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Influence of sintering temperature on dielectric properties and crystal structure of corundum-structured $Mg_4Ta_2O_9$ ceramics at microwave frequencies

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Abstract

Microwave dielectric properties of corundum-structured $Mg_4Ta_2O_9$ ceramics were investigated as a function of sintering temperatures by an aqueous sol–gel process. Crystal structure and microstructure were examined by X-ray diffraction (XRD) technique and field emission scanning electron microscopy (FE-SEM). Sintering characteristics and microwave dielectric properties of $Mg_4Ta_2O_9$ ceramics were studied as a function of sintering temperature from 1250 °C to 1450 °C. With increasing sintering temperature, the density, ε_r and Qf values increased, saturating at 1300 °C with excellent microwave properties of $\varepsilon_r = 11.9$, $Qf = 195{,}000$ GHz and $\tau_f = -47$ ppm/°C. Evaluation of dielectric properties of $Mg_4Ta_2O_9$ ceramics were also analyzed by means of first principle calculation method and ionic polarizability theory.

Keywords: A. Sol–gel process; First principle calculation method; Ionic polarizability theory; $Mg_4Ta_2O_9$ ceramic; Microwave dielectric properties

1. Introduction

Recently, the rapid progress in mobile and satellite communication system has been creating a high demand for the development of microwave dielectric materials with a high quality factor (Q), an appropriate dielectric constant (ε_r), and a near-zero temperature coefficient of resonant frequency (τ_f). The corundum-like phase of magnesium tantalate ($Mg_4Ta_2O_9$; MT) with a high product of quality factor and frequency (Qf), is a suitable material for microwave applications, such as substrates and resonators at high frequency, due to suitable dielectric constant and quality factor values comparable to those of sintered Al_2O_3 [1]. Some research regarding MT ceramics achieved by the conventional solid-state method were reported [2–4] in the literature to date. However, it has a sintering temperature of over 1400 °C. Obviously, high sintering temperature of these ceramics limits their practical application and the reduction of the sintering temperature is desirable to enable commercial applications such as in integrated circuits. Many investigations have described the development of lowering the sintering temperature such as using chemical process, adding glass flux, etc. As we know, adding glass flux usually causes the detrimental effect on the microwave properties of ceramics. Therefore much attention has been paid to chemical process and other special milling methods by using starting materials with smaller particle sizes [5,6].

The goal of this research was also to take advantage of the sol–gel method for preparing MT ceramics as reported in $MgO–Nb_2O_5$ and $MgO–TiO_2$ systems before [7,8]. In our previous work, synthesis and characterization of MT powders by an aqueous sol–gel process were reported as precursors and $Mg_4Ta_2O_9$ nanopowders with the size of 20–30 nm were obtained at 800 °C [9]. Now in this work, MT nanoparticles were used to prepare MT ceramics, and microwave dielectric properties as a function of sintering temperatures were investigated in detail. Additionally, first principle calculation method and ionic polarizability theory were used for the evaluation of dielectric properties of MT ceramics.

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2. Experimental

Powders in composition of MT phase were prepared through the aqueous sol–gel process with high-purity $Mg(NO_3)_2 \cdot 6H_2O$ and Ta_2O_5 as raw materials. The xerogel was decomposed at 800 °C in a muffle furnace for crystallization reported in our previous work [9]. The as-prepared powders were ball milled in a polyethylene jar for 4 h using ZrO_2 balls in ethanol medium to reduce the conglobation phenomena. The powders were then mixed with polyvinyl alcohol as a binder, granulated and pressed into cylindrical disks of 10 mm diameter and about 5 mm height at a pressure of about 200 MPa. These pellets were preheated at 600 °C for 4 h to expel the binder and then sintered at selected temperatures for 4 h in air at a heating rate of 5 °C/min. Phase analysis of MT sample was conducted with the help of a Rigaku diffractometer (Model D/MAX-B, Rigaku Co., Japan) using Ni filtered Cu Kα radiation (λ=0.1542 nm) at 40 kV and 40 mA settings. Based on XRD analysis, the morphology were examined by transmission electron microscopy (Model Jeol JEM-2010, FEI Co., Japan). Bulk densities of sintered ceramics were measured by the Archimedes method. A HP8720ES network analyzer (Hewlett–Packard, Santa Rosa, CA) was used for measurement of microwave dielectric properties. Dielectric constants were measured using Hakki–Coleman post-resonator method by exciting the TE011 resonant mode of dielectric resonator using an electric probe as suggested by Hakki and Coleman [10]. Unloaded quality factors were measured using the TE01d mode by the cavity method [11]. All measurements were carried out at room temperature at a frequency of 8–10 GHz. Temperature coefficients of resonant frequency were measured in the temperature range of 25–85 °C.

First-principle calculations were performed to investigate the electronic structure of $Mg_4Ta_2O_9$ using CASTEP (Cambridge Serial Total Energy Package) software package, which was a plane wave pseudo-potential method. For the calculations, the density functional theory (DFT) was used, in which plane wave basis set was chosen for the expansion of valance-electron wave functions at the local density approximation (LDA) level. Energy cut off value of plane wave basis set was selected as 650 eV and the criterion for self-consistency was eigenenergy convergence within 10^{-8} eV/atom. The *k*-point set was chosen as $4 \times 4 \times 3$ Monkhorst–Pack grids and the pseudopotential was constructed from the CASTEP database. The cluster model of $(Mg_8Ta_{16}O_{72})^{-48}$, which was constructed on the basis of the refined lattice parameters [12] and crystal structure parameters in this study, was shown in Fig. 1. In this crystal structure, the Ta^{5+} and Mg^{2+} ions were surrounded by the six (O1 and O2) oxygen ions and these ions comprise the TaO_6, $Mg(1)O_6$ and $Mg(2)O_6$ octahedra. Cations were located in the centers of the octahedra.

3. Results and discussion

Curves for the relative density and diametric shrinkage ratio of MT ceramics as a function of sintering temperatures were shown in Fig. 2, through which the optimized sintering temperature was determined. Here MT ceramic had theoretical density of 6.18 g/cm^3 and its shrinkage tendency was characterized by the ratio of diametric size before and after the ceramic sintering. It was found that the relative density increased from 76.3% to 94.1% as sintering temperature

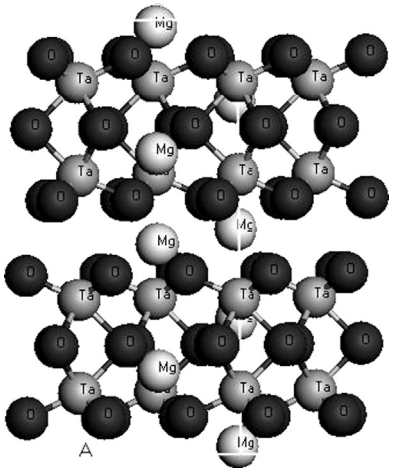

Fig. 1. Cluster model used in the calculation: $(Mg_8Ta_{16}O_{72})^{-48}$.

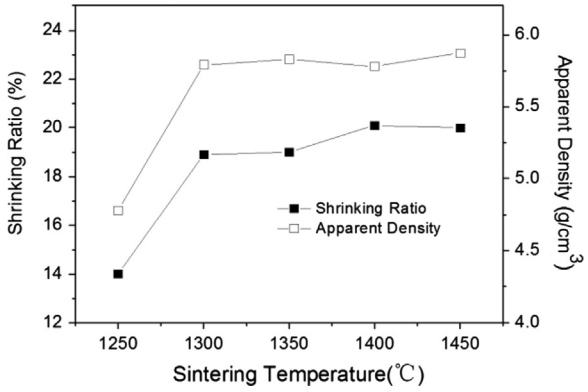

Fig. 2. Relative densities and diametric shrinkaging ratio of MT ceramics as a function of sintering temperatures from 1250 °C to 1450 °C.

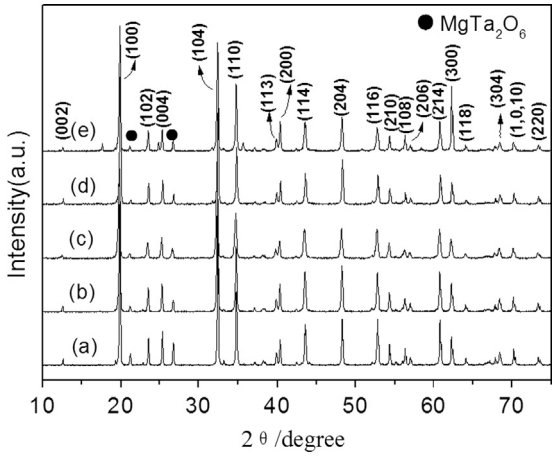

Fig. 3. XRD patterns of MT ceramics sintered at different temperatures ((a)–(e) corresponding to 1250 °C, 1300 °C, 1350 °C, 1400 °C, and 1450 °C).

increasing from 1250 °C to 1300 °C. At 1300 °C a saturated value of relative densities was found and the curve of diametric shrinkage ratio also showed a similar tendency. The XRD patterns of MT ceramics sintered at 1250–1450 °C were shown in Fig. 3. The predominant phase was identified as corundum-structured $Mg_4Ta_2O_9$ with space group P-3c1(165) and the minor secondary phase $MgTa_2O_6$ with tetragonal symmetry existed. The X-ray diffraction patterns of $Mg_4Ta_2O_9$ ceramics did not exhibit significant changes throughout the sintering temperature range from 1250 °C to 1450 °C. To characterize the microstructure of MT ceramics sintered at different temperatures, SEM micrographs were illustrated in Fig. 4(a–e). It was easily seen that the apparent porosity decreased as sintering temperature increased from 1250 °C to 1450 °C and all pores had almost disappeared at 1300 °C on the surface of MT samples. With the increase of sintering temperature, the grain size increased rapidly and the average measured grain size was about 2–3 μm at 1300 °C as shown in Fig. 4(b). However, it was seen that the grains were melt due to excessive sintering temperature of 1450 °C as shown in Fig. 4(e). Therefore, it was obvious that MT ceramics were successfully prepared with high density through the sol–gel process at 1300 °C and the sintering temperature was reduced significantly compared with solid-state reaction methods [2–4].

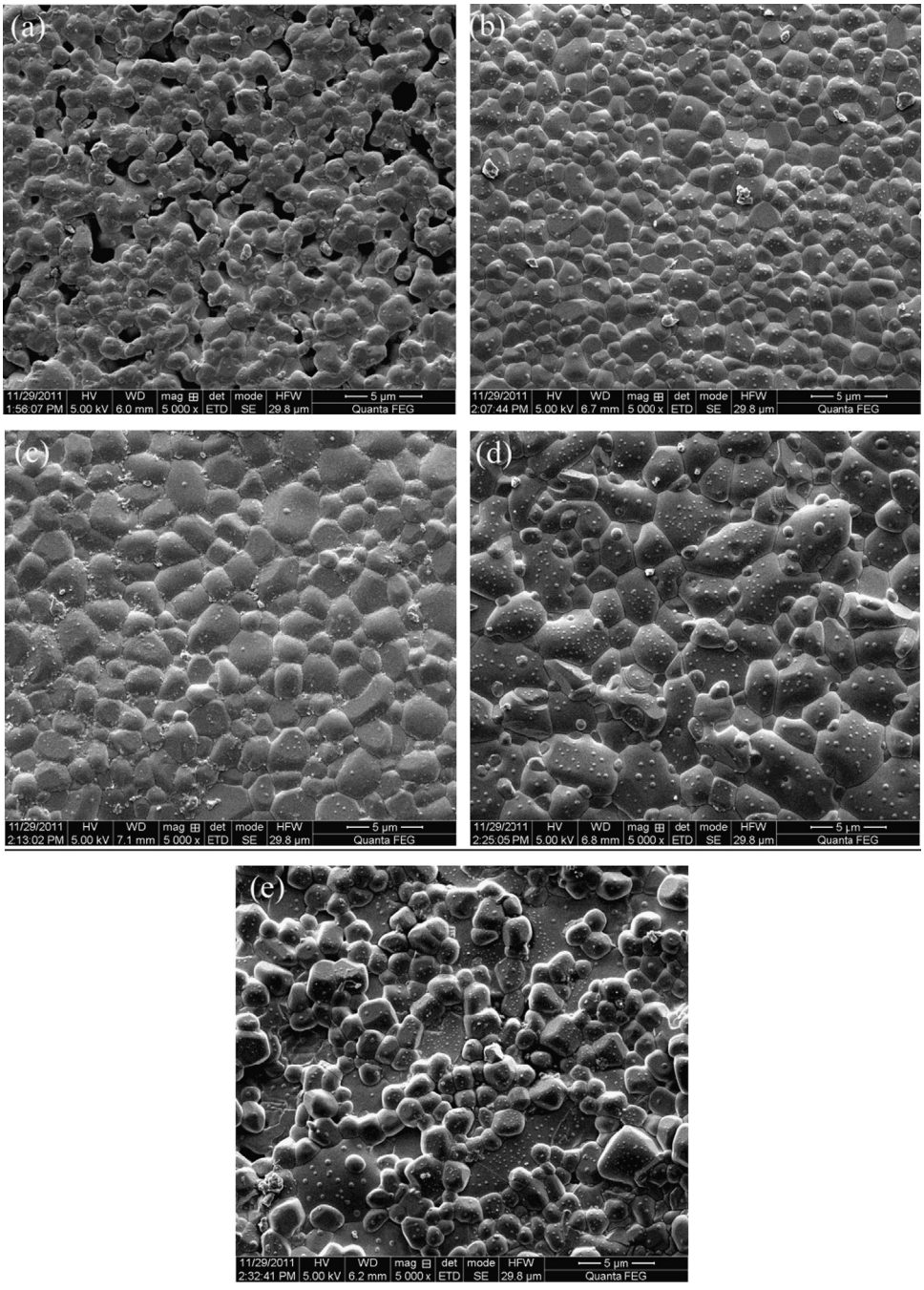

Fig. 4. FE-SEM micrographs of MT ceramics sintered at different sintering temperature for 2 h ((a)–(e) corresponding to 1250 °C, 1300 °C, 1350 °C, 1400 °C, and 1450 °C).

Changes of ε_r, Qf and τ_f values as a function of sintering temperature were shown in Fig. 5. It was found that the ε_r values of MT ceramics steadily increased from 8.5 to 11.8 with the increase of the sintering temperature from 1250 °C to 1300 °C, and then saturated at ≈12. Based on the sintering characteristic curves and microstructures shown in Figs. 1 and 3, it was obvious that the low ε_r values were caused by pores (ε_r≈1) at sintering temperatures lower than 1300 °C. The curve of ε_r values showed a tendency similar to those of relative density and shrinkage ratio, showing significant sensitivity to the dense degree of the ceramics. In addition, the effect on the dielectric constants caused by the second phase of $MgTa_2O_6$ could be negligible due to its minor quantity although its dielectric constant was approximate 30 as reported [7]. The results of ε_r values obtained at 1300 °C by the sol–gel process were comparable with these sintered at 1400 °C by the solid-state reaction method [2–4]. For the samples with nearly full density, to clarify the effects of crystal structure on dielectric constant, theoretical dielectric polarizability ($\alpha_{theo.}$) was calculated to be 11.55 according to the additive rule based on the ionic polarizability of the constituent ions or oxides [13] as formulated in Eq. (1). The observed dielectric polarizability ($\alpha_{obs.}$) was calculated to be 11.8 by the Clausius–Mossotti equation as formulated in Eq. (2) with measured dielectric constant at microwave frequencies [14]. By comparison values of $\alpha_{theo.}$ and $\alpha_{obs.}$ were in good agreement with each other, and the minor discrepancy from the $\alpha_{obs.}$ and $\alpha_{theo.}$ could be attributed to the relative density because the $\alpha_{obs.}$ value depended on the specimen and fabrication process used.

$$\alpha_{theo.} = \alpha(Mg_4Ta_2O_9) = 4\alpha(MgO) + \alpha(Ta_2O_5) \quad (1)$$

$$\alpha_{obs.} = \frac{1}{b} V_m \frac{\varepsilon - 1}{\varepsilon + 2} \quad (2)$$

where α (MgO) and α (Ta_2O_5) represented the oxides polarizabilities reported by Shannon [14]. Moreover, V_m, ε and b indicated the molar volume of the samples, the dielectric constant and constant value ($4\pi/3$), respectively.

With the increase of sintering temperatures, Qf values increased from 128,600 GHz to 195,000 GHz from 1250 °C to 1300 °C and then decreased slightly in the sintering temperature region of 1350–1450 °C as shown in Fig. 5. As for Qf values of dielectric ceramics, it was well known that porosity, secondary phase and structure defect usually result in deterioration of Qf values [15]. Among these factors, porosity was suggested to affect Qf values obviously below 1300 °C. It was found that the relative density was one of the most important factors controlling dielectric loss as demonstrated for many other microwave dielectric materials. The remarkable increase in Qf values ranging from 1250 °C to 1300 °C was also related to the reduction of porosity according to results of SEM microstructures shown in Fig. 4(a) and (b), while the decrease in Qf values could be attributed to the destroy on grains caused by excessive sintering temperature of 1450 °C as shown in Fig. 4(e). As for the secondary phase of $MgTa_2O_6$, the crystal structure was trirutile and had a Qf value of nearly 57,400 GHz sintered at 1200 °C [7]. According to the well-known general empirical model for multiphase ceramics, the presence of the $MgTa_2O_6$ phase inevitably had a significantly detrimental effect on the Qf values due to its poor microwave properties. Compared with the results by the solid-state reaction method, Ohsato et al. [2,3] reported a higher Qf value more than 200,000 GHZ. Once the as-prepared samples reached nearly full density, Qf values were mainly affected by intrinsic factors, such as crystal structure and lattice vibrations, especially the covalence of cation–oxygen bonds besides extrinsic process parameters. Here the total density of states (DOS) and energy level diagrams of MT were calculated using the DFT method as shown in Fig. 6(a) and (b). In the energy level diagrams in Fig. 6(a), the band gap of MT was calculated to be 4.322 eV. In the density of states (DOS) in Fig. 6(b), it was seen that the highest occupied molecular orbital (HOMO) levels lay on the top of O-2p valence band. The occupied bands located from 4 eV to 7 eV, 0 eV to −7 eV and −18 eV to −15 eV, were mainly composed of O-2p, O-2s and Ta-5d orbitals, respectively. The occupied orbitals located from 0 eV to −7 eV and from 4 eV to 7 eV were also made up of Mg-3s orbitals. Significant amounts of Ta-5d states were found in the O-2p band, suggesting that the Ta–O bonds were covalent. Thus, the covalent interactions of the Ta–O bonds were considered to be strong and the Mg–O bond might be an ionic interaction. From these results, it was considered that the covalent interactions of the Ta–O exerted an influence on the average bond strength of Ta–O bonds in the TaO_6 octahedra. The bond strength of Ta–O due to strong covalent interactions made greater contributions to the higher Qf values of dielectric ceramics, which was also demonstrated by other reports [16]. Moreover, remarkable changes in τ_f values of MT ceramics were not found with the increase of sintering temperatures from 1250 °C to 1450 °C and these values were ranged from −40 ppm/°C to −50 ppm/°C, which was similar to the results by other methods [2–4]. Similarly, there was not significant effect on the τ_f values of MT ceramics due to its minor quantity although its τ_f value was approximate 29 ppm/°C as reported [7]. Thus, it was considered that additional improvement in τ_f value by adjusting the ratio of $MgTa_2O_6$ as second phase was beneficial for dielectric resonator applications at high frequency.

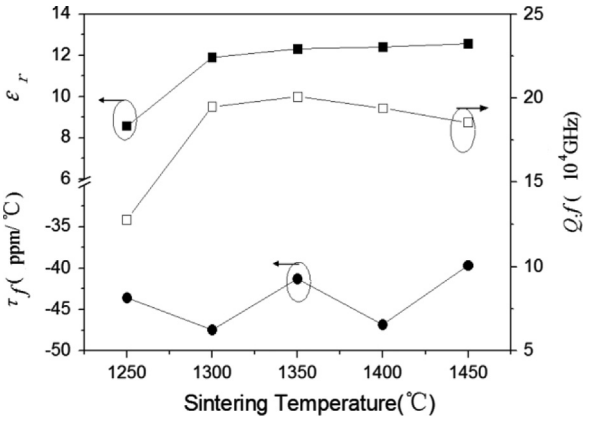

Fig. 5. Curves of ε_r, Qf and τ_f values as a function of sintering temperatures for MT ceramics in the temperature region of 1250 °C–1450 °C.

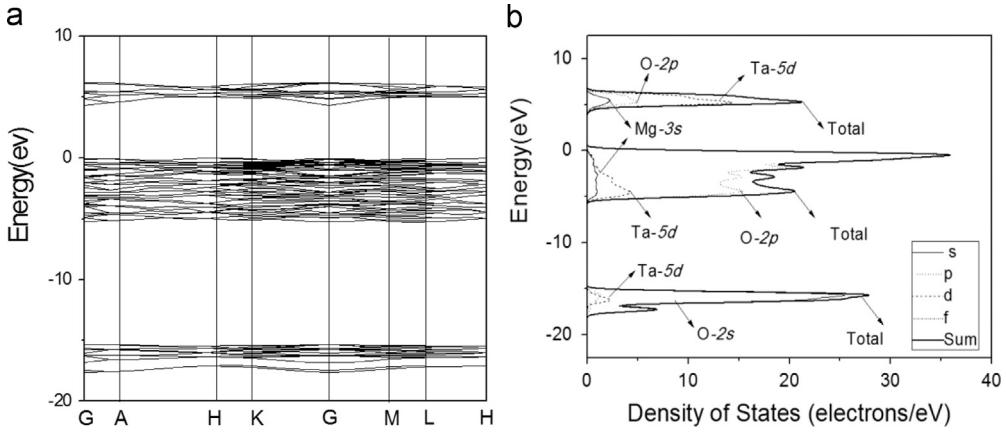

Fig. 6. (a) Band structures, (b) total density of states (TDOS) and partial density of states(PDOS) of MT crystals.

4. Conclusions

Corundum-structure MT ceramics were prepared using nanopowders and microwave properties of MT ceramics were systematically investigated depending on sintering temperatures. The results showed that MT samples with nearly full densities were obtained at 1300 °C and had excellent microwave dielectric properties of $\varepsilon_r = 11.9$, $Qf = 19{,}5000$ GHz and $\tau_f = -47$ ppm/°C. In addition, first principle calculation method and ionic polarizability theory were used for evaluation of dielectric properties. The observed dielectric polarizability was nearly in accord with theoretical dielectric polarizability of 11.55 and higher *Qf* values of dielectric ceramics could be attributed to be the bond strength of Ta–O due to strong covalent interactions.

Acknowledgments

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