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Effects of heating rate on microstructures and microwave dielectric properties of $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics

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Abstract

$(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics were synthesized at 1500 °C for 3 h using the solid-state reaction at a heating rate from 1 to 7 °C/min. The effects of heating rate on the microstructure, phase composition and oxidation state of titanium in the ceramics were investigated. The XRD results show that this system is composed of two phases, i.e. $ZnAl_2O_4$ spinel and rutile. The ''black core'' phenomenon resulting from reduction of Ti^{4+} ion valence appears after the ceramics are sintered at the speed of 1 and 3 °C/min. As the heating rate increases, the density and quality factor ($Q{\cdot}f$) increase initially and reach the maximum value when the heating rate is 5 °C/min, and then reduce quickly to the minimum, while the dielectric constant (ε_r) and temperature coefficient of resonator frequency (τ_f) nearly do not change. The optimal microwave dielectric properties can be achieved in $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics sintered at a heating rate of 5 °C/min with an ε_r value of 11.6, a $Q{\cdot}f$ value of 74,000 GHz (at about 6.5 GHz), and a τ_f value of −0.4 ppm/°C.

Keywords: Dielectric properties; Ceramics; X-ray diffraction; $ZnAl_2O_4$–TiO_2

1. Introduction

Nowadays microwave dielectric materials with low dielectric constant ($\varepsilon_r < 15$) have attracted much scientific and commercial attention. In the case of microwave substrate and antenna application, low dielectric constant can minimize cross-coupling with conductors and shorten the time for the electronic signal transition. In additional, high quality factor ($Q{\cdot}f$) to increase selectivity and near-zero temperature coefficient of resonator frequency (τ_f) to ensure the stability of the frequency against temperature change are also required [1,2].

$(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics with low ε_r value is a promising candidate for microwave substrate and antenna [3]. In light of Zn ion evaporates [4] and the valence of Ti element changes [5] easily at high temperature, heating rate is of great importance to control the microstructures and microwave dielectric properties [6,7]. In the present study, the effects of heating rate on the microstructures, the oxidation state of Ti element and microwave dielectric properties in the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics were investigated.

2. Experimental

Reagent grade ceramic powders ZnO (99.5%), Al_2O_3 (98.5%) and TiO_2 (Rutile, 99.5%) were used as raw materials. Stoichiometric starting powder according to the composition of $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) was milled with agate balls in ethanol for 3 h at a speed of 360 rpm (rotation per minute). The slurry was dried at 80 °C in an infrared stove, and then calcined in air at 1150 °C for 3 h. After milling and drying again, the calcined powder added with 7 wt.% polyvinyl alcohol whose concentration of the aqueous solution is 5 wt.% as a binder was uniaxially pressed into the samples with dimensions of 20 mm in diameter and about 11 mm in height under a pressure of 150 MPa. These samples were sintered at 1500 °C for 3 h in air, with different heating rate of 1, 3, 5 and 7 °C/min. The samples were cooled at a rate of 2 °C/min up to 1000 °C and then they were furnace cooled.

The bulk densities of the sintered samples were measured using the Archimedes method. The crystalline phases were analyzed by means of the X-ray diffraction method using Cu

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Kα radiation (XRD; X'Pert PRO). The microstructure observation was performed by scanning electron microscope (SEM; FEI-Sirion 200). The chemical state of Ti element was confirmed by X-ray photoelectron spectroscopy (XPS; VG Multilab 2000). The dielectric constant (ε_r) and the unloaded $Q{\cdot}f$ value were measured in the TE011 mode by Hakki and Coleman method [8] using an Advantest R3767C network analyzer and parallel silver boards. The temperature coefficient of resonant frequency (τ_f) in the temperature range of 20–80 °C was calculated by formula (1):

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

where f_1 and f_2 represent the resonant frequency at T_1 and T_2, respectively.

3. Results and discussion

X-ray diffraction patterns of the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics sintered at 1500 °C for 3 h by different heating rate are shown in Fig. 1. According to JCPDS card No. 82-1043 and No. 89-4920 respectively, $ZnAl_2O_4$ and rutile phases exist in the sintered samples. As a whole, the X-ray diffraction intensity of $ZnAl_2O_4$ phase decreases whereas that of rutile phase increases gradually with an increase in heating rate. However, it is interesting that the diffraction intensity of $ZnAl_2O_4$ and rutile phases in the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics sintered at a heating rate of 5 °C/min both enhances dramatically which indicates the improvement of crystallizability. Moreover, the rutile X-ray diffraction spectra in Fig. 1(a–c) exhibit noticeable difference in the peak intensity, compared with the standard spectra. That is, the TiO_2 grains in the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics only except for the one sintered at a heating rate of 5 °C/min have preferential orientation along the [1 0 1] direction. The orientation of crystalline grains may depend on the direction and position of the measured samples. To further understand the phenomenon, the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics sintered at different heating rate of 1, 3, 5 and 7 °C/min were grinded in crucible and then sieved through 325 mesh, respectively. The X-ray diffraction analysis of the above ceramic powders was performed and the results are shown in Fig. 2. It is known from Fig. 2 that the X-ray diffraction intensity of rutile does not nearly change while that of the $ZnAl_2O_4$ phase initially enhances with increase of heating rate and reaches the maximum at a heating of 5 °C/min, and then reduces slightly at 7 °C/min, which confirms further the best crystallizability in the ceramics sintered at a heating rate of 5 °C/min. Moreover, it can be found in Fig. 2 that the preferential orientation of grains do not appear in the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) system. The Al_2TiO_5 phase in the ceramic powders could result from the crucible.

Fig. 3 shows SEM micrographs in cross-section of the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics sintered at 1500 °C by different heating rate and etched at 1400 °C for 1 h. Clearly, bigger and smaller grains are comprised in the system of $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics. EDX analysis has confirmed that the bigger grains are TiO_2 and the smaller are $ZnAl_2O_4$ [3]. The TiO_2 grain size is very sensitive to the heating rate while the $ZnAl_2O_4$ grain size nearly does not change with the heating rate, as shown in Fig. 3. As the heating rate increases from 1 to 3 °C/min, the TiO_2 grain size slightly decreases and then quickly increases over 3 °C/min. Moreover, many pores can be observed in the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics sintered at the heating rate of 1 °C/min in which condition the vaporization of zinc ions easily happens [4]. With an increase of the heating rate, the number of the pore reduces gradually.

Fig. 4 illustrates the densities and microwave dielectric properties of the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics sintered at 1500 °C as a function of the different heating rate.

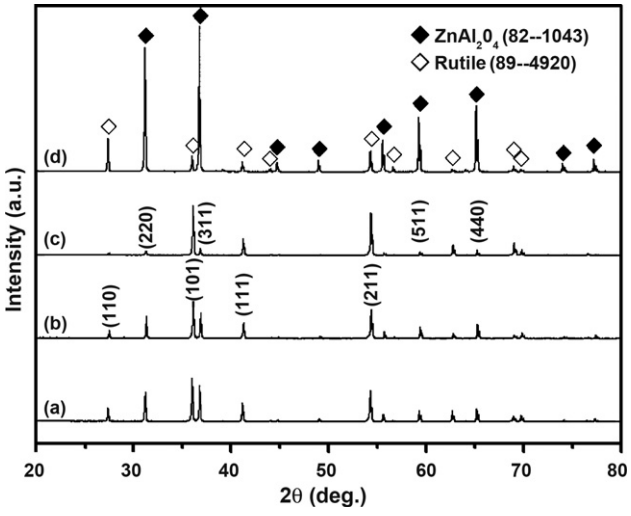

Fig. 1. X-ray diffraction patterns of the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics sintered at 1500 °C by different heating rate: (a) 1 °C/min; (b) 3 °C/min; (c) 7 °C/min; (d) 5 °C/min.

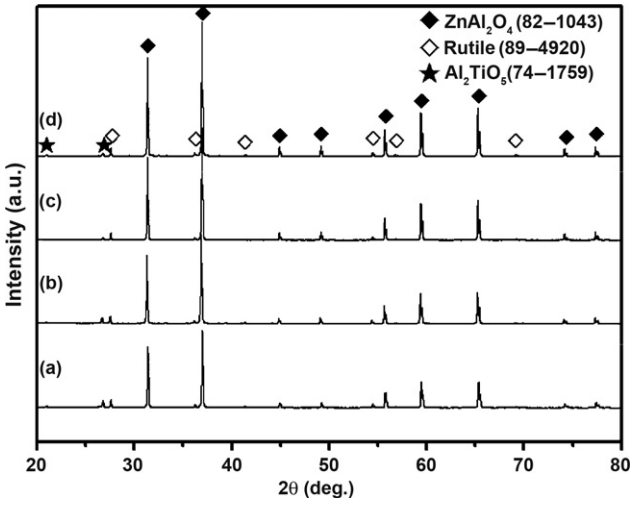

Fig. 2. X-ray diffraction patterns of the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramic powders sintered at 1500 °C by different heating rate: (a) 1 °C/min; (b) 3 °C/min; (c) 7 °C/min; (d) 5 °C/min.

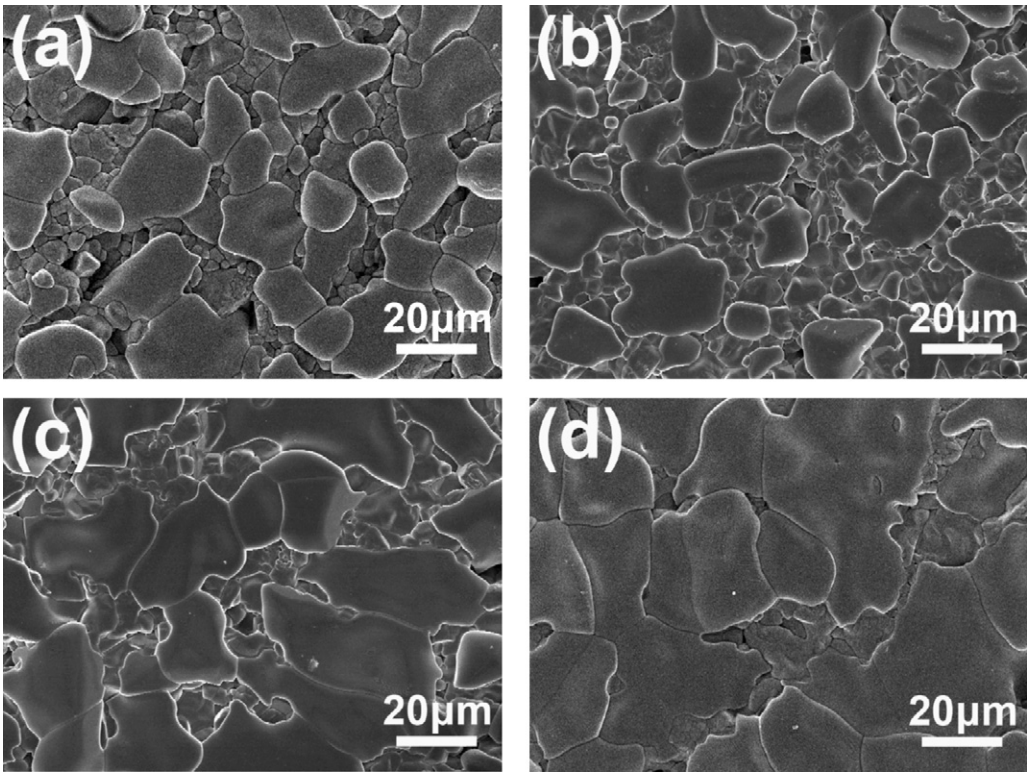

Fig. 3. SEM micrographs of the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics sintered at 1500 °C by different heating rate: (a) 1 °C/min; (b) 3 °C/min; (c) 5 °C/min; (d) 7 °C/min.

The density increases slightly with increasing the heating rate and reach the maximum value 4.42 g/cm^3 when the heating rate is 5 °C/min, and then reduces quickly to the minimum, as shown in Fig. 4(a). In general, an increase in the heating rate retards densification and grain growth during the heating stage. This has the consequence that more powder sintering activity is being preserved within the microstructure of the compact. Subsequently, during the dwell time at the top temperature, densification and grain growth take place at higher rates resulting finally to increased density, coarser microstructure [9]. However, when the heating rate is higher than 5 °C/min during sintering, the molding sample cannot obtain enough thermal energy [10], which is not beneficial to atom diffusion and therefore results in appearance of many micropores and decrease of densification, as also observed in the document by Wang et al. [11]. Furthermore, the dielectric constants of the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics sintered at 1500 °C are nearly independent on the heating rate and all about 11.6, as shown in Fig. 4(a).

The influence of the heating rate on the quality factor ($Q{\cdot}f$) of the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics sintered at 1500 °C is shown in Fig. 4(b). A significant variation in $Q{\cdot}f$ value which arisen from the heating rate can be found in the heating rate range of 1–5 °C/min, and then a maximum $Q{\cdot}f$ value of 74,000 GHz is obtained when the sample is sintered at the heating rate of 5 °C/min. Moreover, it can be observed that the ''black core'' phenomenon appears in the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics sintered at the heating rate of 1 °C/min and the black color weakens gradually with the increase of the heating rate and disappears up to 5 °C/min. It is considered that reduction of Ti^{4+} ion valence can take place in the ceramics sintered at lower heating rate such as 1 and 3 °C/min which reduces the $Q{\cdot}f$ value [5,12]. In order to clarify the chemical state of Ti element, XPS was performed for the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics sintered at the heating rate of 1 and 5 °C/min, respectively and the results are demonstrated in Fig. 5. The instrument was calibrated with the C 1s peak at binding energy of 284.6 ± 0.02 eV. From Fig. 5, it is known that the binding energy of Ti $2p_{2/3}$ in the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics sintered at the heating rate of 1 and 5 °C/min is 456.15 and 458.30 eV in agreement with Ti^{3+} and Ti^{4+} respectively, which confirms the above contemplation. High temperature sintering with lower heating rates easily leads to the formation of oxygen vacancies, which is accompanied by the formation of Ti^{3+} ions, due to the reduction caused by equilibrium with a low oxygen activity in air [5]. When the heating rate reaches 7 °C/min, the $Q{\cdot}f$ value dramatically reduces to 32,180 GHz, which can result from the reduction of density and the inhomogeneous atom diffusion in the ceramics. Nevertheless, with increasing of the heating rate, the temperature coefficient of resonant frequency for the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics changes slightly and lower than 3.3 ppm/°C as shown in Fig. 4(b). Therefore, the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics is a temperature-stable material and good candidate for advanced substrate and antenna.

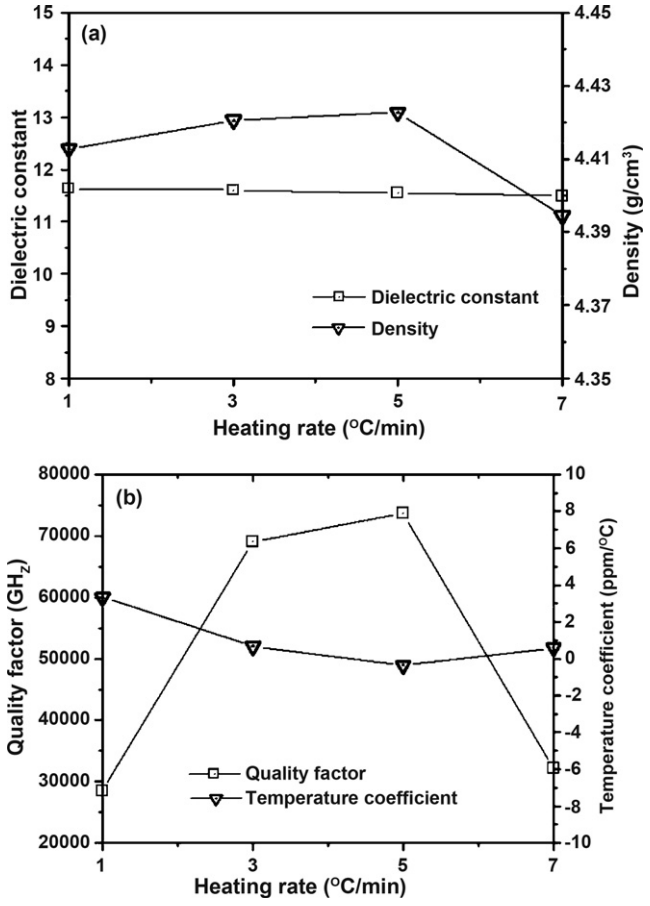

Fig. 4. Densities and microwave dielectric properties of the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics sintered at 1500 °C as a function of the different heating rate.

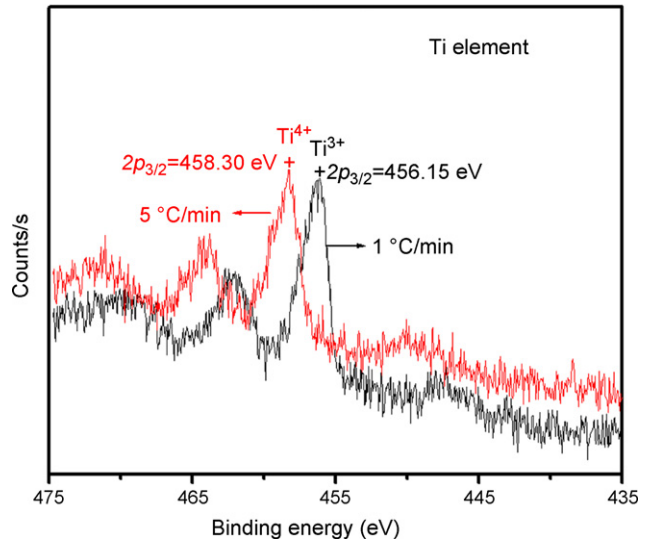

Fig. 5. XPS spectra of Ti $2p_{2/3}$ for the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics sintered at the heating rate of 1 and 5 °C/min.

4. Conclusions

For the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics, its microstructures and microwave dielectric properties are very sensitive to the heating rate. The bigger TiO_2 and smaller $ZnAl_2O_4$ grains are comprised in the system of $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics. As the heating rate increases from 1 to 3 °C/min, the TiO_2 grain size slightly decreases and then quickly increases over 3 °C/min while the $ZnAl_2O_4$ grain size nearly does not change. The density and quality factor ($Q{\cdot}f$) increase initially and reach the maximum value 4.42 g/cm^3 and 74,000 GHz (at about 6.5 GHz) respecively when the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics sintered at 1500 °C for 3 h by a heating rate of 5 °C/min, and then reduce quickly to the minimum, while the dielectric constant (ε_r) and temperature coefficient of resonator frequency (τ_f) nearly do not change and keep about 11.6 and lower than 3.3 ppm/°C, respectively. Moreover, it can be observed that the "black core" phenomenon appears in the $(1-x)ZnAl_2O_4$–$xTiO_2$ ($x = 0.21$) ceramics sintered at the heating rate of 1 °C/min and the black color weakens gradually with the increase of the heating rate and disappears up to 5 °C/min. It is confirmed that reduction of Ti^{4+} to Ti^{3+} has taken place in the ceramics sintered at lower heating rate such as 1 and 3 °C/min which reduces the $Q{\cdot}f$ value.

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