Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 37 (2011) 481–486
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Effects of aqueous gelcasting and dry pressing on the sinterability and microwave dielectric properties of $ZnAl_2O_4$-based ceramics

Jia-Min Wu, Wen-Zhong Lu *, Wen Lei, Jian-Ping He, Jun Wang

Department of Electronic Science and Technology, Huazhong University of Science and Technology, Wuhan 430074, China

Received 14 July 2010; received in revised form 5 August 2010; accepted 6 September 2010
Available online 29 September 2010

Abstract

The effects of aqueous gelcasting and dry pressing on the sinterability and microwave dielectric properties of 90 wt.% ($0.75ZnAl_2O_4$–$0.25TiO_2$)–10 wt.% $MgTiO_3$(ZTM) ceramics have been investigated. It is found that aqueous gelcasting could effectively decrease the sintering temperature of ZTM ceramics by 100 °C and acquire more excellent microwave dielectric properties of ZTM ceramics compared with conventional dry pressing. X-ray diffraction (XRD), environment scanning electron microscope (ESEM) and energy-dispersive X-ray spectroscopy (EDX) were used to analyze the phase compositions and microstructures of ZTM ceramics. The results illustrate that the phase compositions are completely uniform no matter what sintering temperature and forming method are adopted. However, the densities, ε_r and $Q \times f$ values are greatly affected by different forming methods, whereas there are few effects on the τ_f values. It is observed that ZTM ceramics prepared by aqueous gelcasting exhibit greater densities, more excellent and stable microwave dielectric properties compared with that prepared by dry pressing at the relative low sintering temperatures. However, when the sintering temperature becomes higher, the opposite phenomenon would gradually appear.

Keywords: Aqueous gelcasting; Dry pressing; Sinterability; Microwave dielectric properties; $ZnAl_2O_4$

1. Introduction

With the rapid development of microwave application in the area of microwave substrate and antenna, high performance microwave dielectric ceramics with low dielectric constant (ε_r), high quality factor ($Q \times f$) and near-zero temperature coefficient of resonator frequency (τ_f) are required. Recently, Surendran et al. [1,2] had found that $ZnAl_2O_4$ ceramics present low dielectric constant ($\varepsilon_r = 8.5$) and high quality factor ($Q \times f = 56300$ GHz). However, the sintering temperature of $ZnAl_2O_4$ is so high (1650 °C) that they could not be used in real application. Meanwhile, the τ_f value of $ZnAl_2O_4$ ceramics is too negative ($\tau_f = -79$ ppm/°C) [1]. TiO_2, which has high positive τ_f value ($\tau_f = +398$ ppm/°C) [2], has often been used to adjust the τ_f value of microwave dielectric materials with negative τ_f value and lower the sintering temperature of ceramics [3–7]. In addition, it had been reported that gelcasting could decrease the sintering temperature for Al_2O_3 ceramics [8]. Therefore, gelcasting would be another promising method to decrease the sintering temperature of $ZnAl_2O_4$ ceramics.

Gelcasting, which was invented by researchers of Oak Ridge National Laboratory [9], has been successfully used to form various ceramics including Si_3N_4-SiC [10], SiC [11], and Al_2O_3 [12], etc. In this process, the high solids loading slurry is solidified by the polymerization of monomers to form green bodies. This forming method has many outstanding advantages, such as high strength of the dried green body, facile fabrication of devices with complicated shape and comprehensive application in a wide range of materials, etc. Generally, non-aqueous solvents and aqueous solvents are used in gelcasting. Non-aqueous gelcasting has several disadvantages such as health problems, environmental hazards and high cost, so aqueous gelcasting, which has the advantages of low toxicity and low cost, has been widely used to gradually substitute non-aqueous gelcasting to form various materials.

So far, some researches have been done on the microwave dielectric properties of $ZnAl_2O_4$-based ceramics prepared by conventional dry pressing method. However, there are few researches about the effects of different forming methods on the sinterability and microwave dielectric properties of microwave

* Corresponding author. Tel.: +86 27 87542594; fax: +86 27 87543134.
E-mail address: lwz@mail.hust.edu.cn (W.-Z. Lu).

0272-8842/$36.00
doi:10.1016/j.ceramint.2010.09.006

dielectric ceramics. In this paper, aqueous gelcasting and dry pressing were used to prepare 90 wt.% ($0.75ZnAl_2O_4$–$0.25TiO_2$)–10 wt.% $MgTiO_3$(ZTM) ceramics. In order to satisfy the requirements of our project, $MgTiO_3$ was used to adjust the ε_r and τ_f values of $0.75ZnAl_2O_4$–$0.25TiO_2$ ceramics. The effects of different forming methods on the sinterability, phase compositions, microstructures and microwave dielectric properties of ZTM ceramics were investigated.

2. Experimental procedure

The monomer used in aqueous gelcasting was acrylamide (AM) and cross-linker was *N*,*N*′-methylenebisacrylamide (MBAM). 3 wt.% ammonium persulfate (APS) aqueous solution and *N*,*N*,*N*′,*N*′-tetramethyl ethylenediamine (TEMED) were used as initiator and catalyst, respectively. The dispersant used in aqueous gelcasting was ammonium polyacrylate (PAA-NH_4). The ZTM powder was prepared by the conventional solid state reaction method. Reagent grade ceramic powders ZnO (99.5%), Al_2O_3 (98.5%), TiO_2 (rutile, 99.6%) and MgO (98.5%) were used as raw materials. TiO_2 and MgO in a molar ratio of 1:1 were milled with zirconia balls and alcohol for 5 h at a speed of 365 r/min. After the slurry was dried, the mixture was calcined at 1190 °C for 3 h to synthesize $MgTiO_3$. Stoichiometric starting powders according to the compositions of $0.75ZnAl_2O_4$–$0.25TiO_2$ were also milled with zirconia balls and alcohol for 5 h at a speed of 365 r/min and then dried. The powders were calcined at 1130 °C for 3 h. Afterwards, 10 wt.% $MgTiO_3$ prepared before was added into 90 wt.% $0.75ZnAl_2O_4$–$0.25TiO_2$ calcined powder. After mixing and drying, some dried powders were uniaxially pressed into samples with dimensions of 20 mm diameter and 10 mm height under a pressure of 150 MPa, the other powders were used to prepare the same samples by aqueous gelcasting. The flow chart of aqueous gelcasting is shown in Fig. 1. The premix solution was prepared by mixing the monomer, cross-linker and deionized water. The concentration of the premix solution was about 14 wt.% and the ratio of AM and MBAM was 20:1. The ZTM powder and dispersant were added into the premix solution to make slurry with solids loading of about 50 vol.%. Strong aqua ammonia was used to adjust the pH value of the slurry at about 8–10 [13]. After ball milling for 1 h, the high solids loading slurry was obtained, then degassing was subsequently carried out for 10 min under vacuum. Afterwards, the catalyst and initiator were added into the slurry to initiate the gelation. After casting, demolding and drying, the green samples were removed binder at 600 °C for 1 h and then all the samples prepared by two forming methods were sintered at 1370–1470 °C for 3 h to form ceramics.

The densities of the sintered samples were measured with Archimedes method. The crystalline phase analysis of the sintered samples was achieved with X-ray diffraction (XRD) (X'Pert PRO, PANalytical B.V., Holland). The microstructure observation and quantitative analysis of the sintered samples were performed using environment scanning electron microscope (ESEM) (Quanta 200, FEI, Holland) and energy-dispersive X-ray spectroscopy (EDX) (Genesis 7000, EDAX Inc., USA), respectively. The ε_r and the $Q \times f$ values were measured in the TE_{011} mode with the Hakki and Coleman method [14], a vector network analyzer (Advantest R3767C, Advantest Corporation, Japan) and parallel silver boards were used for the measurement. The temperature coefficient of resonant frequency (τ_f) was calculated with the following formula in the temperatures ranging from 25 °C to 75 °C:

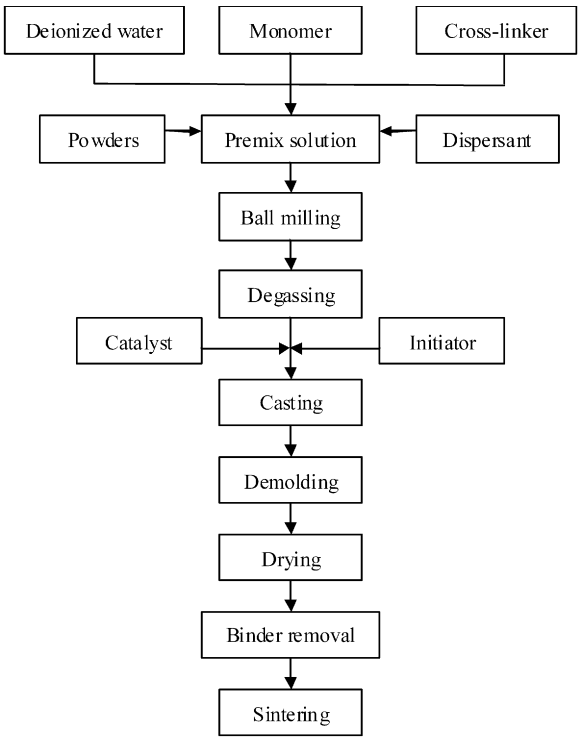

Fig. 1. The flow chart of aqueous gelcasting.

$$\tau_f = \frac{1}{f(25)} \times \frac{f(75) - f(25)}{75 - 25} \quad (1)$$

where $f(25)$ and $f(75)$ represent the resonant frequency at 25 °C and 75 °C, respectively.

3. Results and discussion

The densities of ZTM ceramics prepared by aqueous gelcasting and dry pressing are shown as a function of sintering temperature in Fig. 2. With the increase of sintering temperature, the densities of ZTM ceramics prepared by aqueous gelcasting increase firstly and then decrease slightly. The densities of ZTM ceramics prepared by dry pressing increase with the increase of sintering temperature until 1420 °C, and then decrease slightly until 1445 °C. Afterwards, the densities increase again. The anomalous phenomenon appearing at 1445 °C is attributed to the increase of the volume ratio of TiO_2 phase and decrease of the volume ratio of $ZnAl_2O_4$ phase, which will be pointed out in the XRD results shown in Fig. 3. Because the theoretical density of TiO_2 (4.26 g/cm^3) is lower than that of $ZnAl_2O_4$ (4.58 g/cm^3) [1], the densities of ZTM ceramics prepared by dry pressing and sintered at