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The effects of dispersants on sinterability and microwave dielectric properties of $Zr_{0.8}Sn_{0.2}TiO_4$ ceramics

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ABSTRACT

This study investigated the effects of dispersants (deionised water and ethanol) on the sinterability, phase compositions and microwave dielectric properties of $Zr_{0.8}Sn_{0.2}TiO_4$ ceramics prepared by a solid-state reaction. Results showed the presence of impurity phases in low-density ceramics with ethanol as dispersant sintered from 1500 °C to 1550 °C. However, pure phase was detected in samples prepared with deionised water as dispersant when sintering temperature ranged from 1512 °C to 1550 °C. The microwave dielectric properties of the samples with deionised water significantly improved compared with those with ethanol. Thus, deionised water was suitable for preparing $Zr_{0.8}Sn_{0.2}TiO_4$ ceramics with a high density of approximately 98%, ϵ_r of 39.83, $Q \times f$ of 33,700 GHz and τ_f of + 3.5 ppm/°C.

1. Introduction

The rapid development of modern industrial technology has led to the shift of mobile communication towards fast and stable equipment that requires miniaturisation, reliable chip, nontoxic constituents and low-cost microwave devices. Microwave dielectric ceramics are used extensively as components in the filter units of communication systems. In order to meet the requirements, many microwave dielectric ceramics with different relative permittivity have been researched [1–6]. $Zr_{(1-x)}Sn_xTiO_4$ (ZST) ceramics are good candidates for applications in the microwave field [7,8] because of their high quality, medium dielectric constant and near-zero temperature coefficient of resonant frequency. When $x = 0.2$, $Zr_{0.8}Sn_{0.2}TiO_4$ has a high temperature stability, and the temperature coefficient of resonant frequency is almost zero [9,10]. However, full densification of these ceramics without using sintering aid is difficult because the needed sintering temperature is over 1600 °C.

Scholars have investigated the effects of dispersants on the properties of ceramics [11–14]. In 2013, Lei et al. [15] found that dispersants affected $BaAl_2Si_2O_8$ microwave dielectric ceramics in terms of shrinkage, phase evolution and microwave dielectric properties. In this study, $BaAl_2Si_2O_8$ ceramics prepared with ethanol as dispersant through a solid-state reaction were characterised by near-zero shrinkage and single phase. $BaAl_2Si_2O_8$ ceramics with deionised water as dispersant exhibited high density, ϵ_r and $Q \times f$ values. Moreover, $BaAl_2Si_2O_8$ ceramics calcined at temperatures higher than 1175 °C

underwent phase evolution and showed reduced $Q \times f$ value.

In our previous work, we compared sintered samples with ethanol and deionised water as dispersants. Among the samples tested, $Zr_{0.8}Sn_{0.2}TiO_4$ microwave dielectric ceramics exhibited deference of the optimum sintering temperature and microwave dielectric properties. In this regard, the present study investigated the effect of dispersant on the phase composition, microstructure, relative density and microwave dielectric properties of ceramics.

2. Experimental procedure

2.1. Sample preparation

$Zr_{0.8}Sn_{0.2}TiO_4$ ceramics were prepared through a solid-state reaction with reagent-grade ZrO_2 , SnO_2 and TiO_2 ceramic powders as raw materials. The starting materials were mixed according to the desired stoichiometry and milled with zirconia balls in deionised water or ethanol at 365 rpm for 5 h. After drying and sieving, the milled powders were calcined at 1300 °C for 3 h to obtain $Zr_{0.8}Sn_{0.2}TiO_4$ powders (hereinafter, ZST with deionised water as dispersant is called DZST and ZST with ethanol as dispersant is called EZST). The calcined powders were ball milled in the two dispersants and dried again. The powders were added with 8 wt% PVA as binder and uniaxially pressed at 200 MPa to obtain samples with 12 mm diameter and approximately 8 mm height. The samples were sintered at densification temperatures from 1500 °C to 1550 °C for 3 h at a heating rate of 5 °C/min in air and

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cooled to 1000 °C at a rate of 2 °C/min, then furnace cooled.

2.2. Characterisation

Experimental bulk density (ρ_b) was measured by Archimedes method using distilled water as liquid. Crystalline phases were identified by X-ray diffraction using an automated diffractometer (XRD-7000, Shimadzu Corporation, Japan) equipped with a crystal monochromator under $\text{CuK}\alpha$ radiation. Theoretical density (ρ_t) was determined using the XRD data. Microstructures were examined by scanning electron microscopy (SEM, Quanta 200, FEI, the Netherlands). Dielectric constant (ϵ_r) and quality factor $Q \times f$ value at microwave frequencies were measured using Hakki–Coleman dielectric resonator method with microwave network analyser (Agilent E8362B, Agilent Technologies, USA). τ_f within 20–80 °C was calculated by Formula (1):

$$\tau_f = \frac{1}{f(T_0)} \frac{[f(T_1) - f(T_0)]}{T_1 - T_0} \quad (1)$$

where $f(T_1)$ and $f(T_0)$ represent the resonant frequency at T_1 (80 °C) and T_0 (20 °C), respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns of $\text{Zr}_{0.8}\text{Sn}_{0.2}\text{TiO}_4$ ceramics prepared using two types of dispersants and sintered at different temperatures. DZST samples formed pure orthorhombic $\text{Zr}_{0.8}\text{Sn}_{0.2}\text{TiO}_4$ phase after sintering at higher than 1500 °C. At 1500 °C, TiO_2 appeared [Fig. 1(b)]. The generation of the TiO_2 could be due to the insufficient driving force of the low sintering temperature for synthesis of pure phase. When ethanol was used as dispersant, other phases besides $\text{Zr}_{0.8}\text{Sn}_{0.2}\text{TiO}_4$ were found as the sintering temperature increased from 1500 °C to 1550 °C. At sintering temperature higher than 1525 °C, monoclinic TiO_2 phase disappeared and orthorhombic $\text{Zr}_5\text{Ti}_7\text{O}_{24}$ phase was generated [Fig. 1(a)]. $\text{Zr}_5\text{Ti}_7\text{O}_{24}$ is the specific composition within the $(\text{Zr}, \text{Ti})\text{O}_2$ solid solution which is the intermediate compound of the ZrO_2 – TiO_2 system. It is ordered superstructure of α - PbO_2 and a fersmite-type structure. The ordered phase has a smaller molar volume and is slightly more Ti-rich compared to the disordered polymorph [16,17]. The appearance of the immediate compound $\text{Zr}_5\text{Ti}_7\text{O}_{24}$ resulted from the fact that the sintering temperature was too low to synthesize the disordered ZrTiO_4 .

Fig. 2 shows the fracture surface SEM and BSE micrographs of EZST samples sintered at 1500 °C, the black shadow areas were the second phase [Fig. 2(b)].

Comparing Fig. 1(a) with (b), the impurity phases TiO_2 and $\text{Zr}_5\text{Ti}_7\text{O}_{24}$ present in EZST indicated that the sintering driving force of EZST was insufficient under the same sintering condition. In addition,

there were not any compounds contain Sn in the impurity phases. We predicted that the insufficient driving force originated from the inhomogeneous dried ZST powder obtained after the first ball milling with ethanol as dispersant. The inhomogeneous dried powder led to inhomogeneous reaction during calcination and thus affected the entire result. To confirm this conjecture, we performed a sedimentation experiment of ZST dispersions using deionised water and ethanol as dispersants at 22 °C.

ZST suspensions were obtained by ball milling of ZST raw powder in deionised water and ethanol. The suspensions were placed in a quartz graduated cylinder ready to be analysed. The sedimentation was then immediately monitored for 48 h. Stratification was recorded by the scale of the graduated cylinders. Particles in the suspension with ethanol quickly subsided within few minutes and completely settled within 24 h. Meanwhile, particles in the suspension with deionised water underwent consistent slow subsiding in the experiment. It is suggested that during drying process, heavier agglomerated particles precipitated first, and the other particles remained in the suspension when ethanol was used as dispersant. This phenomenon resulted in non-uniform dried ZST raw powders and consequent inhomogeneous reaction during calcination. Thus, EZST, regardless of the sintering temperature, possessed impurity phases [Fig. 1(a)]. Moreover, we did a SEM test on the dried powders, and found that the powders with ethanol as dispersant had obvious agglomeration phenomenon, as shown in Fig. 3.

Based on the sedimentation experiment, ZST aqueous solutions were not prone to sedimentation. We ascertained that water and ethanol molecules formed hydrogen bonds. However, water molecules exhibit higher polarity than ethanol molecules. Therefore, water molecules ionise and generally exist in the form of H_3O^+ in the presence of hydrogen bonds. The hydroxyl group of ethanol molecules forms intermolecular hydrogen bonding; as such, ethanol molecules formed a chain-like structure [18–20] [Fig. 4(a)]. This structure led to viscous ethanol, in which particles cannot disperse perfectly. Moreover, oxides can form hydrogen bonds with the hydroxyl group [21]. Li et al. [22] found that catechol is adsorbed on the TiO_2 surface by hydrogen bonding. In ZrO_2 and SnO_2 , which are atomic crystals, the electronegativity values of Zr, Sn and O are 1.4, 1.8 and 3.5, respectively. Therefore, the atomic bonds between O and Zr, Sn are polar bonds [23,24]. During ball milling, trapped particles were subjected to high mechanical stress. The resulting shear and plastic deformation and local temperature increases would lead to increased superficial defects concentration and atomic mobilities [25]. Therefore, oxygen atoms were more likely to be exposed, the exposed O possibly formed hydrogen bond with hydroxyl groups in ethanol [Fig. 4(b)]. Thus, oxides were firmly adsorbed by hydrogen bonding, making them difficult to disperse but easy to aggregate and precipitate.

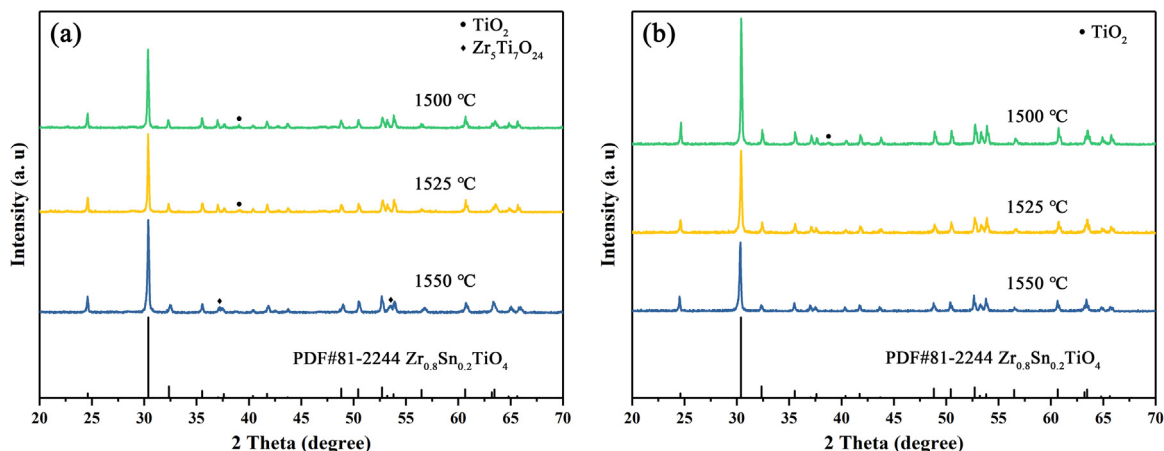


Fig. 1. XRD patterns of $\text{Zr}_{0.8}\text{Sn}_{0.2}\text{TiO}_4$ ceramics sintered at different temperature: (a) ethanol and (b) deionized water.

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