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Microwave dielectric properties of $Mg_4Nb_2O_9$ ceramics produced by hydrothermal synthesis

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Abstract $Mg_4Nb_2O_9$ ceramics have been prepared by a hydrothermal synthesis in order to reduce the sintering temperature. The sintering and microwave dielectric properties of the hydrothermally processed $Mg_4Nb_2O_9$ were studied under various sintering temperatures ranging from 900 to 1300°C. The highest $Q\times f_o$ value of 26,069 GHz was obtained at the sintering temperature of 1300°C and is attributed to the increased density and appropriate grain growth. τ_f value of −17.1 ppm/°C was improved by the addition of TiO_2 and τ_f value of 6.7 ppm/°C was obtained at 20 wt% TiO_2. Chemical compatibility of $Mg_4Nb_2O_9$ with Ag was tested to identity the possibility of using $Mg_4Nb_2O_9$ for an LTCC application. Since any secondary phase was not observed in the XRD pattern of the mixtures of $Mg_4Nb_2O_9$ and Ag powder heat treated at 900°C, it was considered that the $Mg_4Nb_2O_9$ system is applicable to the multilayer microwave devices using Ag as an electrode.

Keywords Hydrothermal synthesis · $Mg_4Nb_2O_9$ · Microwave dielectric properties · Sintering · LTCC

1 Introduction

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 ($Q\times f_o$), an appropriate dielectric constant (ε_r), and a near-zero temperature coefficient of resonant frequency (τ_f). Recent study [1] showed that $Mg_4Nb_2O_9$ ceramics produced by conventional solid-state reaction process had a high $Q\times f_o$ value comparable to Al_2O_3. Although sintering temperature of $Mg_4Nb_2O_9$ is lower than that of Al_2O_3, the temperature is still too high to fully commercialize this material.

There are several approaches [2–7] to reduce the sintering temperature of the microwave dielectric ceramics: the addition of low melting point compounds such as B_2O_3, Bi_2O_3, and V_2O_5, the development of new compositions, and the chemical processing to produce smaller particle size of starting dielectric materials. There have been relatively fewer investigations [8, 9] of the chemical processing methods such as hydrothermal, sol–gel, and precipitation processes for producing ceramics for microwave applications. Most of the microwave dielectric materials are being produced by conventional solid-state reaction process. There was a study [10] to reduce the sintering temperature of $Mg_4Nb_2O_9$ using the precipitation method and the possibility of applying $Mg_4Nb_2O_9$ as a new low temperature co-fired ceramics (LTCC) system was suggested.

The goal of this research was to explore the capabilities of another chemical processing method, hydrothermal method, for reducing the sintering temperature of $Mg_4Nb_2O_9$ without significant degradation of the microwave dielectric properties. Hydrothermal synthesis is undoubtedly a useful process for producing powders with a good control over stoichiometry and homogeneity, yielding very fine particle size as can be seen in the synthesis of ZnO [11]. The sintering and microwave dielectric properties of the hydrothermally processed $Mg_4Nb_2O_9$ system at various sintering temperatures were studied. In addition, the microwave properties at the

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sintering temperatures lower than 950°C were evaluated in order to identify the possibility of using $Mg_4Nb_2O_9$ as an LTCC material.

2 Experimental procedure

Magnesium nitrate hexahydrate $Mg(NO_3)_2{\cdot}6H_2O$ and niobium (V) chloride $NbCl_5$ with 98% purity (Aldrich) were used as the starting materials for hydrothermal synthesis. The precursor solution was prepared by dissolving stoichiometric quantities (4:1 molar ratio) of $Mg(NO_3)_2{\cdot}6H_2O$ and $NbCl_5$ in deionized water at concentrations of 0.5 mol/l. After achieving complete dissolution by stirring with a magnetic stirrer for 5 h, solution with a pH value of 10.98 was prepared by adding aqueous NH_4OH (28%). The volume of the precursor was always maintained at 900 ml to ensure a consistent volume of liquid was present within the hydrothermal container at the start of each experiment. The synthesis took place at 90°C for 24 h in 1000 ml Teflon-lined stainless steel hydrothermal "bombs" (Parr Co.). Powders produced by this reaction were centrifuged, washed with deionized water, filtered, and dried in air for at least 24 h prior to weighing. The powders were subsequently calcined at 700°C for 5 h and milled for 24 h with zirconia balls. The ground powders were dried and pressed into pellets, 15 mm in diameter and 6.7 mm thick. The pellets were sintered at a temperature range of 900 to 1300°C for 5 h in air. The heating rate was 10°C/min.

The morphology of the powders and the microstructure of the sintered body were examined using scanning electron microscopy (JSM 5310, JEOL) and phase identification of the sintered specimens was carried out by X-ray diffractometry (D/MAX-2200, Rigaku) using Cu-Kα radiation. The densities were measured using the Archimedes method. The microwave dielectric properties were measured by the resonant cavity method described by Hakki and Coleman [12] using the TE_{011} propagation mode. The τ_f value was measured over a temperature range of −20 to 80°C.

3 Results and discussion

SEM micrograph of the particles calcined at 700°C for 5 h is given in Fig. 1. The particles were shown to be well dispersed and had a size under 100 nm.

Figure 2 shows the XRD patterns of the pellets sintered at temperatures from 900 to 1300°C for 5 h in air. The major phases were identified as a mixture of $Mg_4Nb_2O_9$, $MgNb_2O_6$, and MgO. As the sintering temperature increased, the amount of $Mg_4Nb_2O_9$ phase increased while that of $MgNb_2O_6$ and MgO phases decreased. It existed almost as a single phase of $Mg_4Nb_2O_9$ at the sintering temperature of 1300°C.

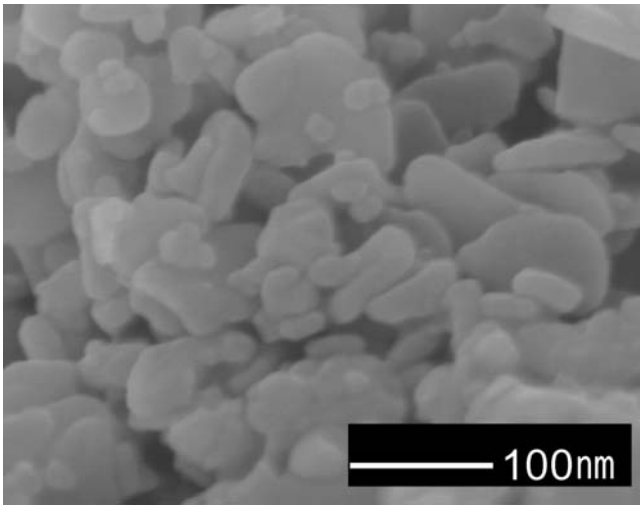

Fig. 1 SEM micrographs of $Mg_4Nb_2O_9$ produced by hydrothermal synthesis. Powders were calcined at 700°C for 5 h

The effect of the sintering temperature on the density and microwave dielectric properties of the specimen is shown in Fig. 3. The apparent densities increased from 2.46 to 3.51 g/cm^3 as the sintering temperature increased from 900 to 1300°C. The value of ε_r increased as the sintering temperature increased, reaching a maximum value of 11.2 at 1300°C. The increase of ε_r with sintering temperature is attributed to the increase in the density. $Q{\times}f_o$ value increased as the sintering temperature increased and reached its maximum value of 26,069 GHz at 1300°C. The steady increase in the $Q{\times}f_o$ value with sintering temperature is related to the increase in the density and appropriate grain growth as reported in previous studies [13, 14]. It is noteworthy that $Q{\times}f_o$ values of $Mg_4Nb_2O_9$ prepared by the precipitation method [10] were lower at most of the sintering temperature range than those of $Mg_4Nb_2O_9$ prepared in this study by the hydrothermal synthesis. This could be attributed to the presence of potassium in the precipitation which caused the reduction of $Q{\times}f_o$ values. When compared to the solid-state reaction processed $Mg_4Nb_2O_9$, although the $Q{\times}f_o$ values of the hydrothermally produced one were lower at the sintering temperatures over 1100°C, a $Q{\times}f_o$ value of 4,493 GHz obtained at the sintering temperature of 900°C suggested the possibility of utilizing this $Mg_4Nb_2O_9$ as an LTCC material. The τ_f values were in the range of −22.8 ~ −16.6 ppm/°C. An improvement in ε_f would be needed for commercial application.

Figure 4 shows the SEM microstructure of the specimens sintered at temperatures ranging from 900 to 1300°C for 5 h. The apparent porosity decreased as the sintering temperature increased and this observation was consistent with the results of the increase in $Q{\times}f_o$ values with

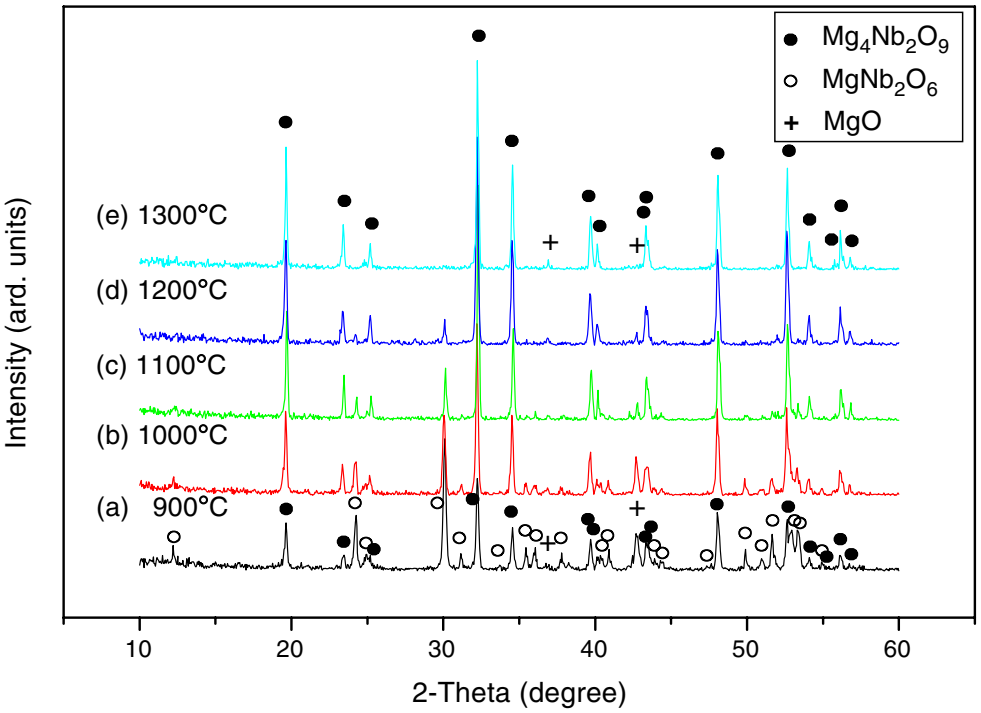

Fig. 2 XRD patterns of $Mg_4Nb_2O_9$ as a function of sintering temperature from 900 to 1300°C

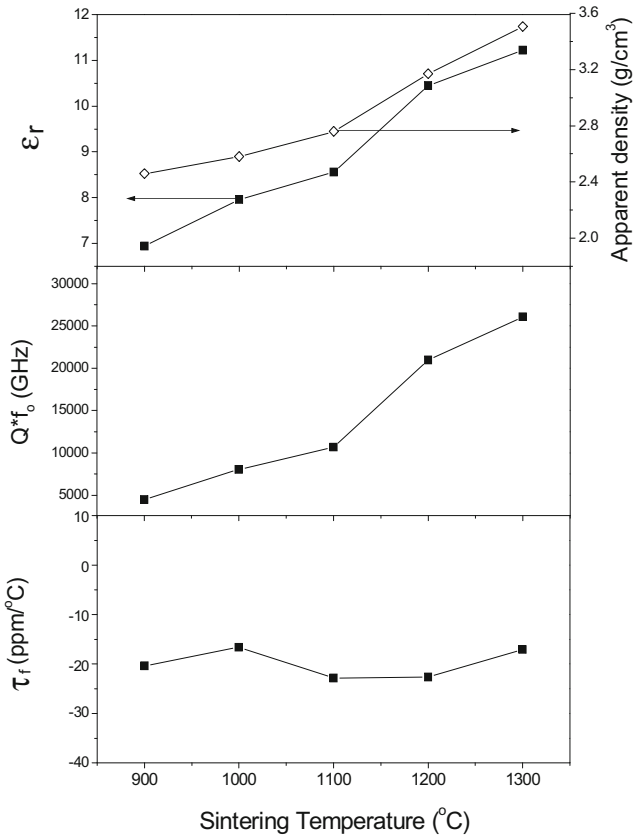

Fig. 3 Sintered densities and microwave dielectric properties of $Mg_4Nb_2O_9$ as a function of sintering temperature from 900 to 1300°C

increasing sintering temperatures. Grain growth was shown to be prominent after 1200°C and the grain size measured by a linear intercept method was ~4.1μm at the sintering temperature of 1300°C.

The improvement in τ_f values was necessary because τ_f values of $Mg_4Nb_2O_9$ were in the range of −22.8 ~ −16.6 ppm/°C. Since the τ_f value of TiO_2 is approximately 450 ppm/°C, TiO_2 was added to improve the τ_f value of $Mg_4Nb_2O_9$ ceramics. The TiO_2 purchased from Aldrich had a mean particle-size less than 40 nm and was mixed with $Mg_4Nb_2O_9$ powders by conventional ball milling with zirconia balls. Figure 5 shows the τ_f and $Q\times f_o$ values of the $Mg_4Nb_2O_9$ containing x wt% of TiO_2 with $0\leq\times\leq20$ at the sintering temperature of 1300°C. Initial τ_f value of −17.1 ppm/°C increased with the addition of TiO_2 and τ_f of 6.7 ppm/°C was attained at $x=20$. However, $Q\times f_o$ decreased to values in the range of 14,967 ~ 15,950 GHz as the amount of TiO_2 increased.

For the commercial application of LTCC, the reaction between the microwave dielectric materials and electrode should be minimized. XRD analysis of the dielectric ceramics and electrode powder mixture sintered at the desired temperature is considered an acceptable way to analyze the interface reaction [15]. This method is widely used for the investigation of any reaction between dielectrics and electrode materials used in multilayer chip capacitors. The XRD patterns of the mixture of $Mg_4Nb_2O_9$ and Ag powders after the heat treatment at 900°C for 5 h are shown in Fig. 6. Since the formation of a secondary

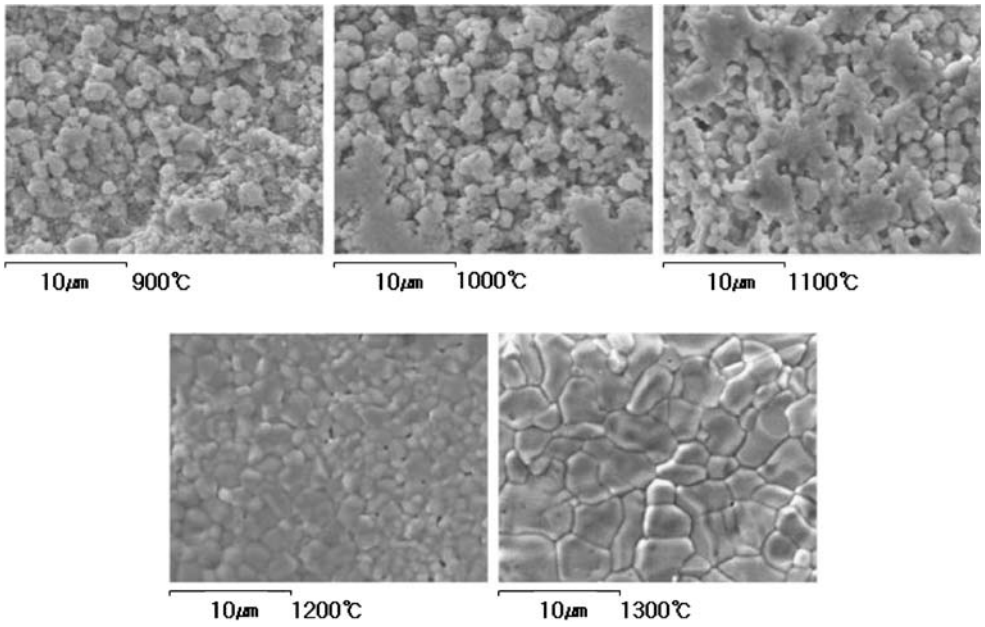

Fig. 4 SEM micrographs of $Mg_4Nb_2O_9$ sintered at temperatures from 900 to 1300°C for 5 h

phase was not observed in the XRD pattern, it is suggested that $Mg_4Nb_2O_9$ has chemical compatibility with a Ag electrode.

4 Conclusions

The sintering and microwave dielectric properties of $Mg_4Nb_2O_9$ prepared by a hydrothermal method have been investigated. A $Q\times f_o$ value of 26,069 GHz with a ε_r of 11.2 and a τ_f of −17.1 ppm/°C was obtained for the hydrothermally processed $Mg_4Nb_2O_9$ after sintering at 1300°C for 5 h. The τ_f value was improved by the addition of TiO_2. $Mg_4Nb_2O_9$ with 20 wt% TiO_2 exhibited microwave dielectric properties of τ_f=6.7 ppm/°C and $Q\times f_o$= 15,950 GHz when sintered at 1300°C for 5 h. The hydrothermally synthesized $Mg_4Nb_2O_9$ was shown to have a high $Q\times f_o$ value even at very low sintering temperature: 4,493 GHz at 900°C for 5 h. $Mg_4Nb_2O_9$ was found to chemically compatible with Ag electrode material; no secondary phase was observed in the XRD pattern of a mixture of $Mg_4Nb_2O_9$ and Ag powder after heat-treated at 900°C for 5 h. Thus, hydrothermally processed $Mg_4Nb_2O_9$ are considered to be an appropriate candidate as an LTCC material for microwave applications.

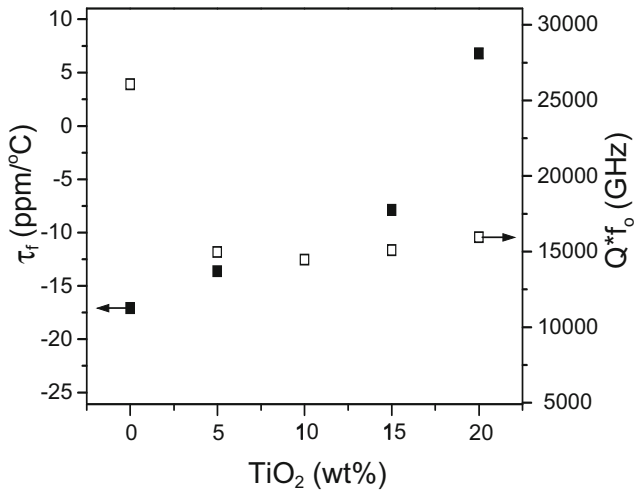

Fig. 5 Variations of $Q\times f_o$ and τ_f values of $Mg_4Nb_2O_9$ with $0\leq\times\leq$ 20 wt% addition of TiO_2 when sintered at 1300°C for 5 h

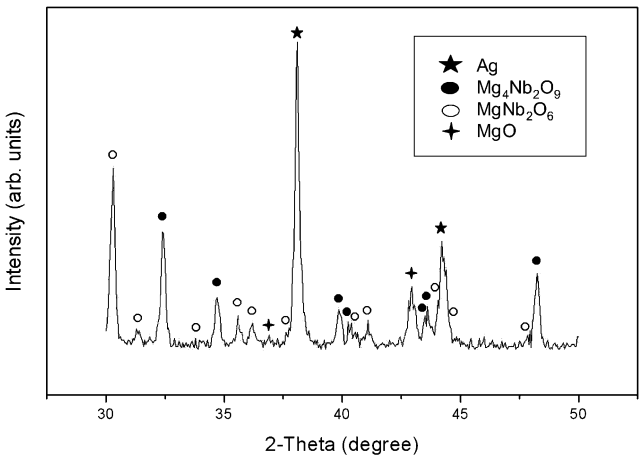

Fig. 6 XRD patterns of the mixture of $Mg_4Nb_2O_9$ and Ag powders after heat treated at 900°C for 5 h

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