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Low temperature sintering and microwave dielectric properties of $(Mg_{3-x}Zn_x)(VO_4)_2$ ceramics

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Abstract

This paper describes the effects of Zn substitution for Mg on the microwave dielectric properties of $(Mg_{3-x}Zn_x)(VO_4)_2$ ceramics. As for the XRPD patterns of $(Mg_{3-x}Zn_x)(VO_4)_2$ ceramics sintered at the sintering temperature of 750 °C, no secondary phase was detected over the whole composition range. However, in the case of the sample sintered at 850 °C, the $Zn_4V_2O_9$ and $Zn_2V_2O_7$ compounds were identified by using XRPD; this result was attributed to the decomposition of $Zn_3(VO_4)_2$ phase. From crystal structure analysis, it was found that the atomic distances of $M(1)$—O (M = Mg and Zn) and $M(2)$—O in MO_6 octahedra increased, though that of V—O in VO_4 tetrahedron decreased. Moreover, the slight tilting of $M(2)O_6$ octahedron was observed by the Zn substitution. As for the covalency of cation–oxygen bond, the covalency of M—O bond in $M(1)O_6$ and $M(2)O_6$ octahedra decreased because of the increase in the atomic distance of M—O, whereas that of V—O increased with increasing the Zn addition. However, as a result, the slight decrease in the covalency of cation–oxygen bond was recognized because the variation in the covalency of M—O bond is predominant in this crystal structure. The dielectric constants of the samples range from 4.4 to 11.1. The decrease in the covalency may be related to the difference in the dielectric constant of each composition. The maximum $Q \cdot f$ value of bulk densities is effected by varying the chemical composition of $(Mg_{3-x}Zn_x)(VO_4)_2$ ceramics and it shifts toward lower sintering temperature with an increase in x within the temperature region of 800–1050 °C. The temperature coefficient of resonant frequency (τ_f) of the samples decreased with increasing of Zn, and then a variation in τ_f value was attributed to the tilting of $M(2)O_6$ octahedron caused by Zn substitution for Mg.

Keywords: Powders-solid state reaction; Grain growth; ZnO; X-ray method

1. Introduction

In recent years, an increasing effort has been directed toward attaining the miniaturization of components with the multilayer microwave integrated devices, i.e., integrations of passive components such as inductors, resistors, capacitors and line resonators into the substrate which carries the integrated circuits. However, in order to make the multilayer microwave integrated devices, the development of low temperature co-fired ceramics (LTCC) is required. The sintering temperature for LTCC has to be lower than 960.5 °C, which is the melting point of Ag which is used as an electrode material. For the commercial application such as a resonation at microwave frequency, a requirement of a high $Q \cdot f$, a high permittivity and a stable temperature coefficient of resonant frequency (τ_f) is necessary. For LTCC material, which are widely used as a substrate for the application to the multilayered microwave devices, a low dielectric constant with high $Q \cdot f$ is required. Thus, there is considerable interest in a development of a new LTCC material with high $Q \cdot f$.

In MgO–V_2O_5 system, Kerby and Wilson[1] reported that the $Mg_3(VO_4)_2$ compound was partially melted at 980 °C. Therefore, the $Mg_3(VO_4)_2$ compound was considered to be an appropriate candidate for new LTCC material. The microwave dielectric properties of $Mg_3(VO_4)_2$ compound sintered at 1050 °C for 5 h were reported to have a dielectric constant (ε_r) of 9.3 and a quality factor($Q \cdot f$) of 65440 GHz with a temperature coefficient of resonant frequency (τ_f) of −89.5 ppm/°C.[2] However, the sintering temperature of $Mg_3(VO_4)_2$ is still too high to use together with an internal conductor such as a silver because the melting point of silver is 960.5 °C. In the case of the ZnO–V_2O_5 system, it was reported that the $Zn_3(VO_4)_2$ compound decomposed to form the $Zn_4V_2O_9$ and $Zn_2V_2O_7$ compounds at 815 °C, followed by a partial melting at 860 °C.[3] Thus, the Zn substitution for Mg may be effective in reducing the sintering temperature of a new $(Mg_{3-x}Zn_x)(VO_4)_2$ ceramic. The effects of Zn substitution for Mg on the crystal structure, microstructure, reduction of sintering temperature

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and microwave dielectric properties of $(Mg_{3-x}Zn_x)(VO_4)_2$ were investigated in this paper.

2. Experimental method

The samples of $(Mg_{3-x}Zn_x)(VO_4)_2$ ceramics were prepared by a conventional solid state reaction method from individual reagent-grade oxide powders: MgO (99.9% purity), ZnO (99.9% purity) and V_2O_5 (99.99% purity). The powders were weighed according to the stoichiometric compositions of $(Mg_{3-x}Zn_x)(VO_4)_2$, and then mixed with a mortar for 45 min in ethanol. The obtained powers were calcined at the temperature of 700 °C for 20 h in air. The calcined powders were ground for 45 min in ethanol with a suitable amount of 5% solution of polyvinyl alcohol (PVA) as the binder and formed into pellets (12 mm in diameter and 7 mm thickness) via uniaxial pressing at 100 MPa in a stainless-steel die. These pellets were sintered in the temperatures range of 750–1075 °C for 5 h in air, using the heating and cooling rates of 5 °C/min. The crystalline phases of the samples were identified by X-ray powder diffraction (XRPD) using Cu Kα radiation, where the crystalline phases of the samples were refined by Rietveld analysis.[4,5] The microstructure observations of the sintered surfaces were performed by means of field emission scanning electron microscope (FE-SEM) and energy dispersive X-ray analysis (EDX). The bulk densities of the sintered samples were measured by Archimedes method. The temperature coefficient of dielectric constant (τ_ε) of the sample was measured at a frequency of 1 MHz using LCR meter. The microwave dielectric properties of the samples were evaluated in terms of the Hakki and Coleman method.[6]

3. Results and discussion

The crystal structure of $(Mg_{3-x}Zn_x)(VO_4)_2$ ceramics was investigated by using XRPD. Fig. 1 shows the XRPD patterns of $(Mg_{3-x}Zn_x)(VO_4)_2$ ceramics sintered at 750 °C for 5 h in air. No secondary phase was detected in the composition range of 0–3. In order to confirm the solid solutions, the lattice parameters of $(Mg_{3-x}Zn_x)(VO_4)_2$ ceramics sintered at 750 °C for 5 h in air were refined by using Rietveld analysis. The plot of refined lattice parameters versus composition x of $(Mg_{3-x}Zn_x)(VO_4)_2$ ceramics are shown in Fig. 2. The lattice parameters, a and b, linearly increased with increased x, whereas the lattice parameter c decreased. Fig. 3 shows the crystal structure of $Mg_3(VO_4)_2$ ceramic which has an orthorhombic structure with space group of *Cmca* (No. 64). The crystal structure of the ceramic is composed to the $M(1)O_6$ (where M = Mg and Zn) and $M(2)O_6$ octahedra, and VO_4 tetrahedron, where these polyhedra linked each other as shown in Fig. 3. The influence of Zn substitution for Mg on the atomic distances of cation–oxygen bonds is shown in Table 1 where an increase in the atomic distance of M–O is observed with increasing Zn and the atomic distance of V–O was decreased. Moreover, with increased x, a slight tilting of $M(2)O_6$ octahedron was recognized as shown in Fig. 4. Thus, it is considered that the increase in the lattice parameters a and b are due to the increase in the atomic distances of M–O bond in MO_6 octahedron. Moreover, the decrease in the lattice parame-

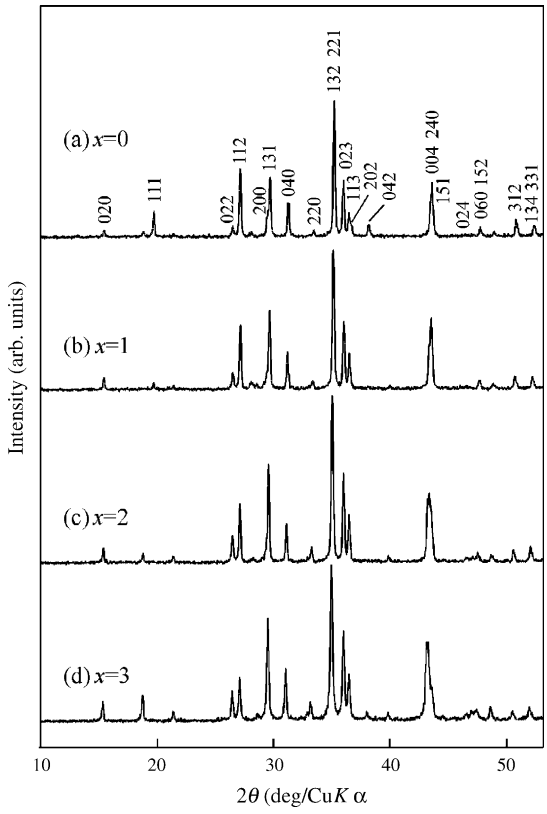

Fig. 1. XRPD patterns of the $(Mg_{3-x}Zn_x)(VO_4)_2$ ceramics sintered at 750 °C for 5 h in air.

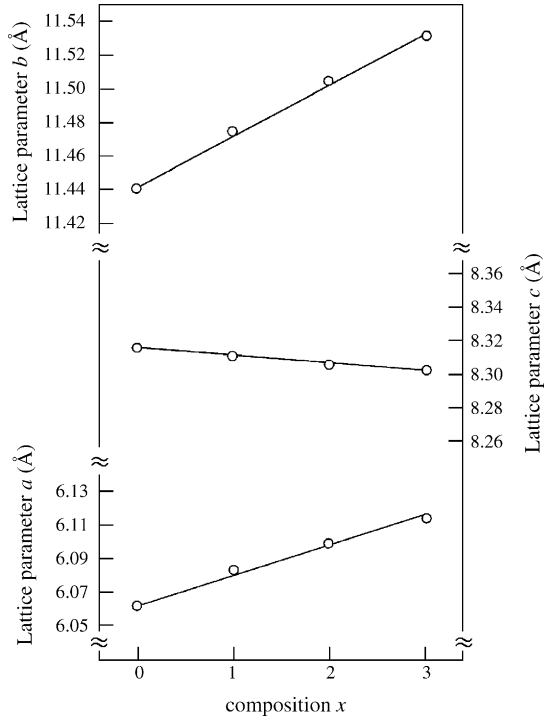

Fig. 2. Lattice parameters of $(Mg_{3-x}Zn_x)(VO_4)_2$ ceramics sintered at 750 °C for 5 h in air as a function of composition x.