J Mater Sci (2009) 44:328–330
DOI 10.1007/s10853-008-3142-8

LETTER

A new glass-free low-temperature fired microwave ceramic

Y. Z. Li · J. J. Bian · L. L. Yuan

Received: 27 August 2008 / Accepted: 26 November 2008 / Published online: 20 December 2008

Reducing the sintering temperature without affecting the properties is a challenging problem in LTCC material research. Low melting glass addition, chemical processing and small particle size of starting materials are three main methods normally used to reduce the sintering temperature of these dielectric ceramics. However, fine powders prepared by wet chemical processing such as the sol–gel process complicate the fabrication method and increase the cost. Addition of low melting glass either leads to poor microwave dielectric properties or significantly increases the possibility of chemical interaction with the metal electrode due to the presence of complicated phases in the LTCC system [1, 2]. So, a glass-free LTCC material with appropriate microwave dielectric properties is strongly desired for the multilayer structure applications. A number of glass-free LTCC materials have been reported [3–10]. However, most of these materials have a high τ_f, which is a key parameter of microwave dielectric ceramic. The search for an ideal glass-free low-temperature fired material with good properties is still continuing. In the present communication, we report the microwave dielectric properties of $x\mathrm{ZrTe_3O_8}$–$(1-x)\mathrm{CeTe_2O_6}$ for the first time. Also, the τ_f of the $CeTe_2O_6$ ceramics has been tailored by TiO_2 addition.

$0.45\mathrm{TiO_2}$–$0.55\mathrm{CeTe_2O_6}$ and $x\mathrm{ZrTe_3O_8}$–$(1-x)\mathrm{CeTe_2O_6}$ powders with compositions of $x = 0$, 0.1, 0.15, 0.2 and 1.0 were prepared by conventional solid-state reaction process from the starting materials including TiO_2 (99.7%), TeO_2 (99.99%), ZrO_2 (99.6%) and CeO_2 (99.99%). These compounds were weighed and mixed with ZrO_2 balls in ethanol for 24 h, dried and calcined at the temperature of 600–700 °C for 2 h in an alumina crucible with subsequent ball milling in ethanol with zirconia balls. After drying, mixed with 7–10 wt% PVA and sieving, the granulated powders were uniaxially pressed under a pressure of 120 MPa into compacts with 10 mm in diameter and 4.5 mm thickness. The compacts were sintered ranging from 650 to 850 °C for 2 h. The sintering temperature was optimized by the maximum bulk density and $Q \times f$ value. In order to prevent tellurium evaporation during sintering, the compacts were covered with powder of the same composition. The chemical compatibility with silver was investigated by co-firing the mixed powders with pure silver powders (30 wt% Ag) in ambient atmosphere at temperatures at around 700 °C.

The densities of the ceramics were measured by the Archimedes method. The phase constituents of the sintered samples were identified by X-ray powder diffraction (XRD) with Ni-filtered Cu Ka radiation (Rigaku D\max2550, Japan). Microwave dielectric properties of the sintered samples were measured between 4 and 10 GHz using network analyzer (Agilent 8720ES, USA). The quality factor was measured by the transmission cavity method. The relative dielectric constant (ε_r) was measured according to the Hakki-Coleman [11] method using the TE_{011} resonant mode, and the temperature coefficient of the resonator frequency (τ_f) was measured using invar cavity in the temperature range from 20 to 80 °C.

Figure 1 shows the powder XRD patterns of $x\mathrm{ZrTe_3O_8}$–$(1-x)\mathrm{CeTe_2O_6}$ ($x = 0$, 0.1, 0.15, 0.2, 1) sintered samples. The powder diffraction pattern of $x = 0$ sample is very similar to monoclinic ($P2_1/n$) $CeTe_2O_6$ [12]. The patterns of $x = 1$ samples are in good agreement with that of the cubic (Ia-3) $ZrTe_3O_8$ [12]. The $x = 0.1$, 0.15, and 0.2 samples

---

Y. Z. Li · J. J. Bian (✉) · L. L. Yuan
Department of Inorganic Materials, Shanghai University,
149 Yanchang Road, Shanghai 200072, China
e-mail: jjbian@shu.edu.cn

Y. Z. Li
e-mail: lyzsunny@shu.edu.cn

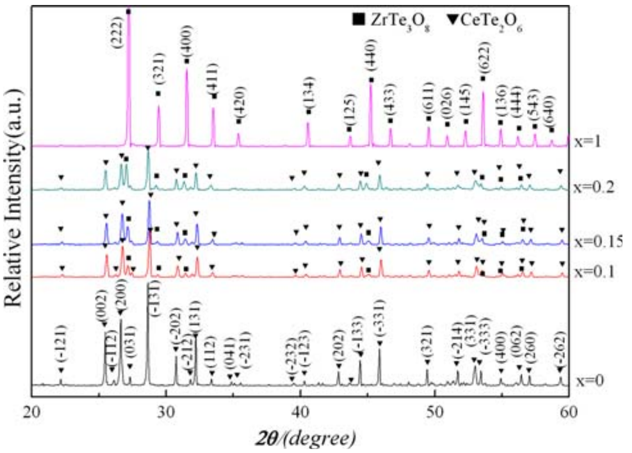

Fig. 1 XRD patterns of ceramics sample xZrTe$_3$O$_8$–(1 − x)CeTe$_2$O$_6$

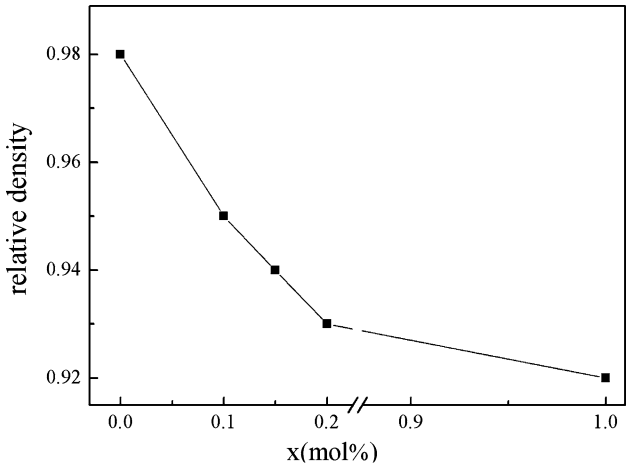

Fig. 3 Relative density of xZrTe$_3$O$_8$–(1 − x)CeTe$_2$O$_6$ as function of x

exhibit mixture phases of CeTe$_2$O$_6$ and ZrTe$_3$O$_8$ without any observable formation of second phase. Figure 2 shows the SEM image of 0.15ZrTe$_3$O$_8$–0.85CeTe$_2$O$_6$ sample sintered at 675 °C. Multiphase microstructure is observed in the sample, which is agreement with the XRD results. The relative densities of xZrTe$_3$O$_8$–(1 − x)CeTe$_2$O$_6$ sintered at different temperatures are shown in Fig. 3, as function of x. The theoretical densities (ρ_{th}) of the xZrTe$_3$O$_8$–(1 − x) CeTe$_2$O$_6$ ceramics were obtained from $\rho_{th} = \frac{w_1+w_2}{(w_1/\rho_1+w_2/\rho_2)}$ [13], where w_1 and w_2 are the weight fraction of CeTe$_2$O$_6$ and ZrTe$_3$O$_8$ in the mixture, respectively. ρ_1 and ρ_2 represent the theoretical density of CeTe$_2$O$_6$ and ZrTe$_3$O$_8$, respectively. As seen in Fig. 3, the relatively density decreases with the increase of ZrTe$_3$O$_8$ addition. For CeTe$_2$O$_6$ ($x = 0$) ceramics, relative densities of 98% TD could be obtained after sintering at 700 °C for 2 h. For ZrTe$_3$O$_8$ sample about 93% of theoretical density could be obtained after sintering at 800 °C. Figure 4 shows the variation of dielectric constant and temperature coefficient of xZrTe$_3$O$_8$–(1 − x)CeTe$_2$O$_6$ as function of x. Dielectric constant of CeTe$_2$O$_6$ and ZrTe$_3$O$_8$ are about 15.2 and 57.6, respectively. The dielectric constant increases with the increase of ZrTe$_3$O$_8$ content. CeTe$_2$O$_6$ exhibits negative τ_f value (−67.5 ppm/°C) and ZrTe$_3$O$_8$ exhibits positive 278.4 ppm/°C. The τ_f value increases almost linearly with increasing x. A minimum τ_f value of −8 ppm/°C is obtained when $x = 0.1$. Variation of $Q \times f$ value as function of x is shown in Fig. 5, the $Q \times f$ value dramatically decreases up to $x = 0.1$ and then decreases slowly with the further increase of x. Maximum $Q \times f$ values of 45,400 GHz were obtained for CeTe$_2$O$_6$ ($x = 0$). Also, the τ_f of the CeTe$_2$O$_6$ ceramics was tailored by TiO$_2$ addition. The temperature coefficient of resonant frequency (τ_f) of pure CeTe$_2$O$_6$ is −67.5 ppm/°C and that of TiO$_2$ is 400 ppm/°C [13]. τ_f of the mixture phase can be predicted using a general mixture formula: $\tau_f(\text{mixed}) = \sum\left\{(\tau_f)_i V_i\right\}$ [14], where V_i and $(\tau_f)_i$

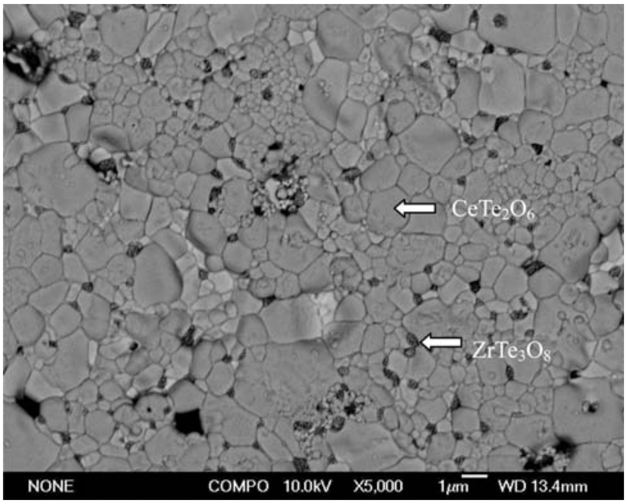

Fig. 2 Back-scattered SEM images of sintered sample 0.15ZrTe$_3$O$_8$–0.85CeTe$_2$O$_6$ (sintered 675 °C/2 h)

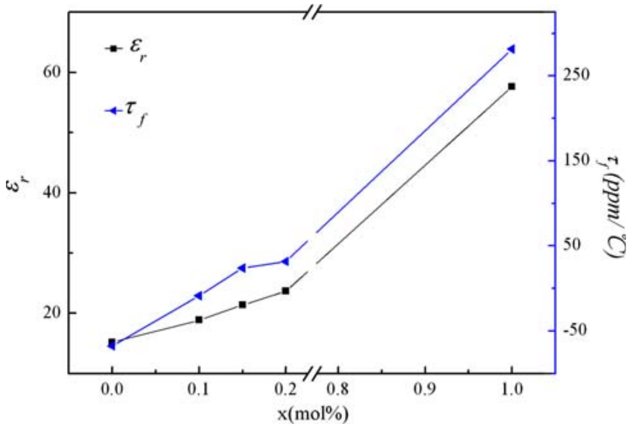

Fig. 4 Variation of dielectric constant and temperature coefficient of xZrTe$_3$O$_8$–(1 − x)CeTe$_2$O$_6$ as function of x

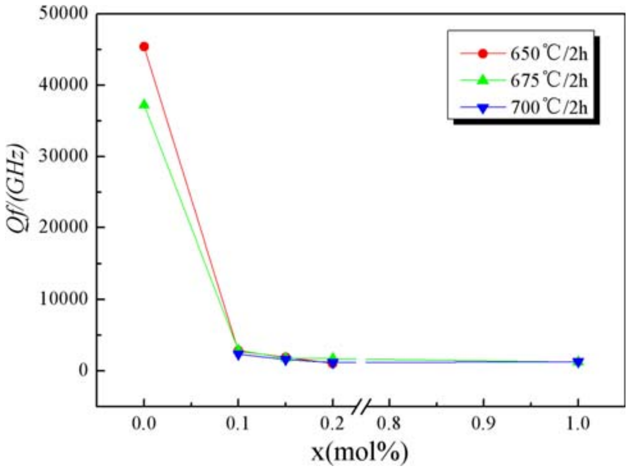

Fig. 5 Variation of $Q \times f$ of xZrTe$_3$O$_8$–(1 − x)CeTe$_2$O$_6$ as a function of x

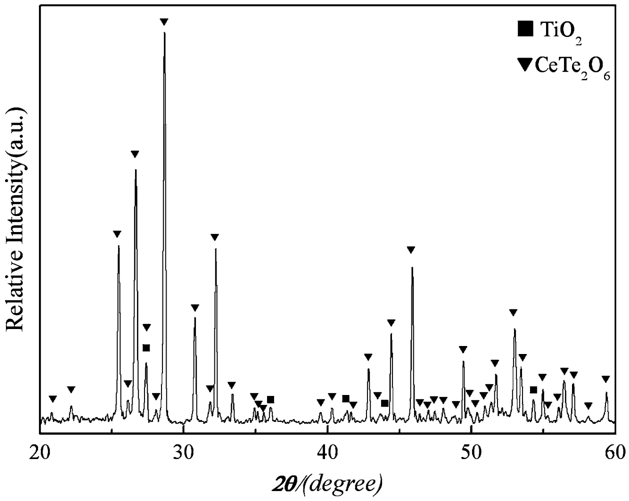

Fig. 6 XRD patterns of ceramics sample 0.45TiO$_2$–0.55CeTe$_2$O$_6$

are the volume fraction and temperature coefficient of resonant frequency of CeTe$_2$O$_6$ and TiO$_2$ in the mixture. And the τ_f of the mixture phase can be approximated to zero by 45 mol% TiO$_2$ addition theoretically. The XRD pattern and the SEM image of polished and thermally etched surface of the 0.45TiO$_2$–0.55CeTe$_2$O$_6$ sintered 730 °C/2 h are illustrated in Figs. 6 and 7, respectively. Mixture phases of CeTe$_2$O$_6$ and TiO$_2$ are observed. 0.45TiO$_2$–0.55CeTe$_2$O$_6$ sample exhibit bulk density (96%) when it is sintered at 730 °C/2 h. It exhibits good microwave dielectric properties: $\tau_f = 24.9$ ppm/°C, $\varepsilon_r = 22.8$ and $Q \times f = 8400$ GHz. However, serious chemical reactions were observed in the mixture powders of 0.45TiO$_2$–0.55CeTe$_2$O$_6$/xZrTe$_3$O$_8$–(1 − x)CeTe$_2$O$_6$ with Ag sintered at 700 °C in ambient atmosphere.

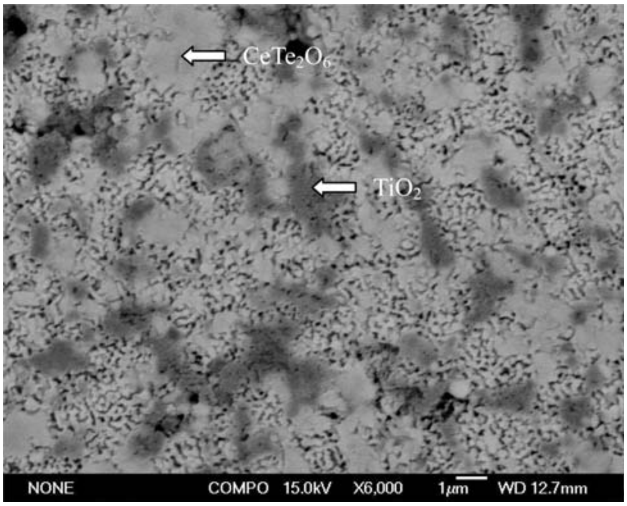

Fig. 7 Back-scattered SEM images of sintered sample 0.45TiO$_2$–0.55CeTe$_2$O$_6$ (sintered 730 °C/2 h)

References

1. Valant M, Suvorov D (2004) J Eur Ceram Soc 24:1715
2. Bian JJ, Kim DW, Hong KS (2005) Mater Res Bull 40:2120
3. Kwon DK, Lanagan MT, Shrout TR (2005) J Am Ceram Soc 88:3419
4. Kwon DK, Lanagan MT, Shrout TR (2007) Mater Lett 61:1827
5. Udovic M, Valant M, Suvrov D (2001) J Eur Ceram Soc 21:1735
6. Udovic M, Valant M, Suvrov D (2004) J Am Ceram Soc 87:591
7. Kwon K, Lanagan MT, Shrout TR (2005) J Ceram Soc Jpn 113:216
8. Subodh G, Sebastian MT (2007) J Am Ceram Soc 90:2266
9. Maeda M et al (1987) Jpn J Appl Phys Suppl 26:76
10. Sebastian MT (2008) Dielectric materials for wireless communication. Oxford, London
11. Hakki BW, Coleman PD (1960) IRE Trans Microw Theory Tech 8:402
12. Powder Diffraction Database – PDF, International Centre for Diffraction Data – ICDD, 12 Campus Boulevard, Newtown Square, PA 19073-3273, USA
13. Cho I-S, Kang S-K et al (2006) J Eur Ceram Soc 26:2007
14. Wu JM, Chang MC, Yao PC (1990) J Am Ceram Soc 73:1599