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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

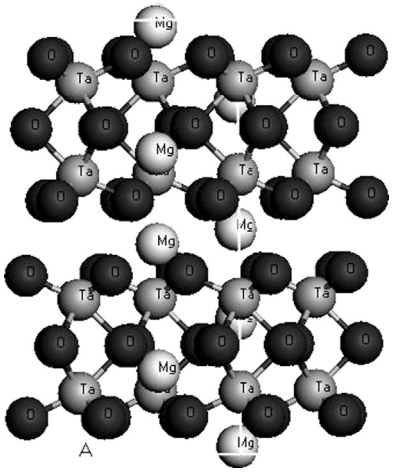

Fig. 1. Cluster model used in the calculation: $(Mg_8Ta_{16}O_{72})^{-48}$.

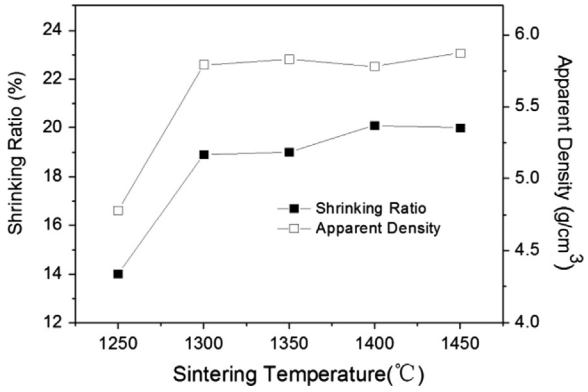

Fig. 2. Relative densities and diametric shrinkaging ratio of MT ceramics as a function of sintering temperatures from 1250 °C to 1450 °C.

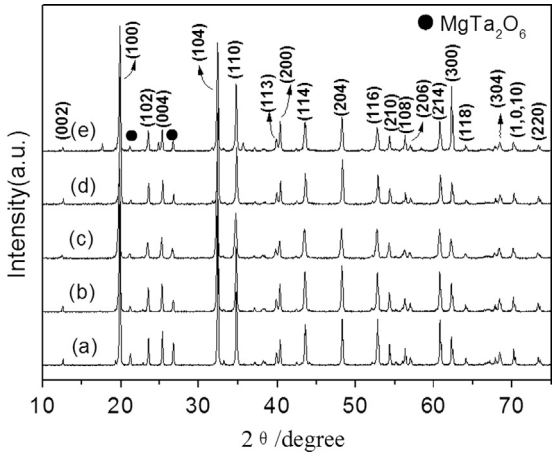

Fig. 3. XRD patterns of MT ceramics sintered at different temperatures ((a)–(e) corresponding to 1250 °C, 1300 °C, 1350 °C, 1400 °C, and 1450 °C).