



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

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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].

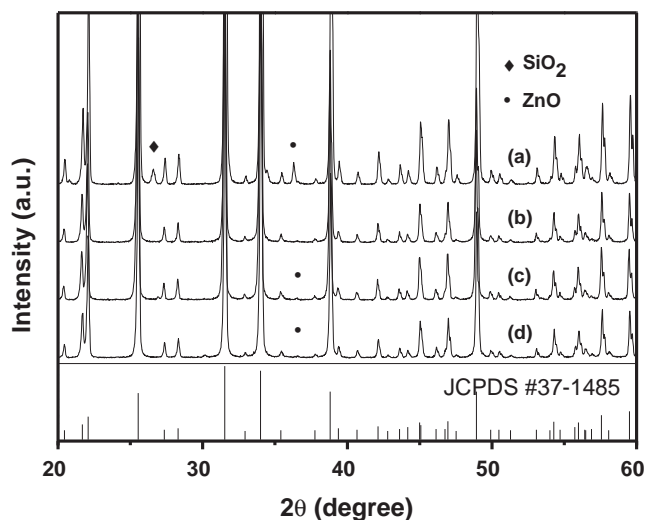


Fig. 1. XRD patterns of $\text{Zn}_{2-x}\text{SiO}_{4-x}$ powders (a) $x = 0.13$ calcined at 1150 °C for 2 h, (b) $x = 0.13$, (c) $x = 0.11$, and (d) $x = 0.09$ calcined at 1175 °C again for 2 h.

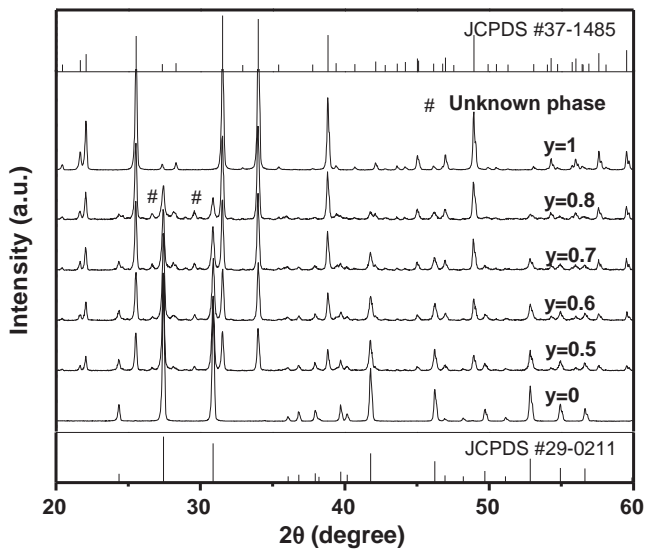


Fig. 2. X-ray diffraction patterns of $(1-y)\text{Ba}_3(\text{VO}_4)_2-y\text{Zn}_{1.87}\text{SiO}_{3.87}$ ceramics sintered at 1100°C for 4 h, as compared to the standard patterns of $\text{Ba}_3(\text{VO}_4)_2$ and Zn_2SiO_4 .

However, Zn_2SiO_4 has a rhombohedral symmetry and Zn^{2+} occupies the tetrahedral site of $[\text{ZnO}_4]$ units in which the Si–O covalent bonding is strong, making the $[\text{SiO}_4]$ tetrahedrons highly stable [18]. Both the difference and stability in the crystal structure of two phases guarantee the formation of the composite ceramics [24,25]. However, it can be found that the content of unknown secondary phases in the composite ceramics increases with increasing the y value in the raw powder mixture, suggesting that the unknown phase might be silicon-rich.

The bulk densities of the $(1-y)\text{Ba}_3(\text{VO}_4)_2-y\text{Zn}_{1.87}\text{SiO}_{3.87}$ ceramics ($y = 0.4\text{--}0.6$) sintered at various temperatures are shown in Fig. 3. It can be observed that the bulk densities of the samples increase with increasing the $\text{Zn}_{1.87}\text{SiO}_{3.87}$ content. Moreover, the densification of all samples could be enhanced with increasing the sintering temperature and then started to decline after a maximum value was reached. The maximum density was found to appear in the temperature range of $1050\text{--}1100^\circ\text{C}$. The density of the composite is roughly between those of each single-phase ceramic (see the inset of Fig. 3). However, compared to the stoichiometric Zn_2SiO_4 ceramic [16,17], the optimum sintering temperature of the

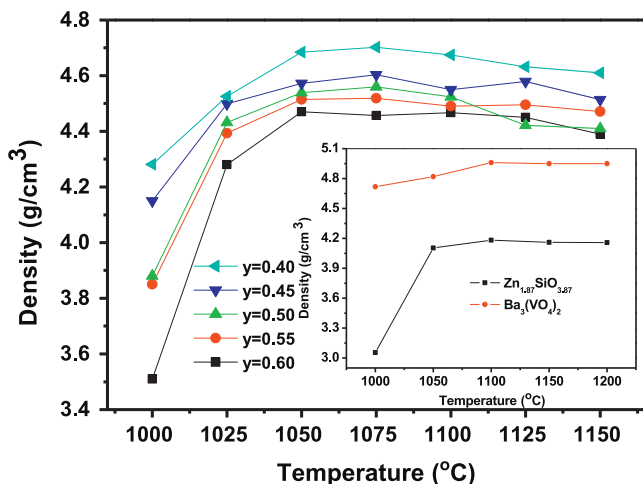


Fig. 3. Variations in bulk density of the $(1-y)\text{Ba}_3(\text{VO}_4)_2-y\text{Zn}_{1.87}\text{SiO}_{3.87}$ ceramics sintered at $1000\text{--}1150^\circ\text{C}$ for 4 h.

composite was obviously decreased. The enhanced sintering behavior might be attributed to two factors. One could be related to the existence of silicon-rich secondary phases from the Zn-deficient $\text{Zn}_{1.87}\text{SiO}_{3.87}$, which might have a relatively low melting point. Another could be associated with the relatively low sintering temperature of $\text{Ba}_3(\text{VO}_4)_2$ itself [14]. As the sintering temperature is too high, the fast or discontinuous grain growth would inhibit the extraction of pores from the sample body, causing the degradation of the sintering density [26].

Fig. 4 shows the SEM micrographs of the $(1-y)\text{Ba}_3(\text{VO}_4)_2-y\text{Zn}_{1.87}\text{SiO}_{3.87}$ composite ceramics sintered at 1100°C . It can be observed that all samples exhibit a bimodal grain size distribution. Two types of grains (Fig. 4(b)) own different grain sizes: $\sim 5\ \mu\text{m}$ for one marked 1 and $\sim 2\ \mu\text{m}$ for another marked 2. The composition analysis of these types of grains was carried out by EDS, as shown in Table 1. On the one hand, it is indicated that the big grain with an approximate ratio of Ba:V:O = 3:2:8 should belong to the $\text{Ba}_3(\text{VO}_4)_2$ phase. The element ratio of Zn:Si:O for small grains approximately reaches 2:1:4, meaning that they belong to the Zn_2SiO_4 phase. The similar result was apparently shown in the backscattered electron image (Fig. 4(d)), in which brighter grains containing heavy atoms should be $\text{Ba}_3(\text{VO}_4)_2$, while the dark ones should be Zn_2SiO_4 . On the other hand, the existence of a small amount of Ba and V in the small grain or the existence of a small amount of Zn in bigger grains could be ascribed to the interdiffusion between the grains. Previous studies have demonstrated that the pure-phase Zn_2SiO_4 ceramic has a much higher sintering temperature (1300°C) than that of the $\text{Ba}_3(\text{VO}_4)_2$ ceramic (1100°C) [14,16,17]. But the nonstoichiometric $\text{Zn}_{1.87}\text{SiO}_{3.87}$ ceramic can be sintered well at 1100°C (Fig. 4(g)). The blurred grain morphology indicates the symptom of the liquid phase sintering. This to some extent accounts for the contribution of silicon-rich secondary phases. This also explains why the nonstoichiometric $\text{Zn}_{1.87}\text{SiO}_{3.87}$ ceramic can be sintered at a relatively low temperature compared to the stoichiometric one. Noticeably, the backscattered electron image of the $(1-y)\text{Ba}_3(\text{VO}_4)_2-y\text{Zn}_{1.87}\text{SiO}_{3.87}$ ($y = 0.45$) sample (Fig. 4(d)) showed that there exist two distinct kinds of grains, which supports the conclusion from the XRD results that the sintered samples contain two separate phases of $\text{Ba}_3(\text{VO}_4)_2$ and Zn_2SiO_4 . As the sintering temperature rises to 1150°C , the composite sample has more porosity and much bigger average grain sizes (Fig. 4(f)). This observation keeps good consistence with the measurement of the density (Fig. 3).

The Raman spectra of the $(1-y)\text{Ba}_3(\text{VO}_4)_2-y\text{Zn}_{1.87}\text{SiO}_{3.87}$ composite ceramics are shown in Fig. 5. The respective Raman spectrum of the pure $\text{Ba}_3(\text{VO}_4)_2$ ceramic and $\text{Zn}_{1.87}\text{SiO}_{3.87}$ ceramic was also plotted for comparison. The Raman bands of the pure $\text{Ba}_3(\text{VO}_4)_2$ phase can be distributed in three well-separated frequency regions corresponding to the internal stretching of $[\text{VO}_4]$ modes (V–O stretching modes, $850\text{--}750\ \text{cm}^{-1}$), the internal bending of $[\text{VO}_4]$ modes (O–V–O bending modes, $450\text{--}300\ \text{cm}^{-1}$), and translational and rotational modes of the $[\text{VO}_4]$ units mixed with the Ba^{2+} displacements ($250\text{--}120\ \text{cm}^{-1}$) [27]. However, the main Raman-active modes of $\text{Zn}_{1.87}\text{SiO}_{3.87}$ at $864\ \text{cm}^{-1}$, $901\ \text{cm}^{-1}$ and $940\ \text{cm}^{-1}$ can be ascribed to the stretching and bending vibrations of the $[\text{SiO}_4]$ tetrahedra [28]. According to the Raman spectrum of the single phase, all the Raman-active modes in the $(1-y)\text{Ba}_3(\text{VO}_4)_2-y\text{Zn}_{1.87}\text{SiO}_{3.87}$ composite ceramics can be identified, which belong to the $\text{Ba}_3(\text{VO}_4)_2$ phase (marked by the red wavenumber) and the Zn_2SiO_4 phase (marked by the blue wavenumber), respectively. This further confirmed that the composite ceramics were generally formed. Compared to single-phase $\text{Ba}_3(\text{VO}_4)_2$ ceramics, the Raman spectra of the $\text{Ba}_3(\text{VO}_4)_2$ phase in the composite were barely changed. A slight shift of low frequency peaks from $92\ \text{cm}^{-1}$ for the $\text{Ba}_3(\text{VO}_4)_2$ ceramics to

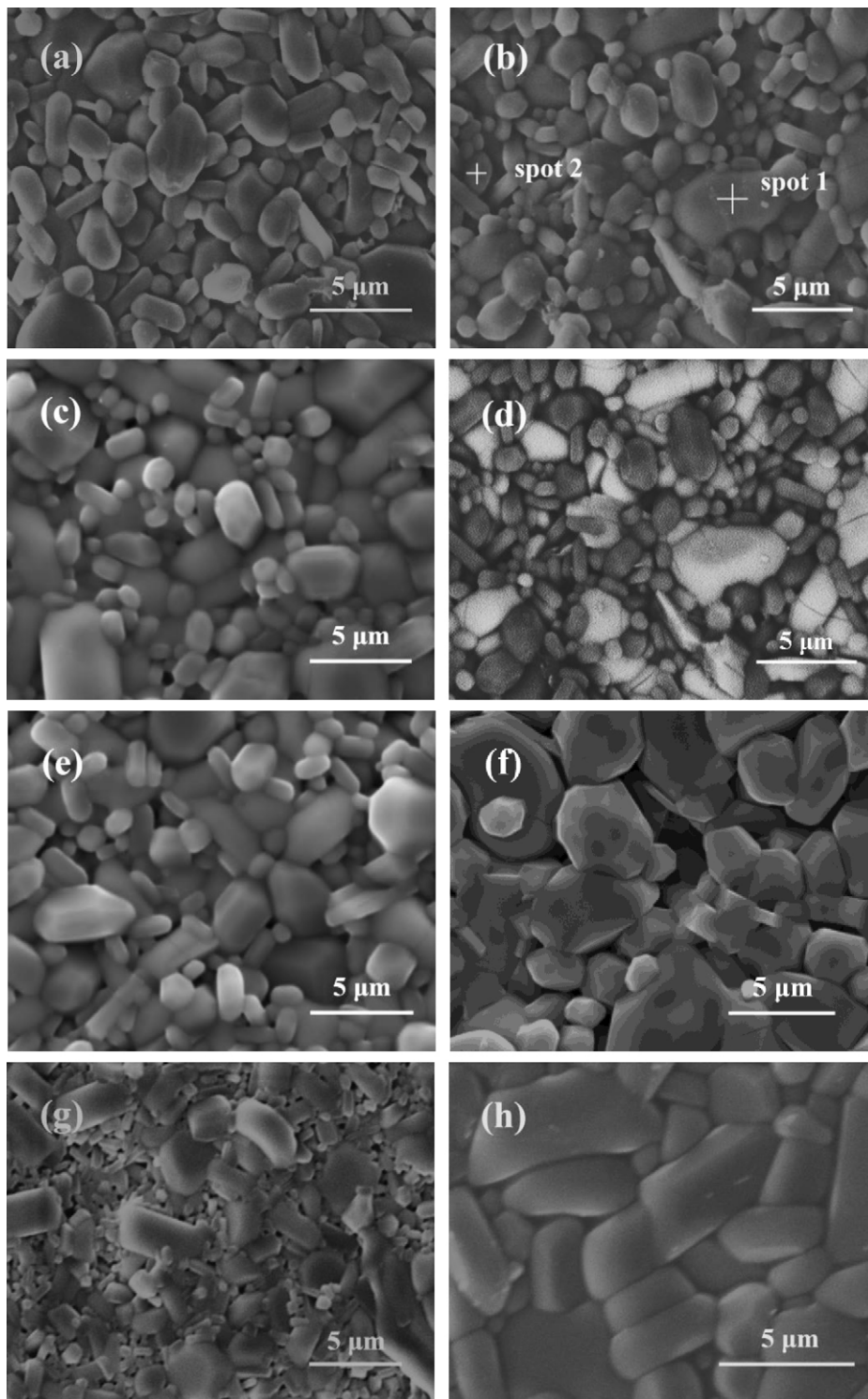


Fig. 4. Scanning electron microscopy images of the $(1 - y)\text{Ba}_3(\text{VO}_4)_2 - y\text{Zn}_{1.87}\text{SiO}_{3.87}$ ceramics: (a) $y = 0.40$, at 1100°C , (b) $y = 0.45$, at 1100°C , (c) $y = 0.50$, at 1100°C , (d) $y = 0.45$, at 1100°C , (e) $y = 0.55$, at 1100°C , (f) $y = 0.45$, at 1150°C , (g) $y = 1$, and (h) $y = 0$, at 1100°C .

102 cm^{-1} for the composite can be explained by the displacements of a small amount of Ba^{2+} , as confirmed by the EDS result. Moreover, The vibration band at 864 cm^{-1} corresponding to the Zn_2SiO_4 phase in the composite was spilt into some multiple bands with higher frequencies (see the inset of Fig. 5), such as 870 cm^{-1} , 883 cm^{-1} , and 891 cm^{-1} vibration bands. This can be explained by the distorted tetrahedral groups possibly caused by the silicon-rich secondary phases [28].

The dielectric constants of the $(1 - y)\text{Ba}_3(\text{VO}_4)_2 - y\text{Zn}_{1.87}\text{SiO}_{3.87}$ composite ceramics sintered at different temperatures are shown in Fig. 6. With increasing y from 0.4 to 0.6, the ϵ_r values of the composite specimens can be adjusted from 9.8 to 6.8. It can be also seen that the ϵ_r values are highly dependent on the relative density of the sintered bodies. Therefore, the tendency of the dielectric constant versus the sintering temperature (Fig. 6) is very similar to that of the bulk density versus the sintering temperature (Fig. 3).

Table 1
EDS analysis of $0.55\text{Ba}_3(\text{VO}_4)_2-0.45\text{Zn}_{1.87}\text{SiO}_{3.87}$ ceramics sintered at 1100°C .

| Elements | Atom % | |
|----------|---------|---------|
| | Point 1 | Point 2 |
| Zn | 1.97 | 22.82 |
| Si | 0 | 14.23 |
| Ba | 26.36 | 6.27 |
| V | 16.98 | 2.80 |
| O | 54.69 | 53.88 |
| Total | 100.00 | 100.00 |

Moreover, it can be found that the dielectric constant of the $(1-y)\text{Ba}_3(\text{VO}_4)_2-y\text{Zn}_{1.87}\text{SiO}_{3.87}$ composite ceramics is approximately in between those of $\text{Ba}_3(\text{VO}_4)_2$ and $\text{Zn}_{1.87}\text{SiO}_{3.87}$ ceramics (see the inset of Fig. 6). This is basically ascribed to the mixing rule of dielectrics as expressed by the Maxwell–Wagner’s equation [29]. For the same reason, the dielectric constant of the composite ceramics at the same sintering temperature was found to increase with increasing the content of $\text{Ba}_3(\text{VO}_4)_2$, owing to higher ϵ_r values of $\text{Ba}_3(\text{VO}_4)_2$ than $\text{Zn}_{1.87}\text{SiO}_{3.87}$ (see the inset of Fig. 6). As a result, the adjustment of the volume ratio of $\text{Ba}_3(\text{VO}_4)_2$ and $\text{Zn}_{1.87}\text{SiO}_{3.87}$ phases can not only help achieve a modified sintering behavior and but also obtain an appropriate dielectric constant value.

The $Q \times f$ value is usually affected not only by the lattice vibrational modes but also by the pores, the second phases, the impurities, the lattice defect and crystallizability [30]. The relationship between the $Q \times f$ values, the sintering temperature and the compositions of the ceramics is shown in Fig. 7. It is obvious that the $Q \times f$ value of the composite ceramics generally increases with increasing the sintering temperature and the content of $\text{Zn}_{1.87}\text{SiO}_{3.87}$ phase, probably because of the variation of the sample density. The maximum $Q \times f$ values can be achieved for the specimens sintered at $1075-1100^\circ\text{C}$. A further increase of the sintering temperature tends to cause a decrease of the $Q \times f$ value. Moreover, higher sintering temperatures tend to aggravate the reaction between two single-phase grains. This explanation might also apply to the variation of the dielectric constant (see Fig. 6). Although the $Q \times f$ values of the composite ceramics are roughly between those of single-phase materials (see the inset of Fig. 7), they seem too low. Even for those composites with larger amount

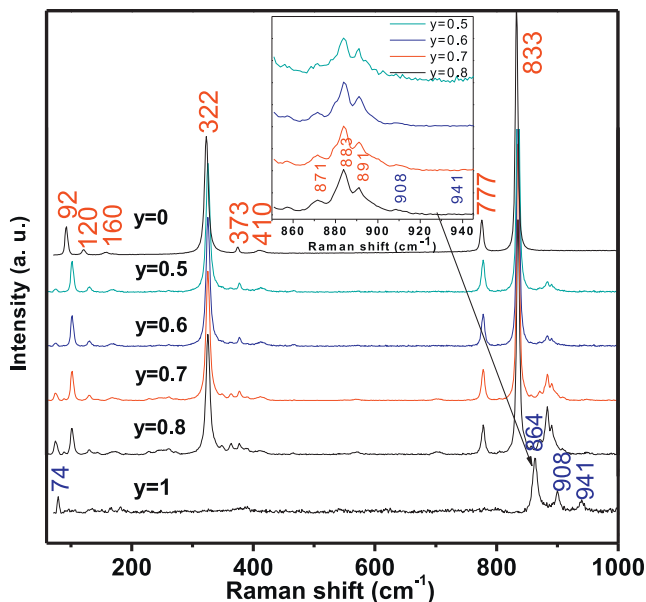


Fig. 5. Raman spectra of the $(1-y)\text{Ba}_3(\text{VO}_4)_2-y\text{Zn}_{1.87}\text{SiO}_{3.87}$ ceramics sintered at 1100°C for 4 h.

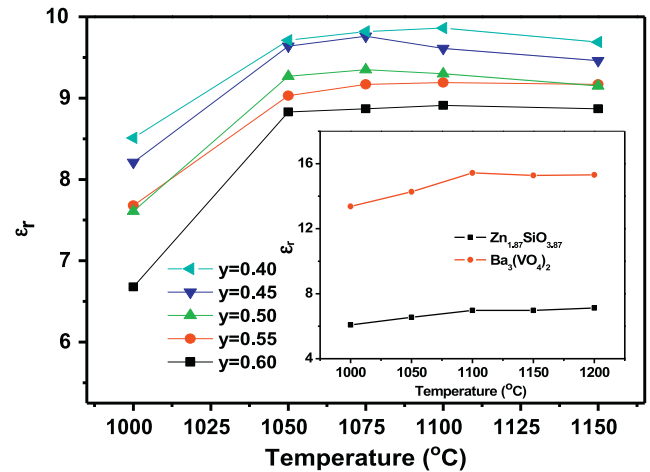


Fig. 6. Dielectric constant of $(1-y)\text{Ba}_3(\text{VO}_4)_2-y\text{Zn}_{1.87}\text{SiO}_{3.87}$ ceramics as function of sintering temperature.

of $\text{Zn}_{1.87}\text{SiO}_{3.87}$ ($y = 0.6$), their $Q \times f$ values ($\sim 25,000$ GHz) are still far away from those ($90,000-100,000$ GHz) of the $\text{Zn}_{1.87}\text{SiO}_{3.87}$ ceramics prepared in this study. By comparing Figs. 6 and 7, it can be found that the sintering of the composite ceramics has a bigger effect on the $Q \times f$ values than the dielectric constant. A small amount of secondary phases (see Fig. 2) might have an influence on both of them but should not make such a big difference. EDS analysis in Table 1 has indicated that the interdiffusion of a slight amount of elements such as Ba, V and Zn occurs during cofiring of two phases. The results mean that the diffusion of Ba and/or V into the lattice of $\text{Zn}_{1.87}\text{SiO}_{3.87}$ phase has significantly deteriorated its $Q \times f$ values compared to its dielectric constant. The polarizability (α_D) and molar volume (v_m) determine the dielectric constant, according to the Clausius–Mossotti equation [31]:

$$\frac{\epsilon_r - 1}{\epsilon_r + 1} = \left(\frac{4\pi}{3}\right) \left(\frac{\alpha_D}{v_m}\right) \quad (1)$$

The molecular polarizabilities of the complex substances can be broken up into the polarizabilities of constituent ions. As a result, even though the ion diffusion exists in the composite, the molecular polarizabilities of the composite are nearly constant. According to the XRD results of the composite, the molar volume of

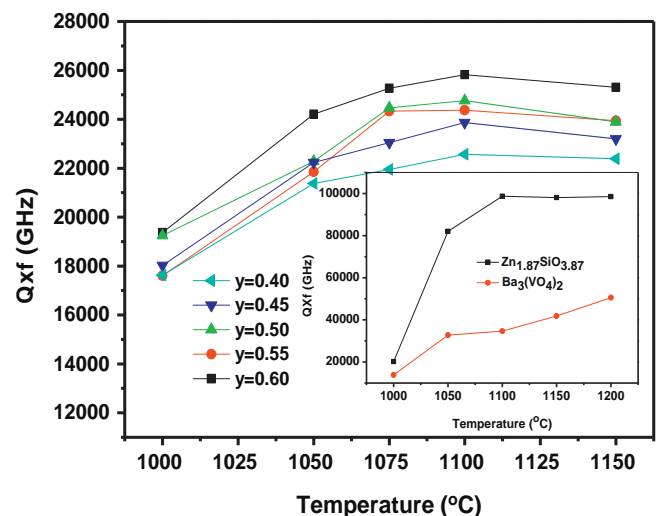


Fig. 7. $Q \times f$ values of $(1-y)\text{Ba}_3(\text{VO}_4)_2-y\text{Zn}_{1.87}\text{SiO}_{3.87}$ ceramics sintered under various temperatures.

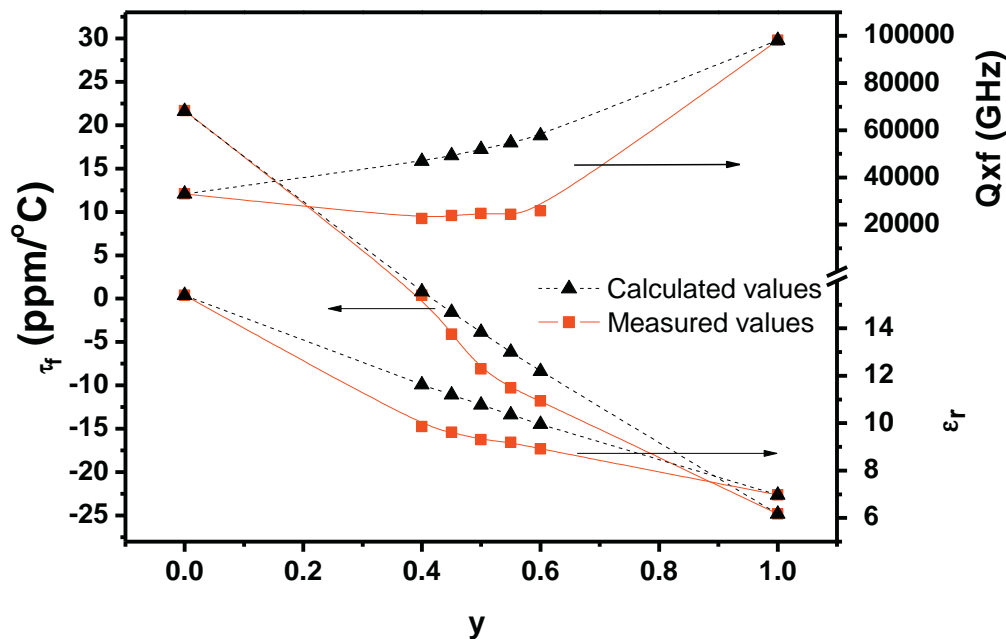


Fig. 8. The calculated or measured microwave dielectric properties of $(1-y)\text{Ba}_3(\text{VO}_4)_2-y\text{Zn}_{1.87}\text{SiO}_{3.87}$ ceramics sintered at 1100°C for 4 h.

the two phases only slightly changes from $205.8 \text{ \AA}^3/\text{mol}$ to $206.07 \text{ \AA}^3/\text{mol}$ for $\text{Ba}_3(\text{VO}_4)_2$, and $86.95 \text{ \AA}^3/\text{mol}$ to $86.99 \text{ \AA}^3/\text{mol}$ for $\text{Zn}_{1.87}\text{SiO}_{3.87}$, respectively. On the basis of the high density of the sintered composites (Fig. 4), the fluctuation of the dielectric constant caused by the ion diffusion is thus negligible. However, the Zn deficiency would introduce a series of lattice defects in the crystal, apart from the distortion of the $[\text{ZnO}_4]$ tetrahedron. Therefore, the inner stress in the willemite crystals tends to increase such that the $Q \times f$ values are deteriorated. The Zn-deficient $\text{Zn}_{1.87}\text{SiO}_{3.87}$ ceramic has much lower microwave dielectric properties than the stoichiometric Zn_2SiO_4 ceramics ($Q \times f \sim 198,000 \text{ GHz}$, $\epsilon_r \sim 6.6$) [14]. This becomes one of the reasons for the relatively low $Q \times f$ values of $(1-y)\text{Ba}_3(\text{VO}_4)_2-y\text{Zn}_{1.87}\text{SiO}_{3.87}$ composite ceramics. Moreover, the grain sizes of the $(1-y)\text{Ba}_3(\text{VO}_4)_2-y\text{Zn}_{1.87}\text{SiO}_{3.87}$ composite ceramics become smaller than those of single phase $\text{Ba}_3(\text{VO}_4)_2$ or $\text{Zn}_{1.87}\text{SiO}_{3.87}$ ceramics (Fig. 4(g) and (h)). Smaller grains would introduce more grain boundaries, which also contribute to the low $Q \times f$ value. The grain boundaries in polycrystalline ceramics usually act as a sink for impurities and thus have a deleterious effect on the microwave loss.

In addition to the above-mentioned two parameters, the τ_f value of the composite ceramics can be also adjusted by changing the relative content of two phases. This is also the reason why we chose $\text{Ba}_3(\text{VO}_4)_2$ and $\text{Zn}_{1.87}\text{SiO}_{3.87}$ to prepare microwave composite ceramics, both of which exhibit τ_f values with opposite signs except for their low dielectric constants and high $Q \times f$ values. It can be seen from Fig. 8 that with increasing the content of $\text{Ba}_3(\text{VO}_4)_2$, the τ_f values of the composites change from large

negative values close to positive values. A near zero τ_f value was achieved in the composition range of $y = 0.4\text{--}0.5$. According to the above discussion, the variation in microwave dielectric properties of the composite ceramics is basically related to the relative phase content of $\text{Ba}_3(\text{VO}_4)_2$ and Zn_2SiO_4 . The microwave dielectric properties of the composite ceramics can be therefore predicted by using the following equations [32]:

$$\ln \epsilon_r = V_1 \ln \epsilon_1 + V_2 \ln \epsilon_2 \quad (2)$$

$$Q^{-1} = V_1 Q_1^{-1} + V_2 Q_2^{-1} \quad (3)$$

$$\tau_f = V_1 \tau_{f1} + V_2 \tau_{f2} \quad (4)$$

where V is the volume fraction of each phase. The subscripts 1 and 2 stand for $\text{Ba}_3(\text{VO}_4)_2$ and Zn_2SiO_4 phases, respectively. The volume fractions could be calculated from the weight fraction of each phase, respectively. The Q values in the equation can be replaced by the $Q \times f$ values. The properties of single-phase ceramics were measured (see the inset of Figs. 6 and 7). It can be found that almost all experimentally measured values are smaller than the calculated ones. These differences might be attributed to various factors. The parasitical secondary phases and slight inter-diffusion of elements, which have been confirmed by XRD and EDS, would be responsible for the above deviation. The change of the grain morphology and size, the porosity, the distribution uniformity of two phases and even element doping effects would make additional contributions. Nevertheless, the composite ceramics with excellent microwave dielectric properties of $\tau_f \sim 0.4 \text{ ppm/}^\circ\text{C}$, $Q \times f \sim 23,000 \text{ GHz}$, and

Table 2

A comparison of microwave dielectric properties of some ceramics.

| Materials | ϵ_r | $Q \times f$ (GHz) | τ_f (ppm/ $^\circ\text{C}$) | S.T. ($^\circ\text{C}$) |
|--|--------------|--------------------|-----------------------------------|---------------------------|
| Zn_2SiO_4 [17] | 6.6 | 219,000 | -61 | 1300 |
| MgAl_2O_4 [33] | 7.9 | 82,000 | -73 | 1500 |
| $0.6\text{Ba}_3(\text{VO}_4)_2-0.4\text{Zn}_{1.87}\text{SiO}_{3.87}$ [this work] | 9.3 | 23,000 | 0.4 | 1050 |
| $0.83\text{ZnAl}_2\text{O}_4-0.17\text{TiO}_2$ [34] | 11.7 | 90,000 | 1.4 | 1450 |
| $0.6\text{BaMoO}_4-0.4\text{TiO}_2$ [35] | 13.8 | 40,500 | -6.1 | 1250 |
| $0.95\text{Zn}_2\text{SiO}_4-0.05\text{CaTiO}_3$ [36] | 8.2 | 20,000 | 0.8 | 1200 |

$\epsilon_r \sim 9.3$ have been obtained by adjusting $y = 0.4\text{--}0.5$ and controlling the sintering temperatures at 1100°C . A comparison between the literature work and the current work was made, as shown in Table 2. By comparison, the composites prepared in this study not only have desirable microwave dielectric properties but also have a relatively low sintering temperature. The potential of these composites would be significantly magnified by further increasing the $Q \times f$ values. We have realized that it would be a hopeful measure to optimize the phase-purity of the willemite phase and its stoichiometry. The relevant work is underway.

4. Conclusions

The novel microwave dielectric composite ceramics have been manufactured by cofiring the mixed-powder compacts of $\text{Ba}_3(\text{VO}_4)_2$ and of $\text{Zn}_{2-x}\text{SiO}_{4-x}$. The phase structure, sintering behavior, grain morphology and various microwave dielectric properties were investigated. The XRD, SEM and Raman spectra results indicate that Zn_2SiO_4 with a willemite structure could be obtained by controlling a slight amount of Zn deficiency, and that a small amount of unknown secondary phases exist in the final composite except for two expected phases. Several factors such as non-stoichiometry, element inter-diffusion and varied grain size or morphology, etc., make the predicted property values deviate from the experimentally measured ones although the tendency of the properties with the fraction of the respective phase is generally right. The $(1-y)\text{Ba}_3(\text{VO}_4)_2-y\text{Zn}_{2-x}\text{SiO}_{4-x}$ composite ceramics ($y \sim 0.4\text{--}0.5$ and $x = 0.13$) sintered at 1100°C exhibited excellent microwave dielectric properties of $Q \times f \sim 23,000$ GHz, $\epsilon_r \sim 9.3$, and $\tau_f \sim 0.4$ ppm/ $^\circ\text{C}$.

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References

- [1] H.F. Zhou, X.L. Chen, L. Fang, X.B. Liu, Y.L. Wang, *J. Am. Ceram. Soc.* 93 (2010) 3976–3979.
- [2] W. Lei, W.Z. Lu, D. Liu, J.H. Zhu, *J. Am. Ceram. Soc.* 92 (2009) 105–109.
- [3] M. Guo, S.P. Gong, G. Dou, D.X. Zhou, *J. Alloy. Compd.* 509 (2011) 5988–5995.
- [4] K.P. Surendran, P.V. Bijumon, P. Mohanan, M.T. Sebastian, *Appl Phys. A* 81 (2005) 823–826.
- [5] A. Kan, H. Ogawa, H. Ohsato, S. Ishihara, *J. Euro. Ceram. Soc.* 21 (2001) 2593–2598.
- [6] V.M. Ferreira, F. Azough, J.L. Baptista, R. Freer, *Ferroelectrics* 133 (1992) 127–132.
- [7] F. Zhao, Z.X. Yue, J. Pei, Z.L. Gui, L.T. Li, *Appl. Phys. Lett.* 90 (2007) 142908.
- [8] A. Kan, H. Ogawa, K. Mori, H. Ohsato, Y. Andou, *J. Mater. Res.* 18 (2003) 2427–2434.
- [9] Y.Y. Zhou, S.Q. Meng, H.C. Wu, Z.X. Yue, *J. Am. Ceram. Soc.* 94 (2011) 2933–2938.
- [10] E.S. Kim, S.H. Kim, B.I. Lee, *J. Eur. Ceram. Soc.* 26 (2006) 2101–2104.
- [11] C.L. Huang, J.J. Wang, C.Y. Huang, *J. Am. Ceram. Soc.* 90 (2007) 1487–1493.
- [12] S.H. Yoon, G.K. Choi, D.W. Kim, S.Y. Cho, K.S. Hong, *J. Eur. Ceram. Soc.* 27 (2007) 3087–3091.
- [13] L. Li, X.M. Chen, X.C. Fan, *J. Eur. Ceram. Soc.* 26 (2006) 3265–3271.
- [14] S.Q. Meng, Z.X. Yue, H. Zhuang, F. Zhao, L.T. Li, *J. Am. Ceram. Soc.* 93 (2010) 359–361.
- [15] H. Zhuang, Z.X. Yue, S.Q. Meng, F. Zhao, L.T. Li, *J. Am. Ceram. Soc.* 91 (2008) 3738–3741.
- [16] M.Z. Dong, Z.X. Yue, H. Zhuang, S.Q. Meng, L.T. Li, *J. Am. Ceram. Soc.* 91 (2008) 3981–3985.
- [17] Y.P. Guo, H. Ohsato, K.I. Kakimoto, *J. Eur. Ceram. Soc.* 26 (2006) 1827–1830.
- [18] N.H. Nguyen, J.B. Lim, S. Nahm, J.H. Paik, J.H. Kim, *J. Am. Ceram. Soc.* 90 (2007) 3127–3130.
- [19] B.W. Hakki, P.D. Coleman, *IEEE. Trans. Microwave. Theory. Technol.* 8 (1960) 402–410.
- [20] W.E. Courtney, *IEEE. Trans. Microwave. Theory. Technol.* 18 (1970) 476–485.
- [21] J.S. Kim, N.H. Nguyen, J.B. Lim, D.S. Paik, S. Nahm, J.H. Paik, J.H. Kim, *J. Am. Ceram. Soc.* 91 (2008) 671–674.
- [22] K.X. Song, X.M. Chen, X.C. Fan, *J. Am. Ceram. Soc.* 90 (2007) 1808–1811.
- [23] M.H. Whitmore, H.R. Verdun, D.J. Singel, *Phys Rev. B* 47 (1993) 11479–11482.
- [24] I.H. Park, B.S. Kim, K.Y. Kim, B.H. Kim, *Jpn. J. App. Phys.* 40 (2001) 4956–4960.
- [25] H. Ogawa, A. Yokoi, R. Umemura, A. Kan, *J. Eur. Ceram. Soc.* 27 (2007) 3099–3104.
- [26] H. Zhuang, Z.X. Yue, F. Zhao, L.T. Li, *J. Am. Ceram. Soc.* 91 (2008) 3275–3279.
- [27] A. Grzechnik, P.F. McMillan, *J. Solid. State. Chem.* 132 (1997) 156–162.
- [28] T.A. Sidorov, *Russ. J. Inog. Chem.* 52 (2007) 1586–1594.
- [29] Y.G. Wu, X.H. Zhao, F. Li, Z.G. Fan, *J. Electrom.* 11 (2003) 227–239.
- [30] J.D. Breeze, J.M. Perkins, D.W. McComb, N.M. Alford, *J. Am. Ceram. Soc.* 92 (2009) 671–674.
- [31] R.D. Shannon, *J. Appl. Phys.* 73 (1993) 348–366.
- [32] L. Huang, Y.W. Tseng, Y.C. Kuo, *J. Am. Ceram. Soc.* 94 (2011) 2963–2967.
- [33] C.W. Zheng, S.Y. Wu, X.M. Chen, K.X. Song, *J. Am. Ceram. Soc.* 90 (2007) 1483–1486.
- [34] S. Thomas, M.T. Sebastian, *Mater. Res. Bull.* 43 (2008) 843–851.
- [35] J. Guo, D. Zhou, H. Wang, Y.H. Chen, Y. Zeng, F. Xiang, Y. Wu, X. Yao, *J. Am. Ceram. Soc.* 95 (2012) 232–237.
- [36] G. Dou, D.X. Zhou, M. Guo, S.P. Gong, *J. Alloy. Compd.* 513 (2012) 466–473.