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Cation distribution of high-performance Mn-substituted $ZnGa_2O_4$ microwave dielectric ceramics

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ABSTRACT

In current study, only 5 mol% Mn^{2+} was applied to fabricate high performance microwave dielectric $ZnGa_2O_4$ ceramics, via a traditional solid state method. The crystal structure, cation distribution and microwave dielectric properties of as-fabricated Mn-substituted $ZnGa_2O_4$ ceramics were systematically investigated. Mn^{2+}-substitution led to a continuous lattice expansion. Raman, EPR and crystal structure refinement analysis suggest that Mn^{2+} preferentially occupies the tetrahedral site and the compounds stay normal-spinel structure. The experimental and theoretical dielectric constant of $Zn_{1-x}Mn_xGa_2O_4$ ceramics fit well. In all, this magnetic ion, Mn^{2+}, could effectively adjust the τ_f value to near zero and double the quality factor from 85,824 GHz to 181,000 GHz of $Zn_{1-x}Mn_xGa_2O_4$ ceramics at the meantime. $Zn_{1-x}Mn_xGa_2O_4$ ($x = 0.05$) ceramics sintered at 1400 °C for 2 h exhibited excellent microwave dielectric properties, with $\varepsilon_r = 9.7$(@9.85 GHz), $Q \times f = 181{,}000$ GHz, $tan\delta = 5.44 \times 10^{-5}$,and $\tau_f = -12$ ppm/°C.

1. Introduction

Low-K microwave dielectric ceramic materials have long been studied as millimeter wireless communication systems [1–5]. It is required to possess low dielectric constant , high quality factor and near zero temperature coefficient, so that these materials can widen the wave width, utilize frequency resource sufficiently, and shorten the relaxation time. And it is crucial to advancing the properties of intelligent transport systems, excellent ultra-stable oscillators, and ultrahigh-speed wireless local area networks.

Spinel compounds, one of the typical low-K dielectric ceramic materials, with general formula AB_2O_4 or $B(AB)O_4$, is applied in many scientific and commercial fields, such as magnetic materials, catalysts, semiconductors, superconductors and microwave dielectric ceramics. Common spinel ceramics for millimeter region application include M_2SnO_4 [6–8] M_2SiO_4 [9–11] and MAl_2O_4 [12–15] (M = Zn, Mg). Compared with M_2SnO_4, M_2SiO_4 and MAl_2O_4 (M = Zn, Mg), MGa_2O_4 (M = Zn, Mg) [16–23] have high quality factors over 90,000 GHz, low sintering temperature and a wide sintering temperature region. Therefore, MGa_2O_4 (M = Zn, Mg) spinel materials are promising candidates for millimeter-wave region application. However , the crystal structure of these two spinel ceramics are different. The crystal structure of $ZnGa_2O_4$ and MGa_2O_4 are normal-spinel and partial normal-spinel, respectively.

Researches have been studied the dielectric performance of $ZnGa_2O_4$ [16–18], $MgGa_2O_4$ [19,20] and their solid solutions, such as (Zn, Mg)Ga_2O_4 [21] and Zn (Ga, Al)$_2O_4$ [22]. These compounds are all spinel structured ceramics, and researchers believed that cation distribution play an important role in the enhancement of the $Q \times f$ value. Crystal structure refinement was applied to clarify the relationship between the crystal structure and the microwave dielectric properties of $MgGa_2O_4$. Akinori Kan etc. use crystal structure refinement to investigate $MgGa_2O_4$ spinel materials [20]. In their research, although the relative density is the same value of about 96%, $MgGa_2O_4$ ceramics with 0.86° of inversion show greater microwave dielectric performance than samples with higher (0.88) or lower (0.84) inversion parameter. Takahashi [23] investigated the cation distribution of spinel-structured $Zn_{1-3x}Al_{2+2x}O_4$ (x = 0–0.2) ceramics with defective structures and found that an intermediate spinel structure with preferential occupancy of tetrahedral sites by trivalent cations exhibits an enhanced $Q \times f$ value.

In the case of $ZnGa_2O_4$, fewer studies investigated the relationship between the cation distribution and the microwave dielectric properties. In our previous research, appropriate Cu-substitution can promote the microwave dielectric performance of $ZnGa_2O_4$, especially the $Q \times f$ value which climbed from 85,824 GHz to 131,445 GHz. Moreover, both

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the Raman spectrometer analysis and the crystal structure refinement demonstrate that the preferential site occupancy of Cu^{2+} is the octahedral site [24].

The above investigations were mainly focused on improving the quality factor of spinel structured ceramics, especially the gallium compounds. However, in the case of $ZnGa_2O_4$ microwave dielectric ceramic, the larger negative τ_f value, ~ -60 ppm/°C, has limited its application for millimeter-wave region. Therefore, it is significant to tune its τ_f value to near zero. Usually, these following two ways, substitution with magnetic ion and introducing second phase with positive τ_f value, are widely accepted to shift the large negative τ_f value to near zero [25]. Although introducing second phase with positive τ_f value could adjust the τ_f value to near zero, the $Q \times f$ value always be decreased in the meanwhile. Therefore, almost all of the commercial microwave dielectric products on the market today tune τ_f through the addition of varying amounts of magnetic additives, such as Ni, Co, and Mn, for magnetic additives could promote the $Q \times f$ value at the same time. Therefore, it came to us that whether or not can magnetic additives adjust the τ_f value to near zero and improve other dielectric performance at the same time.

Thus, in this paper Mn was introduced at the level of x = 0, 0.01, 0.05, 0.1 and 0.15, the effects of the preferential site occupation and magnetic ion Mn role on the microwave dielectric properties were investigated.

2. Materials and methods

2.1. Powder synthesis

$Zn_{1-x}Mn_xGa_2O_4$ (x = 0–0.15) spinel ceramics were prepared via traditional solid state method. ZnO, $MnCO_3$, and Ga_2O_3 powders were selected as the starting material. Analytical grade powders were weighted precisely using an analytical balance on the basis of stoichiometric proportions, to form a $Zn_{1-x}Mn_xGa_2O_4$ (x = 0–0.15) formula in the resultant Mn-substituted $ZnGa_2O_4$ spinel solid solutions. The substitution amount of $MnCO_3$ in this work was employed as 0.00 mol %, 0.01 mol%, 0.05 mol%, 0.10 mol%, 0.15 mol%, denoted as ZGO, 1ZMGO, 5ZMGO, 5ZMGO and 15ZMGO, respectively.

The mixed powders were milled for 12 h with ethanol in polyethylene jars with agate balls in a planetary milling machine (QM-1SP4; Jialing, Nanjing, China) with a rotation speed of 300 rpm. The obtained slurry was dried at 100 °C in an oven for 24 h in air, followed by sieved though a 100 mesh screen. The sieved powders were mixed with 7 wt% polyvinyl alcohol as adhesion agent and pressed into pellets of 13 mm in diameter and 6 mm in thickness with an automatic machine (DY-20; Tianjin Keqi Instrument, Tianjin, China) under 75 MPa. The green bodies were calcined at 1000 °C for 3 h in air to remove the volatile impurities in a muffle furnace and form the solid solutions. After calcining, the pellets were sintered at 1250–1350 °C for 4 h in air with a high-temperature electric furnace (KSX4-16, Allfine, Wuxi, China). Densities of the ceramics were evaluated via the Archimedes method and 5 samples were measured for every sintering temperature and give the average density. The relative densities were obtained based on bulk and theoretical density. Microstructural evolution of obtained ceramics was investigated by a scanning electron microscope (SEM, Hitachi SU8010, Japan).

2.2. Structure analysis

The XRD profiles of the ceramics were obtained by a step scanning method in the 2θ range of 5–80° with a step size of 0.02° and a counting time of 3.0 s/step, using X-ray diffraction (XRD, RigakuD/Max 2500 type, Japan) with Cu Kα radiation. Raman spectra were excited with an argon laser (20 mW laser power) and recorded using a Raman spectrometer (HR800, Horiba Labram, 514 nm He-Cd laser, 20 mW laser power). The manganese oxidation state and its position in the Mn-doped spinel structure were examined with EPR spectroscopy. It was carried out with standard X-band EPR spectrometer at a frequency of 9.7 GH (Bruker Elexsys FT/CW 580). The effect of Mn substitution on the crystal structure was investigated with General Structure Analysis System (PC-GSAS) software. Fourier transform infrared (FT-IR) spectroscopy was performed by NICOLET 5700 (Thermo, America).

2.3. Dielectric performance analysis

To investigate the microwave dielectric performance, ε_r, $Q \times f$, f_0 and τ_f were detected using cavity resonator method [26] by using Lightwave Component Analyzer (Hewlett Packard 8703 A, 1550 nm/130 MHz–20 GHz) and the resonator size is ϕ36 mm × h25 mm. The temperature coefficient of resonant frequency (τ_f) was calculated in the temperature range from 20 °C to 90 °C.

3. Results and discussion

3.1. Phase composition and sintering behavior

The spinel structured Mn-substituted $ZnGa_2O_4$ ceramics have been analyzed by XRD patterns (shown in Fig. 1). Obviously, all the diffraction peaks could be well indexed to spinel structured $ZnGa_2O_4$ (JCPDS No.86-0413) or $MnGa_2O_4$ (JCDPS No. 72-1521) with the space group *Fd3m*, and no $ZnMn_2O_4$ phase ((JCDPS No.77-0470, space group *I*41/*amd*) was detected in these specimen. $ZnGa_2O_4$ and $MnGa_2O_4$ both belong to normal spinel compounds. Notably, the reflection of $Zn_{1-x}Mn_xGa_2O_4$ shifted significantly to lower diffraction angles as *x* increased, especially the main diffraction peaks (shown in Fig. 1b). The reflections shift could be ascribed to the lattice expansion.

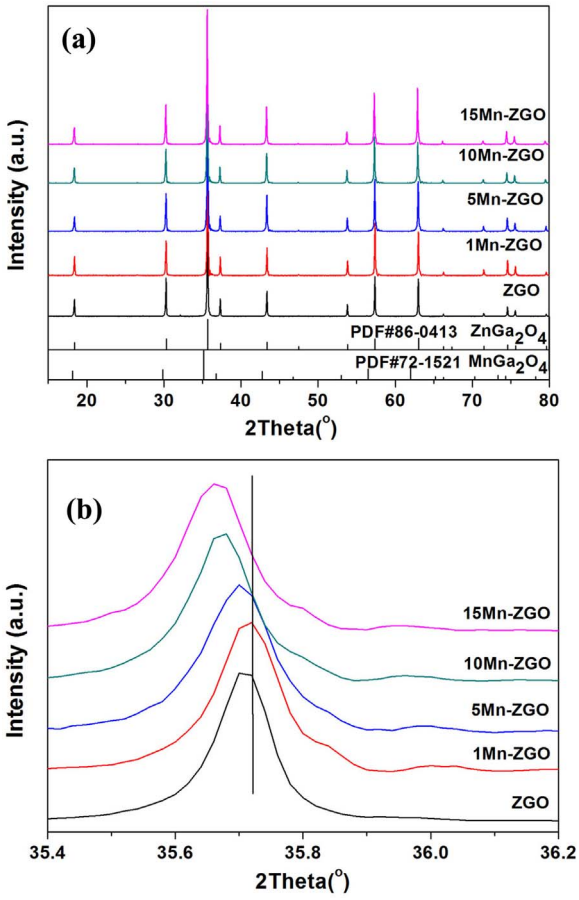

Fig. 1. XRD patterns (a) and their enlarged XRD patterns (b) of $Zn_{1-x}Mn_xGa_2O_4$ (x = 0–0.15) ceramics sintered at 1400 °C for 2 h in air.