



Review

Structure and microwave dielectric properties of $\text{Ba}_3(\text{VO}_4)_2\text{-Zn}_{2-x}\text{SiO}_{4-x}$ ceramic compositesYang Lv^a, Ruzhong Zuo^{a,*}, Zhenxing Yue^b^aInstitute of Electro Ceramics & Devices, School of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, PR China^bState Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China

ARTICLE INFO

Article history:

Received 14 July 2012

Received in revised form 22 December 2012

Accepted 11 February 2013

Available online 26 February 2013

Keywords:

A. Ceramics

A. Composites

C. Raman spectroscopy

D. Dielectric properties

ABSTRACT

Microwave dielectric ceramic composites with compositions of $(1-y)\text{Ba}_3(\text{VO}_4)_2\text{-yZn}_{2-x}\text{SiO}_{4-x}$ ($y = 0.4-0.6$, $x = 0.13$) have been prepared by firing mixtures of $\text{Ba}_3(\text{VO}_4)_2$ and $\text{Zn}_{1.87}\text{SiO}_{3.87}$. The X-ray diffraction (XRD) analysis revealed that Zn_2SiO_4 with a willemite phase can be obtained by appropriately controlling the ZnO deficiency. The starting $\text{Zn}_{1.87}\text{SiO}_{3.87}$ powder should be thus composed of the ZnSiO_4 crystal phase and redundant SiO_2 amorphous phase at room temperature. The scanning electron microscopy studies demonstrated the coexistence of Zn_2SiO_4 and $\text{Ba}_3(\text{VO}_4)_2$ phases in the sintered bodies, as further confirmed by the XRD and Raman results. The near-zero temperature coefficients of the resonant frequency (τ_f) could be achieved by adjusting the relative content of the two phases owing to their opposite τ_f values. The existence of a slight amount of secondary phases, element interdiffusion and non-stoichiometry such as Zn deficiency altogether made the predicted property values deviate from the experimentally measured ones. The composite ceramics with 40 wt% $\text{Zn}_{1.87}\text{SiO}_{3.87}$ sintered at 1100 °C exhibited desirable microwave dielectric properties of the quality factor $Q \times f \sim 23,000$ GHz, dielectric constant $\epsilon_r \sim 9.3$, and $\tau_f \sim 0.4$ ppm/°C.

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1. Introduction

Microwave dielectric ceramics have received much attention in the past decades because of the rapid development of microwave technologies such as wireless LAN, microwave-integrated circuits, and intelligent transport system [1,2]. These applications require a low dielectric constant (ϵ_r) to increase the signal propagation velocity and to minimize the cross-coupling effect, a high quality factor ($Q \times f$) to increase the frequency selectivity, and a near-zero temperature coefficient of the resonant frequency (τ_f) to obtain the

stability of the frequency against temperature [3]. So far, a number of dielectric ceramics with a low ϵ_r and a high $Q \times f$ value have been investigated, such as Al_2O_3 , MgAl_2O_4 , Y_2BaCuO_5 , Mg_2SiO_4 and Zn_2SiO_4 [4–6]. In spite of their high $Q \times f$ values, the common shortcomings of these materials are their large negative τ_f values, which limited their applications in microwave devices. A couple of studies have been focused on various processing methods such as the substitution of B-site ions [7–9] or the adoption of some additives [10]. The purpose of these methods was usually to achieve modified microwave dielectric properties by forming the phase transition. However, it is very hard to obtain excellent microwave dielectric properties and simultaneously near-zero τ_f values in the final material. By contrast, near-zero τ_f values can be more easily obtained in the ceramic composite composed of two

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phases with opposite τ_f values, such as $\text{Al}_2\text{O}_3\text{-TiO}_2$, $\text{CaWO}_4\text{-TiO}_2$ and $\text{MgTiO}_3\text{-CaTiO}_3$, by altering their relative contents [11–13].

Compared with other ceramics with positive τ_f values such as TiO_2 , CaTiO_3 , etc., $\text{Ba}_3(\text{VO}_4)_2$ can be sintered at a relatively low temperature (1100 °C), except that it has a large positive τ_f value (+52 ppm/°C) and good microwave dielectric properties ($\epsilon_r \sim 14$ and $Q \times f \sim 42,000$ GHz) [14]. It was often used as a τ_f -tailoring material to construct composite ceramics, such as $\text{Ba}_3(\text{VO}_4)_2\text{-Mg}_2\text{SiO}_4$ and $\text{Ba}_3(\text{VO}_4)_2\text{-BaWO}_4$, etc. [14,15]. In these composite ceramics, different crystal structures between two phases have effectively restricted the formation of the solid solutions and the secondary phases, and guaranteed ideal microwave dielectric properties together with near-zero tunable temperature coefficients.

Zn_2SiO_4 is a potential material to be used in microwave-integrated circuits owing to its good microwave dielectric properties. Zn_2SiO_4 ceramic synthesized by the cold isostatic pressing (CIP) or sol-gel method exhibited excellent microwave dielectric properties of $\epsilon_r = 6.6$, $Q \times f = 198,400\text{--}219,000$ GHz and $\tau_f = -41.6$ to 61 ppm/°C. Its large negative τ_f values could be tailored close to zero by adding an appropriate amount of TiO_2 [16,17]. However, TiO_2 has a high sintering temperature up to 1500 °C, which tends to degrade the sinterability and microwave dielectric properties of the composite. The sol-gel method is expensive and difficult to be used in practice. Zn_2SiO_4 ceramics synthesized by a conventional solid-state method show a deteriorated $Q \times f$ value due to the presence of the ZnO secondary phase. In order to remove the ZnO secondary phase, the ceramics with the nominal composition of $\text{Zn}_{1.8}\text{SiO}_{3.8}$ sintered at 1300 °C exhibited an improved $Q \times f$ value of 147,000 GHz, an ϵ_r value of 6.6 and a τ_f value of -22 ppm/°C [18].

To the author's knowledge, no attempt has been so far made to tailor the negative τ_f value of non-stoichiometric $\text{Zn}_{2-x}\text{SiO}_{4-x}$ ceramics. As Zn_2SiO_4 has a large negative τ_f value, one can expect that a dielectric composite material with a near-zero τ_f value and a high $Q \times f$ value could be obtained by incorporating Zn_2SiO_4 and $\text{Ba}_3(\text{VO}_4)_2$. In this work, both $\text{Ba}_3(\text{VO}_4)_2$ powder and non-stoichiometric $\text{Zn}_{2-x}\text{SiO}_{4-x}$ powder without any ZnO secondary phase were separately synthesized by a conventional mixed oxide route. $(1-y)\text{Ba}_3(\text{VO}_4)_2\text{-yZn}_{2-x}\text{SiO}_{4-x}$ ($y = 0.4\text{--}0.6$, in weight percent) composite ceramics were manufactured for the first time and their microwave dielectric properties were investigated systematically.

2. Experimental procedure

$\text{Ba}_3(\text{VO}_4)_2$ and $\text{Zn}_{2-x}\text{SiO}_{4-x}$ ceramics ($0.09 \leq x \leq 0.13$) were synthesized using high-purity (>99%) oxides by means of a conventional solid-state reaction method. The mixture of BaCO_3 and V_2O_5 in a molar ratio of 1:1 was calcined at 800 °C for 4 h. The non-stoichiometric $\text{Zn}_{2-x}\text{SiO}_{4-x}$ powder was obtained by calcining the powder mixture of ZnO and SiO_2 at 1150–1175 °C for 2 h. Subsequently, the $\text{Ba}_3(\text{VO}_4)_2\text{-Zn}_{2-x}\text{SiO}_{4-x}$ composite powders ($x = 1.87$) together with 5 wt% PVA binder were ball milled for 4 h using zirconia balls and alcohol as the milling medium. The slurries were dried, and then pressed into cylinders of 10 mm in diameter and 7–8 mm in height. These specimens were first heated at 550 °C in air for 4 h to burn out the organic binder, and then sintered in air in the temperature range of 1000–1150 °C for 4 h.

The bulk densities of the sintered samples were measured by the Archimedes method. The crystal structure of the calcined powders and the sintered ceramics was examined by an X-ray diffractometer (XRD, D/Max2500V, Rigaku, Tokyo, Japan) using $\text{Cu K}\alpha$ radiation. The grain morphology and compositions were analyzed by a scanning electron microscope (SEM, SSX-550, Shimadzu, Tokyo, Japan) equipped with an energy dispersive

spectrometer (EDS). The Raman spectrum was collected at room temperature using a Raman Microscope (inVia, Renishaw, London, UK) with a backscattering configuration. An HP8720ES network analyzer (Hewlett-Packard, Santa Rosa, CA, USA) was used for the measurement of microwave dielectric properties by means of a Hakki-Coleman method [19,20]. The τ_f value of the samples was measured in the temperature range from 30 °C to 80 °C. It can be calculated by the following relationship: $\tau_f = (f_2 - f_1)/f_1(T_2 - T_1)$ where f_2 and f_1 represent the resonant frequencies at T_2 and T_1 , respectively.

3. Results and discussion

Fig. 1 represents the XRD patterns of the $\text{Zn}_{2-x}\text{SiO}_{4-x}$ powders calcined under different conditions. It can be seen that all the specimens exhibit a rhombohedral structure. A complete interaction between SiO_2 and ZnO seems difficult because the structure of crystalline SiO_2 is very stable [18,21]. As a result, the residual SiO_2 or ZnO can still exist as the secondary phase when the $\text{Zn}_{1.87}\text{SiO}_{3.87}$ ($x = 0.13$) powder was calcined at 1150 °C for 2 h, as shown in Fig. 1(a). When the ball-milled powders were calcined again at 1175 °C for 2 h, the residual ZnO phase disappeared such that all the diffraction peaks can be indexed by a single Zn_2SiO_4 phase (JCPDS #37-1485) (Fig. 1(b)). For other non-stoichiometric $\text{Zn}_{2-x}\text{SiO}_{4-x}$ powders (for example, $x = 0.11$ and 0.09), a tiny amount of ZnO phase still remained even if both the ball milling and calcination process were repeated. Considering the Zn deficiency, redundant SiO_2 should be left in the $\text{Zn}_{1.87}\text{SiO}_{3.87}$ sample although no diffraction peaks of this phase were found, probably because the majority of SiO_2 becomes amorphous after sintering [22]. Although a slight increase of the ZnO content was expected to consume the remaining SiO_2 , it was found that the content of ZnO secondary phase increased as manifested in Fig. 1(c) and (d), because a very stable structure of SiO_2 would limit its reaction with ZnO.

The XRD patterns of $(1-y)\text{Ba}_3(\text{VO}_4)_2\text{-yZn}_{1.87}\text{SiO}_{3.87}$ ($y = 0.5\text{--}0.8$) composite ceramics sintered at 1100 °C for 4 h are shown in Fig. 2. It is obvious that the main diffraction peaks can be indexed in terms of the standard patterns of Zn_2SiO_4 and $\text{Ba}_3(\text{VO}_4)_2$ (JCPDS #29-0211). Some minor peaks for unknown phases appeared at about 29°. This result indicated that the composite ceramic has been basically formed. $\text{Ba}_3(\text{VO}_4)_2$ is a hexagonal structure (R32/m) in which the V^{5+} ions are located in the center of tetrahedral $[\text{VO}_4]$ units linked by sixfold and tenfold coordinated Ba^{2+} ions [23].

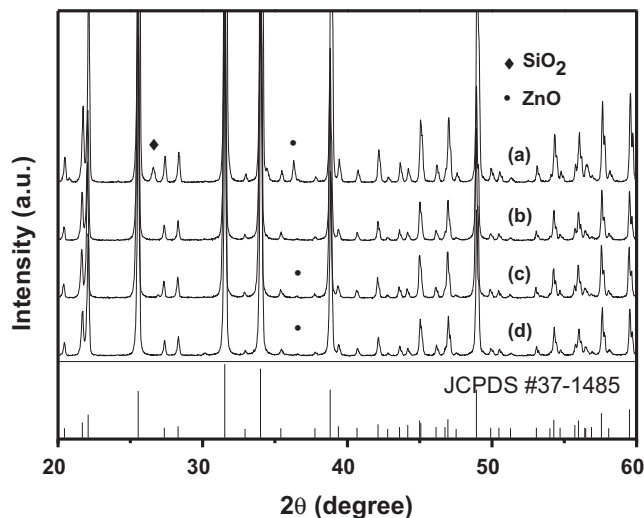


Fig. 1. XRD patterns of $\text{Zn}_{2-x}\text{SiO}_{4-x}$ powders (a) $x = 0.13$ calcined at 1150 °C for 2 h, (b) $x = 0.13$, (c) $x = 0.11$, and (d) $x = 0.09$ calcined at 1175 °C again for 2 h.

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