ELSEVIER

Ceramics International 31 (2005) 905–909

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Low temperature sintering of $(Zn_{1-x}, Mg_x)TiO_3$ microwave dielectrics

Yuh-Ruey Wang*, Sea-Fue Wang, Yen-Ming Lin

Department of Materials and Minerals Resources Engineering, National Taipei University of Technology, 1, Sec. 3, Chung-Hsiao E. Rd., Taipei, Taiwan, ROC

Received 14 April 2004; received in revised form 31 August 2004; accepted 29 September 2004
Available online 12 January 2005

Abstract

The effects of glass additives and milling process on the microwave dielectric properties of (Zn_{1-x}, Mg_x) TiO_3 (ZMT) ceramics were investigated. Three glasses including B_2O_3–SiO_2–ZnO–Na_2O (B–Si–Zn–Na), B_2O_3–SiO_2–ZnO–K_2O (B–Si–Zn–K) and B_2O_3–K_2O–$MnCO_3$ (B–K–Mn) were selected for this study. Host material $(Zn_{0.6}Mg_{0.4})TiO_3$ was selected to be sintered with glasses in the temperature range of 900–1200 °C. For $(Zn_{0.6}Mg_{0.4})TiO_3$ with 5 wt.% glass B–Si–Zn–K sintered at 1100 °C, the ϵ_r and $Q \times f$ values were 18 and 29,375, respectively. Taking advantage of satellite milling, the ZMT ceramics can be sintered at 950 °C with the density of 4.21 g/cm^3, $\epsilon_r = 19$, and $Q \times f = 18{,}957$.

Keywords: A. Sintering; A. Milling; Microwave dielectrics; Zinc titanate; Glass additives

1. Introduction

Due to the rapid development of wireless communication services, the microwave ceramic devices with high performance are desired. The materials used in UHF microwave ceramic devices need to satisfy three requirements, namely the high dielectric constant, ϵ_r, high quality factor, Q, low and as close as possible to zero temperature coefficient of resonant frequency, τ_f. In order to miniaturize the microwave devices, the size of dielectric components must also be reduced. Multilayer devices have been developed to increase the volume efficiency. In multilayer structure, it is necessary to lower the sintering temperature of the dielectrics in order to co-fire with low melting point and highly conductive internal electrode metals, such as silver, copper, and their alloys [1–3].

Introducing low melting glass additives, chemical processing, and fining particle size of the starting materials are three of the methods used to reduce the sintering temperature of the dielectrics. Among these methods, glass additives used in liquid phase sintering is the most effective and least expensive [4]. Zinc titanate ($ZnTiO_3$) is a promising candidate for low temperature sintering dielectrics, because it can be sintered at 1100 °C without sintering aids and can be sintered at temperature <900 °C with B_2O_3 glass. But this phase will decompose as the sintering temperature is above 900 °C. Kim et al. studied in advance the phase stability by adding magnesium, and their microwave properties [5–8]. In order to extend the processing window, this paper studied the effect of ternary B–Si–Zn glass system on the sinterability and also discussed the effect of Mg content on the $ZnTiO_3$ phase stability, processing conditions, and microwave properties.

2. Experimental procedure

$(Zn_{1-x}, Mg_x)TiO_3$ (x = 0–0.5) powder as the host material was prepared by solid-reaction method. High purity oxides, TiO_2 (99.9% Showa Denko G1), ZnO (99.9% Umicore) and MgO (99% PCF) were mixed and then calcined at 700 °C for 2 h, followed by pulverization, pressing and then sintering in the temperature range of 950–1300 °C with intervals of 50 °C for 4 h. Three glasses were used in this study. The composition for glasses A–C are listed in Table 1. These

* Corresponding author. Fax: +886 2273 17185.
E-mail address: yrwang@ntut.edu.tw (Y.-R. Wang).

0272-8842/$30.00
doi:10.1016/j.ceramint.2004.09.017

Table 1
Chemical composition (wt.%) of glass

Glass	SiO_2	B_2O_3	Al_2O_3	ZnO	Metal oxide
A	10.4	45.3	2.5	35.2	Na_2O 6.6
B	9.5	44.0	4.5	33.5	K_2O 8.5
C	–	41.67	–	–	K_2O 41.67
					$MnCO_3$ 6.67

glasses were made by melting mixture of oxides at 1000 °C for 30 min and quenching. The calcined host material with 5 wt.% glasses were mixed by wet ball mill with water as the milling medium for 8 h. The dry-pressed and glass-doped samples were sintered at intervals of 50 °C over the temperature range of 950–1200 °C for 4 h. XRD analysis was undertaken for phase identification using Rigaku D/MAX-B. The microstructure was observed by SEM (Hitachi S-4700) attached with EDS (Horiba 7200-H). The densification behavior was evaluated by determining the bulk density using Archimedes technique. Dielectric properties were measured by a cavity method using Angilent 8722ES network analyzer.

3. Results and discussion

The XRD result of 700 °C and 2 h calcined powders of $(Zn_{1-x}, Mg_x)TiO_3$ with $x = 0$–0.5 shows that the major phase was hexagonal (Zn, Mg)TiO_3 and the TiO_2 and $Zn_2Ti_3O_8$ were minority. TiO_2 phase increased with the increasing Mg content. The existence of TiO_2 phase in Mg-rich systems seems to arise from the insufficient reaction of MgO with other oxides.

The $(Zn_{1-x}, Mg_x)TiO_3$ with $x = 0$ decomposed as the sintering temperature was greater than 950 °C as shown in Fig. 1(a–c). Fig. 2 shows the SEM photo of sample sintered at 1100 °C, where the dark rutile grain can be observed. The MgO additives could uplift the temperature of decomposition. The X-ray diffraction patterns of sample with $x = 0.4$ are showed in Fig. 1(d–f). The pure (Zn, Mg)TiO_3 can be kept until 1200 °C. The SEM photo of 1100 °C sintered

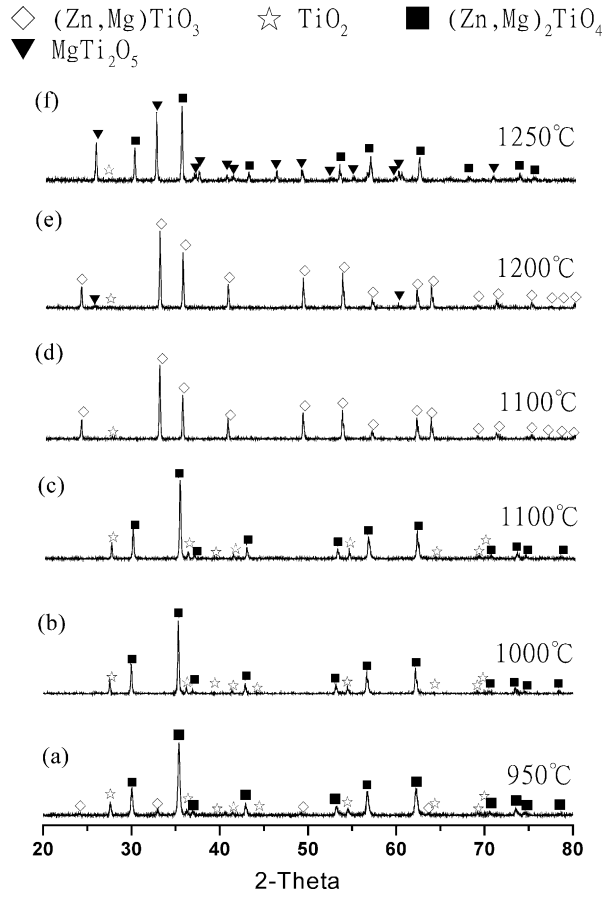
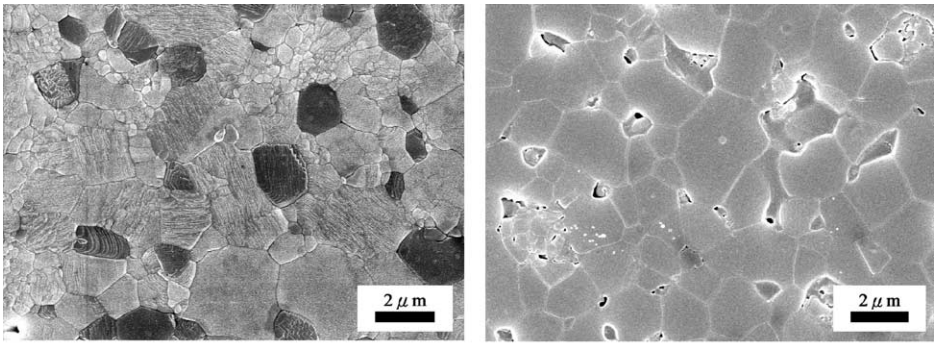


Fig. 1. XRD patterns of specimens with $x = 0$ (a–c) and $x = 0.4$ (d–f).

sample with $x = 0.4$ in Fig. 2b shows the single phase of ZMT. Table 2 shows that the phase components of the ZMT with the different Mg content changing with the increasing temperature. The density of the sintered $(Zn_{1-x}, Mg_x)TiO_3$ ceramics increased with sintering temperature and decreased with the increasing Mg content as shown in Fig. 3. As sample with $x = 0.1$ sintered at 1000 °C and 1050 °C, the density decreased because of the hexagonal ZMT decomposing into cubic Zn_2TiO_4 and rutile. The



(a) (b)

Fig. 2. SEM photos of $(Zn_{1-x}, Mg_x)TiO_3$ specimens of $x = 0$ (a) and $x = 0.4$ (b), both were sintered at 1100 °C for 4 h.