. 27 (2007) 2963-2966.
2. K.M. Manu, P.S. Anjana and M.T. Sebastian, Mater. Lett. 65 (2011) 565-567.
3. G.G.. Yao and C.J. Pei, J. Ceram. Process. Res. 12 (2011) 1-4.
4. D. Zhou, C.A. Randall, H. Wang and X. Yao, J. Am. Ceram. Soc. 93 (2010) 2147-2150.
5. S. Buteea, A.R. Kulkarnia and K.C.R. Jamesd, Mater. Sci. and Eng. B 168 (2010) 151-155.
6. P. Liu, J.L. Ma and H.W. Zhang, Mater. Chem. Phys. 114 (2009) 624-628.
7. W. Lei, W.Z. Lu, D. Liu and J.H. Zhu, J. Am. Ceram. Soc. 92 (2009) 105-109.
8. S. Kumar, R. Kumar and C.G. Lee, J. Ceram. Soc. Jpn. 117 (2009) 689-692.
9. H. Haefie, H.P. Lang, L. Berthold and D. Hesse, Appl. Phys. Lett. 61 (1992) 2359-2361.
10. A. Belous, O. Ovchar and D. Durilin, J. Am. Ceram. Soc. 89 (2006) 3441-3445.
11. C.L. Huang, J.Y. Chen and C.Y. Jiang, J. Alloy. Compd. 487 (2009) 420-424.
12. C.L. Huang and S.S. Liu, J. Am. Ceram. Soc. 91 (2008) 3428-3430.
13. C.L. Huang and J.Y. Chen, J. Am. Ceram. Soc. 92 (2009)

379-383.
14. C.L. Huang and J.Y. Chen, J. Am. Ceram. Soc 92 (2009) 675-678.
15. C.L. Huang and J.Y. Chen, J. Am. Ceram. Soc. 92 (2009) 2237-2241.
16. B.A. Wechsler and R.B. Dreele, Acta. Cryst. B 45 (1989) 542-549.
17. M. Pollet and S. Marinel, J. Eur. Ceram. Soc. 23 (2003) 1925-1933.
18. S. George and M.T. Sebastian, J. Am. Ceram. Soc. 93 (2010) 2164-2166.