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Hydrothermal synthesis of $(Zr,Sn)TiO_4$ nano-powders for microwave ceramics

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Abstract

$(Zr,Sn)TiO_4$ nano-powders for microwave ceramics were prepared by a hydrothermal synthesis route. Raw materials of $ZrOCl_2 < AR >$, $ZrO(NO_3)_2 < AR >$, $SnCl_2 < CP >$, $TiO_2 < CP >$ and de-ionized water were used, and the mixture was stirred in an auto-clave at 160–230 °C. Resulting powders with particle size of 10–120 nm were washed, dried and pressed into pellets, which were then sintered at 1200–1300 °C. The sintering process was analyzed by TGA and DTA. Microstructures of the powder and sintered ceramics were observed by TEM and SEM. Crystalline phases of the ceramics were identified by XRD. Dielectric properties of the samples were: dielectric constant 30–45 and $Q*f = 10{,}000$–$25{,}000$ GHz at 10 GHz.

Keywords: Hydrothermal synthesis; Microwave ceramics; Nano-powder; $(Zr,Sn)TiO_4$

1. Introduction

With the continuous trend of development in wireless communication, it is of key importance to develop microwave ceramics with high quality.[1,2] Several kinds of ceramics have been reported.[3–5] Considerable research had focused on the system of $(Zr,Sn)TiO_4$ with high quality factor.[6,7]

However, a rather high sintering temperature, above 1350 °C, is usually necessary to obtain dense ceramics of $(Zr,Sn)TiO_4$ by conventional solid-state reaction, and even through the sol-gel method.[8] In this paper, $(Zr,Sn)TiO_4$ nano-powders were prepared with a hydrothermal synthesis route,[9] resulting in lower sintering temperature for the ceramics with good microwave properties.

2. Experiment

Raw materials of $ZrOCl_2 < AR >$, $ZrO(NO_3)_2 < AR >$, $SnCl_2 < CP >$, $TiO_2 < CP >$ and de-ionized water were used, in which two kind of TiO_2 with different size of powders were applied, tens of nano-meter and hundreds of nano-meter, respectively. They were weighted according to different ratio of Zr/Sn. The mixture was stirred in an auto-clave at 160–250 °C. Resulting powders were washed and dried. The bulk samples of ceramics were prepared by the solid-state reaction method. Some of powders obtained with hydrothermal synthesis were calcined at 1100–1200 °C for 2 h. They were ground, and then milled with a binder of polyvinyl alcohol (PVA) solution for granulating. Green bodies were hydro-pressed and sintered at 1260 ± 50 °C for 1 h.

The sintering process was analyzed by TGA and DTA (Netzsch, Germany). Microstructures of both the powders and sintered ceramics were observed by TEM (Jeol, Japan) and SEM (Leo, Germany). Crystalline phases were identified by XRD (Rigaku, Japan). Dielectric properties of the samples were also measured with a HP 4284A Meter, and a microwave measurement system at a frequency of 10 GHz.[10]

3. Results and discussion

3.1. Thermal analysis of the powders

The dried powders were analyzed with TGA and DTA, as shown in Fig. 1. It can be seen that there was an endo-thermal reaction around 100 °C, which corresponded to water evaporation from the powder. At the same time, the loss of sample weight also occured. At about 200 °C, however, there was an exo-thermal peak,

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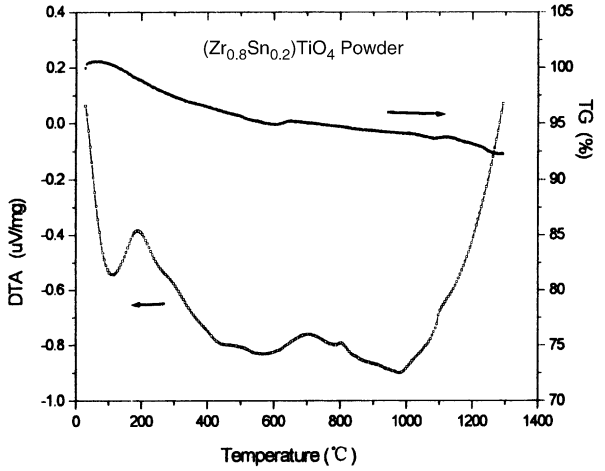

Fig. 1. Thermal analysis of dried powders by TGA and DTA.

which meant the decomposition of PVA binder within the range of temperature. Between 800 and 1200 °C there was an obvious endo-thermal reaction, which corresponded to main stage of the sample sintering and compacting. Meanwhile the sample lost weight slightly but continually.

3.2. XRD characterization of samples

By using X-ray diffraction, the major phases of $(Zr_{1-x}Sn_x)TiO_4$ were determined (Fig. 2) for the samples with ratio of Zr:Sn = 0.8:0.2. Small amounts of TiO_2 and SnO_2 was also fund as minor phase, especially for the samples sintered at lower temperature.

Thermal treatment for the samples had an effect on the amount of $(Zr_{1-x}Sn_x)TiO_4$ in the ceramics. With increasing sintering temperature, the phase $(Zr_{1-x}Sn_x)TiO_4$ become more dominant in the ceramics (Fig. 3).

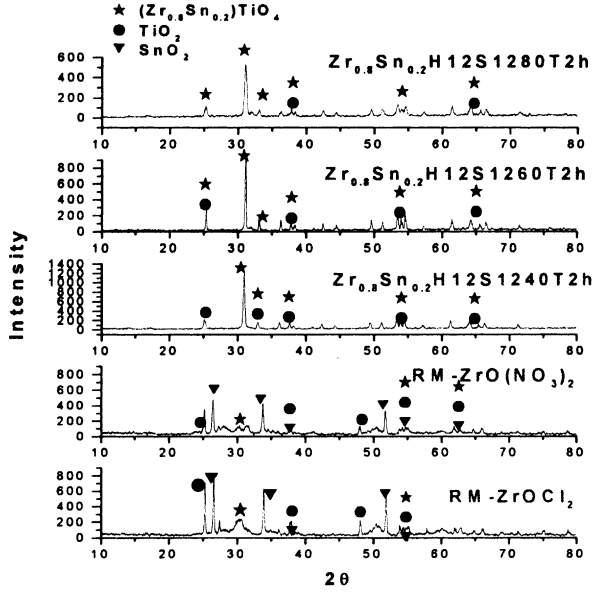

Fig. 2. XRD patterns of the samples.

3.3. TEM images of the powders

Particle sizes of different powders were observed with TEM (Fig. 4). Two kinds of products were obtained using different types of TiO_2 as starting material. Particle sizes of the materials TiO_2 were tens of nano-meter and hundreds of nano-meter, respectively. It is clear that the size of raw chemical has an important influence on the dimension of final powder. The reason maybe that only one kind of raw material is in the solid state and the others are in solution form. Therefore the solutions may diffuse into the solid and chemical reaction takes place within the particles.

3.4. SEM images of the ceramics

Two kinds of ceramics both sintered at 1300 °C for 90 min were investigated by SEM (Fig. 5). They were prepared using the powders of about 100 nm (a) and 10 nm (b), respectively. It can be seen that the ceramics made from the powder of 100 nm in diameter had better microstructure, with fine grains and uniform distribution. However, it seems that excessively small powders may result in abnormal grain growth if they are sintered at excessively high temperatures.

3.5. Dielectric properties of ceramics

Dielectric properties of the samples for different sintering temperatures, prepared with powders of 100 nm, were measured at $f = 10$ GHz (Fig. 6). The dielectric constants varied from $\varepsilon = 35$–45 and the quality factor

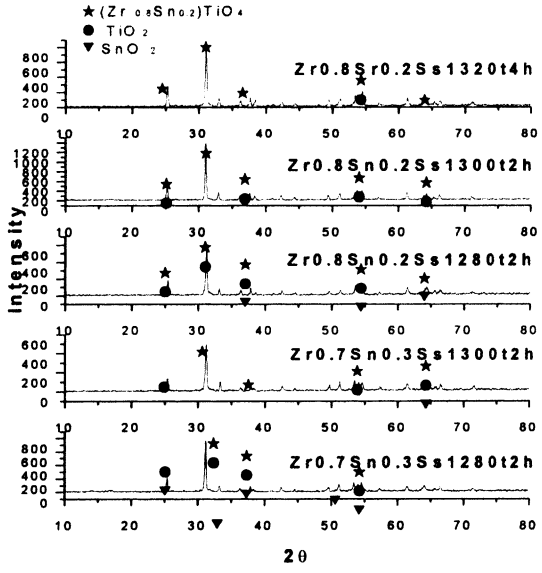

Fig. 3. Effect of sintering temperature on amount of $(Zr_{1-x}Sn_x)TiO_4$ phase.

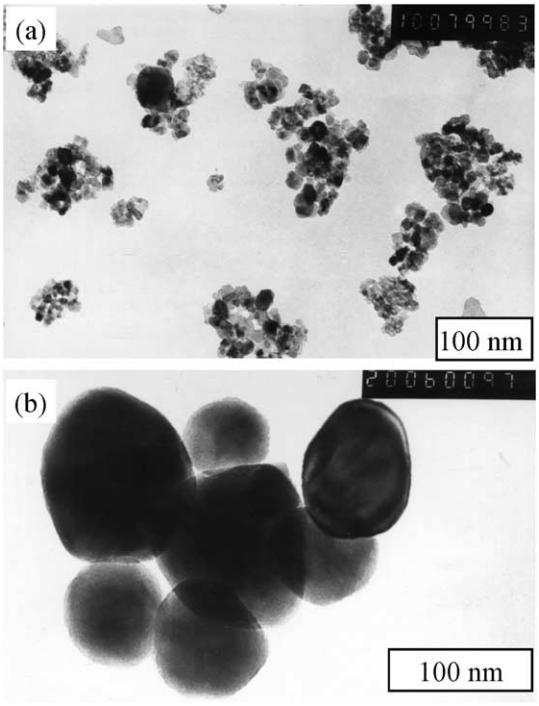

Fig. 4. TEM images of final powders with sizes of about 10 nm (a) and 100 nm (b).

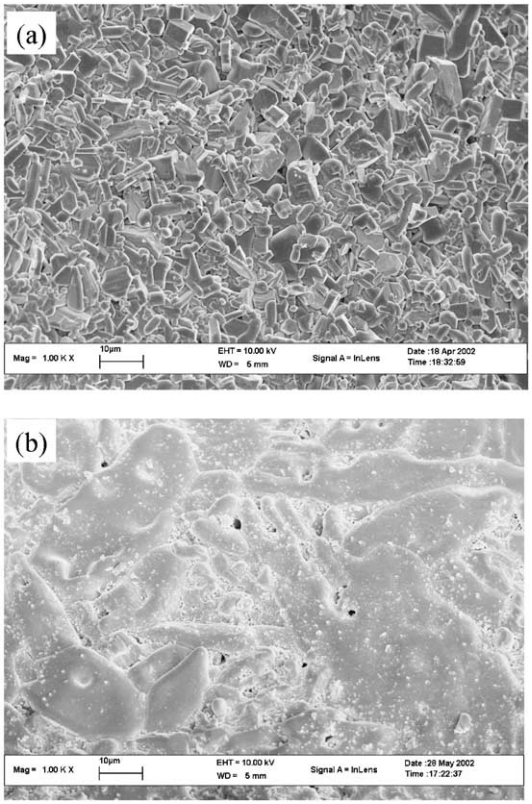

Fig. 5. SEM micrograph of the ceramics sintered from the powders of around 100 nm (a) and 10 nm (b), respectively.

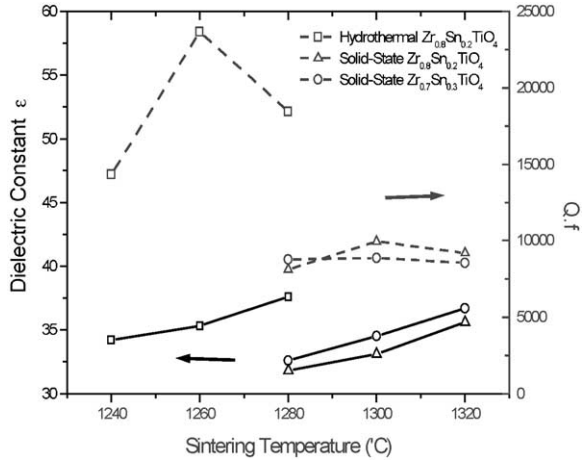

Fig. 6. Dielectric constant and quality factor of the samples for different sintering temperature at $f = 10$ GHz.

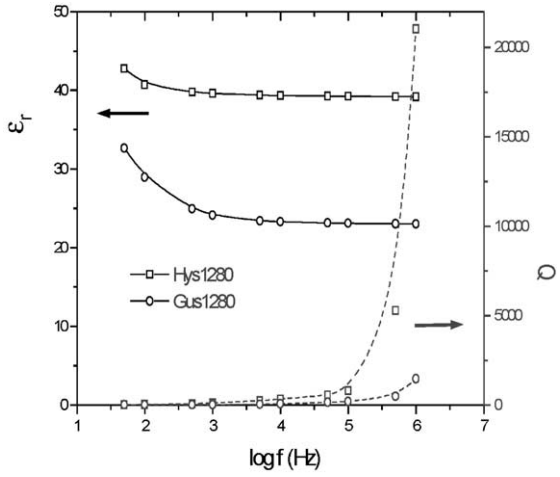

Fig. 7. Frequency dependence of dielectric properties of the ceramics up to 1 MHz.

Q^*f were 10,000–25,000 for different samples. When the ratios of Zr/Sn was around the region of 0.8–0.2, the best dielectric properties were achieved. Two reasons may exist for the lower value of Q^*f in this study, compared with the results of Hirano et al.: one is that the sintered bodies of ceramics in this case had lower density; another possibility may result from using different measurement systems.[8,10]

At low frequency (up to 1 MHz), the dielectric constant of the ceramics decreased slightly with increasing frequency (Fig. 7). The quality factor of the sample increased with increasing frequency. Better dielectric properties were obtained at higher sintering temperature, such as 1280 °C.

4. Concluding remarks

$(Zr_{1-x}Sn_x)TiO_4$ nano-powders for microwave ceramics were prepared by a hydrothermal synthesis route in

an auto-clave at 150–230. Powders with particle size of 10–120 nm were obtained. Dielectric properties of the ceramics were dielectric constant 30–45; $Q^*f = 10{,}000$–$25{,}000$ GHz at 10 GHz.

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