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Reducing-atmosphere resistant mechanism on microwave dielectric enhancement of $CaMgSi_2O_6$ glass-ceramics

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ABSTRACT

This work highlights a reducing-atmosphere resistance using amphoteric ion doping to reduce defects and to enhance microwave dielectric properties in $CaMgSi_2O_6$ glass-ceramics. Amphoteric Al^{3+} ion (Al_2O_3 doping) was selected with both donor and acceptor roles to restrict free electrons and oxygen vacancies in specimens sintered in reducing atmosphere. The X-ray absorption and X-ray photoelectron spectra indicate decreased oxygen vacancies and a valence shift from a mixture of Si^{2+} and Si^{3+} to Si^{4+} in the Al^{3+} −doped $CaMgSi_2O_6$ glass-ceramics sintered in reducing-atmosphere. The amphoteric Al^{3+} ion plays an acceptor role as entering Si^{4+} site to form oxygen vacancies, meanwhile Al^{3+} plays a donor role as entering Mg^{2+} site to compensate free electrons. The amphoteric Al−doped diopside glass-ceramic can increase the electric resistivity and quality factors. This work can provide an efficient approach for the base-metal-electrode (BME) in low-temperature co-fired ceramics (LTCC) and multilayer ceramic capacitors (MLCC).

1. Introduction

Microwave ceramic components have a high demand in the significant growth of telecommunication and satellite broadcasting industries. Recent developments of microelectronic technologies have created a great demand for microwave substrate materials with low dielectric constants (ε_r ~4–9) and high quality factors ($Q \times f$) to reduce the delay time and to increase the speed of electronic signal [1]. In addition, recent advancements of base-metal-electrodes (BME) enable ceramic multilayer capacitors (MLCCs) as a cheaper base electrode (Ni or Cu) to replace expensive noble inner electrodes (Ag-Pd or Ag). BME materials must be sintered in a reducing atmosphere, such as N_2/H_2 or N_2 due to easy oxidization of Ni or Cu electrode [2] and lead to poor insulation in the ceramic systems easily as a semiconductor. For example, the Ti^{4+} ions of $BaTiO_3$ based capacitors can be partly reduced to Ti^{3+}, thus oxygen vacancies and electrons can be formed to increase leakage current and instability. The insulation resistance (IR) was decreases by 10–12 orders of magnitude in $BaTiO_3$ based dielectrics sintered in N_2/H_2 atmosphere [3,4]. The defect chemistry can be expressed as follows:

$$Oo^{*} \rightarrow V_O^{\cdot\cdot} + 2e' + \frac{1}{2}O_2 \quad (1)$$

The mechanisms of donor and acceptor have been thoroughly studied in doped $BaTiO_3$ ceramics sintered in reducing atmosphere [5–9]. Kishi et al. [9] reported that addition of amphoteric ions, such as Y_2O_3, Dy_2O_3, Ho_2O_3, and Er_2O_3 with an intermediate-ionic-size ion can occupy both A and B sites in the $BaTiO_3$ lattice. The doped ions can play a donor and an acceptor role in the lattice by occupying different sites. Oxygen vacancies can be controlled to different degrees by doping concentration and life stability is relatively high in reducing-atmosphere resistant $BaTiO_3$-based dielectrics. Until now, the reducing-atmosphere resistant application is still less except the perovskite $BaTiO_3$ structure. On the other hand, microwave dielectric ceramics are mostly sintered as high temperature co-fired ceramics (HTCC). The low temperature co-fired ceramics (LTCC) can be fabricated with a base-metal copper electrode in a reducing atmosphere, thus it has a great potential to reduce the cost of production. However, the LTCC microwave dielectric materials sintered in reduction atmosphere with base-metal electrode have been rarely developed in the multiphase ceramics (glass + ceramics) [10–13] and glass-ceramics (crystallizable glass) [14–17]. Therefore, reducing-atmosphere resistant

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design is a necessary approach for the base-metal electrode (BME) application in the LTCC development.

Feng et al. [12,13] reported a specific glass with high wettability for adding in $BaTi_4O_9$ ceramics sintered in a nitrogen reducing-atmosphere with Cu electrodes. The specimen exhibited the optimal dielectric properties without Cu diffusion. However, oxygen vacancies and electronic carriers occurred as ceramics sintered in reducing atmosphere and specimen showed decreased quality factors [18]. It was reported that a small degree of porosity may induce a remarkable effect on the dielectric loss tangent. In this work, a single-phase amphoteric Al^{3+} -doped $CaMgSi_2O_6$ glass ceramics [19] have been developed by sintering in reducing atmosphere of N_2. The aim is to increase the microwave dielectric properties, such as quality factor and insulation resistance, and to explore the reducing-atmosphere resistant mechanism in the diopside glass ceramics.

1.1. Experimental procedures

Diopside $CaMgSi_2O_6$ glass-ceramics were prepared through mixing, melting, cooling, pulverizing, and heat treatments. A mixture of $CaCO_3$ (>99%, Komoshina, Japan), $Mg(OH)_2$ (>99%, Ube, Japan), and SiO_2 (>99%, Sibelco, Taiwan) powders are in a specific molar ratio of 1:1:2. ZrO_2 agent (>99.5%, Daiichi, Japan) was added as a nucleating agent and different contents of Al_2O_3 (>99.9%, Sumitomo, Japan) of 0 wt%, 0.25 wt%, 0.5 wt%, 1 wt%, 2 wt%, 3 wt% were added respectively as a reducing-atmosphere resistant agent. The mixed powders were fabricated by ball milling and vacuum drying at 60 °C. The resulting powders were melted at 1500 °C for 2 h followed by furnace cooling, pulverized, and ball milled before pressing to thin circular pellets and rods (φ15 mm) under a load of 1000 kgf. The growth of crystallized glass-ceramics were finished at the sintering temperature of 950 °C for 4 h in 100% nitrogen atmospheres.

For structural study, the wide-angle X-ray diffraction patterns were obtained using a Rigaku Multiplex Diffractometer. The Rietveld refinement analyses were performed with the HighScore Plus software to determine phase quantities and crystalline contents. The surface chemical compositions and bonding states were investigated by using an X-ray photoelectron spectroscope (XPS, VG Scientific Ltd., UK) with Al Kα radiation (energy = 1486.6 eV). The synchrotron soft X-ray absorption spectra of the Si L_1-edge were collected in the total electron yield via current mode at the 20A1 beamline at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The oxygen contents of the sintered ceramic pellets were analyzed using an electron-probe micro-analyzer (EPMA; JXA-8200, JEOL Co., Japan) and wavelength-dispersive spectroscopy (WDS, EDAX Co., NJ, USA). The microwave dielectric constant (ε_r) and quality factor (Q × f) of as-sintered samples were determined using a network analyzer HP8722A (Agilent, USA). The microwave dielectric properties were evaluated at frequency 9 GHz using a dielectric resonator technique according to the dielectric resonator method [20,21]. The dimension of ~12 mm (diameter) × ~12 mm (height) for rod-shape specimens was adopted in the cavity. The dielectric constant was calculated using the resonant frequency of the TE_{011} resonant mode.

2. Results and discussion

Lattice strains, electric properties, and crystalline fractions of the diopside $CaMgSi_2O_6$ glass-ceramics sintered in different reducing atmospheres are shown in Table 1. In our previous study, XRD patterns of the specimen sintered in N_2/H_2 (99:1) atmosphere revealed significant peak broadening than the specimens sintered in air and 100% N_2 atmospheres, indicating that the specimen sintered in N_2/H_2 (99:1) atmosphere exhibits larger internal strain in the lattice. The relation between lattice strain and XRD peak broadening can be expressed by the Williamson-Hall equation [22].

$$\beta_{hkl} \cos \theta_{hkl} = (K\lambda/t) + 4\varepsilon \sin \theta_{hkl} \quad (2)$$

where K is shape factor, λ is X-ray wavelength, θ_{hkl} is Bragg angle, t is effective crystallite size normal to the reflecting planes and ε is root mean square value of microstrain. Plot ($\beta_{hkl} \cos\theta_{hkl}$ as a function of $4\sin\theta_{hkl}$) of Williamson-Hall equation can display strain deformation and microstrain ε can be estimated from the slope of regression line. The result reveals a high lattice strain of 0.00714 ± 0.05% in the specimen sintered in N_2/H_2 (99:1) atmosphere. Lattice strain regressively decreases from 0.00485 ± 0.02% to 0.00383 ± 0.05% for the specimens sintered in 100% N_2 and air atmosphere [19], respectively. The specimens sintered in reducing atmospheres (100% N_2 and 99:1 N_2/H_2) demonstrate higher internal lattice strains than specimen sintered in air, Quin and Szpunar [23] suggested that the origin of lattice strain is due to excess volume of grain boundaries associated with vacancies and vacant clusters, suggesting that the vacancies easily appear in diopside glass-ceramics for sintering in reductive atmospheres.

The higher lattice strain can be attributed to the oxygen vacancies and vacancy clusters, which may cause decreased quality factors. XPS analysis shows predominate Si^{4+} (102.5 eV) valence state for specimen sintered in air. Specimens sintered in 100% N_2 and mixed N_2/H_2 (99:1) atmospheres show a mixture of Si^{4+}, Si^{3+} (101.2 eV), and Si^{2+} (100.2 eV) valence states. Specimen sintered in N_2/H_2 atmosphere exhibits a higher current density of 8.3×10^{-9} A/cm^2, which might be resulted from the valence transition from Si^{4+} to Si^{3+} and Si^{2+} accompanied with free electrons to make a semiconductive behavior in the $CaMgSi_2O_6$ material. Goel et al. [24] reported that the quantitative crystallinity in the specimen sintered in air (85.9 wt%) is higher than specimen sintered in 100% N_2 (79.9 wt%) as X-ray diffraction studies adjoined with the Rietveld method, perhaps due to formation of oxygen vacancies. It is an important issue to acquire less defects and higher Q × f values for the diopside glass-ceramics sintered in reducing atmosphere. According to the previous $BaTiO_3$ studies, the intermediate-ionic-size amphoteric ions doped in the perovskite structure is an efficient design for the reducing-atmosphere resistant method.

To select the amphoteric ions in diopside glass-ceramics, the ideal site-occupancies of pyroxene structures is shown in Fig. 1 based on the different coordinated cations [25]. Diopside phase is one of the pyroxene structures with a formula of M2M1TO6. M2 and M1 represent cations in a regularly distorted octahedral coordination and T represents cations in tetrahedral coordination. Generally, larger cations (Mg^{2+}, Fe^{2+}, Mn^{2+}, Li^{+}, Ca^{2+}, and Na^{2+})

Table 1
Lattice strains, silicon valences, current densities, and dielectric properties of diopside glass-ceramics sintered in air, 100% N_2, and N_2/H_2 (99:1) atmospheres at 950 °C for 2 h according to the report by Feng et al. [19].

Atmospheres	Lattice strain	Silicon binding energy (eV)	Current densities (A/cm^2)	Dielectric constant	Quality factors (GHz)
Air	0.00383	102.5	3.2×10^{-10}	7.42	7342
N_2 (100%)	0.00485	101.2	6.8×10^{-10}	7.43	4231
N_2/H_2 (99:1)	0.00714	100.2	8.3×10^{-9}	7.42	1443