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Preparation and microwave dielectric properties of low-loss $MgZrNb_2O_8$ ceramics

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Abstract

A novel low-loss microwave dielectric material $MgZrNb_2O_8$ was reported for the first time. Single-phase $MgZrNb_2O_8$ was prepared by a conventional mixed-oxide route and sintered in the temperature range of 1280–1360 °C. The microstructure and microwave dielectric properties were investigated systematically. The X-ray diffraction results showed that all samples exhibit a single wolframite structure. When the sintering temperature was lower than 1340 °C, the $Q \times f$ value mainly depended on the relative density. However, when the sintering temperature was above 1340 °C, the $Q \times f$ value mainly relied on the grain morphology in addition to the density. The $MgZrNb_2O_8$ ceramic sintered at 1340 °C for 4 h exhibited excellent microwave dielectric of $\varepsilon_r = 26$, $Q \times f = 120{,}816$ GHz (where $f = 6.85$ GHz), and $\tau_f = -50.2$ ppm/°C. These results demonstrate that $MgZrNb_2O_8$ could be a promising candidate material for the application of highly selective microwave ceramic resonators and filters.

Keywords: A. Sintering; C. Dielectric properties; D. Niobates; E. Functional applications

1. Introduction

Because of the continuing development in modem wireless communication technologies, microwave dielectric ceramics were increasingly used for resonators, filters, duplexers and antennas in systems for wireless communications. Recently, the application of passive components in microwave and millimeter band has been widely studied. The dielectric passive components have several advantages such as small size, low conductor losses, high radiation efficiency, large bandwidth, flexible feed arrangement, wide range of dielectric constants, ease of excitation and easily controlled characteristics [1]. Requirements for the microwave dielectric ceramics are that they should have a high dielectric constant (ε_r) and high quality factor (Q) for miniaturization and better selectivity, respectively. Especially, for those used in the base stations of mobiles, the ceramics are required to have a high $Q \times f$ value of more than 40,000 GHz [2,3]. In addition, the resonant frequency of devices should not depend strongly on temperature such that the temperature coefficient of resonant frequency (τ_f) should be $< \pm 10$ ppm/°C [4,5]. In order to meet the specifications of current and future systems, improved or new microwave components based on excellent dielectric materials and new designs are necessary.

Although several materials such as $Ba(Zn_{1/3}Ta_{2/3})O_3$, $BaTi_4O_9$, $Ba_2Ti_9O_{20}$, $(Zr,Sn)TiO_4$, $CaTiO_3$-$NdAlO_3$, and $Ba_{6-3x}Re_{8+2x}Ti_{18}O_{54}$ (Re=Nd, Sm, La) have been reported for practical applications [6,7], active research is still going on for new ceramics due to great demands for a variety of materials with varying dielectric constants. Recently, there has been a growing interest in the dielectric properties of the columbite materials. Although some columbite ceramics have been reported, such as $ZnTiNb_2O_8$ (ε_r=34.3, $Q \times f$=42,500 GHz, and τ_f=−52 ppm/°C), $ZnZrNb_2O_8$ (ε_r=30, $Q \times f$=61,000 GHz, and τ_f=−52 ppm/°C) [8,9], yet the dielectric properties of $MgZrNb_2O_8$ have not yet been reported so far. In this work, a new low-loss microwave dielectric material $MgZrNb_2O_8$ with a wolframite structure was reported to own excellent microwave dielectric properties as it was sintered at 1340 °C.

2. Experimental procedure

The $MgZrNb_2O_8$ ceramics were prepared by a traditional solid-state method. High-purity $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$

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(purity > 99.9%), ZrO_2 (purity > 99.9%), and Nb_2O_5 (purity > 99.9%) were used as the starting materials. Stoichiometric amounts of the chemical powders were weighed and ground by a planetary ball miller using zirconia balls in ethanol for 4 h. The resultant slurry was then dried. The mixed powders were calcined at 1200 °C for 4 h. The calcined powders were ground again by planetary ball milling for 6 h and then mixed together with poly vinyl alcohol (PVA) binder. The granulated powders were subsequently pressed into cylinders with dimensions of 10 mm in diameter and 7–8 mm in height. Their 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 1280–1360 °C for 4 h. The bulk densities of the sintered pellets were measured by the Archimedes method.

The crystal structure of the sintered ceramics was examined by an X-ray diffractometer (XRD, D/Max2500 V, Rigaku, Japan) using CuKα radiation. The grain morphology was analyzed by a scanning electron microscope (SEM, JSM-6490LV, JEOL, Tokyo, Japan). Microwave dielectric properties of the sintered samples were measured by a network analyzer (N5230C, Agilent, Palo Alto, CA) in the frequency range of 6–7 GHz. The dielectric constant was measured by the Hakki–Coleman method modified by Courtney [10], and the unloaded Q values were measured by the cavity method [11]. The τ_f value of the samples was measured in the temperature range from 20 °C to 80 °C. It can be calculated by the following relationship: $\tau f = (f2-f1)/(f1(T2-T1))$ where f_1 and f_2 represent the resonant frequencies at T_1 and T_2, respectively.

3. Results and discussion

The XRD patterns of the $MgZrNb_2O_8$ ceramics sintered at 1280–1360 °C for 4 h are shown in Fig. 1. All the patterns can be indexed as a monoclinic wolframite structure [12] (JCPDS-PDF #48-0329) which belongs to the space group p2/c (13).

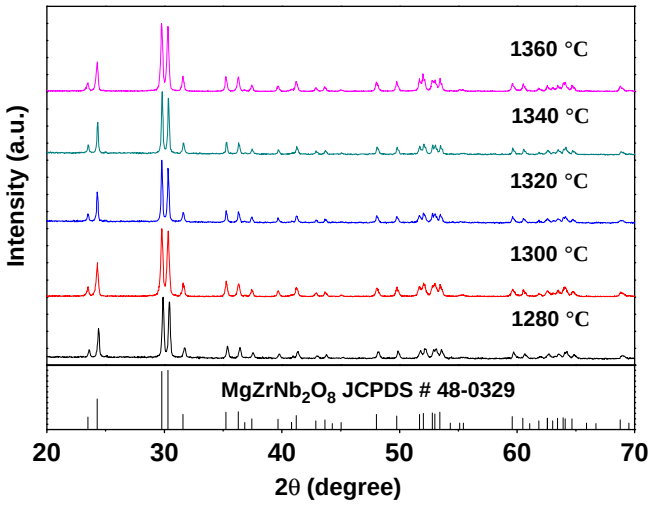

Fig. 1. The XRD patterns of $MgZrNb_2O_8$ ceramics sintered at different temperatures, as compared to the standard pattern of $MgZrNb_2O_8$.

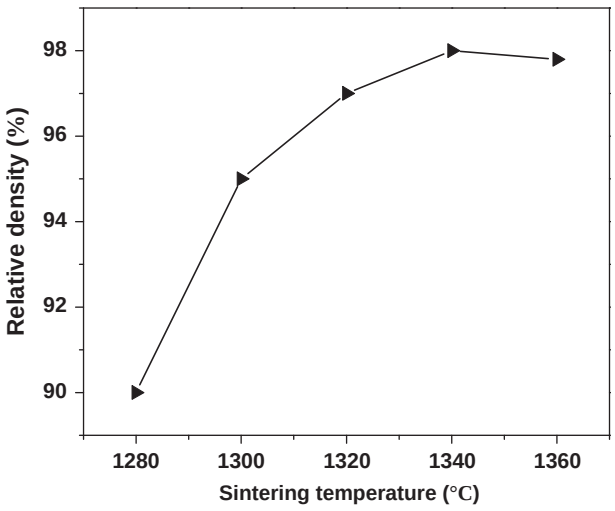

Fig. 2. The variation of the relative density of $MgZrNb_2O_8$ ceramics sintered at different temperatures.

It means that pure-phase $MgZrNb_2O_8$ was obtained. Moreover, the crystal structural parameters do not change with varying the sintering temperature.

Fig. 2 shows the relative densities of the $MgZrNb_2O_8$ ceramics as a function of sintering temperatures. For all the samples, the relative density increases with increasing the sintering temperature and then reaches the maximum relative density (≥98%) at 1340 °C. A further increase of the sintering temperature would lead to a slight decrease of the density probably because of a competition from the grain growth at high temperatures.

Fig. 3 illustrates typical SEM images on the surface of the $MgZrNb_2O_8$ ceramics sintered at various temperatures. From Fig. 3(a), the sample sintered at 1280 °C exhibits a porous structure and its average grain size is ~2 μm. When the sintering temperature was increased to 1340 °C, uniform and dense grain morphology could be observed. However, it can be seen from Fig. 3(e) that non-uniform grain size distribution was obtained as the sample was sintered at 1360 °C. Such a high sintering temperature tends to induce inhomogeneous grain growth, finally leading to a slight decrease in the pellet density.

Fig. 4 illustrates the dielectric constant of the $MgZrNb_2O_8$ ceramics as a function of sintering temperature. The dielectric constant should be mainly determined by the relative density, dielectric polarizabilities and structural characteristics such as the distortion, tilting, and/or rattling spaces of oxygen octahedron in the unit cell [13–15]. In this work, the dielectric constant was mainly dependent on the density of the samples. With an increase of the relative density, the dielectric constant obviously increased. It can be seen that the dielectric constant had almost the same trend as the relative density when the sample was sintered at different temperatures.

For high-frequency applications and for the selectivity of the resonant frequency of microwave dielectric ceramics, a low loss value is very important due to the requirement of better component properties. The $Q \times f$ and τ_f values of the

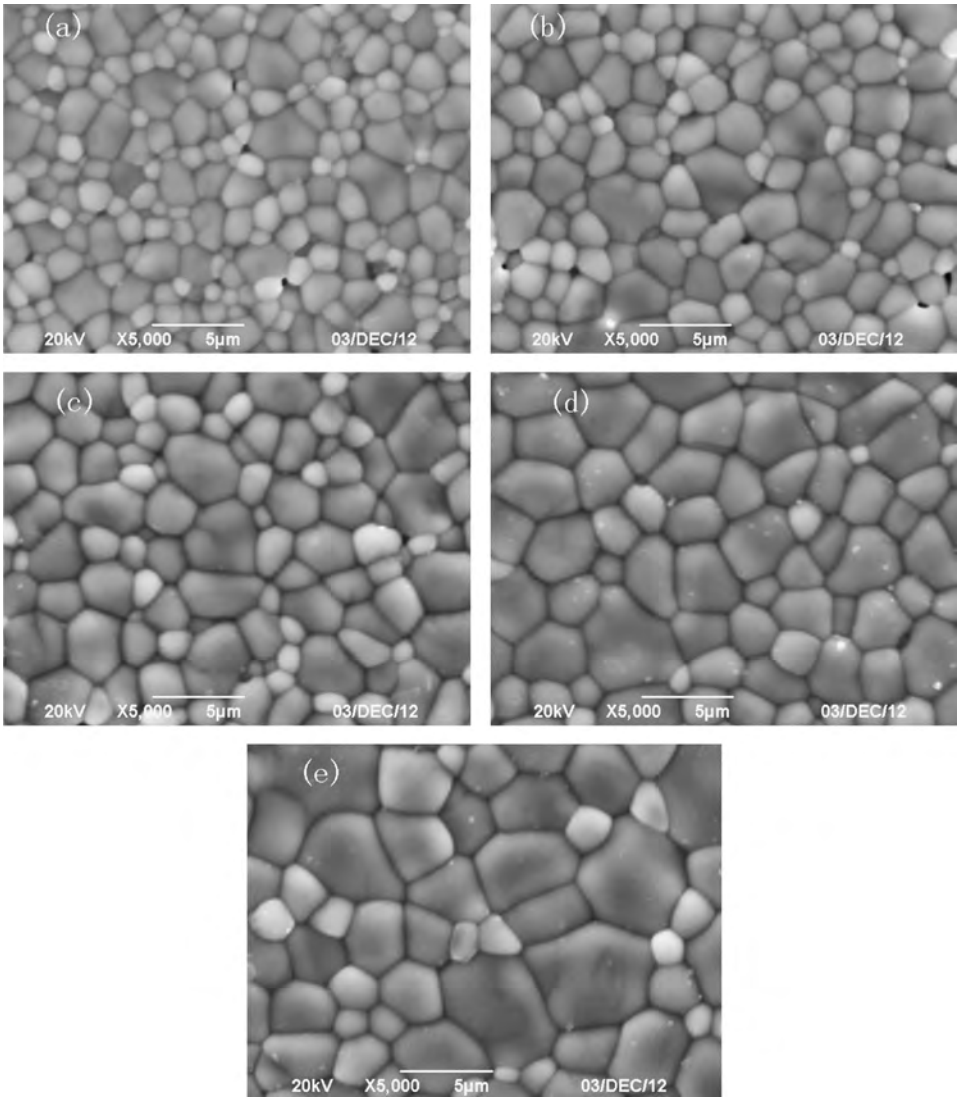

Fig. 3. The SEM images of $MgZrNb_2O_8$ ceramics sintered at (a) 1280, (b) 1300, (c) 1320, (d) 1340, and (e) 1360 °C.

$MgZrNb_2O_8$ ceramics as a function of sintering temperature are also shown in Fig. 4. It is known that the impacts on the quality factor values at microwave frequencies contain intrinsic and extrinsic contributions. The extrinsic factors usually include defect concentration, impurities, grain size, and porosity secondary phase. The intrinsic factors of the quality factor values are generally related with the lattice anharmonicity [16–18]. In this work, the variation of the quality factor was basically consistent with the change of the relative density at different temperatures. The $Q \times f$ values of the $MgZrNb_2O_8$ ceramics began to increase from 92,592 GHz and then reached the highest value of 120,816 GHz as the sintering temperature increased from 1280 ° to 1340 °C. It is clear that the densification behavior of the samples plays a significant role in the dielectric loss. The same phenomenon has been observed in other microwave dielectric ceramics [19–21]. However, it was reported that density has little influence on the quality factor when the relative density is above 95% [18]. Under these circumstances it is probably dominated by some extrinsic factors. As shown in Fig. 4, when the sintering temperature was higher than 1340 °C, the $Q \times f$ values began to decrease. Because the relative density of the sample sintered at 1360 °C was higher than 95%, and the second phases and charge unbalance are also not possible, so the grain morphology would be suggested to dominate the $Q \times f$ values of the $MgZrNb_2O_8$ ceramic. As seen from Fig. 3(e), non-uniform grain size distribution was obtained as the sample was sintered at 1360 °C, which revealed an increase in the lattice imperfection probably because of insufficient crystal growth of small grains. The $Q \times f$ value should be a stronger function of grain morphology than of the sample density as the sintering temperature is above 1340 °C. The decrease in $Q \times f$ values could be then a result of non-uniform grain morphology [22–24]. In general, τ_f is well known to be influenced by the composition, the additive and the second phase of the ceramics. It was not sensitive to the sintering temperature because there were not any secondary phases at different temperatures and the unit cell volume remained constant

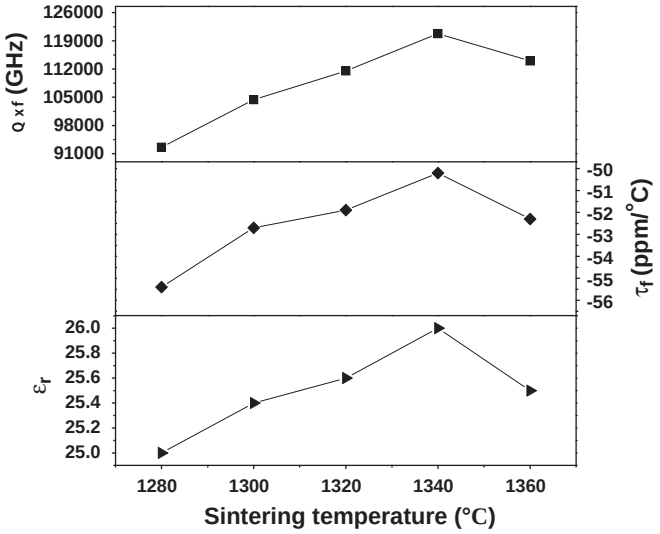

Fig. 4. The variation of the ε_r, $Q \times f$ and τ_f values of $MgZrNb_2O_8$ ceramics sintered at different temperatures.

[25,26]. As a result, the τ_f value of the $MgZrNb_2O_8$ ceramics would remain in a narrow range from −55.4 ppm/°C to −50.2 ppm/°C as the samples were sintered at 1280–1360 °C. The outstanding microwave dielectric properties of $\varepsilon_r = 26$, $Q \times f = 120{,}816$ GHz, and $\tau_f = -50.2$ ppm/°C could be achieved as the $MgZrNb_2O_8$ ceramics were sintered at 1340 °C.

4. Conclusions

The phase structure, grain morphology and various microwave dielectric properties of the $MgZrNb_2O_8$ ceramics were studied as a function of the sintering temperature in this work. The pure-phase $MgZrNb_2O_8$ ceramic samples exhibit uniform and dense microstructural morphology, and own outstanding microwave dielectric properties of $\varepsilon_r = 26$, $Q \times f = 120{,}816$ GHz, and $\tau_f = -50.2$ ppm/°C. The results indicate that $MgZrNb_2O_8$ ceramic could be a suitable candidate for microwave passive component applications.

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